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Degradation and stabilization of polyurethane elastomers

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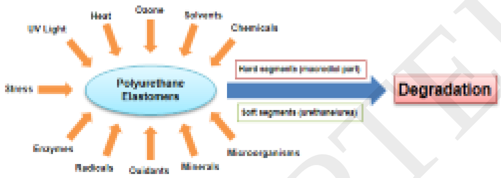
Graphical abstract



Abstract:

Polyurethane elastomers have a combination of excellent mechanical, physical and chemical properties along with exceptional biocompatibility. Therefore, these elastomeric systems are used in a diverse range of indoor, outdoor, underwater and biomedical applications. However, under certain conditions polyurethane elastomers undergo degradation, resulting in modified properties during usage or even complete failure. The degradation will not only severely affect the quality of the associated items, devices, or instruments, but may also cause catastrophic outcomes risking people’s safety and health. This review presents a comprehensive survey of the literature regarding various types of degradation of polyurethane elastomers, including photo-, thermal, ozonolytic, hydrolytic, chemical, enzymatic, *in-vivo*/*in-vitro* oxidative, biological, and mechanical degradation. The stability of polyurethane elastomers based on different building blocks of macrodiols (polyester, polyether, polycarbonate, polybutadiene, and polyisobutylene), isocyanates (aromatic and aliphatic), and chain extenders (diols, triols, and diamines) are summarised, and the mechanisms of different types of degradation are presented. The chemical components significantly influence not only the material structure and properties but also the degradative stability. Focussing on the components, we explore strategies for the enhancement of polyurethane stability through chemistry and engineering. A range of stabilizers, including both organic and inorganic additives for better stability against different types of degradation, are discussed, with a focus on their efficacy and mechanisms of action. A perspective on novel polyurethane materials with desired structures and properties combined with exceptional stability is also provided.

Keywords: Polyurethane elastomers; photodegradation; thermal degradation; oxidation; ozone; hydrolysis; stabilization

Contents

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Abbreviations

General terms:

T_g	Glass transition temperature
M	Molecular mass
E_d	Dissociation energy of a chemical bond
λ	Wavelength
NCO:OH	isocyanate equivalents/macrodiol equivalents ratio
HS	Hard segment
SS	Soft segment
BDE	Bond dissociation energy
TGA	Thermogravimetric analysis
FTIR	Fourier-transform infrared
SC	Stress cracking

Polyurethanes:

PU	Polyurethane
PUU	Poly(urethane-urea)
PEsU	Poly(ester-urethane)
PEtU	Poly(ether-urethane)
PEsUU	Poly(ester-urethane-urea)
PEtUU	Poly(ether-urethane-urea)
PBU	Poly(butadiene-urethane)
PIBU	Poly(isobutylene-urethane)
PCU	Poly(carbonate-urethane)

Polyesters:

PEA	Poly(ethylene adipate) [Poly(oxyethyleneoxyhexanedioyl)]
PBA	Poly(1,4-butylene adipate) [Poly(oxybutane-1,4-diyloxyhexanedioyl)]
PCL	Polycaprolactone [Poly(1,7-oxepan-2-one)]
PLA	Poly(lactic acid) [Poly(2-hydroxypropionic acid)]

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Polyethers:

PEG	Polyethylene glycol [Poly(ethylene oxide), Poly(oxyethylene)]
PPG	Polypropylene glycol [Poly(propylene oxide), Poly(oxypropylene)]
PTMEG	Poly(tetramethylene ether) glycol [Poly(tetramethylene oxide), Poly(oxytetramethylene)]
PHMG	Polyhexamethylene glycol [Poly(hexamethylene oxide), Poly(oxyhexamethylene)]
POMG	Polyoctamethylene glycol [Poly(octamethylene oxide), Poly(oxyoctamethylene)]
PDMG	Polydecamethylene glycol [Poly(decamethylene oxide), Poly(oxydecamethylene)]

Polycarbonates:

PC	Polycarbonate
PHMC	Poly(hexamethylene carbonate) [Poly(oxycarbonyloxyhexane-1,2-diyl)]
PHEC	Poly(1,6-hexyl-1,2-ethyl carbonate) [Poly(oxycarbonyloxy(2,2-diethylpropane-1,3-diyl)-oxycarbonyloxyhexane-1,6-diyl)]

Other polymers for the macrodiol part:

PB	Polybutadiene
HTPB	Hydroxyl-terminated polybutadiene
PIB	Polyisobutylene
PIP	Polyisoprene
PDMS	Polydimethylsiloxane [Poly[oxy(dimethylsilylene)]]

Aromatic diisocyanates:

4,4′-MDI	4,4′-Diphenylmethane diisocyanate [1-Isocyanato-4-[(4-isocyanatophenyl)methyl]benzene]
TDI	2,4-Toluene diisocyanate [2,4-Diisocyanato-1-methylbenzene] or 2,6-Toluene diisocyanate [2,6-Diisocyanato-1-methylbenzene], usually a mixture of two at 4:1 ratio

Aliphatic diisocyanates:

HDI	Hexamethylene diisocyanate [1,6-Diisocyanatohexane]
IPDI	Isophorone diisocyanate [5-Isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane]
4,4′-H_{12}MDI	4,4′-Dicyclohexylmethane diisocyanate [1-Isocyanato-4-[(4-isocyanatocyclohexyl)methyl]cyclohexane]
LDI	L-Lysine ethyl ester diisocyanate [Ethyl (2S)-2,6-diisocyanatohexanoate]

Chain extender:

ChEx	Chain extender
EG	Ethylene glycol [Ethane-1,2-diol]
EDA	Ethylenediamine [Ethane-1,2-diamine]
1,4-BDO	1,4-Butanediol [Butane-1,4-diol]
1,3-BDO	1,3-Butanediol [Butane-1,3-diol]

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Stabilization:

CB	Carbon black
CNTs	Carbon nanotubes
ESIPT	Excited-state intramolecular proton transfer
CB-A	Chain breaking acceptors
CB-D	Chain breaking donors
PDA	Polydopamine
PPD	*p*-Phenylenediamine [Benzene-1,4-diamine]
IPPD	*N*-Isopropyl-*N′*-phenyl-*p*-phenylenediamine [1-*N*-Phenyl-4-*N*-propan-2-ylbenzene-1,4-diamine]

***In-vivo*/*in-vitro* oxidation:**

MIO	Metal ion oxidation
MDM	Monocyte-derived macrophage
FBGCs	Foreign body giant cells

Other chemicals/solvents/simulated body fluids:

BPA	Bisphenol A [4,4′-(Propane-2,2-diyl)diphenol]
PBS	Phosphate buffer saline
ABS	Acetate buffer solution
TBS	Tris-buffered saline
LA	Lactic acid [2-Hydroxypropanoic acid]
THF	Tetrahydrofuran [Oxolane]

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1. Introduction

Polyurethanes (PUs) are a group of polymers that are highly versatile due to the range of chemistries that can be employed in their synthesis, resulting in a multitude of structures and properties. In particular, PU elastomers have been used in a wide variety of end-use markets such as footwear, transportation, wheels and tires, construction, machinery, sporting, electrical and electronic, marine, and other speciality applications [1, 2]. In addition, PU elastomers have a combination of excellent mechanical, physical and chemical properties and exceptional biocompatibility [3-5]. Therefore, these materials have also been popular in biomedical applications, especially in durable cardiovascular devices such as blood bags, vascular catheters and grafts, ventricular assist bladders, artificial heart diaphragms, the total artificial heart, arteriovenous (AV) shunts, pacemaker leads, and leaflet valves [3, 4, 6, 7]. Moreover, recent research has shown that PU elastomers can be designed to exhibit a shape memory behavior [8-13], electrical conductivity [14] or dielectric properties [15], thus presenting an even greater range of potential applications.

However, PU elastomers, like other organic polymers, are not indefinitely stable under all conditions. In some circumstances, they may undergo reactions that lead to a loss in desirable properties (such as elasticity, tensile strength, color, and shape). This change in properties is often related to degradation or ageing [16]. The most apparent outcome of degradation is to shorten the service lifetime of the PU material. More importantly, the degradation of PU elastomers may cause serious issues in certain circumstances. In marine applications, for example, PU elastomers with high flexibility and acoustic transparency are often used as encapsulation materials for underwater sonar devices [17-19]. However, the strong UV, heat, ozone, and stress conditions encountered during daily use could significantly alter the chemistry and properties of the PU elastomers, and eventually cause the materials to crack and fail. The early failure of the material may not only cause the devices

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to malfunction, but also risk the safety of a vessel's crew. As another example, the biodegradation of PU elastomers in the body usually involves hydrolysis, chemical degradation, enzymatic degradation, oxidation, and calcification [3, 20, 21]. The potential for catastrophic failure that PU elastomers could experience when implanted in the corrosive environment of the human body has become a major roadblock for medical application of these polymers. Therefore, how the degradation processes of PU elastomers can be significantly slowed for this important class of polymers is a relevant and interesting topic both scientifically and in practice.

This review is focused on the degradation of PU elastomers under the influence of various environmental factors (such as UV light, heat, ozone, water, inorganic ions and salts, organic chemicals, acids, alkalis, enzymes, and reactive oxygen species) and explores how the resistance to such degradation can be enhanced through chemistry and engineering. The mechanism of each type of degradation and the enhanced stability of PU elastomers against a wide range of usage conditions for both general and biomedical materials are discussed. It is hoped that this comprehensive review will not only provide essential knowledge related to the science and engineering of durable PU elastomers, but also provide guidance for future research into novel PU materials with desired structures and properties combined with exceptional stability.

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2. Polyurethane chemistry

2.1. General

PU polymers are composed of organic units joined by urethane links. Urethanes are produced by the reaction between an isocyanate (R-N=C=O) and an alcohol (R′-OH) [22] (**Error! Reference source not found.**). When the alcohol is a diol or macrodiol, and the isocyanate functionality comes

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from diisocyanates or polyisocyanates, PU polymers can be synthesized. The simplest formula for a PU is linear and is represented in **Error! Reference source not found.**.

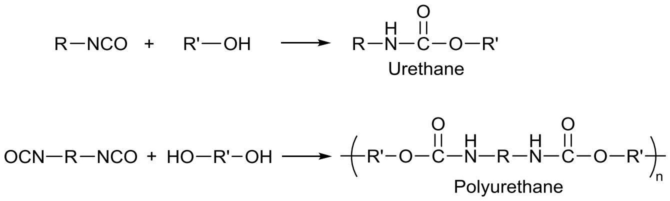

Figure 1. Urethane and polyurethane resulting from the reaction between an isocyanate and an alcohol.

For the synthesis of PU elastomers, the reaction of a diisocyanate (either aromatic or aliphatic), a macrodiol (a polymer diol), and a chain extender (ChEx; typically a small-molecule diol or a diamine) together results in a copolymer of the macrodiol sequence, termed the soft segment (SS), and the diisocyanate-ChEx sequence, termed the hard segment (HS) (**Error! Reference source not found.**) [23]. This segmented polymer chain structure leads to a two-phase system and is highly heterogeneous and dependent on the reaction conditions and the reactivity of the components and the use and choice of catalysts [24-26]. The SS is selected to have a glass transition temperature (T_g) sufficiently below the desired service temperature of the PU to deliver the mechanical properties required, whereas the HS has its T_g or melting temperature (T_m) well above the anticipated service temperature of the PU [26, 27].

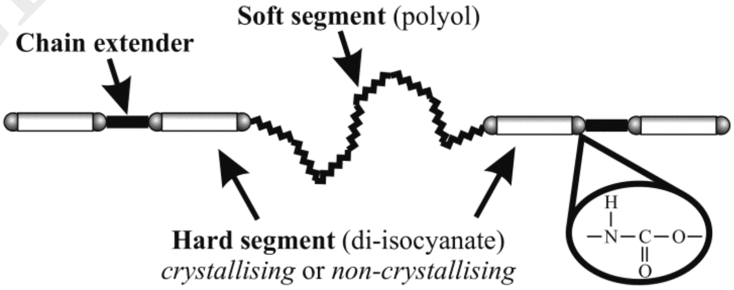

Figure 2. The repeat structure of a typical polyurethane. [23], Copyright 2011 Reproduced with permission from Springer.

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PU elastomers require highly flexible chains in the SS, achieved both through a composition that delivers a low degree of intermolecular interactions, and the presence of physical or chemical crosslinks that prevent sliding of these chains against their neighbors [28]. The crosslinking occurs via the urethane groups, which link the HS and the flexible SS together by means of both covalent (chemical) bonds and hydrogen bonds (physical crosslinks) [28]. Urethane groups are known for their ability to self-associate via hydrogen bonding (through urethane–ester, urethane–ether, and inter-urethane bonding) [29]. By contrast, hydrogen bonding within the HS enhances crystallization and, thus, promotes phase separation between the SSs and HSs [30]. Because of their inherent rigidity as well as this hydrogen bonding, the HSs (either glassy or crystalline) are associated into hard domains acting as physical crosslinks and as filler particles within the rubbery SS matrix [29]. On the other hand, chemical crosslinking can be introduced via tri- or multi-functional constituents (isocyanate, ChEx, and macrodiol) [29].

Due to the incompatibility (different polarity and chemical structure) between the HS and SS, phase separation (immiscibility between the HS and SS) occurs in most PUs [29]. The degree of phase separation and domain formation depends on the HS and SS nature and sizes, the type of the diisocyanate and macrodiol used to produce prepolymers, the type of the ChEx, and the molecular mass (*M*) of the SS. Phase separation is also influenced by the hydrogen bond formation between the urethane linkages, the manufacturing process, and the reaction conditions. In particular, annealing favors stronger hydrogen bonding and increases the PU melting point as it leads to greater uniformity of the polymer network [29].

In the following subsections, different macrodiols, isocyanates and ChEx, especially those involved in the discussion of PU degradation and stabilization in this review, are presented.

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2.2. Macrodiols

The final PU structure depends largely on the macrodiol used, which reacts with the isocyanate initially during the PU synthesis to form the flexible segments [24]. The macrodiols used for manufacturing PU elastomers typically include those with a main chain formed from polyesters, polyethers, or polyalkyls (**Error! Reference source not found.**), for which the T_g's are below room temperature ($T_g = -70$ °C to -30 °C), and are low-melting-point solids or liquids [31, 32]. Mixed copolymer diols containing polyethers and/or polyesters have also been used to form the SS [23]. Polycarbonate (PC) has also been reported for the synthesis of PU elastomers, particularly for biomedical applications [33-40]. To prepare elastomeric materials, the PC diols used are normally aliphatic with long hydrocarbon chains between carbonate groups, such as poly(hexamethylene carbonate) (PHMC) and poly(1,6-hexyl-1,2-ethyl carbonate) (PHEC) diols (**Error! Reference source not found.**). In contrast, the most common bisphenol A (BPA)-based PC has a high T_g (147 °C), and thus is not suitable for making PU elastomers. Also, importantly, this type of PC shows unsatisfactory photo- [41, 42], thermal [43, 44], and hydrolytic [43, 45] stability.

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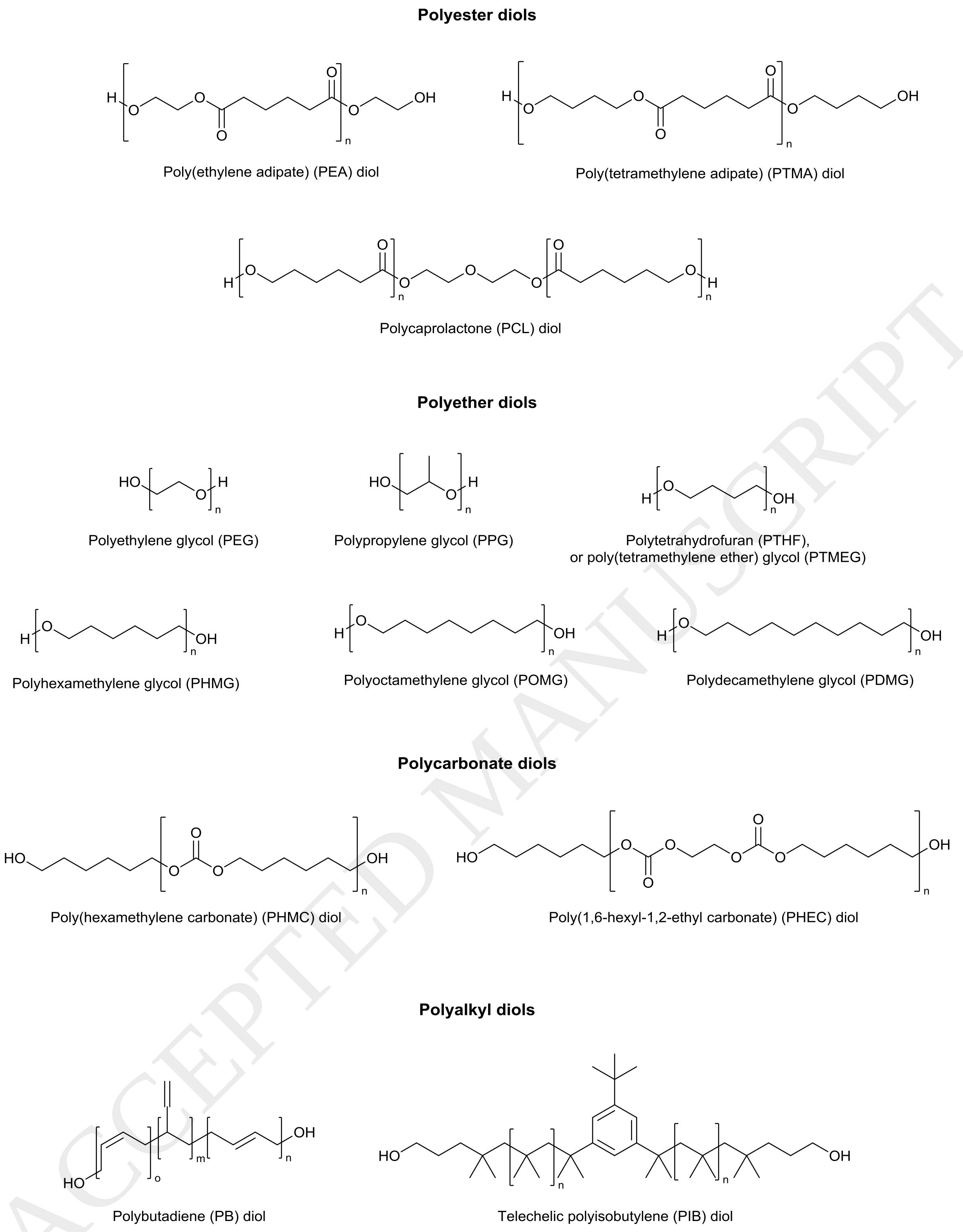

Figure 3. Typical macrodiols used in polyurethane elastomer synthesis. The telechelic polyisobutylene diol is a form of polyisobutylene diol synthesized from 1-tert-butyl-3,5-bis(2-chloropropan-2-yl)benzene and isobutylene. [46].

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Error! Reference source not found. shows some commercial PU elastomers synthesized using different macrodiols, especially for biomedical applications. These commercial products will be referred to in the following sections.

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Generally, polyester-based materials are selected for high strength, and tear, chemical and heat resistance. In contrast, polyether-based materials are selected for low-temperature flexibility, high humidity conditions, and resistance to attack by fungi and bacteria [47-49]. Segregation occurs to a higher degree in the polyether-based elastomers than in the equivalent polyester-based samples [50]. In other words, phase mixing is greater in poly(ester-urethane)s (PEsUs) than poly(ether-urethane)s (PEtUs). This is because urethane NH-ester carbonyl hydrogen bonds are stronger than urethane NH-ether oxygen bonds, as the ester carbonyl group has higher polarity [23, 31]. With the weaker interchain forces, polyether PUs have inferior physical properties [51, 52], although they possess a superior hydrolytic stability [31, 52-54]. The T_g values of PEsUs are also higher than those of PEtUs [52]. Polycaprolactone (PCL) polyesters are considered to be a good compromise, since they allow for elastomers to be synthesized that have both excellent physical properties and hydrolytic stability. Poly(carbonate-urethane)s (PCUs) based on PHMC also display a higher degree of phase mixing compared to PEtUs [55]. The rigidity of carbonate chains also contributes to the increased (although less elastic) mechanical properties and hydrolytic stability compared with PEtUs [56].

Polybutadiene (PB) also offers superior hydrolytic stability to polyesters. Nonetheless, PB is soft and results in PUs with poorer mechanical properties [57-61]. PB is also thermally oxidizable (unless hydrogenated) [62].

Poly(isobutylene-urethane)s (PIBUs) are promising, especially for biomedical applications, due to their hydrolytic and oxidative stability [46, 63-82]. However, the complexity of, and associated

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high costs for, the synthesis of hydroxyl-terminated polyisobutylenes PIBs have significantly limited their large-scale exploitation [71].

The molecular mass (*M*) of macrodiols has a significant impact on the degree of phase separation and properties (including T_g) of PU elastomers [23, 31].

2.3. Isocyanates

Isocyanates represent a class of chemicals that are characterized by high reactivity and versatility. While isocyanates are capable of undergoing many reactions, their significance is usually in the context of their relationship to PU polymerization and structure [62]. During PU synthesis, diisocyanates are responsible for chain extension and the formation of urethane linkages or a variety of crosslinks by further reaction [24]. The HSs are usually formed by the reaction of a diisocyanate with a glycol or a diamine, although occasionally other ChExs are employed [31]. The properties of HSs determine the interchain interactions in the elastomers to a large extent and so determine the network structure in these materials [31]. The HSs may act as a reinforcing filler or physical crosslinking (hydrogen bonding) site [83].

The most important diisocyanates used in PU elastomer manufacturing are shown in **Error! Reference source not found.**. These diisocyanates can be divided into two groups based on their carbon skeletons: aromatic diisocyanates and aliphatic diisocyanates. Aromatic isocyanates are more reactive than aliphatic diisocyanates [29, 84].

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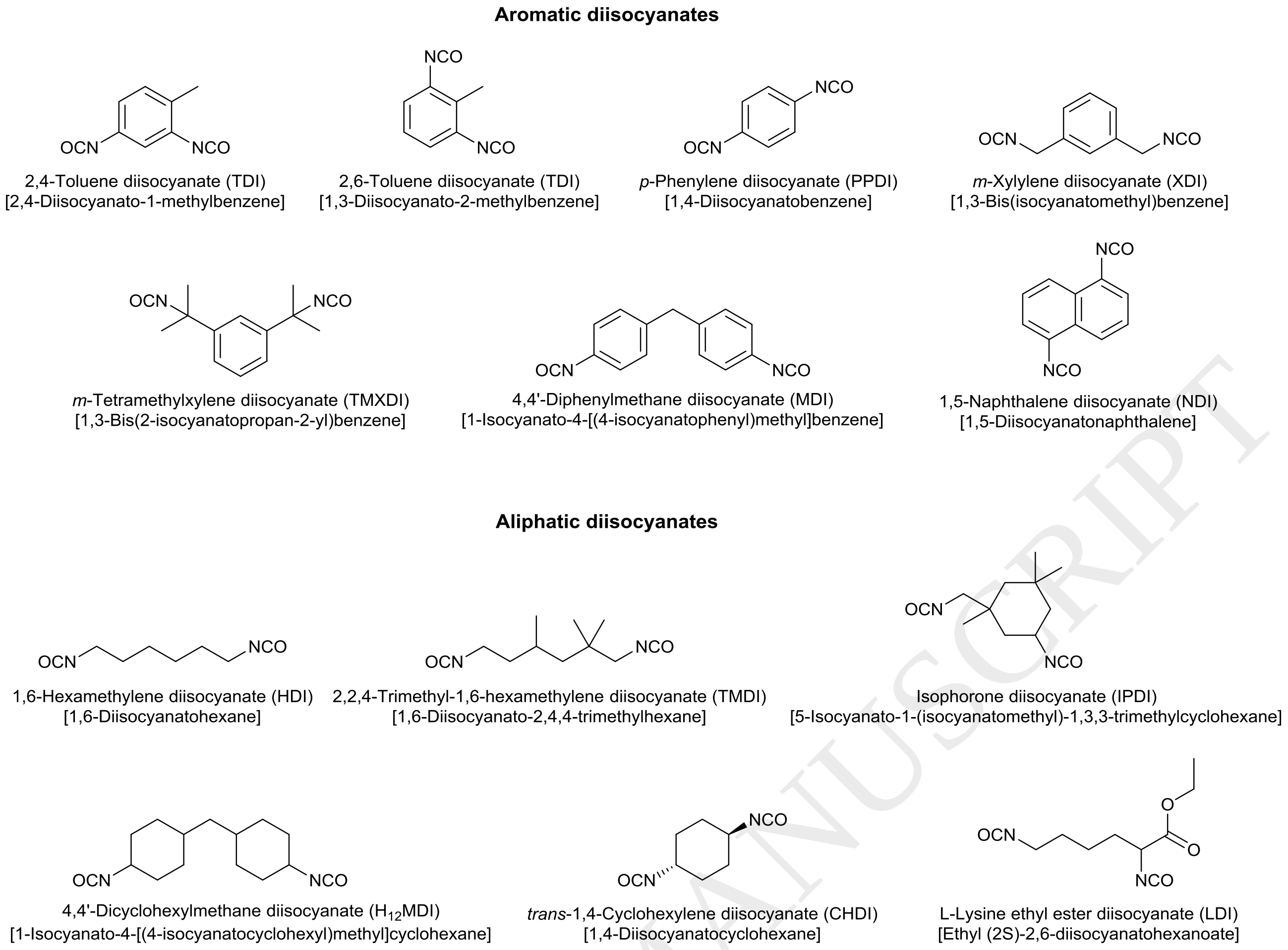

Figure 4. Common diisocyanates used in polyurethane elastomer synthesis.

2.4. Chain extenders

While SSs and isocyanates may make up more than 95% of the polymer volume, very often a low-*M* (< 400 g/mol) component is added that primarily serves as a spacer between neighboring polyisocyanates. The low-*M* diol or diamine that joins diisocyanates together is called the “chain extender” (ChEx) [62]. The ChEx can react with an isocyanate to form the HS, before reaction with a high-*M* SS macrodiol [23, 62]. ChExs typically produce urethane or urea-based HSs, which are highly regular and polar, leading to significant local phase ordering and possibly crystallinity. Without a ChEx, a PU formed by directly reacting a diisocyanate and a macrodiol generally has very poor physical properties and often does not exhibit micro-phase separation [23]. Given this, the

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ChEx structure can have a significant impact on PU properties through its ability to drive phase separation, to complement or interfere with a regular HS structure, and to promote inter-HS hydrogen bonding [62, 85].

Some common ChExs are shown in **Error! Reference source not found.**, with 1,4-butanediol (1,4-BDO) used commonly for elastomer HSs. The ChExs can be categorised into two classes: aromatic diols and diamines, and the corresponding aliphatic diols and diamines. Aromatic ChExs have less reactivity than aliphatic ChExs. Diamine ChExs are much more reactive than diol ChExs [23]. Diol ChExs react with isocyanates to produce urethane groups, whereas diamine ChExs result in urea groups. In this way, PU or poly(urethane-urea) (PUU) can be respectively obtained [62]. Hydroxyl functional ChExs can also serve as crosslinkers. In contrast, secondary amines offer a single isocyanate reaction site and the possibility of maintaining melt processibility [62].

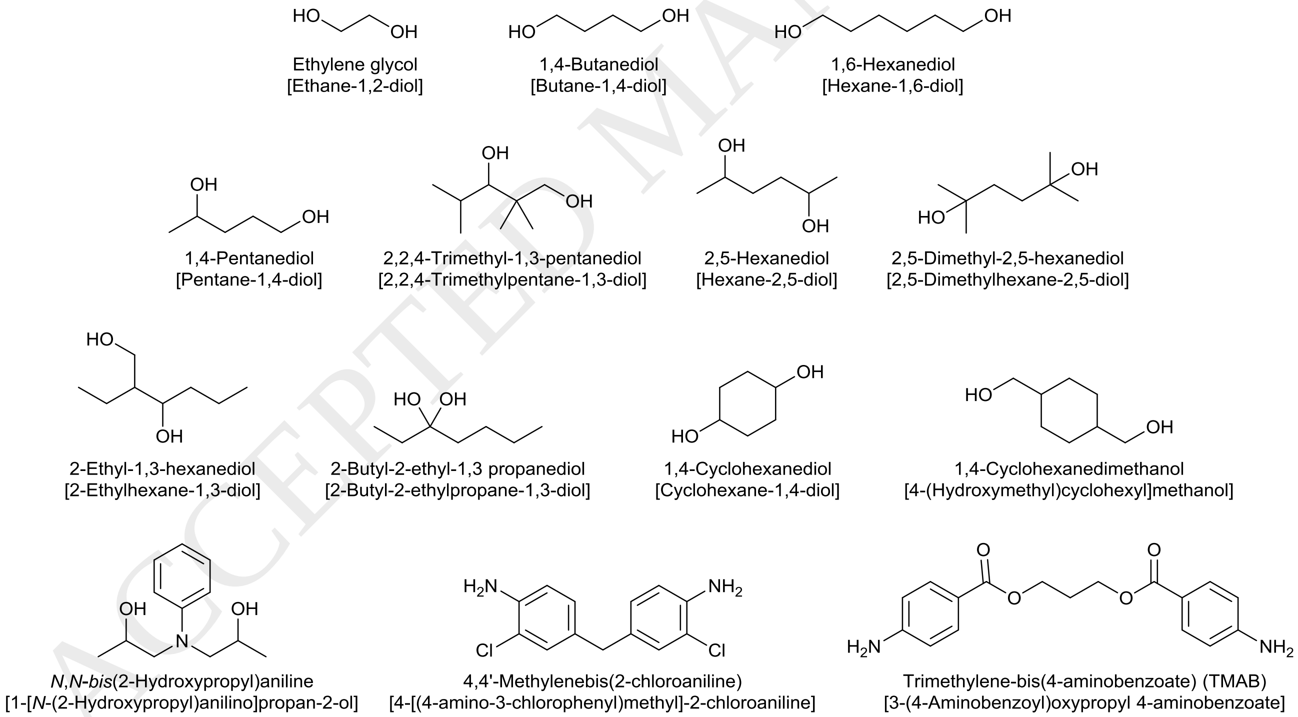

Figure 5. Common chain extenders (diols and diamines) used in polyurethane elastomer synthesis.

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Triols such as trimethylolpropane [2-ethyl-2-(hydroxymethyl)propane-1,3-diol] (TMP) and glycerine can be used in combination with diols. However, strength properties, in particular, tear strength, are reduced [23] when using a higher triol content, while the compression set is decreased [86]. Increasing the triol content can also result in an increase in the T_g and the elastic modulus above the T_g through an increase in the crosslinking density [87].

2.5. Non-isocyanate polyurethanes

Although isocyanate chemistry is the core of traditional PU synthesis, the improper handling of polyisocyanate compounds can cause health issues to exposed PU workers. As a result, there has been a growing interest in non-isocyanate PUs, which can be synthesized from different new routes such as polycondensation, rearrangement, ring-opening polymerization, and polyaddition [88-125]. However, most of the non-isocyanate PU systems developed so far do not offer the advantages of rapid reaction at room temperature from liquid, low-viscosity precursors, industrial viability for both small-scale in-field applications and large-scale industrial applications without generating side-products, and the ability to form elastomeric materials that have a combination of appropriate elongation and tensile strength [99, 103]. While a few non-isocyanate PU elastomers have been reported [94, 96, 98, 99, 109, 111, 113], these new materials have not been fully characterized yet, including their degradation and stability.

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3. Photodegradation and stabilization of polyurethane elastomers

3.1. Photodegradation of polymers

Photodegradation, in the narrow sense, means photolytic degradation occurring in the absence of oxygen. Nevertheless, in most cases, oxygen is present, so a common photodegradation reaction is an oxidation (often referred to as “photooxidative degradation”). In the following text, the term “photodegradation” is used to refer to photoinduced degradation in the broad sense, involving both photolytic degradation and photooxidative degradation, with the general mechanisms of photodegradation of polymers extensively referred to in the literature [126-132].

Photooxidative degradation of polymers, which includes such processes as photooxidation, chain scission, crosslinking and secondary reactions, occurs by free radical mechanisms, similar in many aspects to autoxidation that occurs during thermooxidation. The mechanistic steps for autoxidation, relevant to photo- and thermooxidation in various polymers are shown in **Error! Reference source not found.** [128]. Autoxidation is a free radical-initiated chain reaction, which is slow at the start, generally associated with an induction period, and accelerated with an increase in the concentration of the resulting peroxides [133-139].

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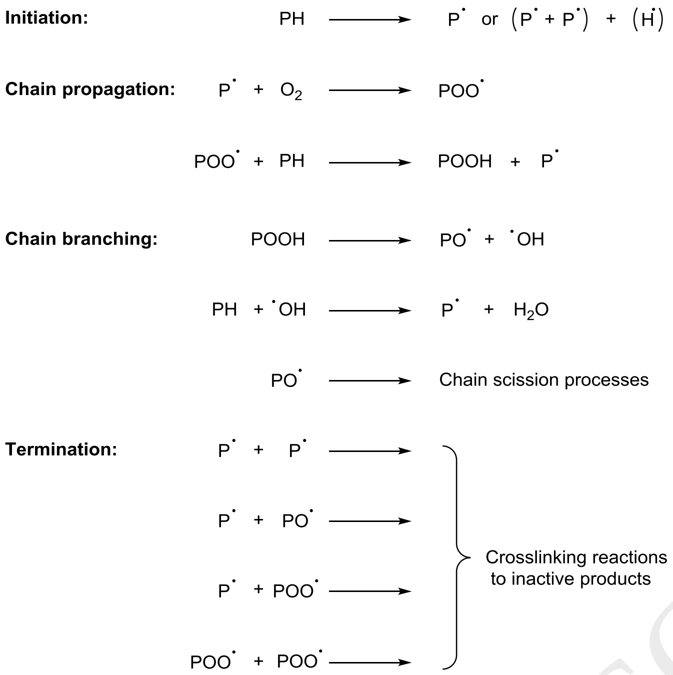

PH	Polymer
P•	Polymer alkyl radical
PO•	Polymer oxy radical (polymer alkoxy radical)
POO•	Polymer peroxy radical (polymer alkylperoxy radical)
POOH	Polymer hydroperoxide
HO•	Hydroxy radical

Figure 6. Mechanistic steps during autoxidation of polymers, relevant to photo- and thermo-oxidation. [128]

Hydroperoxides are formed in a multi-stage process, where alkyl radicals first react with oxygen to form peroxy radicals, followed by abstraction of hydrogen from the polymer backbone [133]. The rate constant for the reaction of most alkyl radicals with oxygen, to form peroxy radicals, is of the order of 10^7–10^9 $\text{L·mol}^{-1}\text{·s}^{-1}$ [140]. The subsequent abstraction of a hydrogen, H, by a peroxy radical, $\text{POO}^\bullet$, requires the breaking of a C-H bond. This reaction is the rate-determining step in autoxidation, with the rate of abstraction decreasing in the following order: hydrogen in the α-position to a C=C double bond (“allyl”) > benzyl hydrogen and tertiary hydrogen > secondary hydrogen > primary hydrogen [133]. Primary and secondary peroxy radicals are more reactive hydrogen abstractors than the analogous tertiary radicals [133, 141], with the most reactive species for hydrogen abstraction

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being acylperoxy radicals [133, 142]. For most common polymers, autoxidation is only propagated as a result of defect structures, predominantly terminal and internal double bonds, which may be formed during the original polymerization procedure and/or the degradation process itself [143]. Additionally, transition metal salts, such as stearates (*e.g.*, from manganese, iron, and cobalt) are shown to be prooxidants for polymers via acceleration of the autoxidation process [144] and therefore should be avoided in PU compositions for better stability.

In photodegradation, photodissociation of chemical bonds (from the singlet or triplet excited states) takes place when the received photoenergy exceeds the bond dissociation energy (BDE), leading to photoinitiation [128, 145, 146]. Both thermal- and photodegradation can also be initiated through the presence of external free radicals ($R^{\bullet}$), which are formed from the thermolysis and/or photolysis of impurities, additives, or photoinitiators (often residual hydroperoxides formed during polymer processing) [128, 145, 146]. In contrast to thermooxidation, photooxidation is often limited to reactions at or near the polymer surface where UV radiation can penetrate [126, 147]. Thus, the concentration of oxidation products, such as hydroxyl and carbonyl groups, varies with depth depending on the diffusion of oxygen and degree of UV penetration [148].

Carbonyl groups accumulate as photooxidation proceeds [149, 150], and these intermediates absorb UV radiation almost four times as efficiently as hydroperoxides [126], and in addition, are considered to be sensitisers for the induced decomposition of hydroperoxides [126, 149]. Although other mechanisms for hydroperoxide sensitization have been suggested, this secondary role of carbonyl groups supports a free-radical, chain-scission mechanism similar to that of thermooxidation [126].

The photochemistry of carbonyl compounds is dominated by Norrish and photo-Fries reactions, which represent two of the most important reactions in the photodegradation of polymers. Norrish reactions describe the photochemistry of ketones and aldehydes, and are subdivided into Type I and II reactions. The Norrish Type I reaction is a photoinitiated carbon-carbon bond cleavage that occurs

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between the α-carbon and the carbonyl of a ketone or an aldehyde to form an alkyl and an acyl radical pair. From this reaction, a variety of products can be formed, including alkanes, alkenes, cyclic acetals, dicarbonyl compounds, and oxetanes [151]. The Norrish Type II reaction is a photoinitiated intramolecular abstraction of a δ-hydrogen of an excited ketone or aldehyde to generate a 1,4-biradical, from which different products can form. These products include alkenes, alkenols, and cyclobutanol [152]. Both types of Norrish reactions are influenced by environmental and structural factors [151, 152]. Depending on the substrate structure, the Norrish Type I and II reactions may occur from the excited singlet (S*) or triplet (T*) states; however the triplet state is much more favored because of its longer lifetime [127, 153].

On the other hand, photo-Fries reactions, or photo-Fries rearrangements, describe the photoinitiated intramolecular rearrangement of phenyl or aryl esters to isomeric acyl phenols or other acyl hydroxyl aromatics via acyl and phenoxy or aryloxy radical pairs [154]. The photo-Fries rearrangement is known to occur via the first excited singlet state [154]. This reaction is affected by the electronic nature of the substrate as well as the reaction environment [154]. Although either *ortho*- or *para*-acyl phenols can be generated, the photo-Fries rearrangement produces *ortho*-acyl phenols as the major products [154].

The longer the UV ray wavelength range, the faster the photoinitiation rate [146]. UV rays ranging from 290–320 nm trigger photooxidation by photolysis of hydroperoxides and Norrish reactions of ketones [146]. α-Diketones derived from further oxidation of the ketones, for example, initiate photooxidation at a surprisingly higher rate under UV irradiation above 350 nm [146]. UV radiation in the range between 320–350 nm also participates in photoinitiation of α,β-unsaturated carbonyls (-C=C-CO-) in addition to the above-mentioned oxidation products, as a result of which the initiation rate is approximately the average between the rates for the above two wavelength ranges [146].

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Temperature can alter the kinetics of photodegradation via its effect on the ability of the free radicals formed to separate, which depends strongly on their mobility in a polymer matrix or solution [155]. Reactions that can be considered to be associated with caged radicals, such as the photo-Fries reaction, require very little free volume and can be expected to be quite efficient in solid polymers below the T_g, whereas photochemical processes such as the Norrish Type II process are generally substantially reduced in glassy polymers below the T_g [155].

In the following sections, the details of photodegradation mechanisms (involving photo-Fries and Norrish Types I and II reactions) will be discussed with reference to PU elastomers synthesized with specific macrodiols, isocyanates and ChExs.

3.2. Photodegradation of polyurethane elastomers

3.2.1. Photodegradation of urethane linkages

The photodegradation mechanisms for aliphatic and aromatic PUs are different [156]. In this section, their mechanisms of degradation will be discussed in detail along with factors that affect the photostability of the urethane groups.

3.2.1.1. Photodegradation of aliphatic urethane linkages

The photodegradation of aliphatic PUs is considered to be similar to that of other polymers such as polyamides (**Error! Reference source not found.**). The reactions that can occur in aliphatic PUs during photodegradation are shown in **Error! Reference source not found.**. Firstly, random chain scission occurs via a Norrish Type I reaction. This photolytic reaction generates free radicals that then abstract hydrogen from the methylene (-CH_2-) groups, followed by the formation of a polymer peroxy radical ($PO_2^{\bullet}$) and polymer hydroperoxide (POOH). UV-induced cleavage of POOH leads to

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the formation of a polymer oxy ($PO^\bullet$) radical, with either β-scission occurring, or the formation of hydroxyl group (POH) via abstraction hydrogen. Both reactions lead to the formation of alkyl radicals. Termination via reaction of different radicals ($P^\bullet$, $PO^\bullet$, and $PO_2^\bullet$) with each other causes crosslinking [156].

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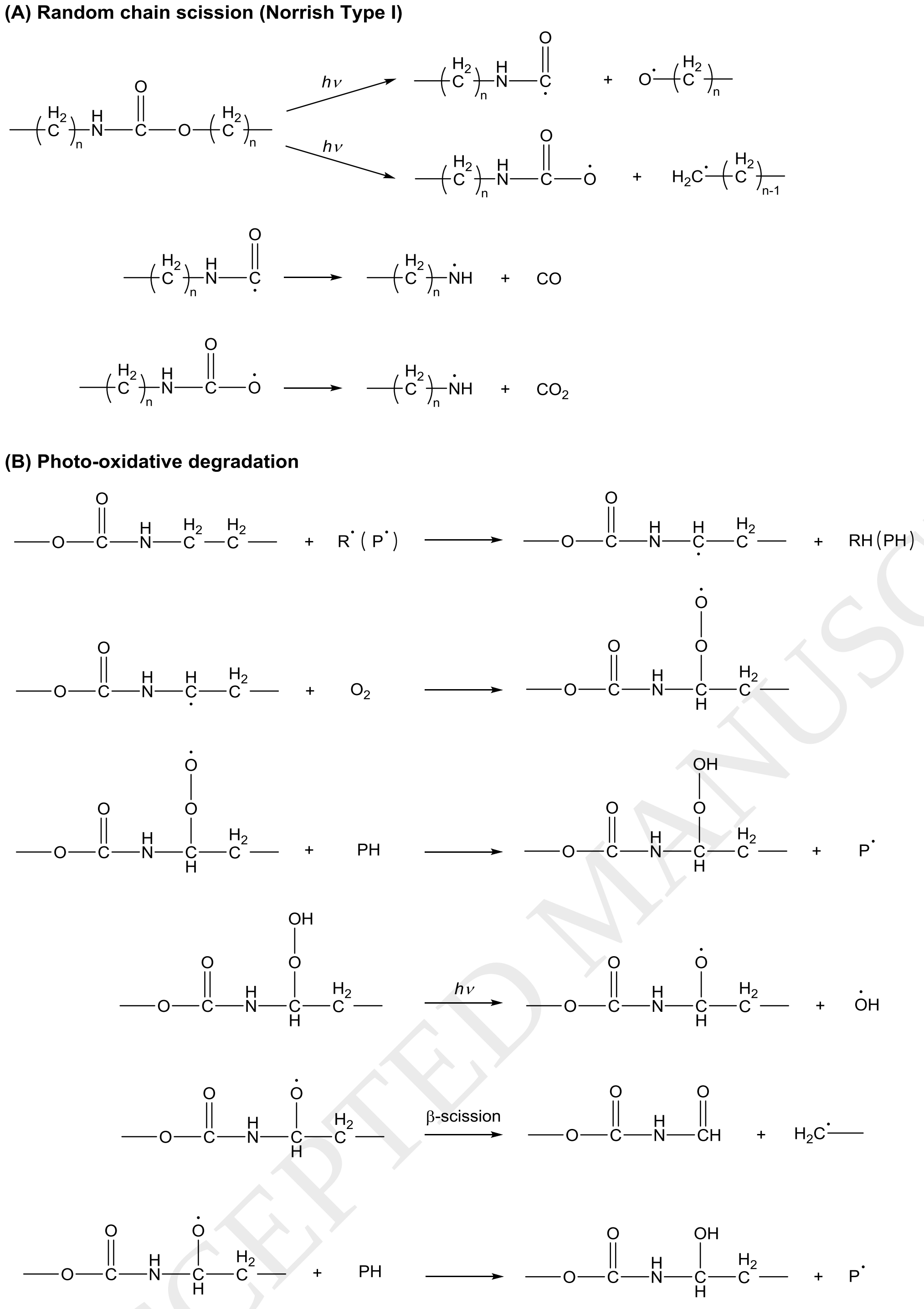

(A) Random chain scission (Norrish Type I)

(B) Photo-oxidative degradation

Figure 7. Photodegradation of an aliphatic polyurethane (R˙ indicates a radical; P˙, a polymer radical; PH, a hydrogen-containing polymer). [156]

Wilhelm and Gardette [157] studied the photooxidation mechanism of aliphatic PEsUs and concluded that long (λ >300 nm) and short (λ = 254 nm) wavelengths of UV irradiation could introduce different routes of photodegradation. Photodegradation that occurs at wavelengths greater

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than 300 nm is relevant to terrestrial conditions (typical outdoor exposure), with degradation at 254 nm being relevant only to artificial exposure and conditions experienced in space (above the ozone layer). Direct homolysis of the urethane linkage was shown to occur at short wavelength (λ = 254 nm), but not at longer wavelengths (>300 nm). Three possible pathways for photoscission were identified, which involve the homolysis of C-N and C-O bonds (**Error! Reference source not found.**). As in the case of polyamides, the scission of C-N bonds leads to the formation of two radicals (I and II) (**Error! Reference source not found.**a). Radical I is the precursor of an amine and radical II evolves by the loss of carbon dioxide, leading to the formation of an alkyl radical (III). Reaction of radical III with oxygen ultimately leads to the formation of several products, including carboxylic acids and hydroxylated products, as well as peresters. Scission of the C-O bond leads to radicals IV and II (**Error! Reference source not found.**b). Radical IV can decarboxylate to form radical V, with the scission of C-C bonds leading to radicals III and VI (**Error! Reference source not found.**c).

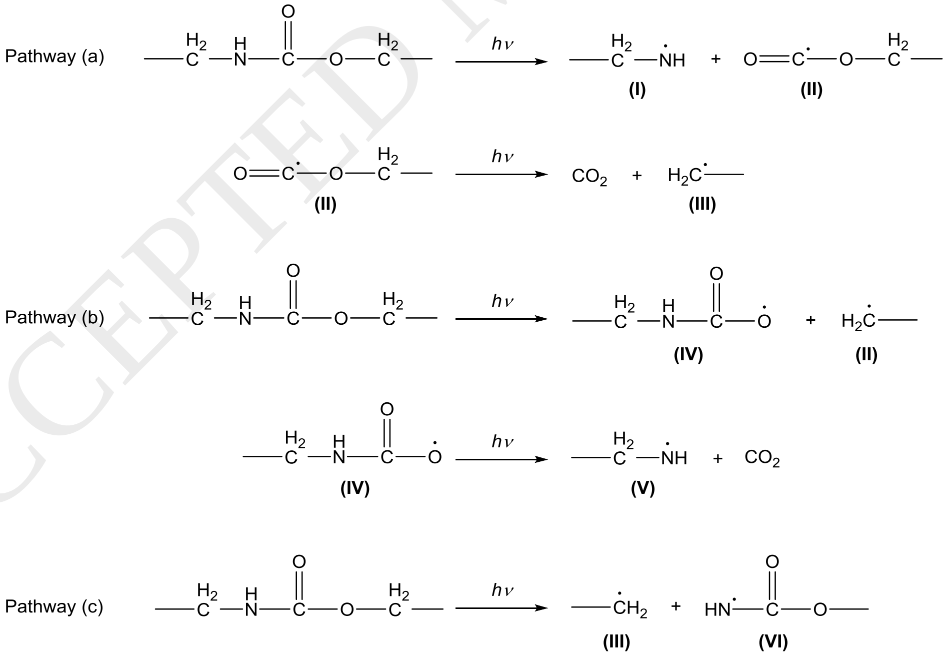

Figure 8. Photoscissions of the urethane linkage at λ = 254 nm. [157], Copyright 1997. Adapted with permission from Elsevier Ltd.

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3.2.1.2. Photodegradation of aromatic urethane linkages

The photodegradation mechanism of aromatic PUs is generally much more complex than that of aliphatic PUs, and the products obtained are difficult to separate and identify, but it has been more extensively studied [157-164]. Compared to PUs with aliphatic diisocyanates, those with aromatic diisocyanates are more unstable with respect to light [62]. As shown in **Error! Reference source not found.**, for either diphenylmethane diisocyanate (4,4′-MDI)- or 2,4-toluene diisocyanate (2,4-TDI)-based PUs, the photo-Fries rearrangement of the phenyl group can occur during irradiation with wavelengths < 340 nm. On the other hand, during irradiation especially with wavelengths > 340 nm, quinone imides can be formed from the phenyl group. The quinoid structures are considered to be responsible for the typical yellow coloration observed during photodegradation of aromatic PUs [157-164], although other factors may also contribute to the yellowing such as the photo-Fries reaction [157, 161]. The color change of aromatic PUs can be correlated with photodegradation by a relative increase in the concentration of carbonyl groups [164]. Further irradiation results in the random chain scission of aromatic PUs, mainly by Norrish Type I reactions (**Error! Reference source not found.**). As for aliphatic PUs, the photooxidative degradation of aromatic PUs occurs in a very similar manner to that of other polymers such as polyamides (**Error! Reference source not found.**) [156].

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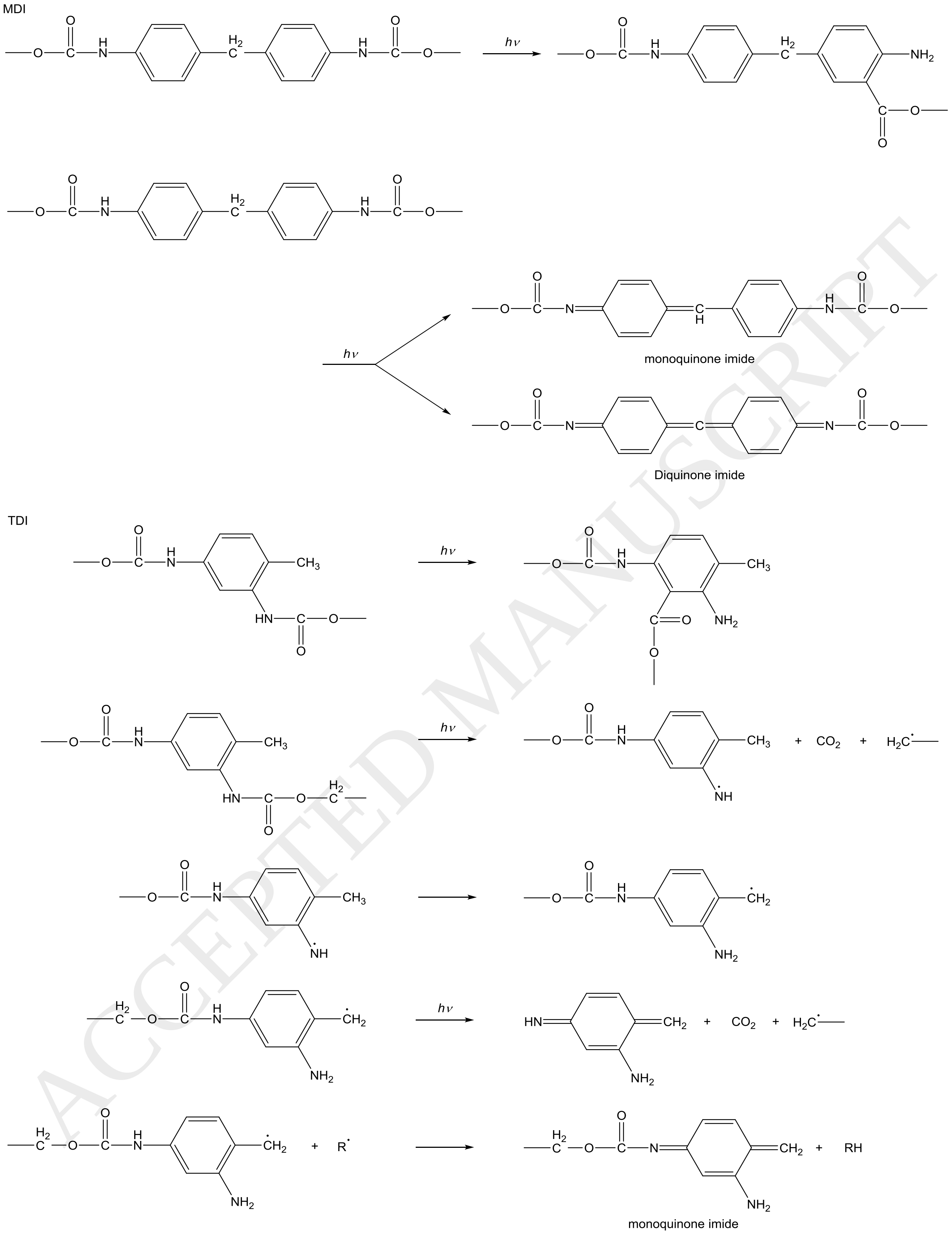
(A) Photo-Fries reaction and the formation of quinone imides



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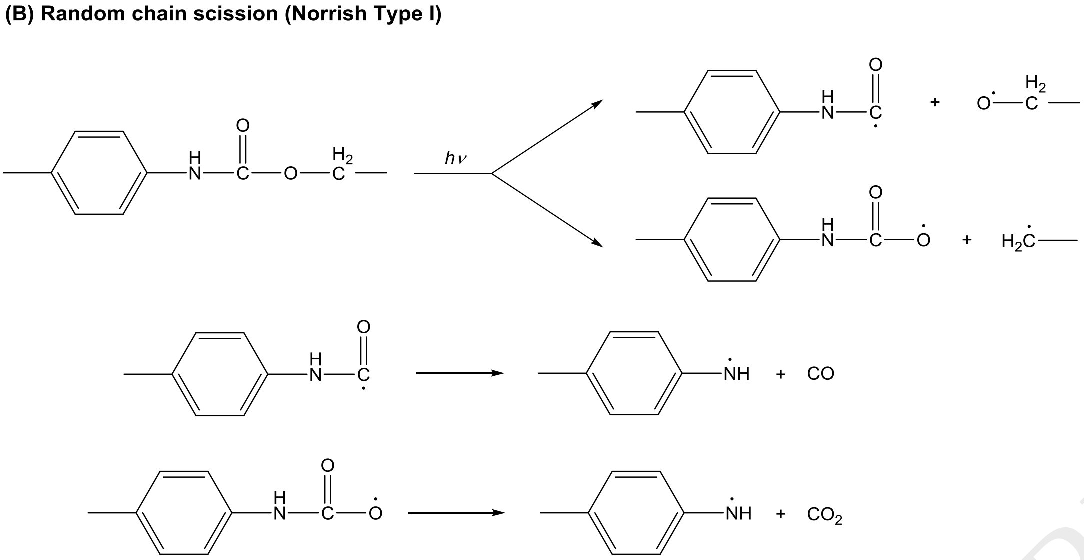

Figure 9. Photodegradation of aromatic polyurethanes. [156].

At shorter wavelengths, besides the photo-Fries rearrangement, the photoinduced oxidation of aromatic PUs may still occur. However, when aromatic PUs are under UV irradiation at wavelengths shorter than 330–340 nm, the photo-Fries rearrangement may interfere with, and thus inhibit, the photooxidation [165].

Rek and Bravar [159] have studied the UV-degradation mechanism of a PU synthesized from 4,4′-MDI and the polyester of adipic acid [hexanedioic acid] and ethylene glycol (EG) [ethane-1,2-diol], which is shown in **Error! Reference source not found.**. While initial irradiation led to the formation of quinoid structures as discussed above, further irradiation resulted in the homolytic scission of bonds in the urethane groups and the creation of free radicals. The decomposition and simultaneous recombination of the free radicals are responsible for the creation of the azo (II), amino (III), and carbodiimide (IV) structures. Along with this, the addition of oxygen to the free radical gives hydroperoxides, the decomposition of which leads to a carbonyl-containing structure (I).

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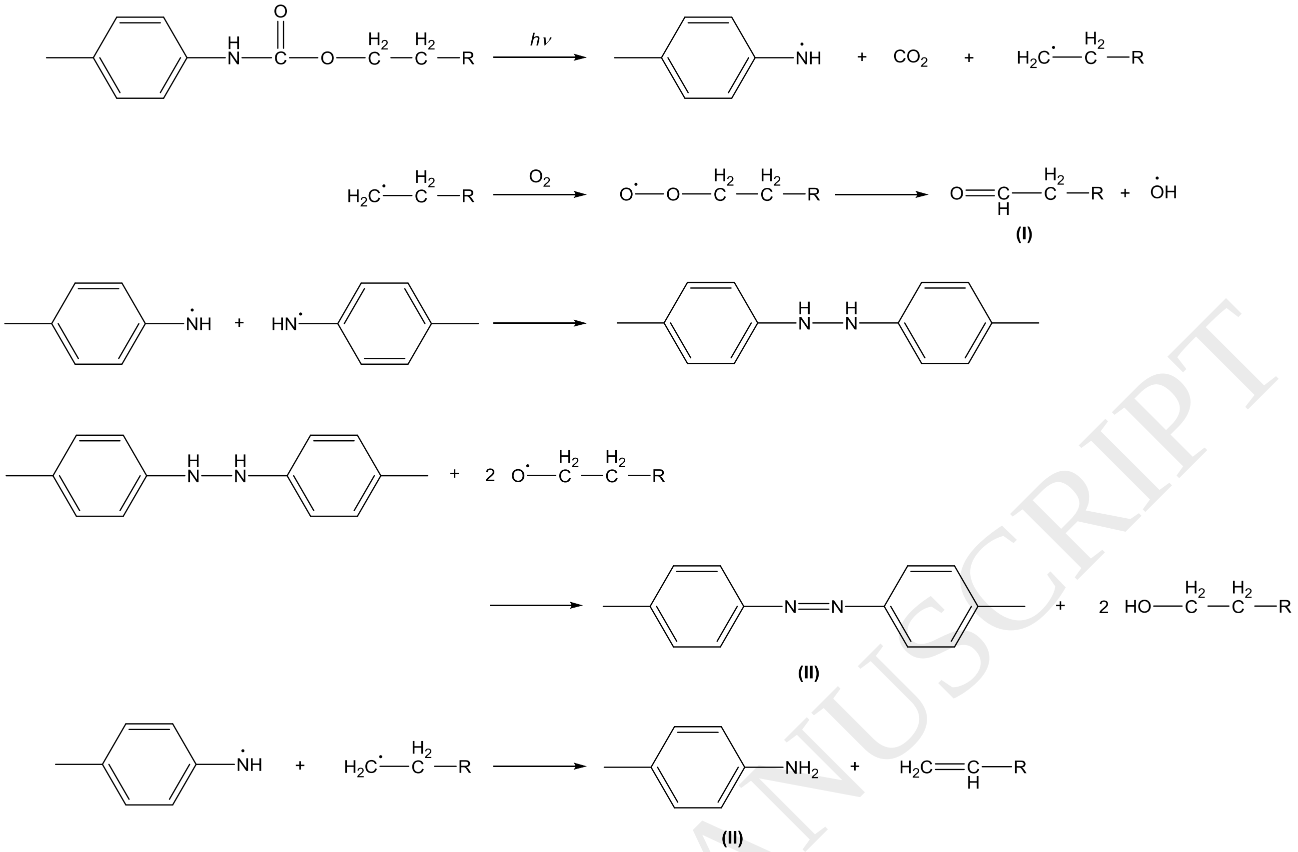
Pathway (a)



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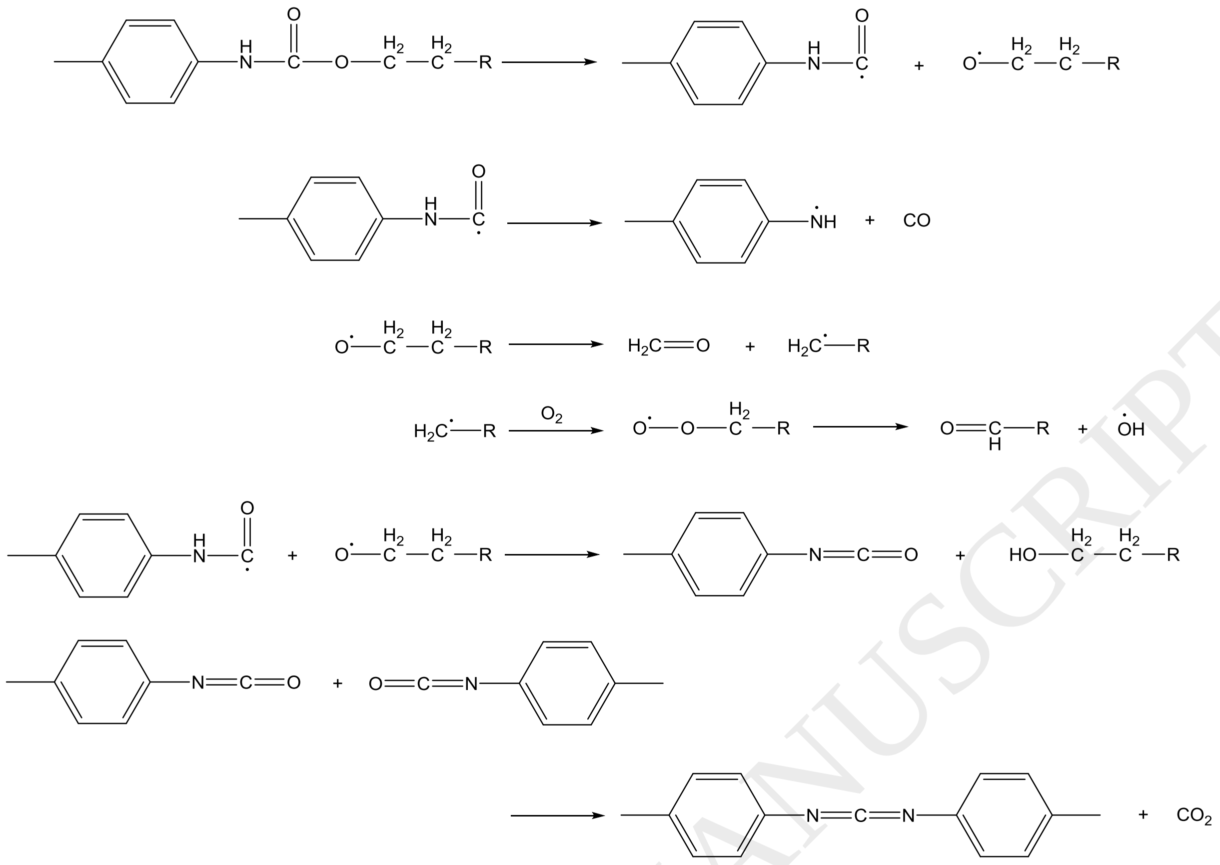
Pathway (b)



(IV)

Figure 10. Photoscission of an aromatic urethane linkage. [159].

3.2.1.3. Factors affecting the photostability of the urethane linkage

The photostability of some common PUs follows the order: 4,4′-MDI < 2,4-TDI < hexamethylene diisocyanate (HDI) [156, 162]. Due to their aromatic isocyanate structures, which are responsible for the formation of quinoid chromophores that are the main causes of yellowing, 4,4′-MDI- and 2,4-TDI-based PUs can experience rapid yellowing during photoageing. Good weatherability of PUs can be hindered by aromatic ring structures, and entirely aliphatic polyisocyanates have been developed for better photostability [23, 62]. PUs based on HDI and 4,4′-dicyclohexylmethane diisocyanate (4,4′-H_{12}MDI), which are aliphatic isocyanates, show less or no coloration under UV exposure [162, 166]. In a patent [167] describing non-yellowing PU adhesives,

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it was claimed that the isocyanate compound used can essentially be any nonaromatic, cyclic or linear aliphatic organic isocyanate compound having an isocyanate functionality of two to four, preferably from two to three.

For aromatic PUs, an increase in the HS content (by means of increasing the diisocyanate and ChEx content, or decreasing the macrodiol *M* can reduce the photodegradation efficiency [168]. In particular, the extent of photodegradation is inversely dependent on the degree of hydrogen bonding in the aryl carbamate groups in the PU backbone [168].

It has been proposed that the limited local mobility resulting from an increased HS content might inhibit the diffusion of oxygen for the photooxidation of PUs [168]. The flexibility of the HSs can be adjusted by altering the length of ChEx used, the crystallinity, and the temperature during photoageing. The photodegradation of aromatic PUs will become less efficient with the use of shorter ChExs, higher crystallinity of the HSs (which can be achieved by annealing), and a temperature that is below the T_g, all of which can decrease the flexibility of HSs [169, 170]. Again, the increased stiffness and crystallinity of the polymer chains may inhibit the oxygen diffusion that is required for photooxidation.

In segmented PUs, the interaction between HSs and SSs makes both the crystallinity and the hydrogen bonding in HSs decrease. Therefore, elastomeric PUs, which have a segmented structure, are more prone to photooxidation than non-segmented PUs (which are prepared simply by reacting a diol and a diisocyanate) [171].

The photostability of urethane linkages can be affected by that of SSs (discussed further in the next section), with the magnitude of the photooxidation of the urethane linkage being higher in PEtUs than in PEsUs [171]. This is due to the highly oxidizable ether group being able to induce photooxidation of the urethane group. In addition, Wilhelm et al. [161] found that the yellowing that results from the formation of quinoid structures is increased as the polyether content increases. This is because the numerous radical species formed by the oxidation of the polyether segments can

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induce oxidation of the aromatic urethane segments by hydrogen abstraction on the central methylene carbon atom of 4,4′-MDI [161].

3.2.2. Photodegradation of the macrodiol component (soft segments)

In this section, the photodegradation mechanisms of different types of SSs will be discussed. These include polyester-, polyether-, and PB-based macrodiols, which are common macrodiols used for the synthesis of PU elastomers. PIB-based macrodiols will also be discussed, considering their saturated chemical structure in comparison with the unsaturated backbone of PB, which makes them promising for the preparation of PUs with better photostability. Other factors that influence the photostability of the macrodiol component will also be discussed.

3.2.2.1. Photodegradation of polyester soft segments

Polyester SSs are rather photostable, and thus the oxidative degradation of PEsUs mostly results from the oxidation of the urethane segments (especially those based on aromatic diisocyanates) [161]. However, Wilhelm and Gardette [157] found that UV irradiation, especially at a short, non-terrestrially relevant wavelength (λ = 254 nm), can provoke the decarboxylation of the polyester segments of an HDI-based PEsU as shown in **Error! Reference source not found.**. In a study of the photodegradation (λ = 300 nm) of a PU synthesized from poly(ethylene adipate) (PEA) diol (M = 2000) and 4,4′-MDI with 1,3-butanediol (1,3-BDO) as the ChEx, alkene group-containing products were found from the decomposition of the aliphatic ester structure, which may be due to Norrish Type II reactions (**Error! Reference source not found.**) [163, 164].

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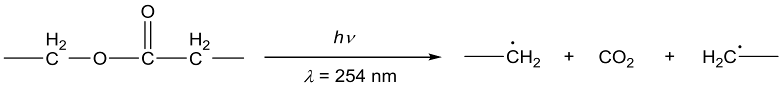

$$-CH_2-O-C(=O)-CH_2- \xrightarrow[\lambda = 254\ nm]{h\nu} -\dot{C}H_2 + CO_2 + H_2\dot{C}-$$

Figure 11. Chain scission of polyester segments in polyurethanes during photodegradation at short UV wavelength (λ = 254 nm). [157].

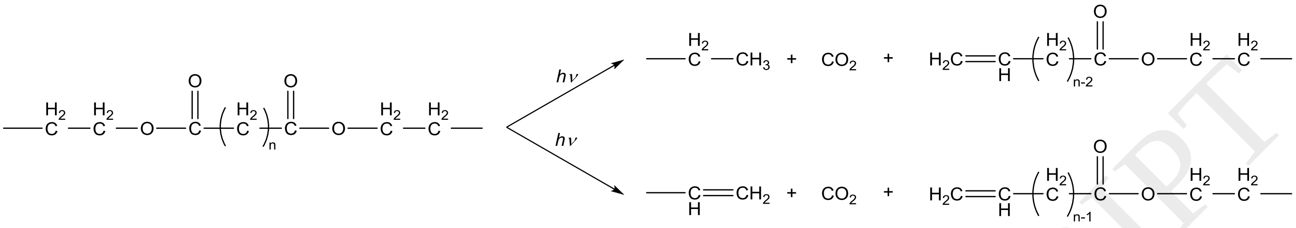

Figure 12. Chain scission of the aliphatic ester structure during polyurethane photoageing. [164], Copyright 2009 Adapted with permission from Elsevier Ltd.

3.2.2.2. Photodegradation of polyether soft segments

Polyether SSs are very sensitive to photochemical oxidation. The photodegradation of PEtUs can lead to a complete loss of all of the infrared absorption bands from both the ether groups and the products formed by photooxidation of the ether groups [172], with the final degradation products being low-*M* substances such as ethylene, formates, and carboxylic acids [172, 173].

The photodegradation of poly(tetramethylene ether) glycol (PTMEG) in PUs has been carefully studied by Wilhelm et al. [161, 172], with the related mechanism shown in **Error! Reference source not found.**. According to their studies, the photoinduced oxidation of PTMEG leads to the formation of secondary hydroperoxides. The decomposition of these hydroperoxides results in the formation of an alkoxy radical (I). The main route of decomposition of this radical (I) is a β-scission reaction, which leads to the formation of formates and an alkyl radical (II) (**Error! Reference source not found.**(A)).

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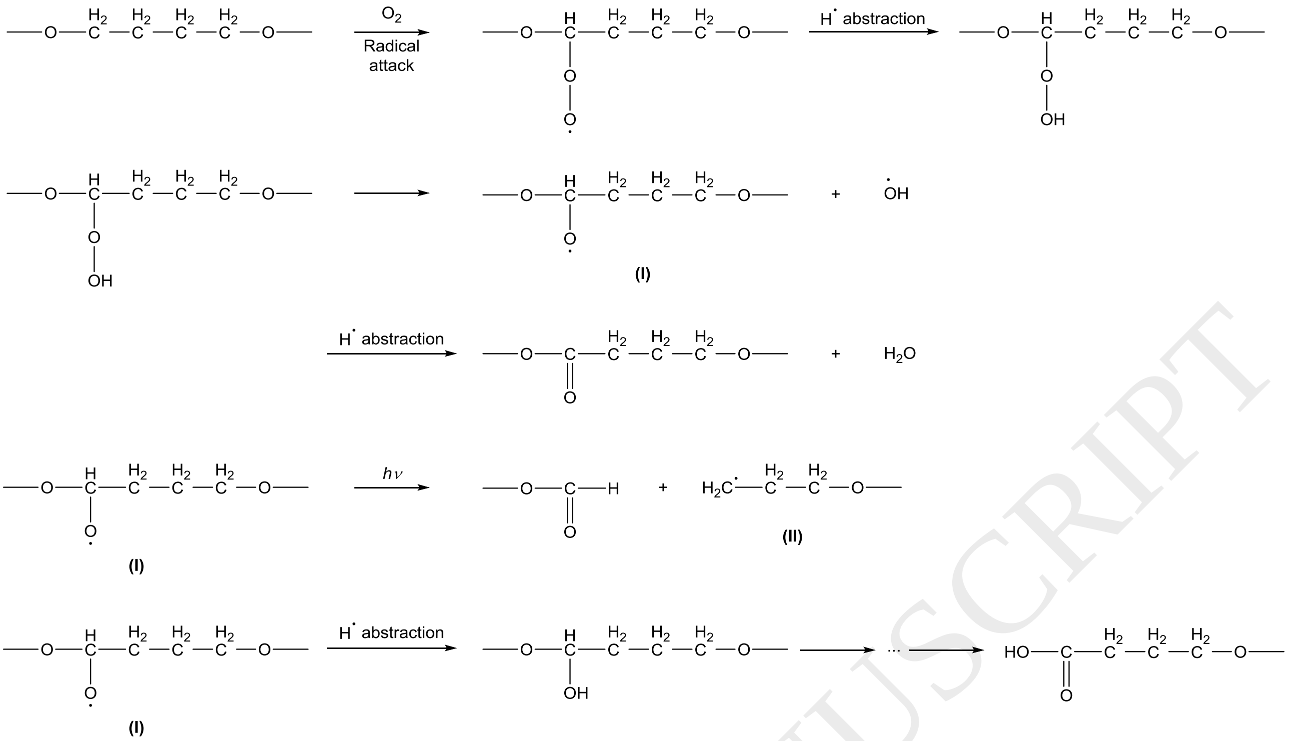
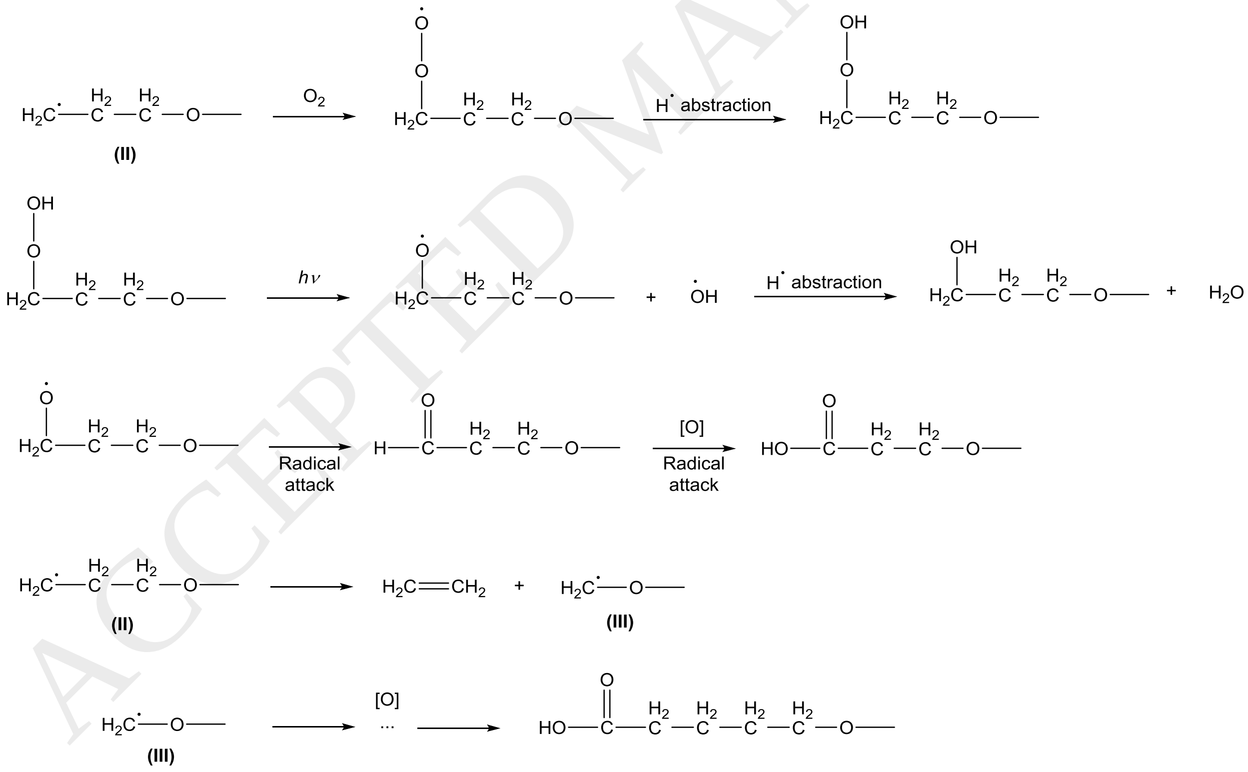
(A) Intial degradation of the polyether sequence



(B) Subsequent reaction of the radical



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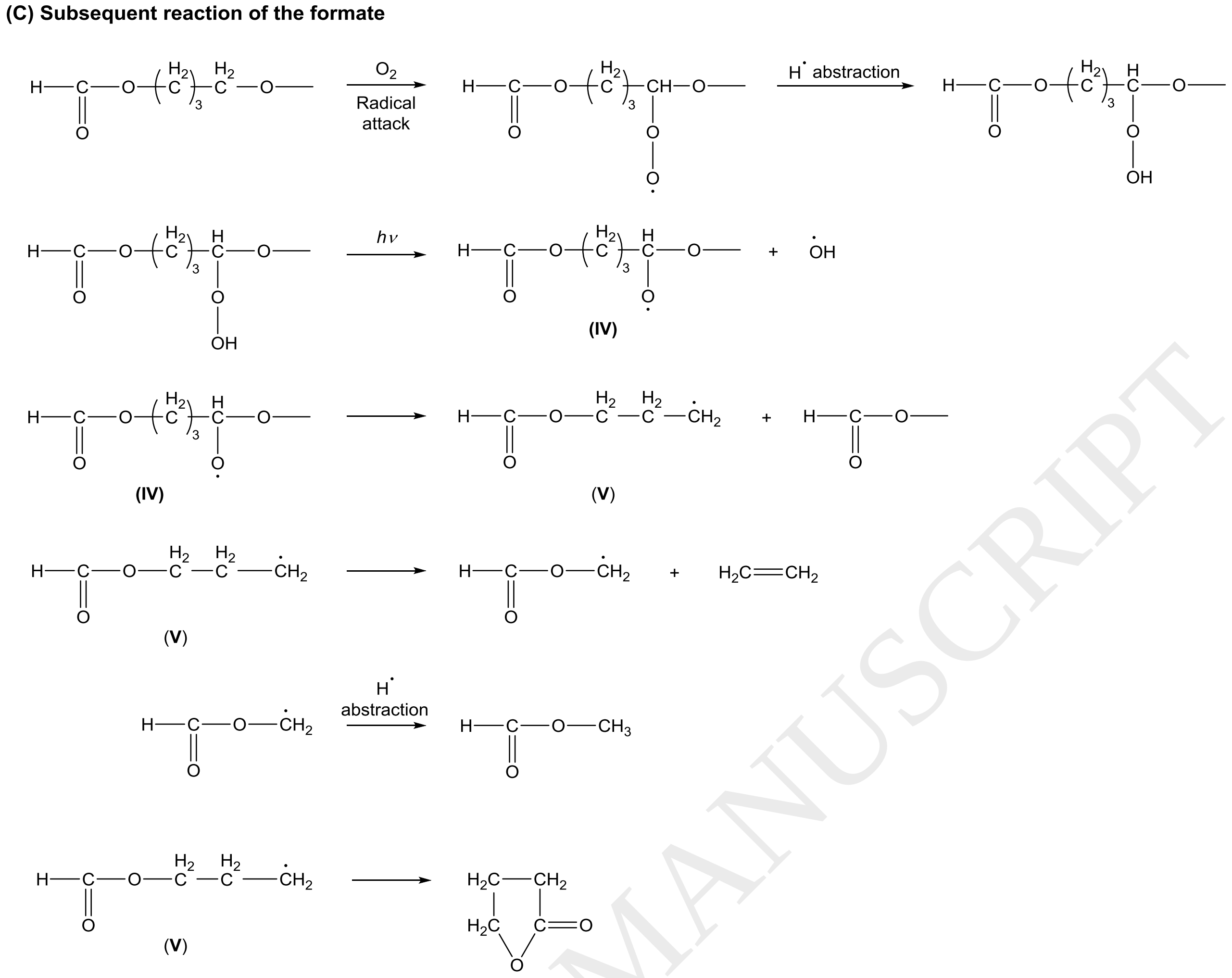

Figure 13. Photodegradation of polyether segments of polyurethanes. [172], copyright 1998. Adapted with permission from Elsevier Ltd. Also with reference to [161].

The oxidation of radical II could lead to primary hydroperoxides, which can be further oxidized into carboxylic acid and aldehydes. A different route of decomposition of the alkyl radical (II) is a β-scission reaction, involving the homolysis of C-C bonds. This scission reaction leads to the formation of ethylene and another alkyl radical (III). This radical (III) may be oxidized to give a formate (**Error! Reference source not found.**(B)).

The formates formed from different routes can then be oxidized by reactions involving an initial hydrogen abstraction on a methylene group α to oxygen. This leads to the formation of a secondary peroxide, which can be decomposed into an alkoxy radical (IV). The decomposition of the radical (IV) by homolysis of the C-C bond in a β-scission process leads to a primary alkyl radical (V) and

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regenerates a formate. The radical (V) can then decompose by a β-scission reaction, which produces in turn ethylene and methyl formate. The radical (V) can also decompose by an internal cyclization that gives a γ-lactone (**Error! Reference source not found.**(C)).

Another route for the decomposition of the alkoxy radical (I) leads to the formation of hemiacetals, which can be oxidized into a carboxylic acid (**Error! Reference source not found.**(A)). This route is considered to be the dominant pathway for the formation of carboxylic acid.

3.2.2.3. Photodegradation of polybutadiene (PB) soft segments

PB and its copolymers are very susceptible to oxidative degradation owing to the unsaturated (alkene) character in their structural units (**Error! Reference source not found.**) [174-178]. Besides the sensitivity of double bonds as a primary UV absorption site as discussed before, the relatively high instability of PB is also attributed to the low dissociation energy of C-H bonds of allylic methylenes (E_d = 350 kJ·mol^{-1}), compared to those in most saturated hydrocarbons, which are more than 380 kJ·mol^{-1} [174].

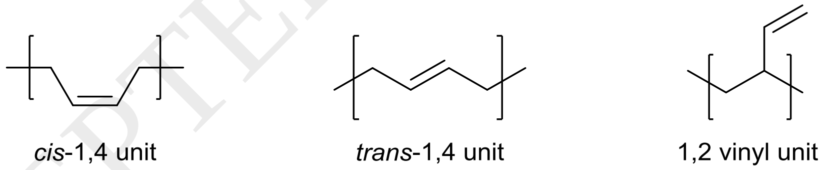

Figure 14. Polybutadiene structural units

Mechanistic studies [179] have shown that oxidative degradation of PB starts from hydrogen abstraction via radical attack, and ultimately leads to the formation of α,β-unsaturated carbonyls (**Error! Reference source not found.**). In this way, hydroperoxides and many intrinsic chromophores are formed (such as unsaturated ketones). While the reactions of 1,2-vinyl units differ from those of the 1,4 units, hydroperoxide formation occurs at the tertiary carbon, which is the most

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reactive of the four carbons in each monomer unit. β-Scission of the subsequent alkoxy radical is believed to be the major chain scission process. This mechanism of initial oxidation of PB applies to both thermal and photooxidative degradation. However, UV exposure can lead to subsequent photolysis of the α,β-unsaturated carbonyls formed throughout degradation, with these being the main chromophores in the degraded PB capable of absorption in the terrestrial solar region, in addition to hydroperoxides. Some related typical photoreactions are shown in **Error! Reference source not found.**C, with the formation of saturated acids as an example. Due to the differences between thermal and photooxidative degradation, α,β-unsaturated carbonyls are the major products of thermooxidation, whereas saturated aldehydes are the predominant products after photooxidation [179, 180]. During the photodegradation of PB, competition between crosslinking and chain scission occurs, with crosslinking due to reaction between vinyl groups and chain scission mainly occurring during the formation of ketones and Norrish Type I reactions [181].

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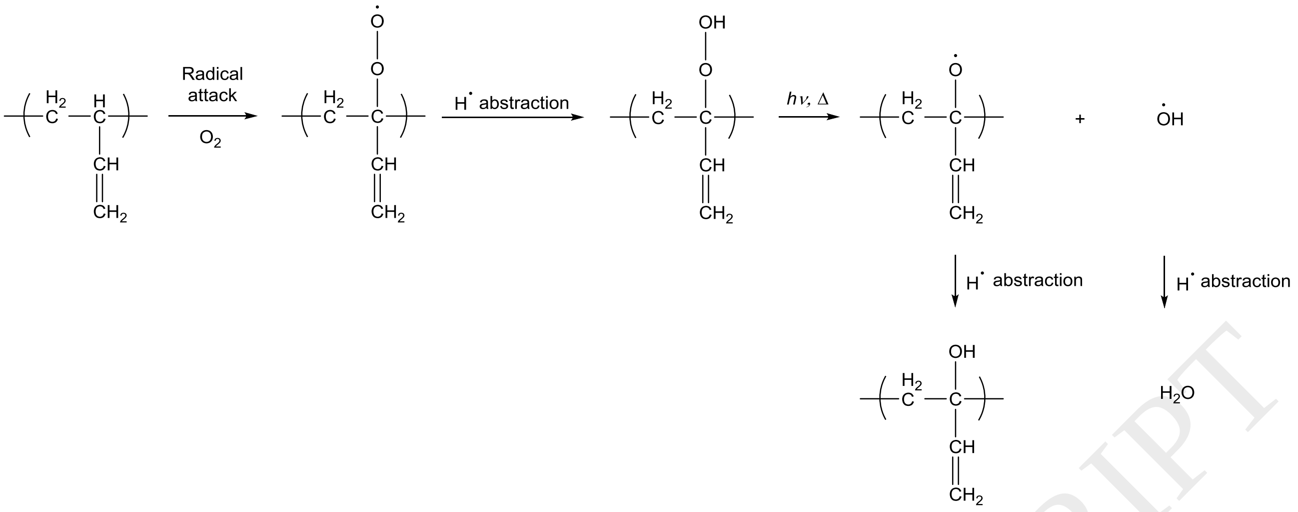
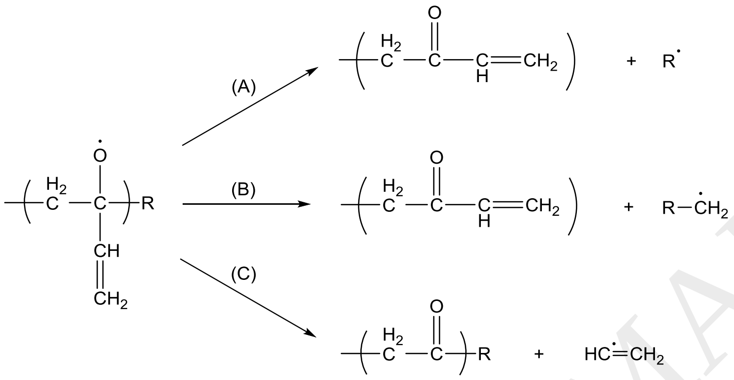
(A) Initial degradation of the vinyl unit



β-scission of alkoxy radical,



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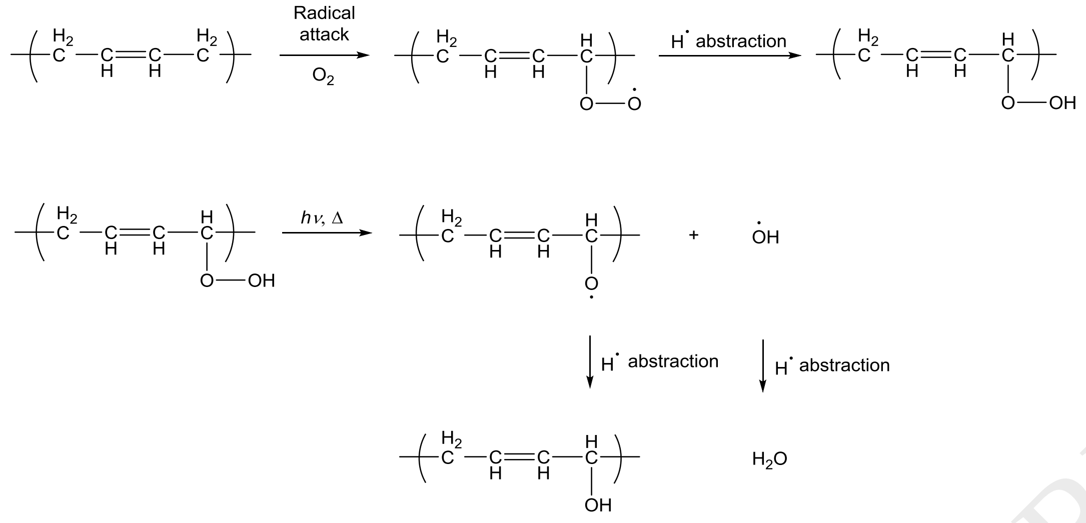
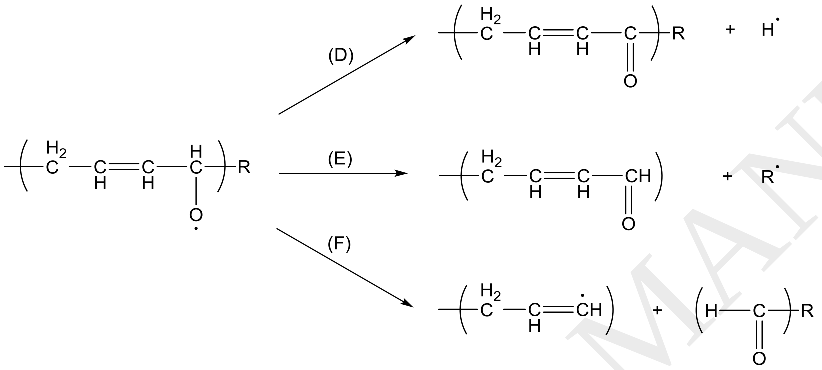
(B) Initial degradation of *cis* and *trans*-1,4 units



β-scission of alkoxy radial,



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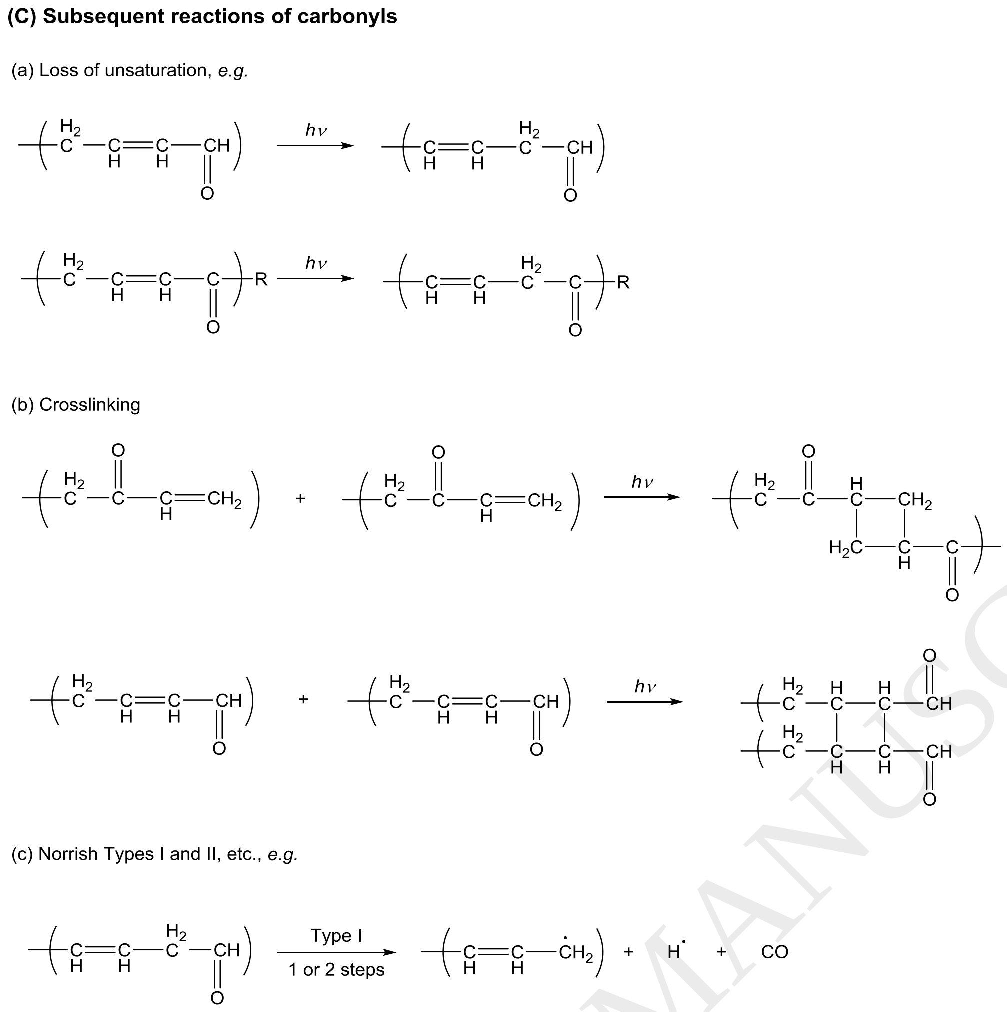

Figure 15. Mechanism of photooxidation of polybutadiene: (A) vinyl unit; (B) *cis*- and *trans*-1,4 units; (C) subsequent photoreaction of carbonyls. [179], Copyright 1974. Adapted with permission from Elsevier Ltd.

Based on evidence from reaction kinetics, Adam et al. [181, 182] have suggested that the rate of photooxidation of highly *trans*- or *cis*-1,4-PB is five times higher than the rate of photooxidation of 1,2-vinyl PB. In PBs with mixed chemical structures, the rate of photooxidation has been inversely correlated with the 1,2-vinyl content [181]. The different rates of reaction of the monomer units can lead to different photooxidation behavior. For PB with a high 1,2-vinyl unit content, the photooxidation rate is low, and passivation via the creation of an outer layer of shield material through photooxidation of the base material, which retards further oxidation does not occur. In other words, the PB remains a homogeneous reactor whose oxidation is not limited by oxygen diffusion.

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Oxidation proceeds in the core of the material and leads to chain scission [181, 182]. In contrast, in the case of PB containing a high concentration of 1,4-double bonds, the photooxidation rate is high, and passivation via extensive oxidation and crosslinking of the surface layer during the early period of exposure is rapid. The bulk of the sample remains unmodified if the passivation is not removed (mechanically, for example) [181, 182]. As the crosslinking of the network limits the diffusion of oxygen, photolysis (without oxygen) of the photooxidation products that formed during initial oxidation (*e.g.*, α,β-unsaturated carbonyls) can occur resulting in the formation of various compounds such as saturated carboxylic acids and α,β-unsaturated anhydrides [180].

According to Bussière et al. [183], while photodegradation results in both chain scission and crosslinking, PB is more sensitive to crosslinking than is polyisoprene (PIP). PB undergoes crosslinking reactions early and before the formation of oxidized products, whereas PIP has an induction period during which no crosslinking is detected despite the formation of carbonyl groups [183]. Oxidation-induced crosslinking of PB is the main factor that changes the material properties, as seen by the substantial increases in storage modulus and T_g [184].

3.2.2.4. Photodegradation of polyisobutylene (PIB) soft segments

PIBUs show greater oxidative resistance compared to poly(butadiene-urethane)s (PBUs) [185], which can be ascribed to the saturated structure of PIB. The UV resistance of PIB is even greater than other aliphatic polymers such as polypropylene (PP) [186]. The mechanism of photodegradation of PIB is shown in **Error! Reference source not found.** [186]. Initially, carbon-carbon bond scission in the main chain gives two end radicals. Also, there is scission of a carbon-carbon bond in a side group, giving a polymer alkyl radical and a methyl radical (**Error! Reference source not found.**a). The methyl radical abstracts hydrogen from the polymer molecules producing new polymer alkyl radicals and methane (**Error! Reference source not found.**b). Then, disproportionation reactions are further responsible for chain scission followed by the increasing

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unsaturation content (**Error! Reference source not found.**c). Meanwhile, the methyl radical can abstract hydrogen from a methyl group, also forming unsaturated structures (**Error! Reference source not found.**d). Chain scission reactions are accompanied by the crosslinking reactions resulting from the termination reactions of different radicals [186]. By studying the accelerated photoageing of PIB in conditions relevant to natural weathering, Gonon et al. [187] suggested that the oxidative degradation of PIB can be explained in terms of induced oxidation. They proposed that temperature has no influence on the mechanism of formation of hydroperoxides but only on their rate of formation, and consequently on the mechanism of their decomposition [187].

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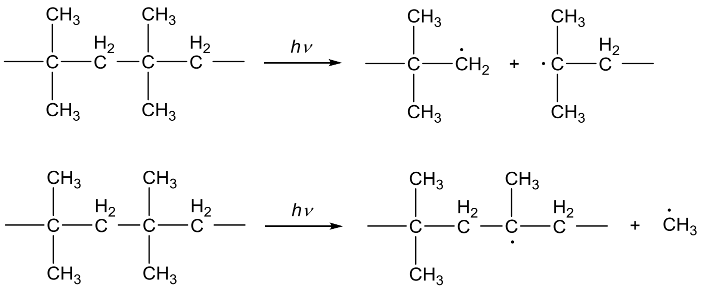
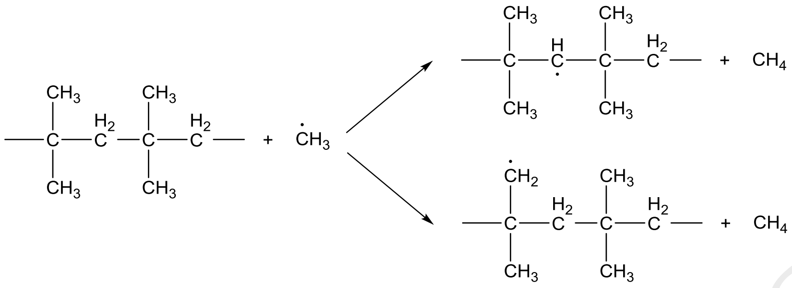
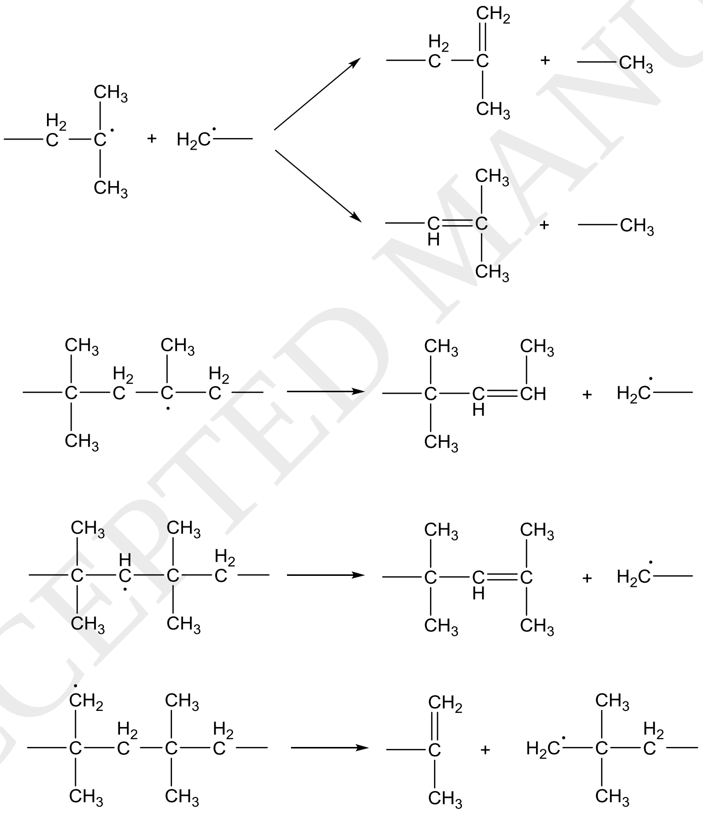
(a) Intial chain scission



(b) Hydrogen abstraction by methyl radicals



(c) Further chain scission and unsaturation



(d) Disproportionation with methyl radicals

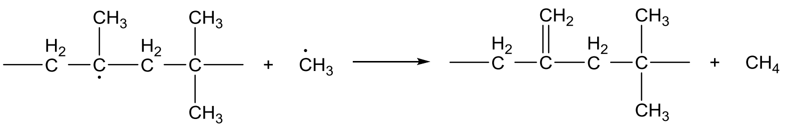


Figure 16. Photodegradation of polyisobutylene [186].

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3.2.2.5. Photodegradation of polycarbonate (PC) soft segments

The photodegradation of BPA-based PCs dominates the literature in this area [41, 42, 156, 188-197] since they are prone to photodegradation, with multiple mechanisms of degradation occurring within terrestrial UV wavelengths. However, as previously discussed, these types of PCs are not relevant for the synthesis of PU elastomers and there has been limited research on the photodegradation of non-BPA poly(carbonate-urethane)s (PCUs). One study showed that PUs based on a commercial polyhexamethylene-polypentamethylene carbonate diol (Eternacoll® PH50) have excellent UV resistance (during up to 200 h in standard weathering tests) [198].

3.2.2.6. Additional Factors that affect the photodegradation of soft segments.

Longer polymer chains are more susceptible to oxidative attack and chain rupture than shorter chains due to the statistically higher probability of longer chains undergoing chain scission [127]. Supporting this, it has been found for PEtUs that the higher the M of polyether, the more rapid is the UV-degradation of polyether in the PU [161].

3.2.3. Effect of photodegradation on the properties of polyurethane elastomers

The most apparent changes of PUs under photoageing are associated with the surface appearance and mechanical properties. As discussed before, photodegradation may result in yellowing of aromatic PUs, mainly due to the formation of quinoid structures by photo-Fries rearrangements. Photodegradation can also cause surface gloss loss, increased surface roughness, and the appearance of microcracks and/or blisters [163, 199-202]. These surface changes could be due to embrittlement as a result of increased crosslinking [200, 201], and the formation of hydrophilic photoreaction

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products, which can lead to absorption of water to form osmotic cells [199]. On the other hand, the competition between chain scission and crosslinking mechanisms may cause the tensile strength and Young's modulus to first decrease and then increase with irradiation time [200], while photodegradation was also observed to result in reductions in elongation at break [203] and tear strength/energy [204, 205].

Rosu et al. [163] studied the influence of polychromatic light (λ > 300 nm) on the surface of a PU based on 4,4′-MDI, PEA diol, and 1,3-BDO as the ChEx. The formation of photo-Fries rearrangement and Norrish Type II reaction products during irradiation was associated with gloss loss, increased surface roughness, and a change in surface wettability (with the contact angle first decreasing and then increasing) (**Error! Reference source not found.**). There were also significant modifications with irradiation time for both T_g (firstly increasing and then decreasing) (**Error! Reference source not found.**) and the swelling coefficient (firstly slightly decreasing and then increasing) (**Error! Reference source not found.**). The changes in the surface wettability, swelling coefficient and T_g could be influenced by multiple factors such as the polarity, photo-crosslinking, surface roughness, and *M*. The initial decomposition of saturated ester structures could decrease the polarity while the formation of chemical products with high polarity could result from photo-Fries rearrangements or from photooxidative reactions, which influence the wettability and swelling coefficient. In addition, while the photoinduced crosslinking increases inter-chain interaction and increases T_g, the decrease in *M* could explain the decrease in T_g and the increased transition range (between the onset and conclusion temperatures) with even longer irradiation time.

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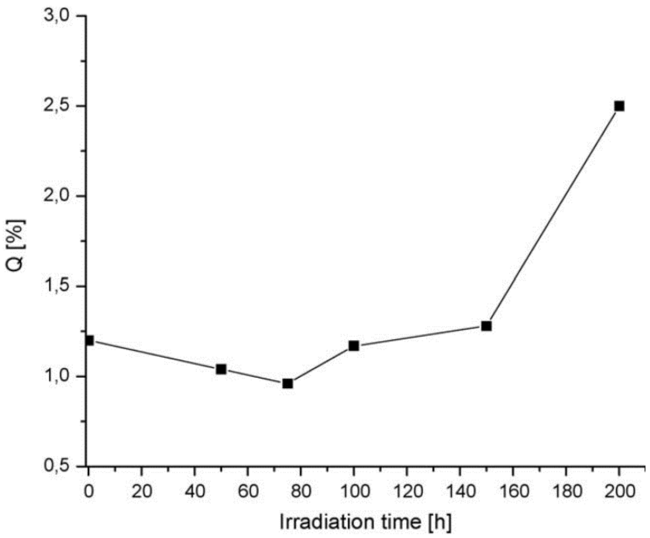

Figure 17. Change in swelling coefficient (Q) as a function of irradiation time. Q (%) = $[(W_s - W_0)/W_0] \times 100$, where W_0 is the weight of the dry film, and W_s is the weight of the film after swelling. [163], Copyright 2009. Reproduced with permission from Elsevier Ltd.

Nakatani et al. [206] reported that the irradiation time dependence of the crystallization behavior was different between PTMEG-based PU samples with different SS chain lengths (prepared by adjusting the *M* of PTMEG). The shorter SSs crystallized more readily during UV-ageing, leading to a reduced amorphous content in the PU. For samples with PTMEG of higher *M*, photoinduced crosslinking dominated, which decreased the mobility of the SSs [206]. These changes in crystallinity and chain stiffness of PUs during photodegradation undoubtedly influence the material properties such as mechanical properties. According to Govorčin, Bajsić and Rek [49], UV-induced crosslinking may also contribute to the observed higher thermal stability of PU elastomers (of both polyester and polyether types) during thermal decomposition as assessed using thermogravimetric analysis (TGA).

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3.3. Stabilization of polyurethane elastomers against photodegradation by polymer modification

As discussed in Section 3.2, the photostability of PUs largely depends on the material chemistry. Generally, PEsUs are more stable under photoageing than PEtU, and aliphatic PUs display better light-stability than aromatic PUs. On the other hand, to the extent that labile or photosensitive groups can be replaced by less reactive groups (bonds with a higher BDE or non-chromophore groups), improved resistance to photodegradation will result [207]. For example, PUs with saturated hydrocarbons have better photostability than unsaturated hydrocarbon materials. Typically, PBUs have poor oxidative stability due to the unsaturated groups in PB. However, hydrogenated PB diols represent a new class of polyhydroxylic hydrocarbon diols, which are more resistant to oxidation due to the absence of double bonds [208-214]. For example, Zou et al. [215] synthesized a hydrogenated HTPB–acrylonitrile copolymer-based PU elastomer, with improved mechanical properties, thermal stability, and oxidative resistance. Nevertheless, reports on the use of hydrogenated PB in the synthesis of PUs have been extremely limited, probably due to the high cost of starting materials. In addition to the high material cost, hydrogenation could increase the T_g of PB, which could limit the applicability of hydrogenated HTPB-based PU elastomers in some situations [215]. Alternatively, PIB can also be used as a replacement macrodiol for PB for PU synthesis [46, 63-82]. However, the complexity of, and associated high costs for, the synthesis of hydroxyl-terminated PIB macrodiols have greatly limited their large-scale exploitation [71].

Alternatively to replacement of PU components, the inclusion of a linear PU in a crosslinked epoxy resin to form semi-interpenetrating networks could be a way to improve the photostability of PUs [216]. Polymers with a higher degree of crosslinking could also display greater resistance to photooxidation [217]. The crosslinking could be either physical (hydrogen bonding) and/or chemical (covalent bonding) [217]. Due to the formation of hydrogen bonding, interchain distances are reduced ("pulling effect"). This may reduce the oxygen permeability and thus restrict photooxidative

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reactions [217]. Strong hydrogen bonding could be obtained in the HS domains when aromatic diisocyanates are used [31] (although aromatic diisocyanates are more photo-labile than aliphatic diisocyanates). Hydrogen bonding between HSs can also be promoted by using isocyanates (especially symmetric isocyanates) with higher polarity, and/or using ChExs that are linear, longer and more flexible and/or have higher polarity and/or an even number of carbon atoms. A greater degree of hydrogen bonding may also be achieved by chemical modification. For example, according to Malkappa and Jana [218], modification of HTPB through the attachment of dinitrobenzene (DNB) groups could allow an additional hydrogen bonding network to be formed between DNB and the urethane backbone, leading to supramolecular crosslinking. On the other hand, chemical crosslinking can be realized by using macrodiols, isocyanates, or ChExs that are tri- or multi-functional. Crosslinked PU-acrylate elastomers have been shown to be remarkably resistant to UV degradation [156, 219], which is in part due to their inherent resistance to photochemistry, but also may be due to the greater number of chain scissions required to reduce mechanical properties in a crosslinked system compared to non-crosslinked materials.

Crystallinity is also important in determining the photostability of PUs [217]. The crystalline structure imposes constraints on chain and therefore radical mobility and the diffusion of oxygen to these radicals [217]. Unless the photoenergy is sufficient to cause a local increase in temperature and melting of the crystal lattice to provide the necessary free volume, it is unlikely that photochemical processes, particularly those requiring large rearrangement of molecular structure, can occur efficiently in crystalline regions of a polymer [217]. The presence of crystalline regions (which, in a sense, behave similarly to a chemical crosslinker) restricts the mobility of the chain segments in the noncrystalline regions. This will have an effect on radical recombination processes [217]. Therefore, increasing the crystallinity could be a viable means to enhance the photostability of PUs, and this may be achieved by annealing [220-222], or by using certain isocyanates [31] and/or ChExs [62, 85] that increase hydrogen bonding.

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However, such obvious approaches as incorporating bonds of a higher BDE, developing structures that would be more crystalline, or avoiding branching in the molecules usually results in the loss of other important properties as well as dramatically increased costs [207, 223, 224]. Alternatively, the addition of additives in small amounts could be more viable for enhancing the photostability of PU materials with minimal variation to their original properties. The different additives/stabilizers for photostability enhancement are discussed in the next section.

3.4. Stabilization of polyurethane elastomers against photodegradation using stabilizers

The use of different additives/stabilizers in PUs (and various polymers) to enhance photostability has been widely reported, with there being three general approaches [207]:

a) blocking or screening out the incident radiation (light screens),
b) the use of additives that preferentially absorb damaging radiation and dissipate the energy in a harmless way (including UV absorbers), and
c) the use of additives that deactivate reactive species or intermediates in the polymer as it undergoes degradation (including radical traps such as hindered amines, quenchers such as organometallic complexes, and hydroperoxide decomposers).

The possibilities available for the inhibition of photoinduced degradation are shown in **Error! Reference source not found.** [133]. Through the use of suitable UV absorbers incorporated into the polymer, penetrating light is absorbed and rapidly deactivated by, for example, transforming it to thermal energy by radiationless processes. These processes compete with the light-induced reactions of the polymer such as photolysis of hydroperoxides, Norrish Types I and II reactions, or photo-Fries rearrangements [133]. Quenchers deactivate excited chromophores such as carbonyl groups, with the excited chromophores being efficient sensitizers for the photolysis of hydroperoxides [133].

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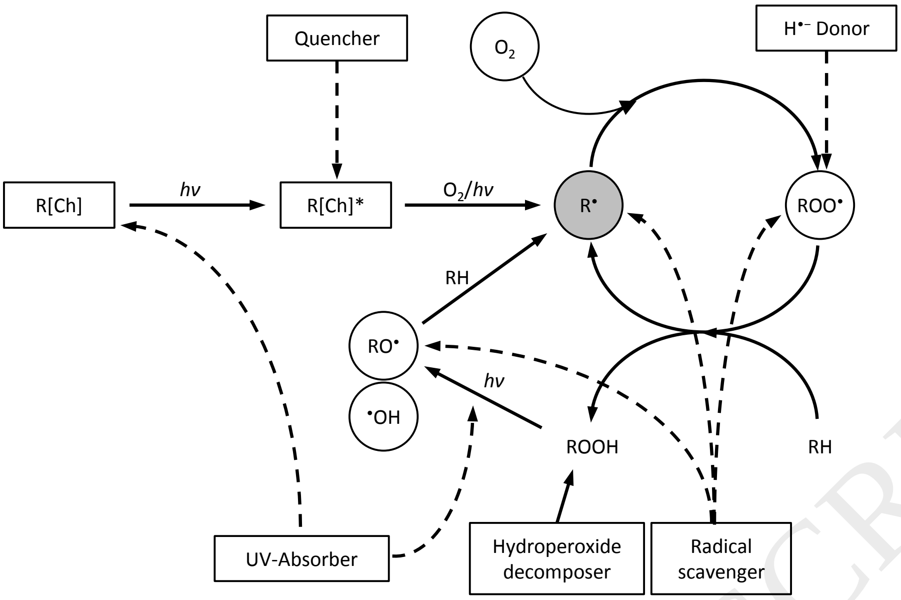

Figure 18. General scheme of inhibition of photooxidation. "[Ch]" represents a chromophore and "[Ch]*" indicates an excited chromophore. [133], Copyright 1988. Adapted with permission from Springer.

In principle, the scavenging of primary macroalkyl radicals, $R^{\bullet}$, would immediately stop autoxidation. However, as the rate of reaction of molecular oxygen is so high ($\sim 10^{7}$–10^{9} $L \cdot mol^{-1} \cdot s^{-1}$), this reaction can hardly be avoided. Only under oxygen-deficient conditions can the use of alkyl radical scavengers contribute significantly to the stabilization of a polymer. In this case, such stabilizers are referred to as chain-breaking acceptors (CB-A). After peroxy radicals are formed, chain-breaking donors (CB-D), which are the predominant type of radical scavengers, are effective in inhibiting further reactions [133]. Scavenging of the $RO^{\bullet}$ and $HO^{\bullet}$ radicals, which are far more reactive than peroxy radicals, $ROO^{\bullet}$, is not practically possible by using radical scavengers. For this reason, to avoid chain branching during autoxidation (**Error! Reference source not found.**), hydroperoxide decomposers are used as co-stabilizers, as these compounds decompose hydroperoxides to form "inert" reaction products [133]. CB-Ds and CB-As are also referred to as primary antioxidants, while hydroperoxide decomposers are classified as secondary antioxidants [133].

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Photostabilizers used for polymers are extensively discussed in the literature [27, 131, 133, 134, 138, 139, 207, 225-247], with a list of the most important photostabilizers for PUs found elsewhere [129, 240]. It is important to note that these photostabilizers may affect other significant physical properties that are also important for some specific applications, such as thermal properties, mechanical strength and color translucency. For example, PUs could show a higher T_g with a higher content of an inorganic UV absorber such as CeO_2 [248]. In recent years, various nanoantioxidants have been developed for diverse applications [249]. However, these nanomaterials have not been applied to the stabilization of bulk polymers including PUs.

In the following sections, typical photostabilizers that can be used for enhancing the UV stability of PU elastomers are discussed. While examples may be sourced from the literature that are focused on wider categories of polymers, the associated UV-protection mechanisms still apply to the design of stabilized PU elastomers.

3.4.1. Light screens

A light screen forms a shield between the polymer and the radiation source [207]. Generally, darker pigments provide more protection [207].

Many organic pigments can be used as light screens, and include azo, anthraquinone and thioindigo compounds, quinacridones, isoindolinones, perylenes, dioxazines, and phthalocyanines [27]. However, carbon black (CB) is the most effective of all light screens, particularly for extended outdoor applications, and may also function in other means as a UV absorber (Section 3.4.2.2), radical scavenger (Section 3.4.3), and/or a quencher (Section 3.4.5)). When CB is properly dispersed in a polymer, UV radiation reaches only the surface layers and there is very little penetration beyond the immediate surface. No other photostabilizer can retard photodegradation as effectively as CB

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[207]. The only issue restricting the more general use of this stabilizer is the color that it introduces into the polymer [207].

The photostability imparted by CB depends upon its particle size (usually as given by primary particle size, 10–100 nm, which is the size of the smaller particles that further form aggregates on a larger scale), concentration, and degree of dispersion in the polymer [250-252]. Small-particle-size CB has a positive influence on the polymer photostability [252, 253]. UV absorption increases until a size of 20 nm is reached, with a further decrease in particle size leading to levelling off of absorption [254, 255]. Good dispersion and dilution quality are also essential for maintaining photostability [252, 255]. Poor dispersion results in larger agglomerates, which have a tendency to scatter UV light rather than absorb it [254, 255]. Higher loadings of CB offer a greater degree of UV protection, but only up to the level of opacity. Adding CB above this level will not significantly improve UV resistance. CB contents of 2 to 3 wt.% are generally sufficient for most polymer systems [255, 256].

3.4.2. UV absorbers

Most polymers are sensitive to UV radiation in the wavelength region between 300 and 360 nm [257]. Individual polymers absorb and are degraded by UV within a much narrower region, often referred to as their activation spectra maxima [257]. For aromatic PUs, the activation spectra maxima vary between 350–415 nm [257]. For effective protection, a UV absorber should either absorb radiation over this broad region or have a peak absorption corresponding to the activation spectra maximum of the polymer to be protected [207]. Dobashi and Ohkatsu [146] has suggested that UV absorbers should be judged based on their absorption maxima (λ_{max}) rather than extinction coefficient (ε) because photoinitiation occurs more rapidly at longer UV wavelengths.

There are a number of organic and inorganic UV absorbers that have been used in a range of polymers, and these are discussed in the following sections. A good UV absorber should be able to

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transform the absorbed UV into less harmful energy, which will not lead to polymer degradation [207].

3.4.2.1. Organic UV absorbers

The most common UV absorbers are low-*M* derivatives of *o*-hydroxybenzophenone, *o*-hydroxybenzotriazole, or *o*-hydroxyphenyl salicylate (**Error! Reference source not found.**) [207]. For example, 2,4-dihydroxybenzophenone [(2,4-dihydroxyphenyl)-phenylmethanone] has been found to be effective for retardation of the photodegradation of PUs [258]. Some examples of derivatives of *o*-hydroxybenzotriazole that have been used for PUs include Tinuvin® 384-2 [octyl 3-[3-(benzotriazol-2-yl)-5-*tert*-butyl-4-hydroxyphenyl]propanoate] [259], Tinuvin® 326 [2-*tert*-butyl-6-(5-chlorobenzotriazol-2-yl)-4-methylphenol] [258], Tinuvin® 327 [2,4-di-*tert*-butyl-6-(5-chlorobenzotriazol-2-yl)phenol] [260, 261], and Tinuvin® 1130 [methyl 3-[3-(benzotriazol-2-yl)-5-*tert*-butyl-4-hydroxyphenyl]propanoate] [262]. A typical hydroxyphenyl-*s*-triazine-type UV absorber is Tinuvin® 400 [6-[2,6-bis(2,4-dimethylphenyl)-1*H*-1,3,5-triazin-4-ylidene]-3-(3-dodecoxy-2-hydroxypropoxy)cyclohexa-2,4-dien-1-one] [263].

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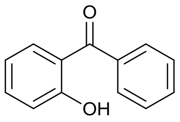
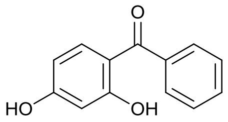
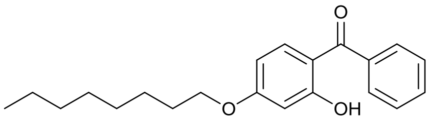
Derivatives of *o*-hydroxybenzophenone



2-Hydroxybenzophenone
[(2-Hydroxyphenyl)-phenylmethanone]

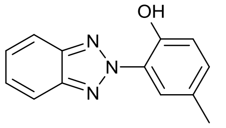


2,4-Dihydroxybenzophenone
[(2,4-Dihydroxyphenyl)-phenylmethanone]

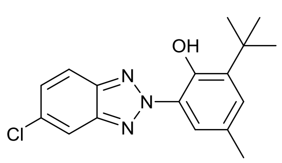


2-Hydroxy-4-(octyloxy)benzophenone (Tinuvin 531)
[(2-Hydroxy-4-octoxyphenyl)-phenylmethanone]

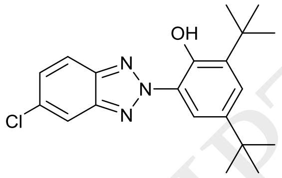
Derivatives of *o*-hydroxybenzotriazole



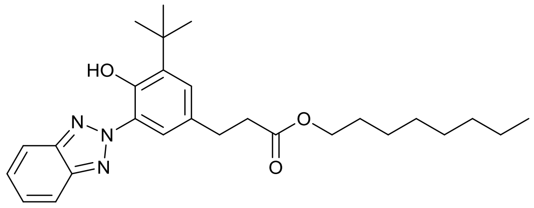
2-(2*H*-Benzotriazol-2-yl)-*p*-cresol (Tinuvin P)
[2-(Benzotriazol-2-yl)-4-methylphenol]



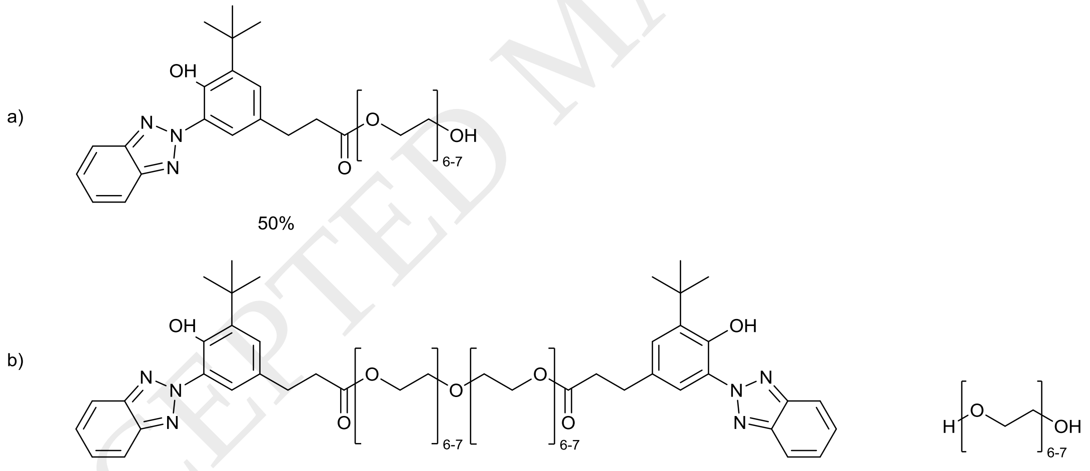
(Phenol, 2-(5-chloro-2H-benzotriazol-2-yl)-6-(1,1-dimethylethyl)-4-methyl) (Tinuvin 326)
[2-*tert*-Butyl-6-(5-chlorobenzotriazol-2-yl)-4-methylphenol]



2-(2'-Hydroxy-3',5'-di-*tert*-butylphenyl)-5-chlorobenzotriazole (Tinuvin 327)
[2,4-Di-*tert*-butyl-6-(5-chlorobenzotriazol-2-yl)phenol]



Benzenepropanoic acid, 3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy-, C9-branched and linear alkyl esters (Tinuvin 384-2)
[Octyl 3-[3-(benzotriazol-2-yl)-5-*tert*-butyl-4-hydroxyphenyl]propanoate]



Tinuvin 1130, A mixture of: a) 50% β-[3-(2-*H*-Benzotriazole-2-yl)-4-hydorxy-5-*tert*.butylphenyl]-propionic acid-poly(ethylene glycol) 300-ester and b) 50% bis{β-[3-(2-*H*-Benzotriazole-2-yl)-4-hydroxy-5*tert*.butylphenyl]-propionic acid}-poly(ethylene glycol) 300 -ester

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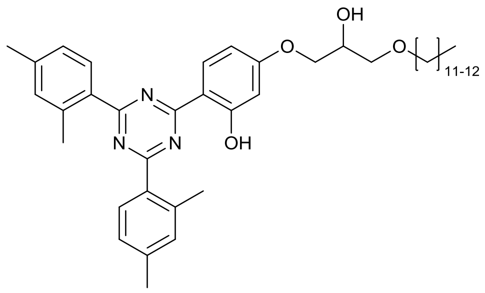

Derivatives of hydroxyphenyl-*s*-triazine

Tinivin 400, a mixture of: 2-[4-[(2-Hydroxy-3-dodecyloxypropyl)oxy]-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine and 2-[4-[(2-Hydroxy-3-tridecyloxypropyl)oxy]-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine

Figure 19. Structures of derivatives of *o-hydroxybenzophenone*, *o-hydroxybenzotriazole*, and hydroxyphenyl-s-triazine, which are used as UV absorbers.

Excited-state intramolecular proton transfer (ESIPT) is commonly accepted as the mechanism responsible for energy dissipation in organic UV absorbers [133, 207, 235, 264]. More specifically, organic UV absorbers can undergo reversible keto-enol tautomerism upon UV radiation or by the release of heat [133, 207, 235, 265-267]. The nature of substituents on the aromatic ring influences the extent to which this keto-enol isomerism contributes to photostabilization [27, 207].

The prices of phenyl esters of benzoic acid are relatively low, which makes them popular for practical use [27]. However, it is noteworthy that these phenyl UV absorbers may yellow on exposure to UV light, as they are subject to photo-Fries rearrangements [27]. Tris-*o*-hydroxyphenyl-*s*-triazines are extremely lightfast, but are inherently yellow and are of insufficient compatibility in most polymers [268]. Better suited are asymmetric *s*-triazines with at least one of the three substituents being nonaromatic [268]. However, due to their inherent color, these UV absorbers may not be suitable for colorless and transparent polymer materials that require color stability [27].

An alternative aminophosphazene UV absorber has been synthesized by Huang et al. [269], with the structure having a rigid phosphazene core and flexible alkoxy shell. They found that molecular dispersion of this aminophosphazene along with sodium montmorillonite (MMT-Na^+) enhanced the UV stability of a 4,4′-MDI/polypropylene glycol (PPG)-based PU. It was proposed that the aminophosphazene could act effectively as a UV absorber due to an energy dissipation mechanism

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similar to organic UV absorbers. Moreover, due to the aminophosphazene having a sterically hindered amine group (further discussed in Section 3.4.3), this stabilizer could additionally function as a free radical scavenger [269].

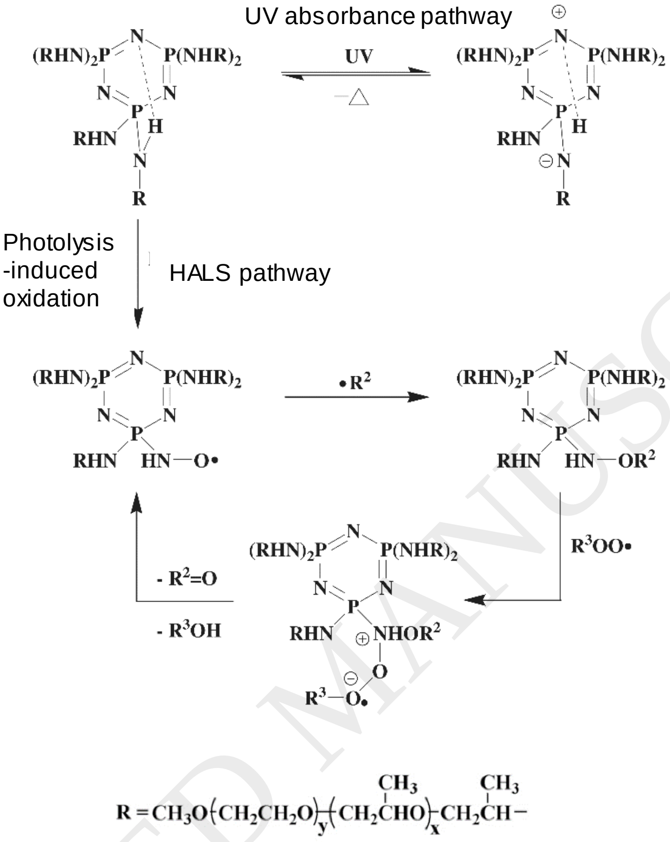

Figure 20. Two possible mechanisms for the UV resistance provided by aminophosphazene. [269], Copyright 2012. Reproduced with permission from Elsevier Ltd.

Besides the inherent stability of organic UV absorbers, another limitation of these photostabilizers in providing long-term protection of polymers is associated with their low *M* (*i.e.*, they are usually volatile), which causes them tend to migrate out of the bulk material [270-272]. These factors are contributors to organic UV absorbers underperforming when compared to inorganic UV absorbers. Some strategies to improve performance by restricting the migration of organic UV stabilizers are discussed in Section 3.4.7.

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3.4.2.2. Inorganic UV absorbers

While the principal role of CB for photo stabilization is as a light screen, its ability to absorb UV warrants its inclusion in the category of UV absorbers. CB converts absorbed energy into heat by an essentially physical process [207], although the mechanism of action of CB via absorbed energy is not well established [235]. It is known that CBs of smaller particle sizes have better absorption and give better protection to polymers [273]. In addition, volatiles on the surfaces of CB particles consist of a complex mixture of chemisorbed, oxygenated groups that may also be chromophores, that also contribute to UV absorption [254]. However, a high volatile content might adversely affect the photostability of polymers [253]. Very similar to CB, carbon nanotubes (CNTs) may also act as UV absorbers, but the absorbed energy may significantly increase the local temperature, which can make CNTs act as a prodegradant [274]. The heat generated by CB or CNTs after UV absorption could possibly contribute to the thermooxidation of polymers. Thus, antioxidants may be required to provide adequate thermal protection [207].

Besides CB, semiconductors such as zinc oxide (ZnO), titania (TiO_2), ceria (CeO_2) and silica (SiO_2) are important inorganic UV absorbers [261, 275-278]. Inorganic oxides are nonvolatile, nonmigratory, and light, thermally and chemically stable. Thus, they have low weight loss in aggressive service conditions [261, 276]. Moreover, while organic UV absorbers have certain absorption peaks in narrow UV ranges, inorganic UV absorbers show relatively broad absorption (up to the proximity with visible wavelengths, *i.e.*, 400 nm) [260, 279]. Therefore, inorganic UV stabilizers usually provide better UV protection than organic UV stabilizers (*e.g.*, hindered amine light stabilizers, or HALS, and organic UV absorbers) [259, 280-282]. For example, Allen et al. [282] suggested that while benzophenone and benzotriazole chromophore-based UV absorbers absorb more strongly in the near UV below 350 nm, rutile TiO_2 nanoparticles absorb more strongly above this range and therefore operate as a strong opacifier.

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Solid band theory can be used to explain why semiconductors such as ZnO and TiO_2 absorb UV radiation [283, 284]. ZnO has a wide band gap (3.37 eV) and large excitation binding energy of 60 meV. Therefore it can absorb light that matches or exceeds the band gap energy and which lies in the UV range of the solar spectrum (<400 nm) [285]. TiO_2 is also effective for UV absorption as it presents a similar band gap (3.23 eV for rutile and 3.57 eV for anatase) [286]. The band gap of inorganic oxides can be slightly affected by the particle size [287]. Besides UV absorption, scattering and reflection mechanisms are significant only in the spectral region where the inorganic oxide has either weak or no absorption [284]. TiO_2 (especially anatase [288]) has a higher refractive index than most other semiconductors [284], which can increase the contribution to stabilization from UV scattering mechanisms.

Studies have shown that inorganic UV absorbers with a smaller particle size (from macro to nano) [277, 281, 289] and higher content [277, 278, 282] in the polymer could result in better UV absorption. Regarding the content, if too few inorganic oxide particles are added, the distance between the particles is too large, and there is not enough opacity. However, an amount that is too great results in lower efficiency due to a particle crowding effect which causes the particles to interfere with each other's scattering efficiency [235]. Regarding the particle size, Goh et al. [287] have shown that the UV absorbance of ZnO particles increases with increasing their size in the range of 15–40 nm. Particles greater than 70 nm become opaque to UV radiation. For particles greater than 70 nm, the absorbance decreases with increasing size because of the decrease in particle density [287].

ZnO nanoparticles are normally effective at reducing or delaying the photodegradation of aromatic PUs [283, 290] and other polymers [291, 292]. In addition, nano inorganic oxides have much weaker scattering intensity than their pigmentary grade counterparts, especially for visible light [284]. Therefore, nano inorganic oxides have no detrimental effect on the transparency of polymer matrices [278, 283, 293, 294]. Moreover, nanocomposites formed by dispersion of

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inorganic nanoparticles in a polymer matrix could improve heat resistance and mechanical properties [277, 278, 289, 293, 295-301].

Good dispersion of inorganic stabilizers can be hard to achieve due to agglomerate formation, crystallinity, hardness, particle size, acid/base interactions, polarity, and process conditions (*e.g.*, intensity of mixing, and mixing schedule) [235]. Therefore, it is important to develop sound processes to maximise the dispersion of nanoparticles in PUs to obtain the desired UV stabilization and other properties (*e.g.*, mechanical and optical). In many studies, mechanical shear forces such as sonication [283, 293, 294] and milling [278] have been applied to break down agglomerated nanoparticles. However, this approach is limited, due to the low interactions between the inorganic materials and the polymeric matrix, compared with the strong interactions between the individual nanoparticles. Better dispersion could be obtained by surface modification of nanoparticles to improve nanoparticle–matrix interactions. Some successful examples include ZnO nanoparticles modified by 2-aminoethyl-3-aminopropyltrimethoxysilane [*N′*-(3-trimethoxysilylpropyl)ethane-1,2-diamine] [302], TiO_2 nanoparticles treated by aminopropyltrimethoxysilane [3-triethoxysilylpropan-1-amine] [299, 300], and CeO_2 nanoparticles with a surface-grafted monolayer of phosphonated poly(oxyalkene) [poly(oxy-1,2,ethanediyl)-α-(3-phosphonopropyl)-ω-hydroxyl] [279]. In addition, a greater degree of dispersion of nanoparticles in PU systems could be achieved with a better match between hydrophilicity/hydrophobicity of the nanoparticles and the matrix (for example, the use of hydrophobic nano-SiO_2 *vs.* hydrophilic nano-SiO_2 [278, 301]).

It is noteworthy that after inorganic oxides absorb UV energy, they can also exert oxidising power and produce reactive free radicals such as perhydroxyl radicals ($HO_2^{\bullet}$), an oxygen radical anion ($O_2^{\bullet-}$) and hydroxyl radicals ($HO^{\bullet}$). [276, 288, 291, 292, 303-311]. These radicals will attack neighboring polymer chains to abstract hydrogen atoms, forming carbon-centred radicals. Subsequently, chain cleavage occurs with the production of hydroxyl derivatives and carbonyl intermediates [281, 288, 292, 308]. For ZnO and TiO_2, this photocatalytic activity is especially

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evident at a particle size of less than 100 nm [288, 309, 310, 312]. Anatase TiO_2 nanoparticles are known to have a strong photocatalytic effect [276, 288, 303-310]. In contrast, rutile TiO_2 nanoparticles have high UV opacity and low photoactivity [288, 308] and are an effective stabilizer for retarding the photooxidation of PUs [282].

The photosensitivity of ZnO or TiO_2 is considered to arise from localised sites on the crystal surfaces [282, 311]. The photocatalytic activity of ZnO or TiO_2 particles might be suppressed by surface treatment or encapsulation of the particles with another material, which could act as an isolation layer, or by passivation of the particle surface through oxidation [235]. For resistance to weathering, TiO_2 or ZnO particles may need to be heavily coated (up to 10% w/w) with alumina, silica, zirconia, ceria, or phosphates of other metals [276, 281, 308, 312]. Among the different techniques used to modify nanoparticles, silane treatment methods offers definite advantages such as simplicity, low cost and low processing temperatures [260, 299, 300, 313]. However, changing the surface properties by coating or doping is not sufficient to entirely prevent degradation (which can only be minimised) [235].

CeO_2 and TiO_2 show a similar UV cut-off threshold at around 370 nm, and they are both semiconductors, with a band gap of *ca.* 3.0–3.2 eV, and present the same UV absorption mechanism under UV radiation. However, CeO_2 does not show any photocatalytic effect [279]. CeO_2 nanoparticles have band gap energies ranging from 2.9 eV to 3.5 eV depending on their particle sizes due to the quantum confinement effect. Among different inorganic UV absorbers, considering energy band gaps and absorption edges, only CeO_2 is a proper UVB absorber [279]. Moreover, CeO_2 presents the property of transparency in the visible spectrum from 400 up to 800 nm, a range greater than TiO_2 [279].

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3.4.3. Radical scavengers

Hindered amine light stabilizers (HALS) act as scavengers for free radicals that may be generated during UV-initiated oxidation of organic compounds [314]. Although there are wide structural differences in the HALS products commercially available, they typically share the 2,2,6,6-tetramethylpiperidine ring structure. Several important, commercial photostabilizers based on this structure are available, as typified by *bis*(2,2,6,6-tetramethyl-4-piperidinyl) sebacate [bis(2,2,6,6-tetramethylpiperidin-4-yl) decanedioate] (**Error! Reference source not found.**) [207]. Some other examples such as Tinivin 123 [bis(2,2,6,6-tetramethyl-1-octoxypiperidin-4-yl) decanedioate] are also shown in **Error! Reference source not found.** [262].

HALS show high efficiency at relatively low concentrations. At only 0.1%, HALS provide protection equivalent to typical UV absorbers used at 3% or 4%. The best of these compounds are claimed to be as effective as CB in inhibiting photodegradation. Although they are expensive, HALS provide the best performance in non-CB formulations based on a cost-efficiency ratio [207]. Nonetheless, as HALS do not appreciably absorb UV irradiation above 290 nm [225], they are usually used with other UV stabilizers for better stabilization performance [259, 261, 263, 270, 272, 315].

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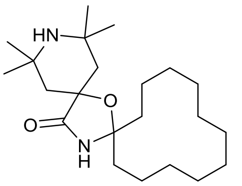
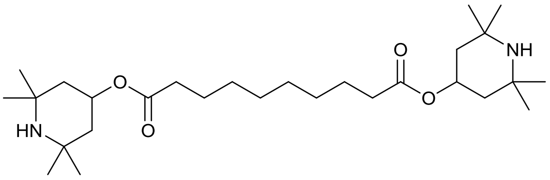
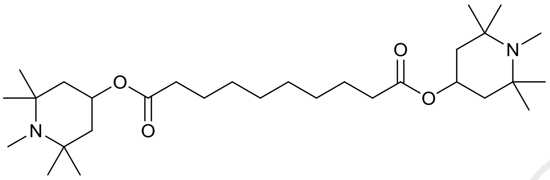


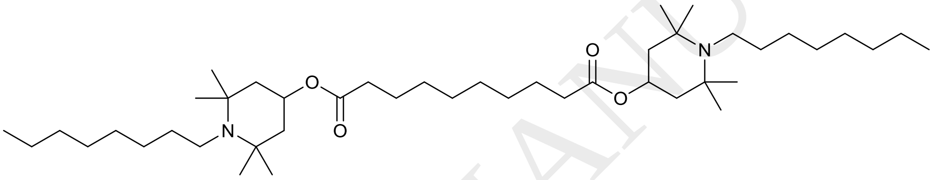
2,2,4,4-Tetramethyl-7-oxa-3,20-diazadispiro[5.1.11^{8}.2^{6}]-henicosan-21-one (Hostavin N 20)



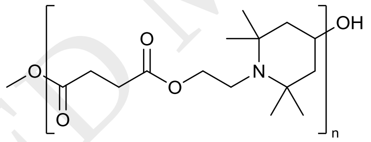
Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (Tinuvin 770)
[Bis(2,2,6,6-tetramethylpiperidin-4-yl) decanedioate]



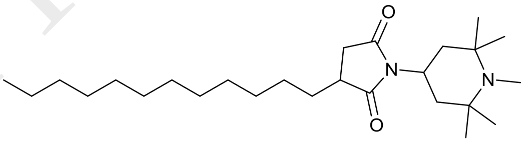
Bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate (Tinuvin 292)
[Bis(1,2,2,6,6-pentamethylpiperidin-4-yl) decanedioate]



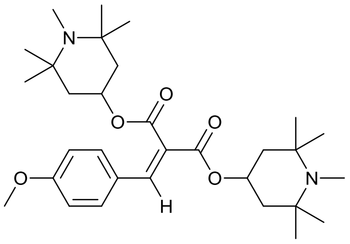
Bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate (Tinuvin 123)
[Bis(2,2,6,6-tetramethyl-1-octoxypiperidin-4-yl) decanedioate]



Poly-(*N*-β-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidyl succinate (Tinuvin 622)
[4-[2-(4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)ethoxy]-4-oxobutanoic acid]



3-Dodecyl-1-(1,2,2,6,6-pentamethylpiperidin-4-yl)pyrrolidine-2,5-dione



Bis(1,2,2,6,6-pentamethylpiperidin-4-yl) 2-[(4-methoxyphenyl)methylidene]propanedioate

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Figure 21. Examples of hindered amine light stabilizers (HALS) based on 2,2,6,6-tetramethylpiperidine. The last HALS compound, developed by Ávár et al. [272], contains a photoreactive site for the fixation of the HALS onto the polymer matrix.

The ability of HALS to scavenge radicals during UV degradation and provide stabilization to polymers occurs via initial formation of aminoxyl/nitroxy radicals (**Error! Reference source not found.**) [235]. The reaction scheme shown in the figure depicts the Denisov Cycle, which indicates cyclical regeneration of the HALS aminoxyl radical, along with trapping and decomposition of polymer alkyl and peroxy radicals during the cyclic process. The detailed chemical processes for aminoxyl radical regeneration during the Denisov Cycle have been the subject of speculation, with more recent work by Coote et al [316, 317] showing that aminoxyl regeneration can proceed via abstraction of the β-hydrogen atom of the alkoxyamine/aminoether by a peroxy radical with subsequent formation of a ketone and an aminyl radical intermediate.

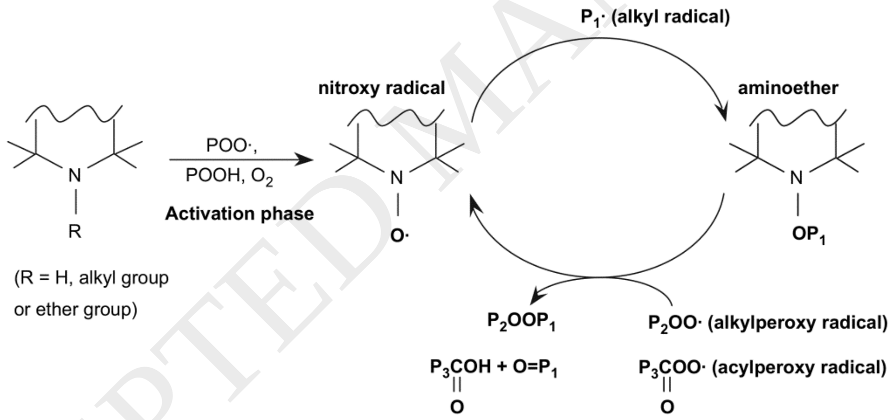

Figure 22. Denisov Cycle for hindered amine light stabilizers (HALS) based on 2,2,6,6-tetramethylpiperidine. [235], Copyright 2015. Reproduced with permission from Elsevier Ltd.

HALS have four methyl groups attached to the two carbons next to nitrogen, which can create a steric hindrance for better stabilizing the related aminoxyl radical (than, for example, three methyl groups) [318]. A stable aminoxyl radical can efficiently trap alkyl radicals [318].

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Hydroxylamines, as well as the aminoxyl radicals that are subsequently formed, can also effectively react with free radicals (see **Error! Reference source not found.** for the mechanism) [319]. Though not important commercially, stable dialkyl nitroxide radicals have been shown to be effective scavengers of radicals [207].

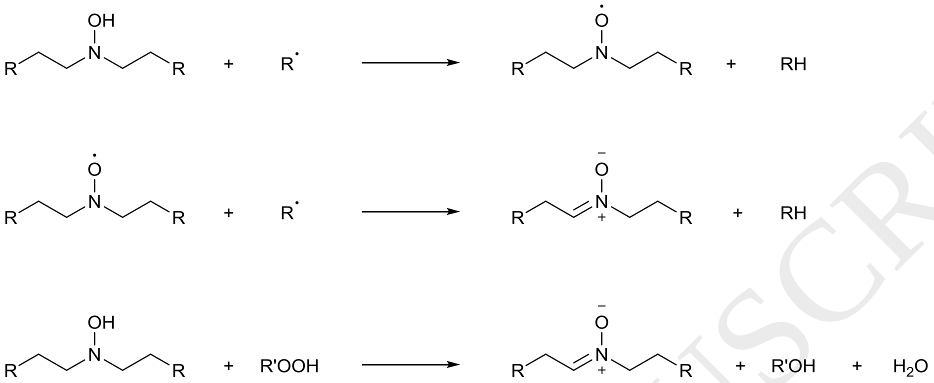

Figure 23. Radical trapping and hydroperoxide decomposition mechanism of hydroxylamines. [319], Copyright 2002. Adapted with permission from Elsevier Ltd.

Besides HALS, other UV stabilizers, such as ferulic acid, phenoxy antioxidants, flavonoids, vitamin C and E and β-carotene, some natural extracts, CB, and copper stearate also show similar UV stabilization mechanisms that involve radical deactivation [235].

Hindered phenols are known as radical scavengers [235, 240]. Typical examples of phenolic antioxidants include methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate and Irganox® 1010 [[3-[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxy]-2,2-bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxymethyl]propyl] 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate], as shown in **Error! Reference source not found.**. They also show cooperation between the parent phenolic antioxidant and its transformation products (benzoquinone and quinone methide, which have a modified radical scavenging activity), which has an antioxidant supporting effect [233, 235]. The radical trapping mechanism of phenolic antioxidants and their transformed products, quinones, are shown in **Error! Reference source not found.**. In particular, the steric hindrance provided by

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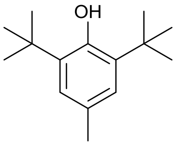
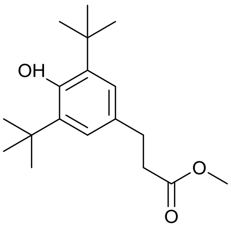
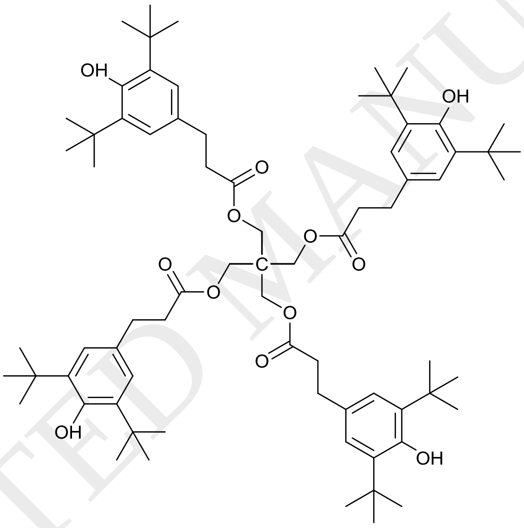
the bulky *t*-butyl groups stabilizes the phenoxy radical formed after reaction with oxygenated or alkyl radicals. It is therefore very unlikely that phenoxy radicals can attack polymer chains [230].



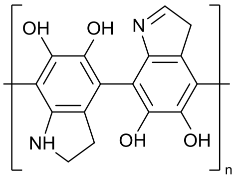
2,6-Di-*tert*-butyl-4-methylphenol



Methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate



Pentaerythritol tetrakis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate)
(Irganox 1010)
[3-[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxy]-2,2-bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxymethyl]propyl] 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate



Polydopamine

Figure 24. Structures of phenolic antioxidants, methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate, Irganox 1010, and polydopamine. The structure of polydopamine is [320].

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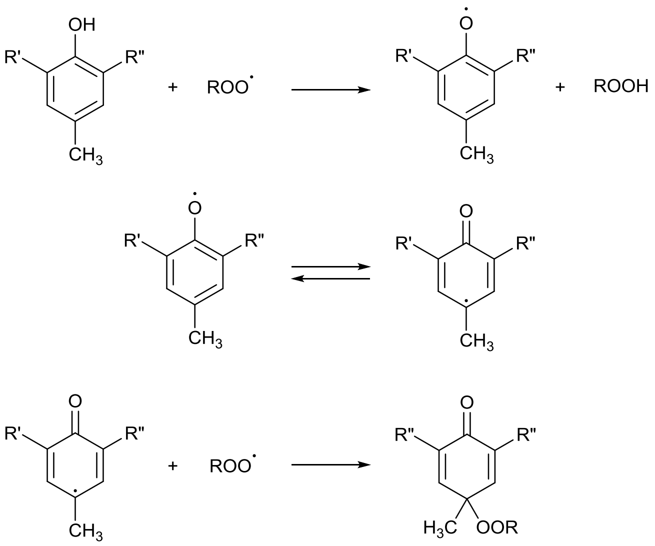

Figure 25. Radical scavenging mechanism of phenolic antioxidants. [207].

Irusta and Fernández-Berridi [321] reported that, for aromatic PEtUs, the UV absorber, 2-hydroxybenzophenone [(2-hydroxyphenyl)-phenylmethanone], decreased the photooxidation on both HSs and SSs, whereas the effect of the radical-scavenging phenolic antioxidant, 2,6-di-*tert*-butyl-4-methylphenol, was more significant on the SSs.

Polydopamine (PDA) (**Error! Reference source not found.**) is a synthetic polymer with a chemical structure similar to melanins that can protect human skin by quenching reactive radicals generated during UV exposure [322] and has recently been found to act as an antioxidant [323-339]. Both PDA and melanins have a phenolic structure, which, in the presence of reactive oxygen species and radicals, can be easily oxidized to the corresponding quinone, quenching the reactive species by hydrogen atom transfer [340]. Demonstration of the effectiveness of PDA as a UV stabilizer has been shown for a PU that contained only 0.8 wt.% PDA-coated graphene and gave high UV resistance [340, 341].

Phenolic compounds from bark extract have also been found to show radical scavenging activity [262, 342], with stability correlating to total phenolic and flavonoid content [342].

CB is frequently mentioned [235, 343] as participating in radical scavenging, although the related mechanism has not been well understood. Oxygen-activated CB has chemical functions on its

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surface [344, 345], which might account for the oxidation stabilization ability of CB (while channel black has more functional groups on its surface than furnace black [224]). The additional UV protection may be ascribed to the volatiles on CB, which consist of a complex mixture of chemisorbed, oxygenated groups [254, 345, 346]. These groups tend to act as radical scavengers, inhibiting any chain reactions caused by UV radiation [254, 255]. In addition, the surface of activated CB usually consists of conglomerates of many condensed polycyclic aromatic rings [224, 345, 346]. The quinoid structures present on the surface of activated CB are considered to participate in radical scavenging [232]. CB can be regarded as a giant phenol and as such should be capable of functioning as a labile-hydrogen donor [224]. Similar to CB, CNTs have been found to have a radical accepting capacity, which may interrupt propagation during autoxidation [274].

3.4.4. Hydroperoxide decomposers

As shown in **Error! Reference source not found.**, hydroperoxide formation is a key reaction in polymer autoxidation. Therefore, decomposition of hydroperoxides to inert or less reactive species is one way to significantly reduce the rate of autoxidation and improve polymer stability.

As discussed above, the major strength of HALS is their participation in peroxide and hydroperoxide decomposition and carbon radical trapping, with hydroxylamines also being shown to be able to decompose hydroperoxides (**Error! Reference source not found.**) [319].

However, phosphites and phosphonites are more commonly used in this way as they effectively decompose hydroperoxides [133, 347, 348]. They reduce the hydroperoxides formed from peroxy radicals to the corresponding alcohol by a redox reaction, being simultaneously oxidized to the corresponding phosphate [133, 319], with the mechanism of decomposition shown in **Error! Reference source not found.**. Because phosphites and phosphonites tend to hydrolyse, in practice mainly hydrolytically stable derivatives are being used [133]. Additional stabilizing capacity can also

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be introduced via chemical combination. Compounds containing both the 2,2,6,6-tetramethylpiperidine ring structure and phosphite were synthesized and showed even better performance in the decomposition of hydroperoxides [349]. This combination also improved the hydrolytic stability of phosphites [349], which has also been shown to increase with increased steric hindrance around their phosphorous atoms [231, 349].

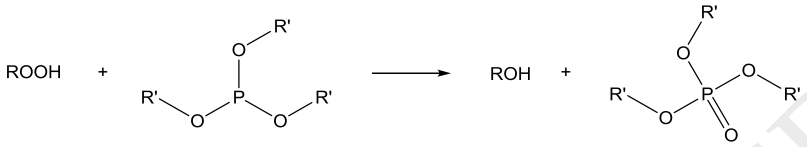

Figure 26. Mechanism of decomposition of hydroperoxides by phosphites. [319].

CB may also function as a chain-terminating and peroxide-decomposing agent [350]. The effectiveness of CB to catalyse hydroperoxide decomposition into nonradical products can be attributed to its acidity resulting from oxygen-containing groups [224]. The activity of CB in hydroperoxide decomposition increases with the amount of chemically bound oxygen [224]. Sulphurised CB is even more effective than oxygen-activated CB for decomposing peroxides, with the sulphur-based chemical groups undergoing reactions similar to those for sulphur-containing antioxidants [224].

3.4.5. Quenchers

As discussed in Section 3.1, many compounds that act as chromophores in polymers, such as polynuclear aromatics, carbonyl groups, reaction products of antioxidants, dyes, and pigments [351] can be sensitisers for photodegradation. Quenchers stabilize polymers by deactivating excited state chromophores (triplet or singlet states) through an energy-transfer mechanism before these

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molecules can undergo reactions that would result in degradation (**Error! Reference source not found.**) [133, 207, 234]. The excited quencher can then dissipate energy as heat [133, 207, 234].

$$\text{Sensitizer} \xrightarrow{hv} \text{Sensitizer*}$$

$$\text{Sensitizer*} + {}^{3}O_2 \longrightarrow {}^{1}O_2 + \text{Sensitizer}$$

$$\text{Quencher} + \text{Sensitizer*} \longrightarrow \text{Quencher*} + \text{Sensitizer}$$

$$\text{Quencher} + {}^{1}O_2 \longrightarrow \text{Quencher*} + {}^{3}O_2$$

$$\text{Quencher*} \longrightarrow \text{Quencher} + \text{Heat}$$

Figure 27. Quenching of excited states of sensitizers and singlet oxygen (${}^{1}O_2$). The excited state is indicated by "*". [133, 207, 234].

Like HALS, quenchers usually do not absorb UV radiation. The primary role of quenchers is to extract absorbed energy from excited-state molecules before they degrade or react to cause degradation [207]. Chelates of transition metals (especially nickel) are the most common class of quenchers [207, 352-354]. Nickel chelates can effectively quench the triplet state of ketones [353]. Metal chelates (such as dibutyldithiocarbamates of Ni [*N*,*N*-dibutylcarbamodithioate;nickel(2+)] or Zn [zinc;*N*,*N*-dibutylcarbamodithioate], and nickel dodecylthiophosphate [nickel(2+);*O*-dodecyl-phosphorothioate]) have also been shown to be effective at quenching singlet oxygen and thus retarding the photooxidative degradation of PUs [27, 258]. In contrast to other types of photostabilizers, metal chelates do not migrate through the polymer to a significant extent and therefore are very effective stabilizers [207].

Quenching of electronically excited states (singlets or triplets) can be in the form of either long-range energy transfer (*e.g.*, a dipole–dipole interaction) or contact (collisional) energy transfer. For long-range energy transfer, the distance between the chromophore and quencher can reach as high as 10 nm, providing that there is significant overlap between the emission spectrum of the chromophore

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and the absorption spectrum of the quencher [353]. For contact energy transfer, the distance between the chromophore and quencher should not exceed 1.5 nm [353].

Nickel quenchers can also contribute to hydroperoxide decomposition [355, 356] and act as radical scavengers [357].

Mendikute et al. [321] indicated that nickel 2,2′-thiobis(4-*tert*-octylphenolate)-*n*-butylamine [butan-1-amine;nickel(2+);2-[2-oxido-5-(2,4,4-trimethylpentan-2-yl)phenyl]sulfanyl-4-(2,4,4-trimethylpentan-2-yl)phenolate] behaved as a photostabilizer in TDI-based PEtUs, whereas it acted as a photoinitiator in 4,4′-MDI-based PEtUs, although the reason for this behaviour was unclear.

Besides metal chelates, there are other compounds that may function as quenchers. For example, salicylic acid esters, amides, and hydrazides have been shown to be effective quenchers of the excited states in aromatic PUs [358].

While it is widely accepted that CB acts as a UV absorber, additional theories suggest that CB presents conjugated double bonds [359] and has a low surface energy [360]; thus, it may also quench certain photoactive species in the polymer.

3.4.6. Combinations of stabilizers

For better protection of polymers against UV degradation, it is not uncommon to use more than one stabilizer in a polymer formulation. When combinations of different UV stabilizers are used, the stability during photooxidation relies on the contribution of each stabilizer, as well as their respective interactions (antagonistic or synergistic) with other stabilizers. Many examples of antagonism and synergism for UV stabilizer combinations in various polymers have been summarised elsewhere [134, 139, 207, 235, 237, 240, 241], although the related mechanisms have not been fully understood.

CB is a very common UV stabilizer and has been discussed extensively already. The nature of CB plays an important role in not only controlling its performance as a stabilizing agent alone, but also its interactions with other UV stabilizers and antioxidants, via adsorption–desorption processes and other chemical interactions [361]. Antagonistic effects may occur with combinations of CB and amines or certain phenolic antioxidants [350]. The acidic or basic nature of CB could determine whether the combined effect of CB and an antioxidant will be synergistic or antagonistic. Generally, inactive (low oxygen content) CB can be more favorably blended with amine-type antioxidants, while medium- or highly-oxidized acidic CB has antagonistic interactions with amines. The combined effect of acidic CB together with a phenolic antioxidant is antagonistic in most cases, and basic CB in combination with phenolic or thioether type antioxidants results in antagonism [350].

Combinations of a UV absorber and a HALS are often used for the photostabilization of PUs [259-261, 263, 272, 315]. While a UV absorber can restrict the accumulation of radicals and hydroperoxides, the reactive products that escape the action of the UV absorber can be subsequently controlled by reaction products formed from HALS. Thus, combinations of HALS and UV absorbers are usually synergistic in UV protection [207, 260, 261, 263, 272]. It is now quite well established that UV absorbers protect the intermediate HALS nitroxide from photolysis [362], with the durability of the UV absorber also increased in the presence of HALS by protection from photo-triggered, free-radical-assisted interruption of the ESIPT mechanism of stabilization [362]. HALS may reduce the quinone derivative of a UV absorber (typically of the *o*-hydroxybenzophenone type), which does not have its original UV-absorption function, to its original state [363]. This protective cooperation provides the greatest effect in photosensitive materials that have increased generation of peroxidic photoproducts [362].

However, the combined effect of inorganic UV absorbers, such as anatase TiO_2 and a HALS (aqueous Hostavin N 20 [2,2,4,4-tetramethyl-7-oxa-3,20-diazadispiro[5.1.11^{8}.2^{6}]henicosan-21-one], Clariant) has been found to be antagonistic [281]. It is possible that this was due to photocatalytic destruction of the HALS via the photoreactive anatase pigments, along with

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deactivation of the HALS via reaction of their amine functionalities with acidic surface sites on the anatase [281].

Combinations of stabilizers for PU have also been described in the patent literature. Prissok and Scholz [364] disclosed in their patent that diglycidyl terephthalate [bis(oxiran-2-ylmethyl) benzene-1,4-dicarboxylate] and/or triglycidyl trimellitate [tris(oxiran-2-ylmethyl) benzene-1,2,4-tricarboxylate] in combination with UV absorbers, preferably of the benzotriazole type, are effective stabilizers for PUs against hydrolysis, thermooxidation, and UV, while maintaining good mechanical properties without introducing significant crosslinking. A combination of diglycidyl terephthalate, triglycidyl trimellitate, and Tinuvin® 328 [2-(2′-hydroxy-3′,5′-dipentylphenyl)benzotriazole] was found to be particularly advantageous and preferably used [364]. However, the mechanism for the synergism was not further elaborated.

3.4.7. Other issues related to photostabilizers

Miscibility, retention, and cost are important factors to consider in the selection of UV stabilizers. However, the stability of UV stabilizers themselves, discussed in detail elsewhere [365], could be more important to consider for the protection of polymers [207]. For organic UV absorbers, the conditions under which energy dissipation occurs, such as polarity and temperature, determine the rate of return to their original state and most likely their survival rates [365], with their UV absorption decreasing with time of exposure [366]. Homolysis of the aryl-carbonyl bond in organic UV absorbers is a major pathway for degradation (**Error! Reference source not found.**) [366].

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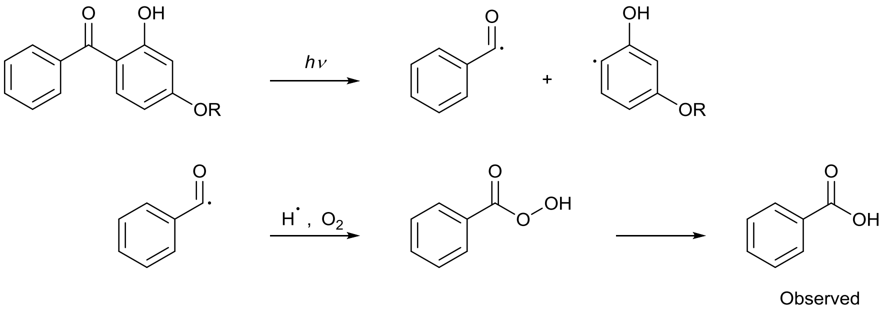

Figure 28. Mechanism of the UV-degradation of organic UV absorbers based on *o*-hydroxybenzophenone. [366], Copyright 1993. Adapted with permission from Elsevier Ltd.

Organic compounds such as UV absorbers and HALS are usually volatile and may be easily lost by migration, which may be promoted by elevated temperature [270, 272, 367]. It is a general property of UV absorbers that decreasing the hydrogen bonding potential within a series of compounds increases the volatility, whereas increasing the *M* has the opposite effect [368]. According to Ávár & Bechtold [272], modifying HALS by introducing a photoreactive site gave the possibility to fix the stabilizing molecule onto the PU matrix, which prevented migration (see the last HALS in **Error! Reference source not found.**). Yaneff et al. [270] revealed that functionalization of UV absorbers and HALS with reactive hydroxyl groups allowed the light stabilizers to efficiently co-condense with coating crosslinkers such as isocyanate or melamine-silane during cure. As a result, the light stabilizer can be retained in a PU coating with an improved stabilization effect [270]. However, it is noteworthy that locking the stabilizer into one position is likely to decrease its efficiency, given that it has to wait for radicals to be in close proximity, rather than being able to diffuse within the matrix.

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4. Thermal degradation and stabilization of polyurethane elastomers

This section focuses on thermooxidative degradation particularly in the air, while hydrothermal ageing will be discussed in Section 6.

4.1. Thermal degradation of polymers

Thermal degradation may result from absorption of infrared radiation, typically from the solar spectrum and heat sources that are close to the material. It is generally accepted that oxidation reactions involved in thermooxidation and photooxidation are similar, both believed to proceed by a free-radical, chain mechanism (autoxidation) [126, 134, 135, 369] (**Error! Reference source not found.** in Section 3.1). Initiation of thermal degradation may result from the thermal dissociation of chemical bonds in macromolecules [126, 235], which may arise through thermal processing or under usage conditions. Free radicals ($R^{\bullet}$), which are formed from the thermolysis of impurities and additives, may also contribute to thermal degradation [128]. Additionally, a combination of thermal and mechanical effects (further discussed in Section 11) could facilitate the scission of polymer chains to macroalkyl radicals, which is an important initiating process leading to the formation of hydroperoxides causing subsequent degradation [370]. Unlike photooxidation, which is primarily a surface reaction, thermooxidation may be initiated across the material depending on oxygen concentration and temperature/rate of reaction [126]. Also, the kinetic chain length (ratio of the propagation rate to the termination rate) during thermooxidation is higher than in photooxidation [126]. While ketones can react further in photochemical conditions, as a result of Norrish reactions, they show higher stability in thermooxidation [371], with other chemical properties such as the concentration of unsaturated bonds dramatically influencing the thermooxidative process [371].

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Ageing temperature greatly influences the rate of thermal degradation. A common approach is to assume that the rate of ageing is increased by a factor of $2^{\Delta T/10}$, where ΔT is the temperature increase (as based on the Arrhenius equation). The result is a mathematical expression of the empirical observation that increasing the temperature by about 10 °C roughly doubles the rate of many reactions. It is equivalent to assuming that the ageing process is a first order chemical reaction with an activation energy of $10R/\log_e 2$, where R is the universal gas constant [372]. However, while doubling of the rate of degradation for every 10 °C can be applied to a non-catalysed decomposition of hydroperoxides, it does not work so well in the presence of a catalyst or for photodegradation. Moreover, it is noteworthy that the application of this assumption does not consider new chain dissociations resulting from the increased temperature.

4.2. Thermal degradation of polyurethane elastomers

Much of this next section will include discussion on thermal degradation of polymers that occurs with time at an elevated temperature based on autoxidation (*i.e.*, long-term, isothermal degradation). This is different from thermal decomposition (combustion) following a progressively increased temperature that takes place immediately when a specific temperature is reached (*i.e.*, nonisothermal degradation), which is usually studied by TGA. A brief discussion related to this is given below.

4.2.1. General discussion of thermal degradation of polyurethane elastomers

According to TGA studies, segmented PUs usually experience a two-stage degradation process with an increase in temperature. The first stage (usually at over 250 °C) is due to the thermolysis of urethane linkages and the second stage is due to the decomposition of the macrodiol component [30, 49, 373-385]. Interurethane hydrogen bonding plays a significant role in the thermal stability of segmented PUs, which can be enhanced by a higher degree of phase separation [384, 386, 387].

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Increasing the macrodiol concentration may increase the degradation temperature of the first stage but decrease that of the latter stage [385, 388]. Aliphatic PU formulations have been reported to show higher thermal stability initially, whereas aromatic formulations displayed better mid-range thermal degradation resistance [389]. The higher the concentration of the urethane group, the lower are both the activation energy for thermal decomposition and the thermal stability of the PU [390]. Additionally, there may be a mutual stabilization effect from the HSs and SSs in segmented PUs [384, 388].

In contrast, in the case of isothermal degradation over a prolonged period, usually at a moderate temperature less than 150 °C, the macrodiol component (*e.g.*, PB) may be less resistant to oxidation than the urethane linkage [374]. Therefore, for understanding thermooxidative degradation and related stability, more attention should be paid to the macrodiol component than the isocyanate/resultant urethane.

Unsaturation level in the macrodiol component may significantly affect thermal degradation, with PBU elastomers being typical rubbers that contain unsaturated C=C bonds. The thermal degradation of these elastomers is discussed below. To avoid thermal degradation of PU elastomers, one patent [391] has documented the preparation of thermally-stable materials utilising low unsaturation level macrodiols (preferably polyether diols) prepared by double metal cyanide complex catalysis. These PU elastomers are more stable against thermal degradation than, for example, PTMEG-based PU elastomers [391].

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4.2.2. Thermal degradation of poly(butadiene-urethane) (PBU) elastomers

As discussed in Section 3.2.2.3, PB and its copolymers are very susceptible to oxidative degradation owing to the unsaturated (alkene) character (**Error! Reference source not found.**). This is related to the low BDE of C-H bonds of allylic methylenes (E_d = 350 kJ·mol^{-1}), compared to those

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in most saturated hydrocarbons, which are more than 380 kJ·mol^{-1} [174]. The thermooxidation of PB leads to double bond consumption, carbonyl and hydroxyl build-up and a mass increase due to oxygen incorporation [174]. In this process, stable unsaturated oxidation products are formed from alkyl radical precursors; and reactions involving polymer radicals ($P^{\bullet}$) are important, especially with exposure to air at atmospheric pressure [174]. Oxidation kinetics are characterized by an induction period, at the end of which oxidation accelerates abruptly and then quickly slows down, which is due to fast substrate consumption. Induction times are about the same for all the investigated characteristics: mass gain, double bond disappearance, and carbonyl and hydroxyl build-up [174].

Some oxidative degradation products of HTPB, including hydroperoxide and peroxides (**Error! Reference source not found.**), can be formed by the reaction between the oxygen and the double bonds of HTPB at high temperatures (typically 180–200 °C) [374]. As hydroperoxides are unstable, subsequent oxidation reactions occur, causing the degradation of the polymer, which follows the same autoxidation process as for photooxidation (**Error! Reference source not found.**) [180].

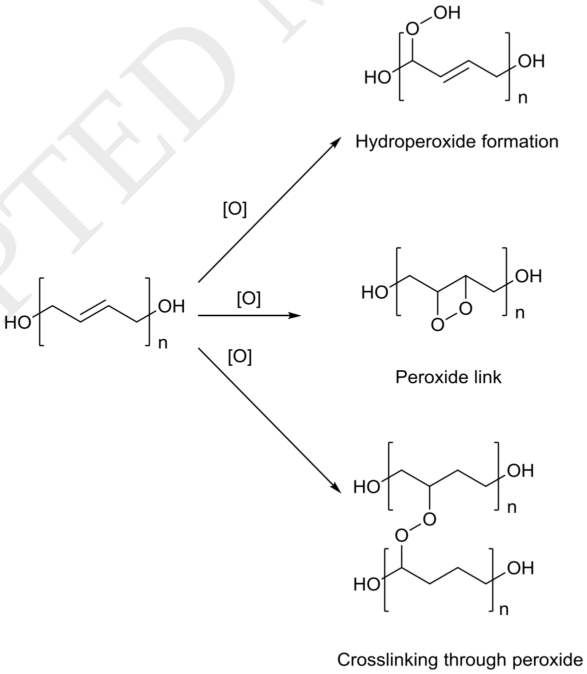

Figure 29. Degradation products from the oxidation of hydroxyl-terminated polybutadiene (HTPB). [374], Copyright 2001. Adapted with permission from Elsevier Ltd.

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Primary unsaturated hydroperoxides derived from PB can be thermally decomposed into α,β-unsaturated carbonyls at moderate temperatures (*e.g.*, 60 °C) [180]. In contrast to photooxidation, subsequent reactions leading to loss of the alkene functionality in these unsaturated carbonyls (such as crosslinking and oxidation) occur to a lower extent under thermooxidative conditions [180]. In addition, when a significant concentration of hydroperoxides has accumulated in PB, thermal decomposition of hydroperoxides leads to a high concentration of radical species and progress to β-scission via Mechanism 2 shown in **Error! Reference source not found.**. In contrast, when the concentration of hydroperoxides is low, Mechanism 1 (**Error! Reference source not found.**) dominates and ketones subsequently form, as discussed for photooxidation of PB (see **Error! Reference source not found.**) [180]. α,β-unsaturated carbonyls are the major products of thermooxidation, whereas these products act as chromophores during photooxidation and react to form saturated aldehydes as the predominant products [179, 180].

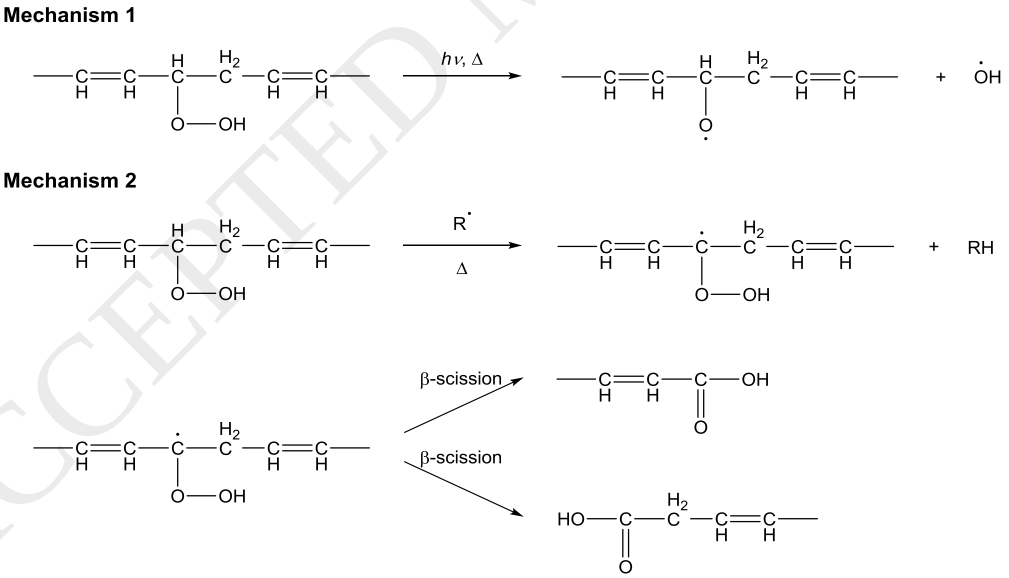

Figure 30. Thermal decomposition of hydroperoxides from polybutadiene. [180]

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It has been reported that, for HTPB/isophorone diisocyanate (IPDI)-based PU elastomers aged in the air at various temperatures up to 110 °C, the urethane linkages were essentially unchanged while the PB component of the polymer had significantly degraded [392, 393]. Both crosslinking and chain scission occurred during degradation [393, 394]. Approximately 60% of the oxidation products were alcohols, independent of temperature and the presence or absence of antioxidants; the remaining oxidative products were principally acids, esters, carbon dioxide, and small amounts of other products containing carbonyl functional groups [392, 393]. The extent of thermooxidation was found to be oxygen-diffusion limited, which led to a gradient of oxidation product concentrations through the film thickness [174, 392]. This heterogeneous oxidation occurs because ambient oxygen cannot permeate into and react with the sample bulk as readily as with the surface layers, so there is a correlation between the oxygen permeation and the oxidation rate of the material [392].

Although urethane linkages are more oxidatively-stable than PB components, the overall oxidative stability of PBUs can still be affected by the urethane linkages. Villar et al. [394] revealed that, for HTPB/IPDI-based PUs kept at various temperatures between 50 °C and 70 °C for up to 34 weeks, a higher number of urethane linkages (a higher NCO/OH ratio, 1.0 *vs.* 0.85) resulted in a lower Arrhenius activation energy (82 ± 10 kJ·mol^{-1} *vs.* 156 ± 30 kJ·mol^{-1}), thus delivering faster oxidation.

There is some disagreement in the literature regarding the rate of thermal degradation of PB with different structural units. Coquillat et al. [174] observed that *trans*-vinylene groups and vinyl groups reacted at practically the same rate. However, in another study by Nagle et al. [392], the *trans* isomer of PB appeared to have a higher degradation rate than the vinyl isomer.

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4.2.3. Effects of thermal degradation on the properties of polyurethane elastomers

Thermal degradation of PUs can result in the loss of mass [374, 395], with gradual mass loss during isothermal ageing possibly being due to the loss of moisture, solvents or plasticiser that were incorporated during the preparation of PUs [374, 395] and/or to the loss of molecules because of chain scission [374, 395].

During thermal ageing, competing effects from crosslinking and chain scission significantly influence the material properties. While crosslinking usually dominates in the initial stage, with a longer period of ageing, the effect of main chain scission overshadows the effect of an increased crosslink density [395]. There is no consensus on how these chemical changes affect the material properties [374, 375, 396-398], as this could depend on multiple factors such as the material formulation and the ageing temperature. For a PCL copolyester-based PU aged at either 70 °C or 90 °C for up to 270 days, there was firstly an increase in the material rigidity and then a decrease in the mechanical properties [395]. For PBU elastomers, thermal ageing between 50 °C and 100 °C will normally result in a decrease in elongation at break and an increase in elastic modulus, with greater changes at higher ageing temperatures (**Error! Reference source not found.**) [374, 396-398]. Thermal ageing may also lead to an increase in T_g [398].

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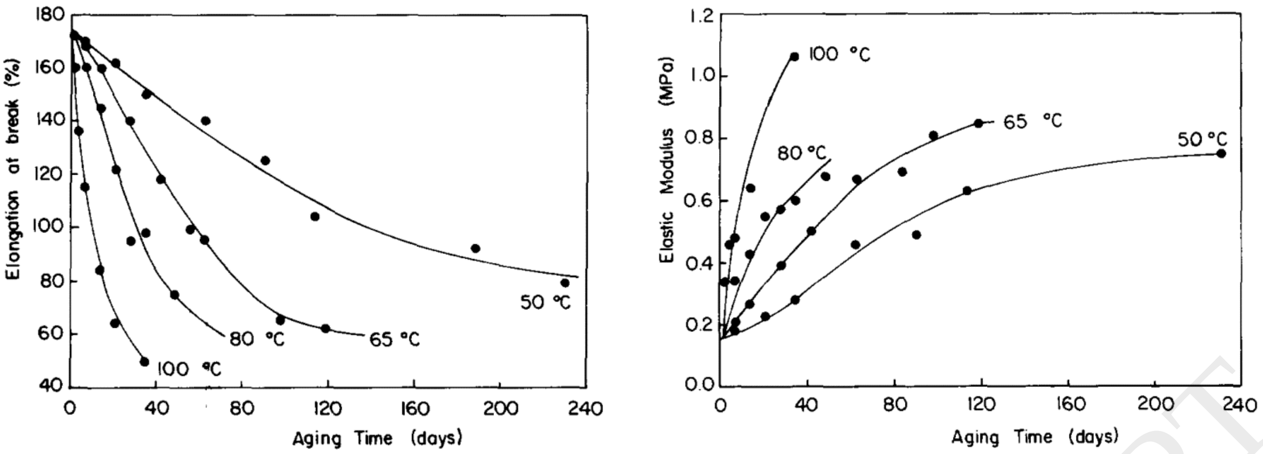

(A) (B)

Figure 31. Effect of thermal ageing on elongation at break (A) and elastic modulus (B) of a HTPB/IPDI-based polyurethane. [396], Copyright 1994. Reproduced with permission from Elsevier Ltd.

For an HTPB/IPDI-based PU elastomer aged at 95 °C for up to 52 days, Assink et al. [397] found a strong correlation between elongation at break and ^{13}C nuclear magnetic resonance (NMR) cross polarization (CP) time, or T_{cp}. While the ^{1}H relaxation times were dominated by high-frequency local motions that were not strongly coupled with the mechanical properties, T_{cp} was dependent on low-frequency cooperative motions that were more strongly coupled to mechanical properties, such as elongation [397]. De la Fuente and Rodríguez [399] indicated that the changes in viscoelastic properties measured by dynamic mechanical analysis (DMA) could well reflect the thermal ageing of HTPB/IPDI-based PU elastomers at different temperatures between 40 °C to 80 °C. The storage modulus (E') firstly decreased due to initial softening and then increased with the ageing time. A higher ageing temperature resulted in higher E' values (**Error! Reference source not found.**A). On the other hand, the loss factor or damping efficiency, tan δ, measured at 22 °C, gradually decreased with the ageing time, and this reduction was at a higher rate at a higher ageing temperature (**Error! Reference source not found.**B).

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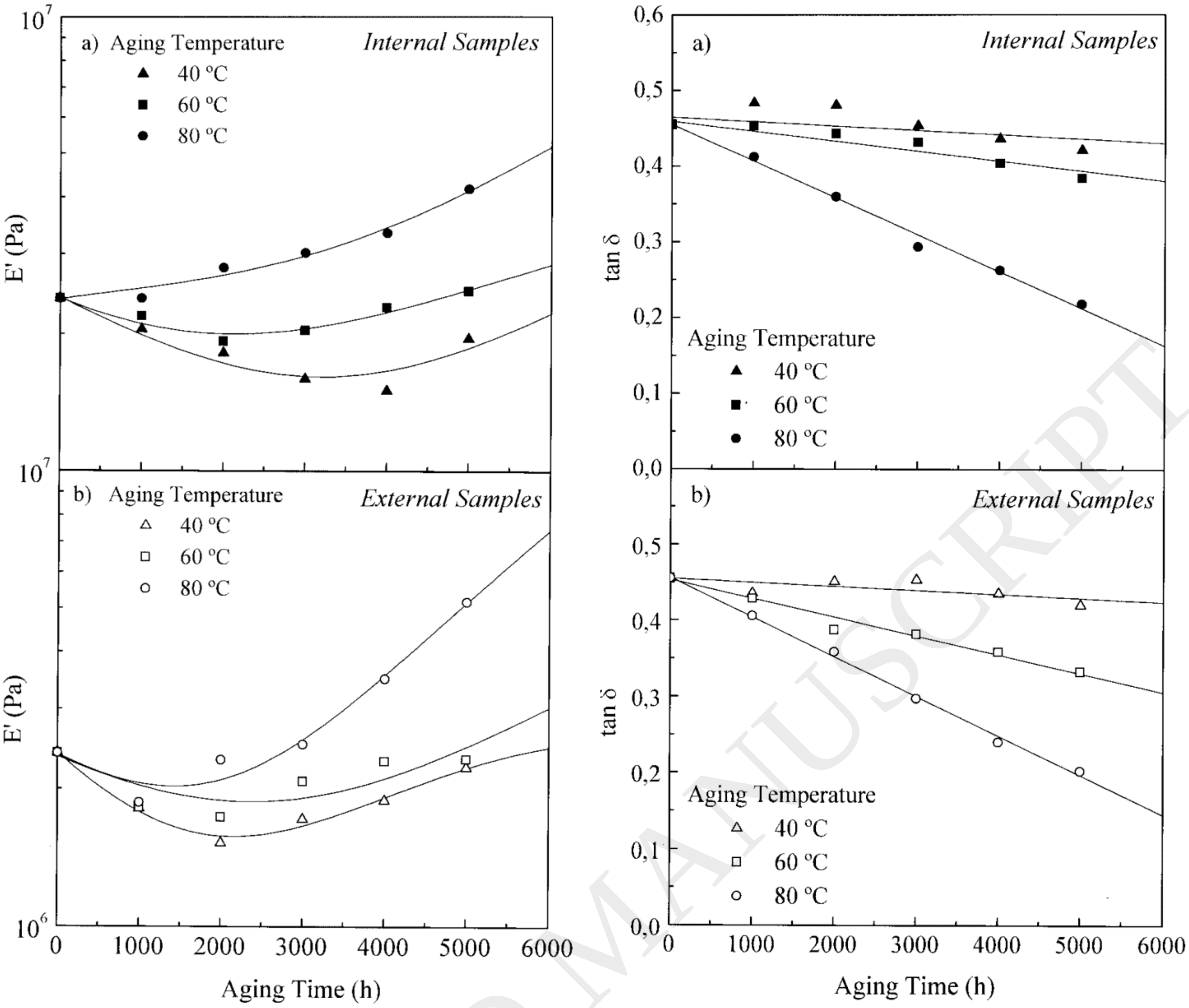

(A) (B)

Figure 32. *E′* (A) and tan δ (B) (measured at a frequency of 0.1 Hz, and 22 °C which corresponded to the secondary relaxation) as a function of the ageing time for (a) internal (core) and (b) external (surface) polyurethane propellant samples aged at different temperatures. [399], Copyright 2003. Reproduced with permission from John Wiley & Sons Inc.

4.3. Stabilization of polyurethane elastomers against thermal degradation by polymer modification

As photodegradation and thermal degradation follow predominantly the same mechanism of autoxidation, the strategies for enhancing the photooxidative stability of PU elastomers (discussed in

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Section 3.3) could also be applied for enhancing thermooxidative stability. Approaches include using materials that have components with higher BDEs and increasing the degrees of crosslinking and crystallinity.

Due to macrodiol components typically being the weak link in the oxidation of PU elastomers, using macrodiols that have high oxidative stability could give PUs with improved thermooxidative stability. Efforts have been made to synthesize new polyester diols that can be used to form PUs that are more thermally stable than traditional PTMEG-based PUs [400]. Macrodiol components may also be prepared by copolymerization with another polymer with higher thermooxidative resistance. For example, Sarkar and Adhikari [374] reported that with the same NCO/OH ratio, adding lignin to build a lignin-*co*-HTPB copolymer to react with TDI could lead to a PU with increased thermal resistance during isothermal ageing at 100 °C for 48 h. Alternatively, hydrogenation of PUs containing unsaturated C=C bonds in the macrodiol segments may give the polymer better resistance to heat and oxidation [215, 401]. This strategy has been demonstrated to be successful for PUs based on PIP (at 150 °C in air for up to one month) [401] and PB (at 120 °C for up to 72 h) [215].

On the other hand, when urethane linkages are subjected to thermal degradation (*e.g.*, during thermal processing with a temperature higher than 200 °C), the use of aliphatic isocyanates may give improved thermal stability. Rische et al. [402] have shown in their patent that PUU dispersions stable to thermal yellowing contain HDI, IPDI, and the isomeric 4,4′-H_{12}MDI and also mixtures thereof, which are all aliphatic isocyanates.

4.4. Stabilization of polyurethane elastomers against thermal degradation using stabilizers

The stabilizers used for enhancing the thermooxidative stability of PUs elastomers are similar to those for improving the photooxidative stability of these materials, and include: radical scavengers,

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hydroperoxide decomposers, and quenchers, as discussed in Section 3.4. **Error! Reference source not found.** shows possible paths for stabilization of thermally degradable polymers within the autoxidation process, with stabilization mainly involving radical scavengers (CB-A and CB-D) and hydroperoxide decomposers [133]. These types of stabilizers have already been extensively covered in the discussion of photostabilization of PU elastomers, with various additives for stabilization against thermooxidation broadly discussed elsewhere [133, 134, 138, 139, 224, 236-238, 246, 247]. The following discussion only involves unique aspects related to using stabilizers for improving the thermooxidative stability of PU elastomers.

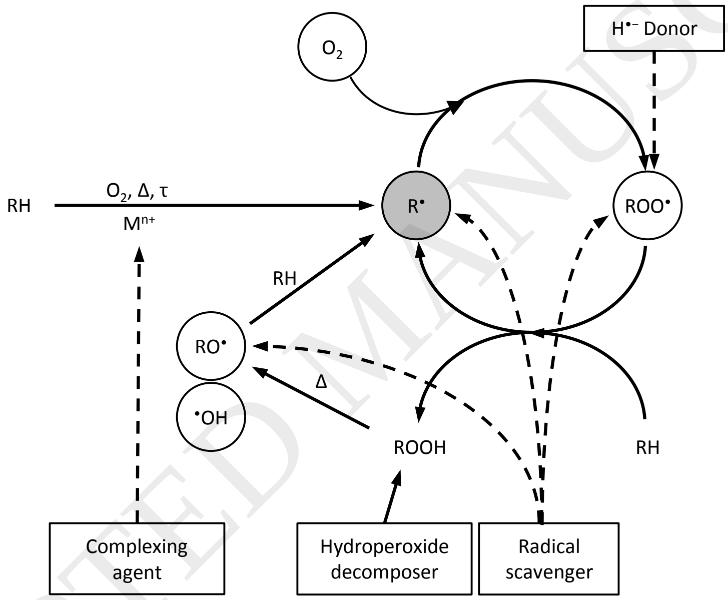

Figure 33. General scheme of inhibition of thermooxidative degradation. [133], Copyright 1998. Adapted with permission from Springer.

4.4.1. Radical scavengers

Various radical scavengers discussed in Sections 3.4.3 and 3.4.4 are also applicable for protection of PU elastomers against thermooxidation. Relatively stable nitroxide radicals are typical CB-As, whereas CB-Ds include secondary amines and hindered phenols. *N,N′*-diphenyl-*p*-

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phenylenediamine [1-*N*,4-*N*-diphenylbenzene-1,4-diamine] and *N*-phenyl-2-naphthylamine [*N*-phenylnaphthalen-2-amine] are typical secondary amine antioxidants [224]. *N,N′*-diphenyl-*p*-phenylenediamine contains two hydrogens, each of which can interrupt oxidation via radical scavenging, as illustrated in **Error! Reference source not found.** [224]. However, it is important to note that the use of amine stabilizers can lead to noticeable discoloration of the substrate due to the transformation products of the aromatic amines [133].

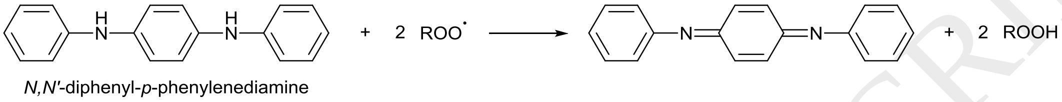

Figure 34. Reaction of *N,N′*-diphenyl-p-phenylenediamine with peroxy radicals. [224].

Irganox® 1010 (**Error! Reference source not found.**) has been found to be an effective antioxidant for polyester/4,4′-MDI-based PUs at temperatures higher than 200 °C, when the HSs became unstable [369]. Calabrese and Boccuzzi [403] have shown in their patent that the radical scavenger, methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate effectively prevents the thermal degradation of PU foams. They claim that this additive can be optionally used with another phenolic and/or an amine and/or phosphite or thioether or lactone stabilizer to form a stabilizer package for macrodiols, PUs and other oxidatively-degradable polymeric materials [403].

While CB is an excellent stabilizer against photooxidation, it also functions as a mild thermal antioxidant [224]. With a variety of oxygenated groups that are chemically attached to its surface, and unpaired electrons within the structure, CB reacts to a minor extent to trap propagating radicals [224]. The primary role of CB, particularly activated CB, is as a CB-D [224].

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4.4.2. Hydroperoxide decomposers

Hydroperoxide decomposers include phosphites and phosphonites as already discussed in Section 3.4.4. Because of their high reactivity, phosphites and phosphonites are usually used as stabilizers during processing in the melt (at temperatures up to 300 °C). As “long-term” stabilizers, their contribution to the stabilization of the end product is small [133]. Their reactivity in hydroperoxide reduction decreases with increasing electron-acceptor ability and steric bulk of the groups bound to phosphorus in the order phosphonites > alkyl phosphites > aryl phosphites > hindered aryl phosphites [348].

Organosulphur compounds such as sulphides, dialkyl dithiocarbamates and thiodipropionates are also well-known hydroperoxide decomposers [236, 348]. Their effect is based on the ability of sulphenic acids to decompose hydroperoxides. To this end, however, the sulphenic acid has to be formed by the decomposition of the intermediate sulphoxides [133, 348]. Regarding this, **Error! Reference source not found.** shows the hydroperoxide decomposition with thiodipropionate esters [133]. Intermediates with a 3,3′-sulphinyldipropionate ester structure are particularly reactive with regard to the sulphenic acid formation. For this reason, compounds such as distearyl, or dilauryl dithiopropionate are mainly used [133]. Because sulphoxides and the subsequent oxidation products are formed relatively slowly, thiosynergists primarily contribute to the extension of the lifetime of plastics in the course of use at temperatures up to 150 °C. During processing in the melt, thiosynergists do not contribute to stabilization, in contrast to trivalent phosphorus compounds [133, 404].

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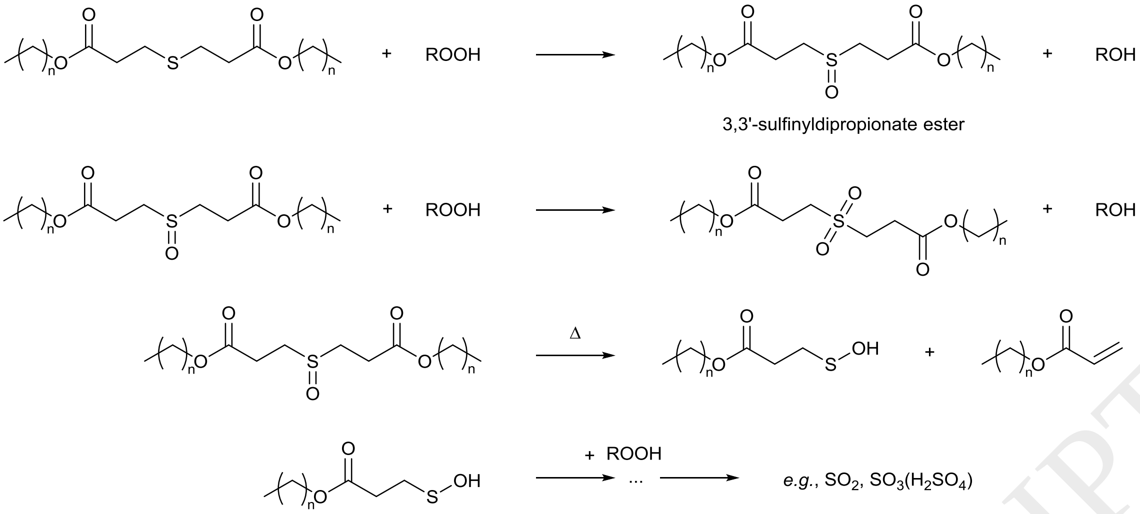

Figure 35. Hydroperoxide decomposition using thiodipropionate esters. [133], Copyright 1998. Adapted with permission from Springer.

Other known hydroperoxide decomposers are based on metal complexes of dialkyl dithiocarbamates [236]. These types of antioxidants have been used in rubbers for many years, with the mechanism by which they inhibit oxidation being quite complex [224].

Activated CB also functions effectively as a hydroperoxide decomposer, with sulphurised CB being more effective, most likely due to mercaptan groups present on the surface of sulphur-activated CB [224]. Hydroperoxide decomposition may also be ascribed to the acidity resulting from oxygen-containing groups on CB [224].

4.4.3. Bifunctional stabilizers

Bifunctional stabilizers combining sterically hindered phenols and sulphur substituents have been investigated for their functionality as both CB-D and hydroperoxide decomposers (**Error! Reference source not found.**) [133, 224, 233, 405].

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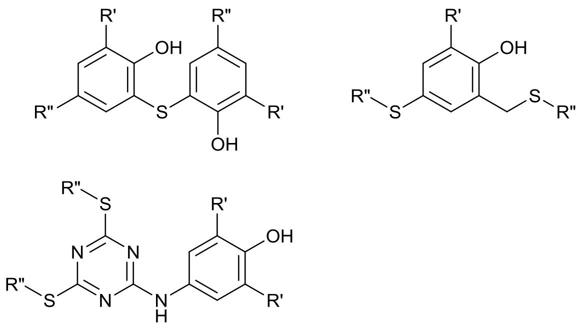

Figure 36. Stabilizers with dual functionality.

4.4.4. Other stabilizers

Inorganic fillers such as silica, layered silicates, CNTs and fullerenes may also be effective in enhancing the thermal stability of PUs [406]. Chen et al. [375] showed a positive effect from sepiolite modified with (3-aminopropyl)triethoxysilane [3-triethoxysilylpropan-1-amine] (KH550-Sp) on the thermooxidative stability of PU nanocomposites based on HTPB, PTMEG (1:1), and TDI. Specifically, KH550-Sp in the nanocomposites could restrict the mobility of polymer chains and prevent the rapid penetration of oxygen into the PU matrix and therefore effectively suppress the oxidation of double bonds [375].

Various additives such as metal-based compounds (metal oxides, metal salts, metal–organic hybrids and metal hydroxides), melamine, and carbon-based additives have also been shown to be effective flame retardants and smoke suppressants during PU thermal decomposition (combustion) [407].

4.4.5. Combination of stabilizers

The effectiveness of combinations of CB with other stabilizers is dependent on the CB chemistry. CB with low volatiles content was shown to increase the thermooxidative stability of polymers, whereas CB with the highest volatiles content adversely influenced the thermal stability [253]. The

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effect observed for the high volatiles content CB may be due to the adsorption of antioxidants (such as secondary amines or certain hindered phenols) used in the formulation onto the surface of CB or to the sensitization of thermooxidative reactions by the surface oxygenated groups present [224, 253]. Catalytic destruction of the antioxidant at the surface may be the major factor responsible for the antagonism [224].

Antagonistic and synergistic effects of combined stabilizers for various polymers have been well documented elsewhere [134, 139, 207, 235, 237]. A typical example of this is that blends of chain-breaking stabilizers (phenols or amines) and hydroperoxide decomposers (phosphites and phosphonites or thiosynergists) generally exhibit a synergistic effect [133]. The combination of CB with sulphur-containing antioxidants also shows synergism [224].

5. Ozonolytic degradation and stabilization of polyurethane elastomers

5.1. General ozonolytic degradation of polymers

Most polymers are resistant to ozone, with ozone degradation limited to unsaturated polymers, especially under stress [126, 408-410]. Elastomeric compounds (natural rubber and synthetic polymers and butadiene and isoprene copolymers) are particularly susceptible to even low concentrations of ozone, down to a few pphm [409, 411].

The mechanism of the reaction of ozone with unsaturated polymers has been well documented in the literature [246, 370, 408, 409, 411-416]. A schematic of such reaction is shown in **Error! Reference source not found.** [412]. Ozone damages these compounds by breaking polymer chains at the C=C double bond, leading to the formation of unstable primary ozonides (molozonide). Ozonides can then cleave to form carbonyl compounds (aldehydes) and carbonyl oxides (zwitterion).

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Aldehydes and carbonyl oxides recombine to form trioxolane rings, which are secondary ozonides. Thus, ozonide groups may be formed together with polymeric ozonides [417, 418]. Ozonides are reasonably stable in neutral environments, but they will decompose readily under the influence of heat or various reducing agents to yield chain scission products such as aldehydes, ketones, acids and alcohols [409, 414]. In unstressed rubbers or elastomers, more than 50% of the fragments recombine to form the secondary ozonide [412]. Ozone reacts with all of the surface double bonds to produce a nonreactive surface coating or frosting [409, 414], which provides an effective barrier against further attack by gaseous ozone [419]. In the unstressed case, the reaction is limited to the surface, and no cracking will occur [126, 409, 414].

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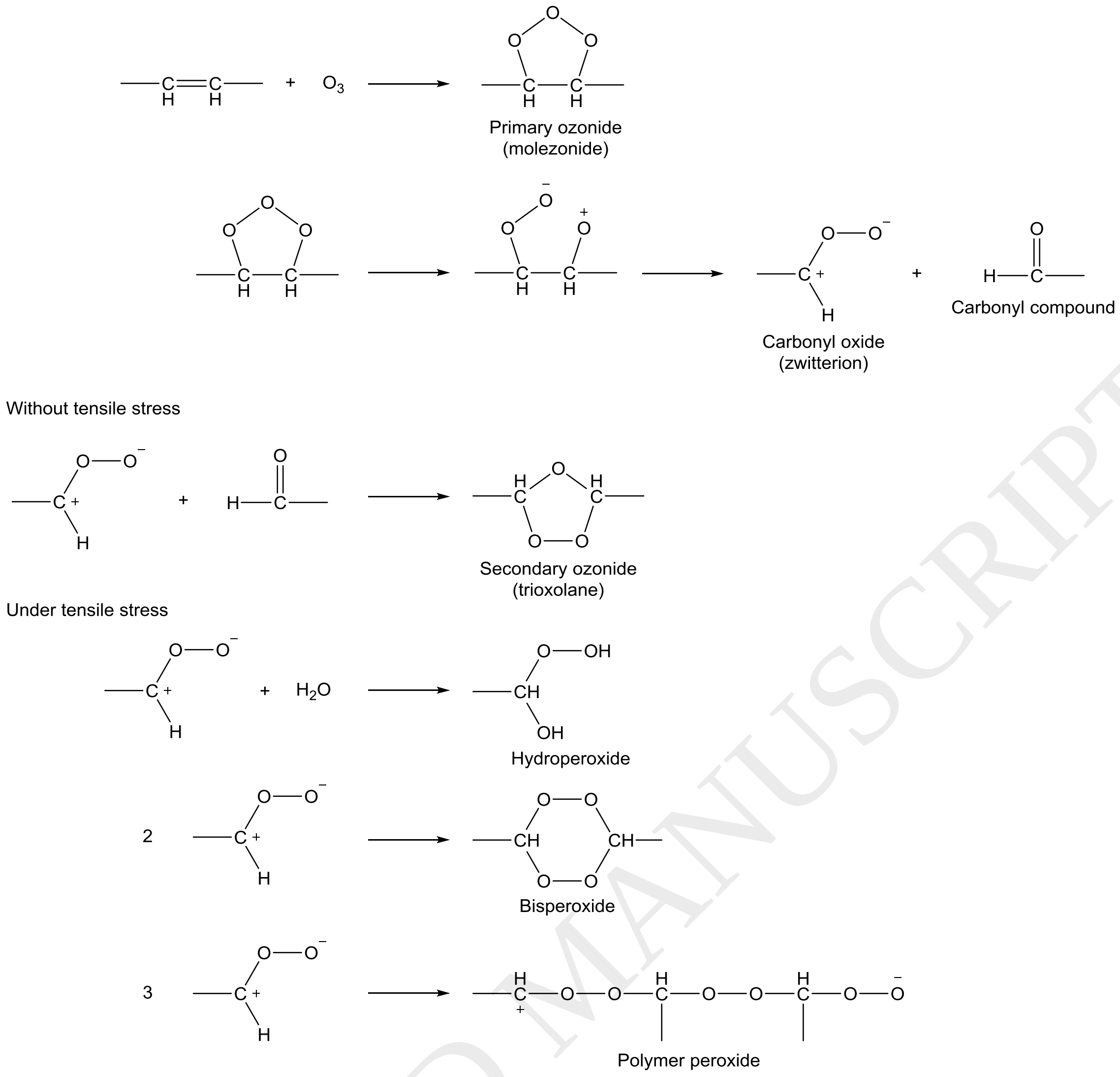

Figure 37. Ozonolysis of diene polymers. [412], Copyright 2001. Adapted with permission from Elsevier Ltd.

Under stress, external force makes the recombination of the two chain end groups to form a secondary ozonide (*i.e.*, the trioxolane ring) difficult and leads to more routes for ozonolysis (**Error! Reference source not found.**) [412]. In this case, one chain end is stabilized because it is already an aldehyde group [412]. However, the chain end with a carbonyl oxide group could react with water to form a hydroperoxide [412]; therefore, the rate of chain scission is increased in the presence of active hydrogen (*e.g.*, water) [409, 414]. Additionally, the chain end with a carbonyl oxide group could recombine with another carbonyl oxide group from another chain end to form a bisperoxide or a polymeric peroxide, which can then be hydrolysed to more stable carbonyl compounds [412].

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As the stressed polymer chains cleave under ozone attack, new highly stressed surfaces are exposed. The localised continuation of this process results in visible cracking, which is always perpendicular to the applied stress [409, 414]. The strain produces cracks on the surface of the rubber that increase in number with increased stress/stretching [409, 411]. After the initial cracking, there is further ozone penetration, resulting in additional cracking and, eventually, mechanical weakening or stress relaxation [411].

The crack growth rate seems to be independent of stress but depends on ozone concentration and temperature [412]. At low or very low temperatures (*e.g.*, 0 °C), even if the ozone concentration is high, the attack on double bonds is hindered by the low reaction rate, low diffusion rate and low solubility of ozone in the elastomer [410]. At temperatures sufficiently above T_g, the availability of ozone becomes the rate-limiting factor for crack growth [412]. However, when the temperature is too high (>70 °C) ozone becomes unstable and decomposes very quickly in air. Consequently, negligible ozone attack is experienced [409, 410].

Both chain scission and crosslinking may occur during ozonolysis [409, 414, 420, 421]. Elastomers containing tri-substituted double bonds (*e.g.*, PIP) are more prone to chain scission [420, 421], as in the pathways described above. Crosslinking may also occur, especially with polymers containing di-substituted double bonds (*e.g.*, PB) [420]. It is proposed that this may be due to the attack of carbonyl oxides, in their biradical form, on the polymer double bonds [420].

The reaction rate constants of unsaturated polymers are usually about 10^6–10^7 times faster than those for relatively saturated polymers [416]. For example, the rate constants of *cis*-PIP and *cis*-PB reacting with ozone in solution at 20 °C are 440,000 $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$ and 60,000 $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$, respectively, whereas that of PIB, a saturated elastomer, is 0.012 $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$ [409]. Research has also shown that solid-state *trans*-polydienes react more readily with ozone both in solution or in the solid state, indicating a lower activation energy in comparison to the corresponding *cis*-polydienes [417, 422].

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5.2. Ozonolytic degradation of polyurethane elastomers

Most PU elastomers are quite resistant to ozone [423], with both PEsUs and PEtUs showing excellent resistance to ozone [53, 424-430]. PU elastomers that are prone to ozonolytic degradation are those based on macrodiols with high degrees of unsaturation, typically PB and PIP. Given this, the discussion in Section 5.1 regarding the ozonolytic degradation mechanisms of general elastomers can also be applied to the PUs based on these polymers.

Ozonolytic degradation is not always problematic for PU elastomers, with ozone sterilization being commonly practised for biomedical applications [431-437]. It has been reported that ozone sterilization could result in surface oxidation of a proprietary PU elastomer leading to a decreased contact angle and increased hydrophilicity, which is favorable for cell attachment [431].

5.3. Stabilization of polyurethane elastomers against ozonolytic degradation by polymer modification

One clear approach to make PU elastomers resistant to ozonolytic degradation is to use macrodiols with a high degree of saturation. As discussed above, the use of polyesters, polyethers and saturated elastomers such as PIB, instead of PB or PIP, can result in PUs with excellent stability against ozone. As discussed already, hydrogenated PB is more resistant to oxidation due to the absence of double bonds [208, 209]. While some of the C=C bonds of an HTPB-based PU were found to be oxidized to form carbonyl functional groups during ozone ageing at a concentration of 50 ppm for 48 h, its hydrogenated counterpart showed no obvious change under the same conditions

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[215]. Elimination of double bonds or crosslinking at the immediate surface could also improve ozone resistance of elastomers [408].

Elastomers such as *trans*-1,4-polyisoprene with higher crystallinity are shown to be less reactive with ozone [412]. Therefore, PUs based on high-crystallinity elastomers should also be more resistant to ozone.

Blending PUs that are susceptible to ozonolytic degradation with polymers with high ozone resistance could also be a useful way to enhance the ozonolytic stability of the overall materials [438]. Maity and Das [438] showed that blends of PU and chlorinated PE (which has excellent thermal and ozone resistance) could be obtained through interchain crosslinking using dicumyl peroxide [2-(2-phenylpropan-2-ylperoxy)propan-2-ylbenzene] (DCP) as a curing agent.

Again, it is important to bear in mind that any physical or chemical modification to the polymer matrix could potentially modify the material properties (such as T_g and mechanical properties) and/or increase the material costs, which could prevent the practical application of these methods.

5.4. Stabilization of polyurethane elastomers against ozonolytic degradation using stabilizers

Stabilizers for protecting polymers against ozonolytic degradation are called antiozonants. They can be divided into two groups: physical antiozonants (hydrocarbon waxes) and chemical antiozonants. Since ozone attack is a surface phenomenon, the antiozonant must migrate to the surface of the rubber to provide protection. Therefore, both physical and chemical antiozonants have to have adequate solubility and diffusivity in the polymer to ensure effective protection [409], with temperature controlling the diffusion rate and solubility of not only ozone but also antiozonants [439].

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5.4.1. Hydrocarbon waxes

Waxes, which are relatively unreactive towards ozone, can protect polymers against ozonolytic degradation by a physical process in which the additive blooms out of the formulation to form a protective film over the surface [408, 409]. If a wax is present in an elastomer at a level exceeding its solubility, some of the wax will migrate to the elastomer surface where it can form a physical barrier to prevent the penetration of ozone [409]. As long as the wax remains intact as a continuous, thick enough film (preferably under static conditions), the elastomers are protected against ozone attack [408, 410].

There are a few advantages to the use of waxes as antiozonants, such as their low cost, non-staining character, and that they have no adverse effects on material processing [409, 415]. However, waxes are ineffective under dynamic stress conditions, due to a lack of adhesion between the wax film and the elastomer and to the inextensibility of the wax bloom [408-410]. Another shortcoming of waxes is their high dependence of protection upon exposure temperature, due to thermally-induced changes in solubility and diffusion coefficients. Protection is difficult to achieve at both very low (<10 °C) and very high (>50 °C) temperatures [409, 415]. Moreover, the damage to the bloom caused by embrittlement, scuffing and delamination during storage and use will affect the protection from ozone provided by the wax [415]. Due to these limitations, waxes are usually used together with chemical antiozonants [409].

Although waxes are commonly used as antiozonants for rubbers, few reports have been found on the effectiveness of waxes for PU elastomers. Nonetheless, research has shown that waxes can diffuse into the PU and migrate to the PU surface [440], demonstrating their capability to protect PUs as well as other rubbers.

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5.4.2. Chemical antiozonants

Chemical antiozonants are mostly based on nitrogen-containing compounds. Compound classes include derivatives of 1,2-dihydro-2,2,4-trimethylquinoline, *N*-substituted ureas or thioureas, substituted pyrroles, and nickel or zinc dithiocarbamate salts [409, 441]. The most effective antiozonants are derivatives of *p*-phenylenediamine (PPD) [409, 413, 415, 416, 441] (**Error! Reference source not found.**), which have also been demonstrated to be effective for PUs [442]. Commercial PPD materials are grouped into three classes: *N,N′*-dialkyl-PPDs, *N*-alkyl-*N′*-aryl-PPDs, and *N,N′*-diaryl-PPDs [246, 409, 410, 415, 441]. *N,N′*-dialkyl-PPDs have the highest reaction rate with ozone, which also results in shorter useful lifetimes [409, 410, 415, 441]. *N,N′*-diaryl-PPDs are only moderately active antiozonants and can only be used at low concentrations (generally < 2%) because of their poor solubility [409, 410, 441]. Nonetheless, *N,N′*-diaryl-PPDs are most stable towards oxygen and are resistant to loss by consumption and vaporization [138, 409, 415, 441]. In contrast, *N*-alkyl-*N′*-aryl-PPDs have balanced properties between *N,N′*-dialkyl-PPDs and *N,N′*-diaryl-PPDs [409, 410, 415, 441]. It is noteworthy that some antiozonants, especially those based on the PPD structure, can yield diimine products, which are strong chromophores. Therefore, this type of antiozonant has a staining effect on the material [408].

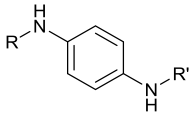

Figure 38. Derivatives of *p-phenylenediamine* [benzene-1,4-diamine].

As ozonolysis is not based on the free radical chain reaction mechanism that can be applied to photo-, thermal, and mechanical degradation, conventional antioxidants except for *N,N′*-diaryl-PPDs provide very little protection against ozone attack [408]. Similarly, *N,N′*-dialkyl-PPDs which are effective antiozonants give little protection against thermooxidation [408]. Even so, there have been

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specifically designed compounds, which are derived from an *N,N′*-substituted PPD and also have an ether or thioether structure. These compounds are of value in elastomeric compositions where they prevent adverse effects due to both oxygen and ozone [443, 444]. It is interesting to note that the most effective antiozonants are also effective antifatigue agents and conversely the molecules that do not act as antiozonants are worse antifatigue agents [410]. In particular, PPDs protect polymers not only from ozone cracking but also from autoxidation and mechanical fatigue [410]. This dual protection is quite unexpected since the fatigue degradation is due to mechanooxidative ageing (discussed in Section 11).

The scavenger theory is believed to be the most important mechanism of antiozonant action, which states that the antiozonant diffuses to the surface and preferentially reacts with ozone, with the result that the rubber is not attacked until the antiozonant is exhausted [246, 408, 409, 414, 441]. Based on this mechanism [408, 409, 441], faster reaction between the antiozonant with ozone provides better protection. The rates of reaction between ozone and an antiozonant (in particular PPD) are typically one to two orders of magnitude higher than the rates for diene elastomers [409, 416].

6. Hydrolytic degradation and stabilization of polyurethane elastomers

6.1. Hydrolytic degradation of polyurethane elastomers

As discussed in Section 2.2, most PUs except for those derived from polyester diols display excellent hydrolysis resistance. In particular, PEtUs display superior hydrolysis resistance to PEsUs [31, 52-54]. The statements here also apply to the hydrolysis of PUs in inorganic salt solutions

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(typically seawater) as most inorganic salts do not affect the degradation of PUs [445]. PBUs are also considered to be hydrolytically stable, although not as good as PEtUs [62].

6.1.1. Hydrolytic degradation of poly(ester-urethane)s

Error! Reference source not found. shows the hydrolysis reaction for PEsUs [446]. Water can react with a carboxylic ester link in the PEsU chain. The reaction breaks the polymer chain at the point of attack, producing two shorter chains. One of these chains ends in a hydroxyl group (-OH). The other end is a carboxyl group (-COOH), which is acidic [446, 447]. This acidic carboxyl group speeds up the further hydrolysis of the polyester segments in the PEsU, and the degradation becomes autocatalytic [446, 448].

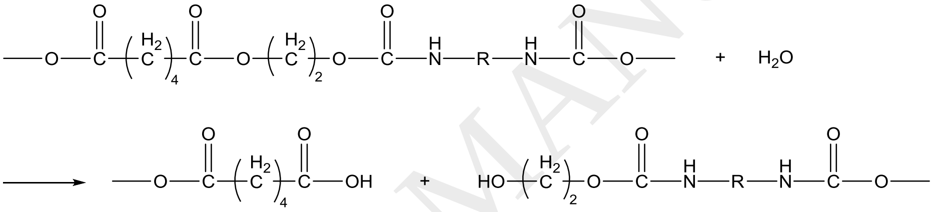

Figure 39. Hydrolysis of poly(ester-urethane)s. [446], Copyright 1973. Adapted with permission from John Wiley & Sons Inc.

The urethane linkage may also be hydrolysed to give an alcohol, an amine, and carbon dioxide [59, 446, 447, 449]; and urea bonds could be hydrolysed into two amines and carbon dioxide [59]. However, ester linkages hydrolyse at about an order of magnitude faster than urethane linkages; and urea linkages hydrolyse faster than urethanes, although under slightly acidic conditions [59]. Therefore, unless a PEsU elastomer contains special sterically hindered carboxylic ester linkages in its chains, the dominant reaction in its hydrolysis in normal service is the cleavage of the carboxylic ester groups as shown in **Error! Reference source not found.** [205, 446, 449, 450]. For example, Pretsch et al. [451] suggested that hydrolytic chain scission of a commercial PU based on

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poly(adipate) diols, MDI, and 1,4-BDO firstly occurred at the ester linkages and was delayed at the urethane linkages, which may be either located initially in the interphase or the SS phase and finally in the crystalline HS domains.

The hydrolysis of PEsUs is acid-catalysed [448]. It is noteworthy that polyester diols are typically acidic due to incomplete esterification in their preparation [446, 449]. While most of the polyester diols formed terminate at both ends in hydroxyl (-OH) groups and have zero acid number, as intended, frequently a few of the polyester diols formed terminate at one end of the chain in free, unesterified carboxyl (-CO_2H) groups. These carboxyl groups are acidic, and their level is represented by the acid number of the polyester diol [446, 449]. The macrodiol acidity adversely affects the hydrolysis stability of derived thermoplastic PEsUs in proportion to the degree of acidity [446, 449, 452]. Similarly, the hydrolysis of PEsUs can also be exacerbated by increasing the acidity of the solution [450].

It has been shown that under humid ageing at 80 °C and 95% relative humidity, the hydrolytic stability of PEsUs based on different polyester diols follows the order: PEA diol < poly(1,4-butylene adipate) (PBA) diol < PCL diol [21]. While all these PEsUs show decreased tensile strength with time due to hydrolytic degradation, the PTMEG-based PEtU experienced little change in tensile strength up to 5 weeks [21].

Unlike esters prepared from diacids and diols, PCL is synthesized by ring opening of the cyclic caprolactone monomer [453]. The hydrophobicity of PCL may also allow it to control the overall hydrolytic stability of the resultant PUs, especially with the HS being more hydrolytically sensitive than PCL [454]. Han et al. [454] synthesized a PU elastomer using lysine diisocyanate (LDI), PCL, and 1,4-BDO. It was found that the mass loss and the water uptake of this PU in PBS at 50 °C decreased with increasing the PCL SS content, which could be ascribed to the hydrophobicity of PCL in comparison with the polar HS [454].

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The hydrophilicity/hydrophobicity of the polyester component plays a major role in the stability of PEsU elastomers. It has been shown that, with an increase in the concentration of methylene groups relative to other groups in the polymer chains, such as ester and urethane groups, the derived PUs (based on, *e.g.*, PCL diol or poly(adipate) diol) would be expected to be increasingly hydrophobic and thus more hydrolysis resistant [446, 449, 455]. The effect of increasing methylene groups relative to other groups has been shown for PU elastomers based on polyether macrodiols. Gunatillake et al. [455] prepared novel PU elastomers based on 4,4′-MDI, 1,4-BDO, and polyether macrodiols such as polyhexamethylene glycol (PHMG), polyoctamethylene glycol (POMG), and polydecamethylene glycol (PDMG). These polyether macrodiols have 6, 8, or 10 methylene groups between the ether oxygens, respectively. The new PUs were demonstrated to be more resistant to neutral, acid (2 M HCl) and basic (5 M NaOH) hydrolysis at 100 °C than were PTMEG-based materials [455]. Similarly, by testing the hydrolytic degradation of different PEtUs, Kim and Kim [456] suggested that hydrolytic degradation decreased with the increase of carbon chain segments in the macrodiol.

Incorporation of extracellular matrix components such as chondroitin sulphate (CS) and hyaluronic acid into a PEA/4,4′-MDI/EG-based PU was found to increase the hydrophilicity and favor the hydrolytic degradation [447]. However, contrary to this, Liu et al. [457] prepared aliphatic PEsUs based on PCL with surface-grafting of hydrophilic polyethylene glycol (PEG), which maintained their mechanical properties for more than six months and only lost 25% weight after 18 months in PBS (pH = 7.4).

6.1.2. Hydrolytic degradation of poly(ether-urethane)s

The superior performance of polyethers over polyesters is well known where hydrolytic stability and fungicidal resistance is concerned [3, 21, 53, 56]. Polyether components are usually highly stable

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under normal moist conditions [6]. For example, Davies and Evrard [458] found that two commercial PEtU samples with two hardnesses (40 and 90 Shore A) retained 100% of their initial tensile properties after five years of immersion in the real sea and estimated that the timescale for 50% property loss at sea temperatures would be more than 100 years [458]. Chaffin et al. [459] studied the *in-vitro* hydrolysis of a commercial PEtU (Elasthane™ 80A, DSM Biomedical) in neutral pH and deoxygenated PBS at temperatures ranging from 37 °C to 85 °C. They suggested that the only obvious backbone chain-scission event occurred at the urethane (carbamate) linkages. Even though PEG-based PUs are highly hydrophilic [83], potentially resulting in the absorption of water to the bulk material, the ether component is still more resistant to hydrolytic degradation than polyesters used in PUs [460].

Conditions that are more aggressive may still cause chemical changes to the polyether components of PUs. Simmons [461] found that autoclaving (with saturated steam at 121 °C for a minimum of 15 min at a pressure of 115 kPa) adversely affected the chemical and mechanical properties and biostability of a commercial PTMEG-based PU (Pellethane® 2363-80A, Dow Chemical Co., USA). The high temperatures and moist environment created by the autoclave sterilization process might promote chain scission, leading to decreased ultimate tensile strength [461]. Le Gac et al. [462] investigated the effect of ageing of a commercial PEtU in natural seawater under hydrostatic pressure up to 100 bars at temperatures ranging from 70 to 120 °C. Again, the results indicated that hydrolysis led to chain scission in the samples and thus induced a large modification of tensile behavior. Additionally, Stevenson and Kusy [450] suggested that the degradation of Pellethane® 2363-80A under the combined effects of an increase in acidity, oxygen content, and temperature for up to 100 days was dominated by a crosslinking mechanism, leading to increased M.

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6.1.3. Hydrolytic degradation of poly(ester-ether-urethane)s

It has been shown that, compared with PEG-based PUs, PCL-based polymers display significantly higher contact angles, indicating greater surface hydrophobicity [83]. Considering the different properties of PCL and PEG, quite a few studies [463-469] have focused on PU elastomers based on PCL blended with PEG for tailored hydrolytic stability (as well as other properties such as transparency, tensile strength, and processibility). The use of hydrophilic moieties like PEG together with a hydrolytically unstable SS like PCL or poly(adipate-ester)s increases the degradation rate [453]. The presence of PEG in the PU could facilitate water absorption and account for the initial hydrolysis of the polymer [470]. *In-vivo* water absorption of the bulk polymer is increased by the presence of the hydrophilic PEG, which exposes the hydrolytically unstable segments to a higher average water concentration while increasing the polymer's permeability. This bulk property change results in faster cleavage of unstable ester bonds [453]. In contrast, a higher PCL content, or a lower PEG content and/or M could lead to an increase in the bulk hydrolytic stability and a reduction in the mass and M loss of the polymer in PBS (pH 7.4) or Tris-buffered saline (TBS) solutions (pH 7.4 or 8.0) [463-468, 471].

In some studies [472, 473] where a PCL-PEG-PCL triblock copolymer or a poly(CL-*co*-LA)-PEG-poly(CL-*co*-LA) was used as the macrodiol component, increasing the PEG chain length or decreasing the PCL chain length in the triblock segment could increase the water absorption and degradation rate of the resulting PUU in PBS (pH 7.4). Hydrolysis-sensitive chemical bonds in the segment could further influence the hydrolytic stability of PUs [474]. Zhou et al. [474] indicated that, for PUs formulated with a PCL-hydrazone-PEG-hydrazone-PCL macrodiol, the hydrazone bond in the polymer chain was more easily cleaved in acidic media.

PU networks based on castor oil (containing ester groups) and PEG with tuneable biodegradation were synthesized through the reaction of epoxy-terminated PU prepolymers (EPUs) with 1,6-hexamethylene diamine curing agent [475]. Still related to the hydrophilicity of the chemical

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composition, increasing the PEG-based EPU content was observed to cause an increase in the hydrolytic degradation rate of this PU [475].

All these studies have shown that the hydrophilicity/hydrophobicity of the macrodiol part plays a major role in controlling the overall hydrolytic stability of PUs.

6.1.4. Effect of isocyanate and chain extender

As discussed in Section 6.1.1, the urethane and urea linkages normally undergo hydrolysis quite slowly. The HSs are usually hydrophobic and difficult to degrade, thus inhibiting the penetration of water into the material. For PCL-based PUs, the use of an aliphatic diisocyanate (4,4′-H_{12}MDI and HDI) instead of an aromatic diisocyanate (4,4′-MDI) was found to increase the hydrolytic degradation of PEtUs [456]. In the case of PCL/HDI-based PUs, the diisocyanate is too flexible to form HSs, and this is considered to be the reason for their high hydrolytic degradability [456]. Similarly, Ibarra et al. [476] reported that the hydrolytic degradability of PUs based on castor oil depends on the isocyanate used (HDI > 4,4′-H_{12}MDI > TDI). Jia et al. [477] investigated the *in-vitro* degradability (PBS, pH 7.4) of two aliphatic segmented PEsUs based on poly(CL-*co*-LA) diol and two novel aliphatic urethane diisocyanate chain extenders (HDI-BDO-HDI and HDI-BDO-HDI-BDO-HDI, respectively). Given that there were more urethane groups in the longer HSs, these could form more hydrogen bonds not only among urethane groups but between urethane and ether groups, which strengthened the interchain attraction and gave a more compact network structure, resulting in slower hydrolytic degradation (~67 days) and lower water absorption (~4 wt.%) [477].

ChExs, especially those that are hydrolytically sensitive, could also play a major role in controlling the overall hydrolytic stability of PU elastomers. Guan et al. [478] synthesized a PUU from PCL and 1,4-diisocyanatobutane, with lysine ethyl ester (Lys) or putrescine as the ChEx. Incubation in PBS (pH 7.4, 37 °C) for 8 weeks resulted in a mass loss, from >50% (lysine ChEx) to

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10% (putrescine ChEx) [478]. Regarding this, the hydrolysis of the ethyl ester to exposed carboxyl groups in the lysine-ethyl-ester-extended PEUUs might have served to catalyse the hydrolysis of the PCL SS [478]. Similarly, in a recent patent on biodegradable PUs and PUUs for tissue engineering, the design of the materials is based on the use of chain extenders including functional monomers with degradable arms [479] or based on ester diols of hydroxyl acids or dicarboxylic acids [480]. For example, a PU based on LDI and a glycolic acid-based macrodiol and ChEx degrades to bioresorbable glycolic acid, lysine, ethylene glycol and ethanol [479]. Tatai [481] developed a degradable ChEx based on D,L-LA and EG to accelerate the HS degradation of PUs. As a result, the PCL-based SS appeared to undergo little change whereas the PU HS was highly susceptible to *in-vitro* degradation (0.1 M PBS, pH 7.4±0.2 at 37 °C), with the mass loss being directly proportional to the HS weight percentage. Zia [482] compared the hydrolytic degradation of PCL-based PUs in PBS (pH 7.4), using chain extension to vary the mass ratios of chitin and 1,4-BDO. The hydrolysis rate of the PU was found to increase with the chitin content [482], which could be attributed to the high hydrophilicity of chitin.

6.1.5. Effect of temperature (hydrothermal treatment)

In many studies of the hydrolysis of polymers, testing temperatures higher than room temperature but lower than the melting temperature have been applied for accelerated hydrolytic degradation, usually referred to as “hydrothermal treatment”. Increased temperature may facilitate the absorption of water by PUs [483]. In addition, higher temperature may slightly increase the solubility of PU in water [451]. More importantly, a higher temperature will result in more severe hydrolysis of PUs [450, 462, 484]. Even for PEtUs tested under the combined effects of increased acidity, oxygen content and temperature, the increase in temperature had the greatest effect of any of the single variables investigated [450].

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The hydrolysis reaction of PUs can be modelled using a first-order reaction with an Arrhenius equation to describe temperature dependence [459, 462]. The use of an Arrhenius model also allows the prediction of the time required for a certain degree of mechanical reduction for PUs [458, 459], which is a very convenient approach for practical applications.

6.1.6. Effect of hydrolysis on the structure and properties of polyurethane elastomers

For PUs, especially those that are relatively hydrolytically stable (based on, *e.g.*, acrylic macrodiols [379], polyether diols [462], or PCL [484, 485]), the immediate changes caused by water are physical changes, mainly due to absorption. The penetration of water into the polymers may cause voids [202, 484]. For PCL-based PUs, the uptake of water reduced the Young's modulus [451], decreased the elastic modulus and the stress at 200% strain [484, 486], and reduced T_g [486]. Slater et al. [483] suggested that water could also act as a plasticiser, resulting in a larger degree of compression set for a thermoplastic PU (formulation unknown).

For a PU based on poly(adipate) diols, MDI, and 1,4-BDO aged in deionised water at 80 °C, Pretsch et al. [451] suggested that there was an initial induction period, where water diffuses quite rapidly into the polymer matrix, with minor changes to the mechanical properties occurring due to the water uptake. Following that, the hydrolytic degradation of SSs caused a decrease in phase separation and deterioration of the mechanical (tensile) properties of the materials [451]. Finally, ageing led to the third phase, where substantial degradation of SSs and access of water to the HS increased the phase separation again. The material became brittle and was slowly destroyed by surface erosion [451].

For a commercial PEtU, Baytec MS-242® (Bayer Material Science LLC, USA), it was reported that the tearing energy suffered a nearly 50% reduction after 5 months of hydrothermal ageing (ASTM D1183-05) [204, 205]. The storage modulus decreased by 15% by Month 5 [204]. Although

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scanning electron microscopy (SEM) could not find any apparent change in appearance [204], the changes in mechanical properties could be due to chain scission under severe conditions as discussed in Sections 6.1.2 and 6.1.5.

6.2. Stabilization of polyurethane elastomers against hydrolytic degradation by polymer modification

When choosing the macrodiol component for the preparation of PUs, avoiding the use of polyester diols will generate PU elastomers with better hydrolytic stability. If PEsUs do need to be used, using PCL diols could be a preferred choice for better hydrolytic stability compared with other polyester diols [23, 31]. It was shown that PU films based on *N*-alkylated oligomeric polyamides are more hydrolytically stable than PEsUs, although not as good as are PEtUs [487]. Compared with PEsUs, PCUs and PEtUs present much better resistance to simple hydrolysis (*e.g.*, in PBS at room temperature) [56, 488]. The hydrolytic stability of PC is probably due to its low water permeability, which is attributed to the rigidity of the polymer chains [56]. Again, it should be noted that the PCUs discussed here are different from the common BPA-based PCUs, which usually show poor hydrothermal stability [43].

Research has shown that PIBUs exhibit unprecedented hydrolytic stability, which is better than other types of PUs (PEsUs, PEtU, PCU, and silicone/polyether-based PUs) [64, 69, 73, 185]. Their outstanding hydrolytic/oxidative stability could be ascribed to the continuous, nonpolar, chemically inert PIB SS, which is an effective barrier to the diffusion of water or other chemicals [69] and can envelop hydrolytically vulnerable segments (including urethane linkages) [64, 73]. Hydrolytic vulnerability is inherent in segmented PUs and mainly occurs at carbamate groups situated at the interface between the HS and SS [73]. As an example of a PU with a PIB SS, Jewrajka et al. [69] reported that after being submerged in boiling water for 15 days, PIBUs experienced insignificant

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changes in mechanical properties and no change in appearance, which was a much better outcome than for Bionate® (DSM), a commercial PCU based on PHMC diol. Kang and Kennedy [73] also demonstrated that, under accelerated conditions (85 °C in buffer solutions, pH = 1.0, 7.4, and 11.0), a PU prepared from a PIB diol, 4,4′-MDI, and 1,4-BDO exhibited lower water absorption and far superior hydrolytic stability than a commercial polydimethylsiloxane **(**PDMS)/PHMG-based PU, Elast-Elon™ (AorTech International Plc, UK; marketed for high bio- and hydrolytic stability).

Crosslinking may also increase the hydrolytic stability of PUs. Crosslinking, leading to an increase in the size of macromolecules, provokes insolubility of the elastomer [489]. Rutkowska et al. [54] demonstrated that for PEsUs based on either poly(ethylene-butylene-adipate) or PCL, the enhanced hydrolysis resistance against seawater was mainly due to the high level of crosslinking by allophanate and biuret bonds (**Error! Reference source not found.**), which largely reduced the swelling of the materials [54]. Jayabalan et al. [490] compared the hydrolytic stability of PUUs synthesized using 4,4′-H_{12}MDI, HTPB and *m*-phenylenediamine [benzene-1,3-diamine] with a PU prepared with 4,4′-H_{12}MDI, HTPB, and 1,4-BDO in Ringer’s and PBS solutions (pH = 7.4). The results suggested the PUUs were more resistant to hydrolytic degradation, which was ascribed to the highly ordered HSs due to increased hydrogen bonding among urea linkages.

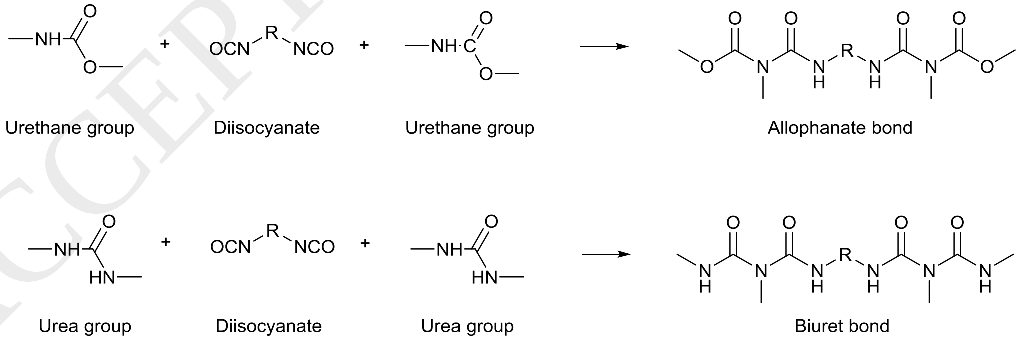

Figure 40. Structure of allophanate and biuret bonds. [54], Copyright 2002. Adapted with permission from Elsevier Ltd.

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The introduction of side chains into the PU backbone can also enhance the hydrolytic stability of PUs [86, 400, 485, 491]. PUs prepared from polyester diols with alkyl side groups may even have better hydrolytic stability than PEtUs [400, 491]. Regarding this, poly(2,4-diethyl-1,5-pentamethylene adipate) glycol (PDEPA) and poly(3-methyl-1,5-pentamethylene adipate) glycol (PMPA) were shown to be more stable than linear poly(1,5-pentamethylene adipate) [491], and poly(2,4-diethyl-1,5-pentamethylene adipate) glycol (PDPA) could have superior stability compared to PBA diol [492].

Hydrolytic stability may also be improved by surface modification. It was reported that, for PU films based on PDPA or poly(2,4-diethyl-1,5-pentamethylene-1,4-cyclohexane dicarboxylate) glycol (PDPCD), the use of a fluoro oligomer could allow the formation of a fluoro-rich layer at the free surfaces, which increases the contact angle/hydrophobicity [493].

The type of isocyanate used could also influence the hydrolytic stability. As discussed already, compared with aliphatic isocyanates such as HDI, aromatic isocyanates such as 4,4′-MDI could be better for the formation of HSs, which are responsible for reduced hydrolytic degradability [456].

For PEsUs, it is possible to reduce the hydrolytic sensitivity of the polyester component by adjusting the chemistry of the ChEx. For example, in poly(lactic acid) (PLA)-based segmented PUs, alkaline ChExs (piperazine and 1,4-butanediamine (BDA) [butane-1,4-diamine]) could neutralize the acidity of hydrolysis products formed form, and the hydrolytic sensitivity of the polyester bonds in double distilled water and PBS (0.1 M, pH = 7.4) [377].

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6.3. Stabilization of polyurethane elastomers against hydrolytic degradation using stabilizers

6.3.1. Organic stabilizers

A very effective class of materials for the stabilization of PUs, especially PEsUs, against hydrolytic degradation are poly(carbodiimide)s [446, 449, 494]. **Error! Reference source not found.** shows one type of sterically hindered, aromatic poly(carbodiimide) structure and the proposed mechanism of the carboxyl-carbodiimide reaction [446]. The carboxyl group when formed during hydrolysis adds across one C=N double bond of the carbodiimide group to form a transitory intermediate. Subsequent rearrangement leads to the formation of a stable, neutral, *N*-acyl aromatic urea structure. Thus, the carboxyl group can been chemically neutralised and bound into the poly(carbodiimide) structure, which prevents autocatalysis of the hydrolysis reaction [446, 449]. Since each stabilizer molecule contains several carbodiimide groups, broken polymer chains that terminate in carboxyl groups can be repaired via chain extension/crosslinking [446, 449].

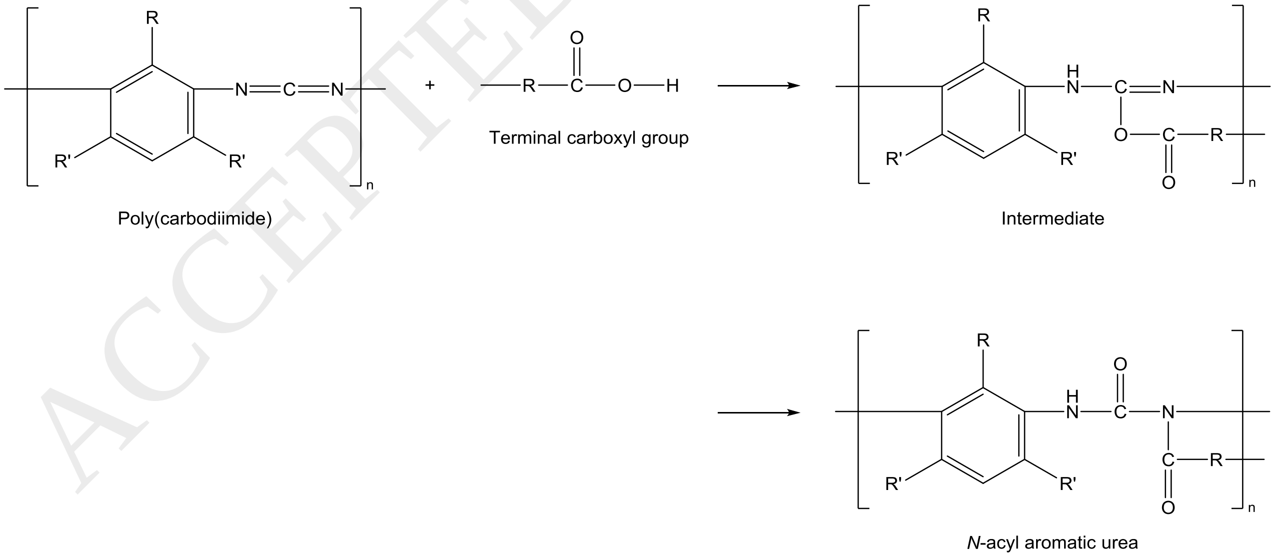

Figure 41. Reaction of a poly(carbodiimide) with carboxyl groups. R and R′ are small alkyl groups. [446], Copyright 1973. Adapted with permission from John Wiley & Sons Inc.

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6.3.2. Inorganic stabilizers

An early patent [495] has shown that the addition of small amounts of acidic silica can improve the hydrolytic stability of PUs. The additive can be micronised silica (average diameter 20 μm) made hydrophobic by silicones absorbed or coated onto the surface of the silica particles [495]. Inorganic fillers such as calcium carbonate, glycerol phosphate calcium salt, and hydroxyapatite were also reported to inhibit the hydrolytic degradation of PEG/PCL-based PUs in PBS (pH = 7.4) [471]. The incorporation of ZnO nanoparticles into PU formulations has also been found to be effective in protecting the PU material against hydrolytic degradation in NaCl solution [293, 296, 496]. Silver nanoparticles were also reported to be effective in stabilizing PEsUs [447]. During hydrolysis, increased hydrogen bonding and crystallinity were observed, especially for silver nanoparticle-stabilized PU matrices [447].

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7. Chemical degradation of polyurethane elastomers

7.1. Chemical degradation by inorganic compounds

The hydrolytic degradation of PU elastomers in mild acids or in solutions of common inorganic salts (*e.g.*, seawater and PBS) have been discussed in Section 6. These hydrolysis conditions normally show little-to-no effect, however, if the acidity or alkalinity is high, the rate of hydrolysis of the PU will be increased, with the temperature playing a large part in the increased rate [445]. For example, Motokucho et al. [497, 498] showed that degrees of hydrolysis up to 98% for PUs based on either HDI, IPDI, or 4,4′-MDI could be achieved at 190 °C for 24 h at 8.0 MPa CO_2 pressure (which generates carbonic acid). In addition, strong acids have different forms of attack. Sulphuric acid will

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dehydrate the structure whereas nitric acid will oxidize it [445]. Peroxides (typically hydrogen peroxide) and bleach (sodium hypochlorite), especially at high concentrations, could also degrade PU elastomers [445] due to, in most cases, their oxidising properties.

Mejis et al. [499] examined the *in-vitro* degradation of a medical-grade PTMEG-based PU elastomer, Pellethane® 2363-80A (Dow Chemicals), using 25 wt.% H_2O_2 at 100 °C with external strain. Treatment for up to 336 h led to significant decreases in ultimate tensile properties and decreases in M [499]. Hydrogen peroxide-induced degradation was found to result in greater order in the HSs and increased mobility in the SSs. The SSs underwent chain scission and no evidence of crosslinking was found [499, 500]. The incubation of Pellethane® 2363-80A in nitric acid also resulted in a sharp decrease of the melting temperature of its HSs, with chain scission mechanisms reported [500].

Some work has been undertaken to monitor the stability of PU elastomers with different structures in strong acids or alkalis or under oxidative environments. Gunatillake et al. [455] found that PUs based on 4,4′-MDI, 1,4-BDO and polyether macrodiols that have 6, 8, or 10 methylene groups between the ether oxygens (PHMG, POMG, and PDMG) showed significantly higher tolerance to H_2O_2 (25%) and NaClO (4% chlorine) solutions at 100 °C for 24 h, compared with a PTMEG-based counterpart. Chan-Chan et al. [501] demonstrated that under either acidic (2 N HCl) or alkaline (5 M NaOH) conditions, PCL/4,4′-H_{12}MDI-based segmented PU elastomers experienced degradation of the PCL part irrespective of the degrees of phase separation and crystallinity resulting from the use of different ChExs (1,4-BDO or dithioerythritol [(2R,3S)-1,4-bis(sulfanyl)butane-2,3-diol] (DTE)). However, an oxidative environment (H_2O_2 30 wt.%) did not affect the SS of these PUs severely but attacked the rigid segments [501].

It has been shown that PCUs normally present better overall stability to chemical oxidants than PEtUs [65, 500, 502, 503]. Faré et al. [502] showed that, under oxidative conditions (0.5 N HNO_3, pH 0.3; or NaClO, 4% Cl_2 available, pH ≈ 13 at 50 °C for 15 days), Pellethane® 2363-80A

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experienced more degradation than commercial PHEC-based PUs (Corethane 80A and Corethane 55D, Corvita Co., USA) and PUU (Coremer™, Corvita Co., USA). Tanzi et al. [503] examined different PCU and PEtU products under strong acidic (0.5 N HNO_3, pH 0.3, oxidation potential E = 0.96 V) or alkaline (0.5 N HNO_3, pH 0.3, oxidation potential $E°$ = 0.96 V) oxidative conditions for 7 days and in the presence of constant strain. While PCUs such as Corethane 80A (Corvita, Co.) and ChronoFlex® AL 80A (CardioTech International) were more affected by the acidic oxidative agent, the PEtU Pellethane® 2363-80A was degraded more in the alkaline oxidative condition in the absence of uniaxial stress [503]. It was reported that the oxidative stability of PCUs could be further enhanced by the integration of polyhedral oligomeric silsesquioxane (POSS) nanocores into the HS to create a novel nanocomposite [504]. These nanocores could shield the SS of the PCU from all forms of degradation while maintaining their elasticity [504].

PIBUs not only exhibit excellent hydrolytic stability (discussed in Section 6.2), but also have strong oxidative stability and chemical resistance [65, 69]. For example, Jewrajka et al. [69] revealed that PIBUs only showed slight yellowing upon exposure to concentrated nitric acid (12%) for 12 h, whereas Elast-Elon™ (a PDMS/PHMG-based product) and Bionate® (a PCU) when treated under the same conditions completely degraded. The high oxidative stability of PIBUs could be due to the presence of the continuous nonpolar PIB matrix, which could effectively shield the diffusion of water and concentrated nitric acid [69].

Takahara et al. [505, 506] reported that PEtUs based on PEG or PTMEG were susceptible to molecular chain scission due to oxidation in 0.1 M $AgNO_3$ solution at 75 °C. The ether linkage was found to be particularly susceptible to oxidation, which was responsible for surface cracking and the largely reduced mechanical strength [505, 506]. PUs that are stable in oxidative and lipid solutions can be prepared from macrodiols containing a linear aliphatic structure, such as hydrogenated PBUs and “Biostable PUR” (a PU based on an aliphatic SS containing no ether linkage, Metronic Inc.) [505, 506].

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7.2. Chemical degradation by organic compounds

Cast PU elastomers (containing primary crosslinks contributed by slightly branched polyesters or polyethers) normally have outstanding resistance to aliphatic hydrocarbon fuels and oils [423]. Organic chemicals that typically cause swelling and degradation of castable PU elastomers include alcohols, organic acids, ketones, and esters [445]. In addition, aromatic hydrocarbons such as toluene can cause swelling, and at higher temperatures, a slow breakdown of the polymer [445, 507]. On the other hand, although thermoplastic PU elastomers (with the absence of primary crosslinks) are insoluble in most common solvents, they are soluble in highly polar solvents such as dimethylacetamide [423].

Troev et al. demonstrated that phosphoric acid esters such as dimethyl phosphite [dimethoxy(oxo)phosphanium] [508-511], diethyl phosphite [diethoxy(oxo)phosphanium] [512], triethyl phosphate [513, 514], tris(2-chloroethyl) phosphate [514], and tris(1-chloropropan-2-yl) phosphate [512] could convert PEsU and PEtU elastomers into liquid at a temperature between 142 °C and 190 °C. The liquefaction was proposed to result from an exchange reaction between the ethoxy groups of phosphorous acid esters and the urethane groups [509-514]. The rate of the exchange reaction depended on the type of the α-carbon atom of the degrading agents [512]. The degraded products were phosphorus- or phosphorus and chlorine-containing oligourethanes [509, 511-514].

Increasing the degree of crosslinking can also enhance resistance to organic solvents [54]. Rutkowska et al. [54] demonstrated that, for PEsUs based on poly(ethylene-butylene-adipate) or on PCL, the high degree of crosslinking by allophanate and biuret bonds (**Error! Reference source not found.**) could lower the swelling degree of the materials in either acetone [propan-2-one] or tetrahydrofuran [oxolane] (THF).

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Seneker et al. [515] studied the solvent resistance of PEtU elastomers based on PTMEG and 4,4′-H_{12}MDI with different contents of *trans*,*trans*-, *cis*,*trans*-, and *cis*,*cis*-isomers. Different solvents were used such as *N*-methylpyrrolidinone [1-methylpyrrolidin-2-one] (NMP), *N*,*N*-dimethylformamide (DMF), THF, isopropanol [propan-2-ol], or dimethyl sulfoxide [methylsulfinylmethane] (DMSO). Increasing the *trans*,*trans*-isomer content was found to increase the solvent resistance of PU elastomers, which could be ascribed to the unique packing of the *trans*,*trans*-H_{12}MDI isomer leading to highly ordered HSs and better HS/SS phase separation [515].

Biomedical applications, in particular, require PU elastomers with minimal lipid-induced swelling and degradation [505, 506, 516-518]. Lipid adsorption was observed to be less severe in Corethane 80A (a PCU) than in Pellethane® 2363-80AE (a PEtU) [505, 506, 518]. PUs that are stable in oxidative, hydrolytic, and lipid solutions can be prepared from macrodiols containing a linear aliphatic structure [505, 506, 518]. PDMS-based segmented PU elastomers have also been found to degrade after lipid sorption. The complete degradation of the material might be due to the high solubility of the PDMS SS in lipid solutions [518].

7.3. Calcification

Calcification (formation of various types of calcium phosphates such as apatite) is a well-documented event in various medical devices, especially in those used in the cardiovascular field [20, 59, 519-524]. In fact, calcification is the leading macroscopic cause of failure for most prosthetic heart valves and blood pumps, limiting the functional lifetime of the device by the loss of elasticity in PU parts [7, 20, 519, 525-527].

In-vitro calcification experiments usually rely on the use of simulated body fluid (SBF), which is supersaturated with the ions necessary to form inorganic calcium deposits on the surfaces of bioactive biomaterials *in vivo* [528-530]. Calcification has been found to occur primarily on the

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surface of PU materials, without affecting the bulk microphase structure [531]. Studies [488, 531] have shown that PEtUs had a high propensity to calcify. Pellethane® 2363-80A, which had a higher ether content, was shown to have more surface deposits and greater levels of calcium than a PHMG-based PEtU and PCUs (Corethane 80A and ChronoFlex® AL-80A) [488]. This difference may be due to the different chemical composition of their SSs affecting their ability to attract Ca^{2+} ions [531]. Along with this, it was shown that a fully aliphatic, ether-free, physically cross-linked, PB-based PUU was resistant to calcification [532]. The susceptibility of PUs to calcification was found to increase with the material hydrophilicity [465, 471]. A higher PEG content in PEG/PCL-based PUs was observed to induce a higher degree of calcification [465, 471]. In addition, metal ions such as Mg^{2+} and Fe^{3+} were shown to be able to inhibit pathological calcification in PU implants [533], with calcification also being overcome by blending a PU with silk fibroin [534].

8. Enzymatic degradation and stabilization of polyurethane elastomers

8.1. General discussion on enzymatic degradation of polyurethane elastomers

The understanding of enzymatic degradation of PU elastomers is of particular importance to the biomedical application of these materials. One of the reasons includes the action of monocyte-derived macrophages (MDMs) on foreign substances such as PU implants in the form of chronic inflammatory response, in which esterases are produced [36]. The biologically active molecules released by MDMs in this activated cell system may be material dependent [36]. Nevertheless, cholesterol esterase (CE) has frequently been selected as a model hydrolytic enzyme because it represents an enzyme that is present in increasing levels as human monocytes differentiate into

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macrophages [535]. CE has been identified as the most active enzyme in PU degradation [536]. In addition, some proteases such as lipases, papain and urease have also been used in the study of the enzymatic degradation of PU elastomers. Lipases perform essential roles in the digestion, transport, and processing of dietary lipids in most living organisms. Papain, a proteolytic enzyme, although being a nonphysiological enzyme [537], is known to be closely related to Cathepsin B, a thiol endopeptidase that is released by the cells during inflammatory response [538]. Urease is found in leukocytes [538] and is responsible for urea hydrolysis.

The ability of the enzyme to adsorb onto the surface in a conformational state that will permit cleavage of the polymer is important in determining the relation between biomaterial chemistry and the stability of the material in the biological environment [539]. The stability of PU elastomers against enzymatic hydrolysis has been found to depend on the hydrophilicity of the SS component [505, 540]. In particular, a PU with hydrophilic PEG segments was more susceptible to enzymatic hydrolysis (in papain solution) than PTMEG- and PB-based PUs [518]. In this case, the dissociation of urethane linkages was also evident. [518]. It has been shown that PUs prepared from macrodiols containing a linear aliphatic structure are stable in enzyme solutions [505, 518].

8.2. Enzymatic degradation of poly(ester-urethane) elastomers

PEsUs are usually readily degraded by enzymes, due to hydrolysis of the ester linkages [21, 541, 542]. Nonetheless, Kim and Kim [456] suggested that the hydrolytic and enzymatic (*Candida cylindracea* lipase) degradation of PEsUs could be restricted by increasing hydrophobicity and HS formation. This could be accomplished by increasing the length of the carbon chains in the macrodiol and/or by using aromatic diisocyanates instead of aliphatic diisocyanates. In this case, the HS, especially in crystalline structures, is difficult to degrade, because it is usually hydrophobic and therefore inhibits the penetration of water into the material [456].

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For biomedical applications, using PCL as the SS for the synthesis of PUs confers biodegradability [454, 474, 543]. Additionally, the use of LDI [454, 474], putrescine [468, 472, 478, 544] and/or L-lysine [543] as the ChEx could allow the formation of degradation products that are likely to be nontoxic. For enzymatic degradation (in PBS with Lipase AK), mass loss was found to increase with a higher PCL fraction [474]. PEG may be incorporated into such PU systems to give a higher overall hydrophilicity and water absorption, thus facilitating the enzymatic (Lipase AK) hydrolysis [543].

PCL-based PEsUs can be quickly degraded in the body by enzymes such as lipases [474, 507, 545]. Lipase AK was found to interact only with the PCL SS in these polymer structures [543]. According to Tetsufumi et al. [507], the degradation of a PCL/norbornene diisocyanate-based PU occurred rapidly in the presence of *Candida antarctica* lipase in toluene at 60 °C, leading to oligomers with M less than 500 [507].

For PCL-based PEsUs, the use of aliphatic diisocyanates (*e.g.*, 4,4′-H_{12}MDI and HDI) instead of aromatic diisocyanates (*e.g.*, 4,4′-MDI) was also found to increase the hydrolytic degradation of these PEsUs in a *Candida cylindracea* lipase solution [456]. In particular, in the case of PCL/HDI-based PEsU, the diisocyanate could be too flexible to form HSs, which was considered to be the reason for the high hydrolytic degradability [456].

Several studies have shown that segmented PCL-based poly(ester-urethane-urea)s (PEsUUs) are susceptible to degradation by inflammatory cell-derived enzymes such as CE, elastase, and carboxylesterase, with CE having a greater effect [542, 546, 547]. The degradation rate of these PEsUs was shown to be significantly higher than that of PTMEG-based PEtUs [542, 548]. The CE activity was found to be greater for PCL-based PEsU substrates that have spacer segments between potential ester-carbonyl cleavage sites and the rigid ring structure [547].

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8.3. Enzymatic degradation of poly(ether-urethane) and poly(carbonate-urethane) elastomers

PEtUs and PCUs are generally more resistant to enzymatic degradation. Christenson [549] examined the effect of CE on unstrained Elasthane™ 80A (a PEtU) and Bionate® 80A (a PCU) films for 36 days. Although the concentration of CE (400 U/mL) used was considerably higher than the estimated physiological level, any effect of enzymatic hydrolysis was confined to the immediate surface with only a small loss in surface SS content [549].

In most cases, the action of enzymes is more specific to the HSs of PEtUs and PCUs. Marchant et al. [550] investigated the degradation of a PTMEG/4,4′-MDI/ethylenediamine (EDA)-based poly(ether-urethane-urea) (PEtUU) elastomer exposed to the proteolytic enzyme, papain, for one month. The results suggested that the degradation of ether linkages was independent of the enzyme, whereas the degradation of urethane and urea groups depended on the presence of papain. Phua et al. [538] found papain was more efficient in degrading Biomer® (a PTMEG-based PU) than urease. It was proposed that papain has a broader specificity and smaller molecular size than urease and can degrade the polymer by hydrolysing urethane and urea linkages to generate free amines and hydroxyl groups [538]. Compared to papain, urease is highly specific for urea and biuret linkages. Urease degraded the polymer by hydrolysing urea linkages, with the degradation products being free amines [538].

The stability of PEtUs and PCU elastomers strongly depends on the polymer structural features such as HS content, hydrogen bonding, and crystallinity. It was suggested that urethane linkages in the SS domains of phase-separated PTMEG-based PEtUU could be more prone to cleavage by CE than the urea/urethane groups in the HS domains [548]. However, Santerre et al. [551] suggested that the ability of a PTMEG/TDI/EDA-based PU to form HS microdomains may contribute to the formation of a protective structure, which reduces the rate of CE hydrolysis of the hydrolytically labile urea and urethane bonds located within the microdomains [551]. Tang et al. [37] proposed that

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increased hydrogen bonding within PCUs led to decreased biodegradation by MDM-associated esterase. The rank of the different chemical groups' susceptibility to hydrolysis was as follows: non-hydrogen-bonded carbonate > non-hydrogen-bonded urethane > hydrogen-bonded carbonate > hydrogen-bonded urethane [37]. They suggested that the crystallinity within the PC phase had less influence than hydrogen bonding on the hydrolytic stability [37].

9. *In-vivo/in-vitro* oxidative degradation and stabilization of polyurethane elastomers

9.1. *In-vivo/in-vitro* oxidative degradation of polyurethane elastomers

It has been suggested that oxidation is the primary biodegradation mechanism of PEtUs and PCUs whereas the effect of enzymes is minimal [3, 549, 552-554]. *In-vivo* oxidative degradation has been attributed to the reactive oxygen species released from adherent cells [555, 556]. In addition, metal ion oxidation (MIO) has been found to occur for specific PU products used as biomedical implants. The mechanism involves interaction between the metal of the conductor coil and hydrogen peroxide [3, 557]. In the case of pacemaker leads, hydrogen peroxide, a known product of inflammatory cells involved in the foreign body response [558], permeates the outer insulation. Reaction with the outer conductor coil produces reactive oxygen species through a Haber–Weiss reaction (shown below) and creates metal ion corrosion products [3, 21, 557].

$$Co^{2+} + H_2O_2 \rightarrow Co^{3+} + HO^{-} + HO\bullet$$

Through a similar mechanism, chemical degradation has been shown to occur in PUs by hydroxyl radicals generated *in vitro* by the decomposition of hydrogen peroxide with a Co^{2+} catalyst [552, 559,

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560]. The hydroxyl radical (•OH) is considered to be the strongest oxidant in biological systems and the $H_2O_2/CoCl_2$ system has been considered to be an excellent choice to accelerate oxidative biodegradation for the prediction of long-term biostability in quantitative comparison among current clinical PUs [3, 549, 552, 554, 561].

As noted previously, PEtUs are prone to oxidative degradation [3, 21, 56]. MIO and environmental stress cracking (ESC) have been cited as leading causes of PEtU pacemaker lead failure [557, 559]. Also, several studies [3, 21, 537, 552, 553, 555-557, 562, 563] have demonstrated that the polyether SS is susceptible to oxidation after extended periods *in vivo*. Elastomers that contain more ether linkages (such as softer compositions) appeared to form microcracks more easily than elastomers with fewer ether linkages (such as harder materials) [564]. Chemical degradation was more advanced on the outer surface of the PEtU [557]. *In-vitro* and *in-vivo* studies showed that oxidation led to chemical changes of PEtUs including the cleavage of polyether SSs and urethane linkages (particularly the urethane bonds joining the HS and the SS) [552, 554, 563, 565-567]. The hydrolysis of aliphatic HSs has also been reported [563] and crosslinking of polyether SSs has been observed [552, 565, 567]. Chain cleavage was found to lead to the development of severe pitting and cracking of the material surface [552, 565]. Fourier-transform infrared (FTIR) results established the following susceptibility of the PEtUU linkages to cleavage *in vivo*: ether > free urethane >> H-bonded urethane >> urea [552].

The results from a cage implant study and cell culture experiments indicated that monocytes adhere, differentiate, and fuse to form foreign body giant cells (FBGCs) on both PEtU and PCU [567, 568]. Despite that, *in-vivo* and *in-vitro* studies [3, 6, 56, 488, 554, 561, 565, 566, 568, 569] have shown better stability of PCUs against oxidation than for PEtUs. For example, the *in-vitro* degradation of Elasthane™ 80A (a PEtU) and Bionate® 80A (a PCU) in a 20% H_2O_2/0.1M $CoCl_2$ solution for up to 24 days were compared [561, 565]. The PCU underwent less chemical and physical degradation, even in biaxial fatigue [561, 565, 568] and the degraded surface layer of the

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PCU was much thinner than that of the PEtU [561]. The better oxidative stability of PCUs could be attributed to their carbonate linkages [568]. However, *in-vivo* studies [566, 567] indicated that evidence for chain scission and crosslinking of the surface of Bionate® 80A was still present in the FTIR spectra of explanted specimens, although occurring at a much lower degree.

The high tendency of PEtUs to degrade via oxidation through the action of reactive oxygen species released by the $H_2O_2/CoCl_2$ system (*in vitro*), or by adherent leukocytes, macrophages and FBGCs (*in vivo*), is mainly related to oxidative attack of the SS (**Error! Reference source not found.**a) [3, 557, 561, 562, 567, 570]. Reactive oxygen species abstract an α-methylene hydrogen atom from the polyether SS [537, 552, 553, 561, 562, 570]. The addition of a hydroxyl radical to the carbon radical forms a hemiacetal, which oxidizes to an ester [561]. Acid hydrolysis of the ester results in chain scission of the SS and formation of acid end groups [561] [552, 553, 562]. Significant chain scission occurs leading to the solubilization and extraction of low-*M* degradation products [561]. A smaller portion of the chain radicals combine with other chain radicals, resulting in crosslinking [552, 561, 571] [552, 553].

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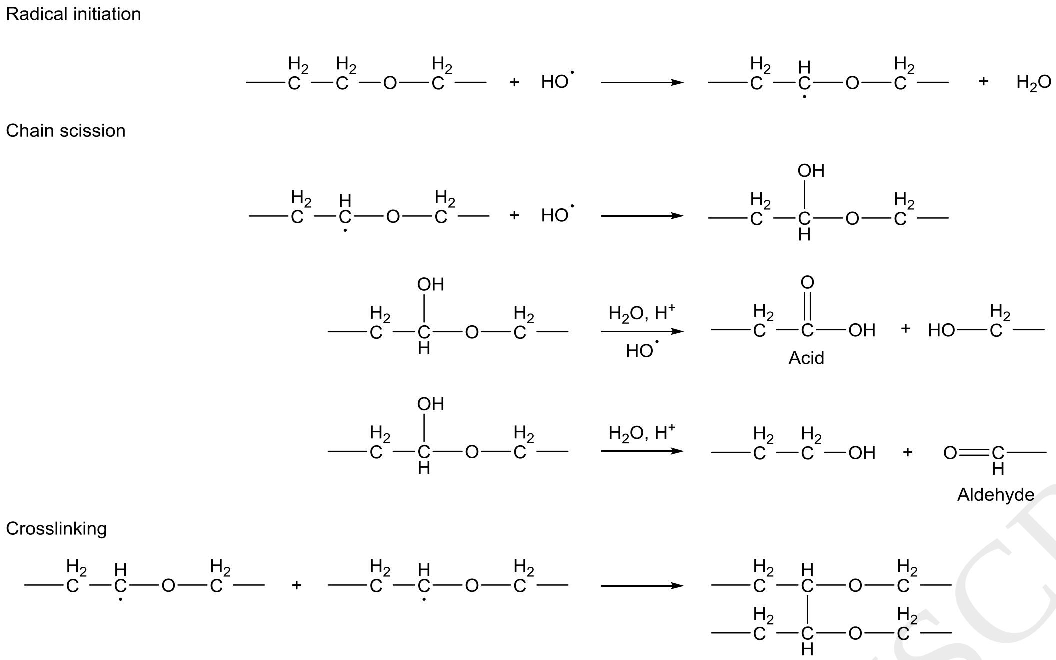
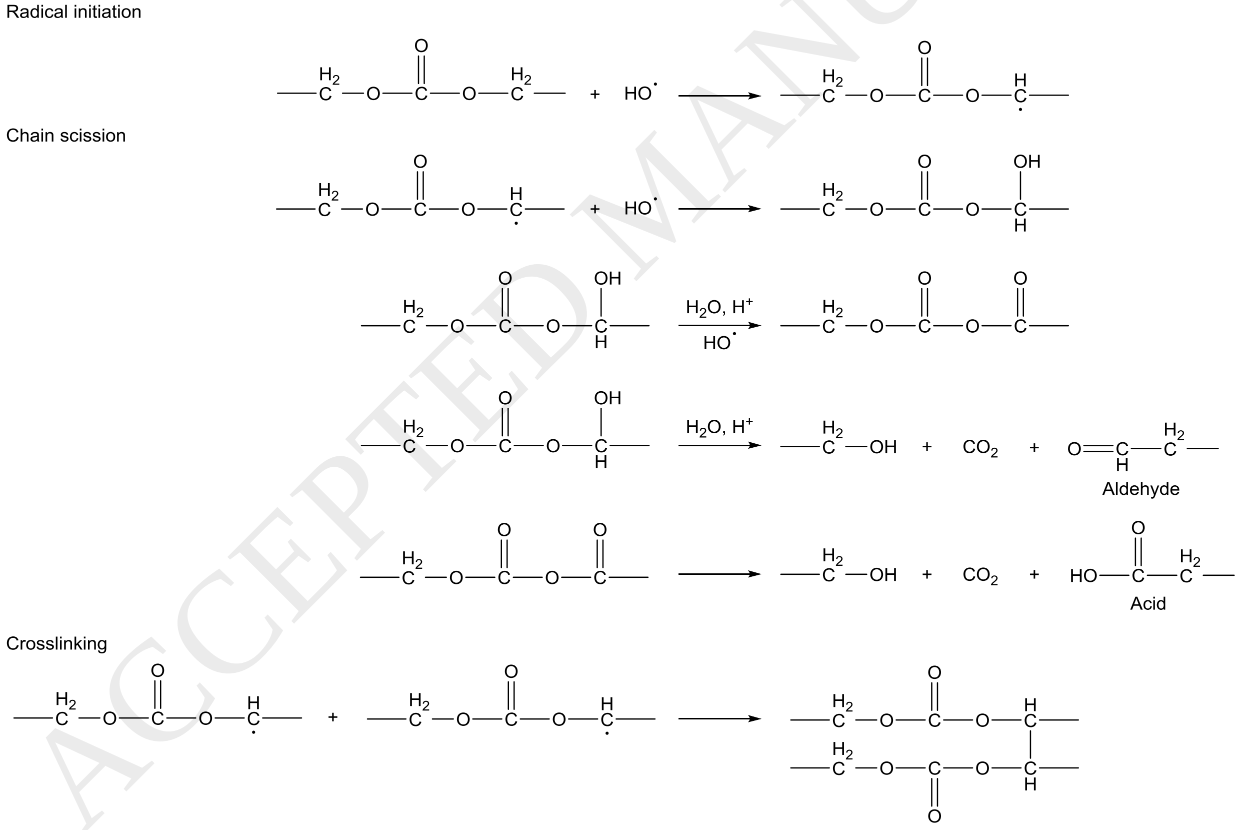
(a) Poly(ether-urethane) soft segment oxidation



(b) Poly(carbonate-urethane) soft segment oxidation



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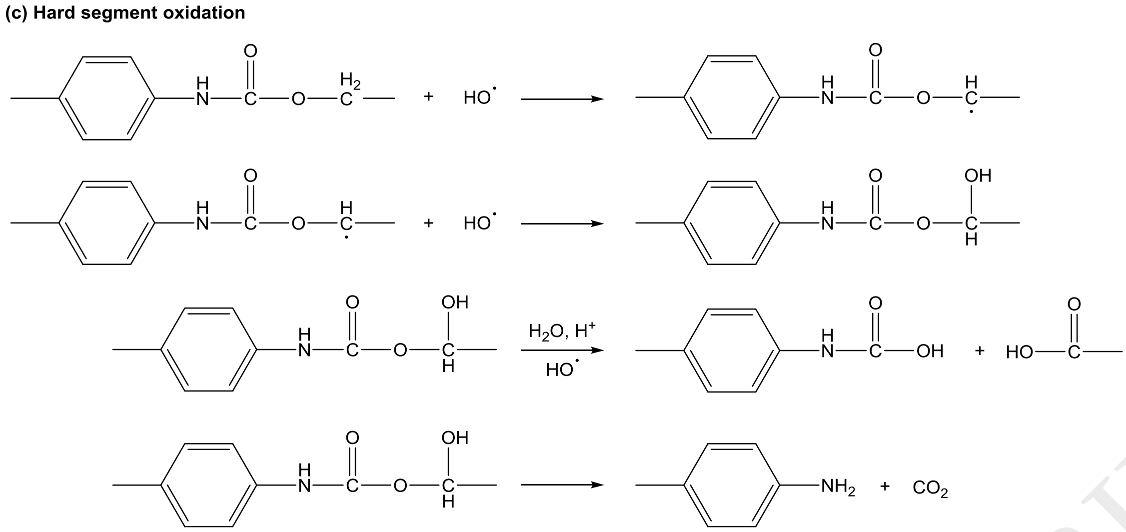

Figure 42. Oxidation of poly(ether-urethane)s and poly(carbonate-urethane)s. [561], Copyright 2004. Adapted with permission from John Wiley & Sons Inc.

α_2-Macroglobulin has been identified as a biological component in human plasma that can act as a stress-cracking promoter for the *in-vitro* oxidative stress cracking of PEtU samples [552, 570]. An additional α_2-macroglobulin treatment before $H_2O_2/CoCl_2$ action was shown to increase the degradation rate and cause greater oxidation to PEtUs [552, 570]. Under such treatment, attack of both α- and β-methylene groups of the polyether segment (Pellethane® 2363-80A or PTMEG/4,4′-MDI/EDA-based PEtUU) by oxygen radicals was also observed [570]. The thiol esters in α_2-macroglobulin are susceptible to hydrolytic cleavage, leading to the formation of free thiol groups, which can then react rapidly with hydroxyl radicals subsequently producing thiyl radicals [552]. Thus, In the α_2-Macroglobulin/$H_2O_2/CoCl_2$ system, both thiyl radicals and hydroxyl radicals participate in the degradation of the polyether SS [552].

The mechanism of oxidation of the SSs of PCUs is shown in **Error! Reference source not found.**b [3, 561]. Reactive oxygen species abstract an α-methylene hydrogen atom from the PC SS. Recombination of the chain radical with a hydroxyl radical forms a hemiacetal, which oxidizes to an ester. Acid hydrolysis of the ester results in chain scission of the SS and the formation of alcohol and carboxylic acid end groups [561]. Although the chemical changes corresponding to the SS chain

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scission and crosslinking were similar in both PEtUs and PCUs, the relative rates of chain scission and crosslinking were different. The lower rate of chain scission in PCUs was attributed to the stabilization of the chain radical by the electrophilic character of the adjacent carbonate. The stabilization of the PCU chain radical increased the radical lifetime, thereby increasing the probability for recombination of chain radicals and crosslinking [561].

With a long enough time, the HSs of PCUs and PEtUs may also undergo degradation through being subjected to reactive oxygen species [567]. According to the mechanism shown in **Error! Reference source not found.**c [561], oxygen radicals abstract an α-methylene hydrogen atom from the ChEx at the urethane [561]. If α_2-macroglobulin is used in addition, thiyl radicals can attack the α-methylene of the urethane ester (analogous to the α-methylene attack on the ether linkage), which enhances the urethane cleavage [552]. Additional hydroxyl radicals combine with the chain radical to form a highly reactive carbonyl-hemiacetal. Oxidative hydrolysis of the carbonyl-hemiacetal results in chain scission and formation of an unstable carbamic acid and carboxylic acid end groups. The carbamic acid decarboxylates readily to form a free amine [561]. However, it was reported that, for PEtUUs, the FTIR results showed no decrease in urea content during any treatment, and the chain-extended HS appeared to be relatively unaffected by implantation or by the *in-vitro* treatment [552].

For both PCUs and PEtUs, the analysis of FTIR spectral changes revealed preferential chain scission of free HS groups compared with hydrogen-bonded HS segments in the hard domains [561]. It was concluded that hydrogen-bonded HSs were inaccessible to degradation due to the crystalline structure of the hard domains [561]. The exposed HSs in the SS phase and at the interphase region were vulnerable to oxidative attack by the proposed mechanism [561].

Although both PCUs and PEtUs appeared to undergo a similar mechanism of HS degradation, evidence for HS degradation was much more prominent in the FTIR spectra of the *in-vitro* or *in-vivo* treated PCU (Bionate® 80A) specimens compared with PEtU (Elasthane™ 80A) samples treated in the same way [561, 566].

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PIBs have again been shown to have better oxidative resistance than both PCs and polyethers. Jewrajka et al. [68] revealed that polyureas containing mixed PIB/PTMG SSs exhibit good oxidative/hydrolytic stabilities in a 20% H_2O_2/0.1 M $CoCl_2$ solution at 50 °C for 40 days, far superior to Bionate® (a PCU) and Elast-Elon™ (a PDMS/PHMG-based PU). Kang et al. [65] found that the presence of chemically inert PIB in the polyether or PC SS protected the vulnerable segments so that PUs with exceptional chemical stability could be obtained. Upon exposure to a 20% H_2O_2/0.1 M $CoCl_2$ solution for up to 14 weeks, the experimental PIB/PC-based PUs exhibited a negligible change in mechanical properties and no surface damage, whereas Elast-Eon™ E2A and Carbothane™ PC-3575A (a PCU, Lubrizol Co.) showed significant surface damage [65].

9.2. Stabilization of polyurethane elastomers against *in-vivo*/*in-vitro* oxidative degradation by polymer modification

As PEtUs are prone to oxidative degradation, they may be substituted with PCUs for better stability. However, the substitution of polyether SSs with PC SSs could result in stiffer thermoplastic PU elastomer materials (typically Elasthane™ 80A *vs.* Bionate® 80A) [567], which may limit the material's potential for application in particular areas. Observed differences in mechanical properties, *i.e.*, higher modulus and reduced ultimate elongation, have been attributed to the reduced flexibility of PC SSs [567].

Another way to enhance the oxidative stability of PEtUs is to employ a polyether with a longer methylene chain (higher CH_2/O ratio) for the SS. A PHMG-based PEtU was shown to be more stable to MIO in H_2O_2/$CoCl_2$ than Pellethane® 2363-80A (a PTMEG-based PEtU) [488].

As discussed above, while the exposed HSs in the SS phase and at the interphase regions were vulnerable to oxidative attack, hydrogen-bonded HSs were inaccessible to degradation due to the crystalline structure of the hard domains [561]. In addition, an *in-vivo* study showed that 4,4′-

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H_{12}MDI-based PEtUs were more susceptible to surface cracking and *M* changes than 4,4′-MDI-based PEtUs, possibly due to the lack of a crystallizable HS [572].

A more widely agreed approach to improve the biostability of PEtU elastomers is the modification with siloxane-based polymers (*e.g.*, silicones such as PDMS). For example, Mathur et al. [568] found that the susceptibility of a PTMEG-based PEtU end-capped by PDMS to *in-vivo* biodegradation was lower than that of the PEtU without modification, although still higher than that of a PHMC-based PCU. The PDMS end caps did not themselves degrade and, moreover, provided a certain degree of protection to the polyether SS [568]. The PDMS end groups imparted a hydrophobic character to the surface of the PEtU that may have resulted in lower FBGC coverage and, effectively, less biodegradation [568]. Pinchuk et al. [573] showed that covalent bonding or grafting of silicone polymers to the surface of PEtUs (Pellethane® 2363-55D, -75D, and -80A) could inhibit the *in-vivo* biodegradation process, whereas the use of an antioxidant (butylated hydroxytoluene, or BHT) at 0.5 wt.% concentration was ineffective in stopping the biodegradation process.

Studies [3, 4, 554, 565, 574] have demonstrated that partial substitution of the polyether SS with PDMS enhanced oxidative stability of PEtUs. According to Martin et al. [574], a formulation with 80% PDMS and 20% PHMG macrodiols (accounting for a total of 60 wt.% of the final polymer), 4,4′-MDI, and 1,4-BDO ChEx produced the best result in terms of a combination of flexibility, strength and biostability, with its properties similar to those of Pellethane® 2363-80A and biostability comparable to that of Pellethane® 2363-55D. Simmons et al. [554] demonstrated that a commercial PHMG/PDMS-based PU, Elast-Eon™ E2 80A, has biostability significantly better than that of Pellethane® 2363-80A and as good as or better than those of Pellethane® 2363-55D and Bionate® 55D. Very minor changes were seen on the surfaces of the Elast-Eon™ E2 80A and Bionate® 55D materials [554]. The presence of PDMS on the film surface, as indicated by contact angle and FTIR, apparently shielded the polyether SS from the effects of the oxidative environment [565]. The

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biostability ranking of different PU materials based on statistical comparisons of chain scission and surface pitting is as follows: PEtU < PEtU-silicone copolymer ≤ PCU < PCU-silicone copolymer [3].

Although both strategies of replacing the polyether SS with PC and of modifying the SS chemistry with PDMS improved the resistance to oxidative degradation, the mechanical properties of the PEtU were compromised to some extent [565].

9.3. Stabilization of polyurethane elastomers against *in-vivo*/*in-vitro* oxidative degradation using stabilizers

A few studies have shown that the addition of antioxidant stabilizers such as Santowhite® [2-*tert*-butyl-4-[1-(5-*tert*-butyl-4-hydroxy-2-methylphenyl)butyl]-5-methylphenol] [549, 561, 562, 566, 575], Methacrol 2138F [decyl 2-methylprop-2-enoate;2-[di(propan-2-yl)amino]ethyl 2-methylprop-2-enoate] [562], and Vitamin E (α-tocopherol) [(2*R*)-2,5,7,8-tetramethyl-2-[(4*R*,8*R*)-4,8,12-trimethyltridecyl]-3,4-dihydrochromen-6-ol] [575] could effectively inhibit *in-vivo* or *in-vitro* degradation of PEtU and PCU elastomers. Santowhite® has been a popular antioxidant, with its chemical structure shown in **Error! Reference source not found.**. Christenson et al. [549, 561, 566] indicated that addition of 2.2 wt % Santowhite® inhibited chain scission and crosslinking of the surface associated with *in-vivo* or *in-vitro* degradation of both Elasthane™ 80A and Bionate® 80A. Schubert et al. [575] showed that vitamin E (**Error! Reference source not found.**) was even more effective than Santowhite® in preventing pitting and cracking to biaxially strained PEtUU elastomers based on PTMEG/4,4′-MDI/diamines, which were tested in 20% H_2O_2/0.1 M $CoCl_2$ at 37°C for 15 days. Vitamin E is more efficient in preventing PEtUU oxidation than Santowhite® possibly because its phenoxy radical is more stable and it can terminate more than one chain per vitamin E molecule [575].

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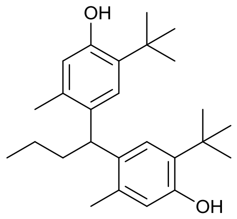
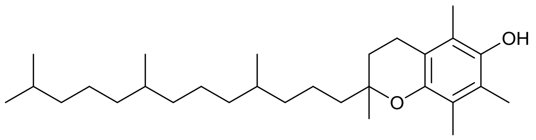


Santowhite
[2-*tert*-Butyl-4-[1-(5-*tert*-butyl-4-hydroxy-2-methylphenyl)butyl]-5-methylphenol]



Vitamin E (α-tocopherol)
[(2*R*)-2,5,7,8-Tetramethyl-2-[(4*R*,8*R*)-4,8,12-trimethyltridecyl]-3,4-dihydrochromen-6-ol]

Figure 43. Chemical structures of Santowhite® and Vitamin E antioxidants.

Antioxidants may also be covalently attached to PU elastomers to provide stabilization against oxidation. For example, Stachelek [576] showed that derivatising Tecothane® TT1074A, an aromatic PEtU, with di-*tert*-butylphenol (DBP) via bromoalkylation conferred significant resistance to *in-vitro* oxidative degradation in $H_2O_2/CoCl_2$ compared with unmodified PU.

10. Biodegradation of polyurethane elastomers

While the previous section was concerned with the *in-vivo* degradation of PU in the body, this section will focus on PU biodegradation under composting and soil conditions. Three types of PU biodegradation have been identified in the literature, namely fungal biodegradation, bacterial biodegradation, and degradation by polyurethanase enzymes [60, 61]. In particular, PEsUs appear to be sensitive to microbial degradation under aerobic conditions [61], with significant weight loss occurring. Esterase activity (both membrane-bound and extracellular) has been noted in microbes, which allow them to utilize PUs as a food source [57]. The microbial degradation of PEsUs is hypothesized to be mainly due to the hydrolysis of ester bonds by these esterase enzymes [57]. This

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is in agreement with a composting (aerobic biodegradation) study of various PEsUs based on either PEA, poly(butylene adipate), poly(hexamethylene adipate), or PCL diol, which showed that the biodegradation rate decreased with decreasing ester content [456]. Moreover, PEsUs composed of an aliphatic diisocyanate showed higher biodegradation rates than those consisting of an aromatic diisocyanate, with the biodegradation rate increasing in the following order of diisocyanate used: 4,4′-MDI < 4,4′-H_{12}MDI < HDI [456].

On the other hand, PEtUs are especially resistant to microbial attack, and the biodegradation of these compounds has been found to be negligible in aerobic and anaerobic conditions [61]. This could be partially explained by the fact that ether links of polyether resins are resistant to attack by microbial enzymes, whereas the ester linkages of polyester resins are more easily cleaved by hydrolases [61].

Nonetheless, the activities of bacteria and fungi against PUs have only been demonstrated under laboratory conditions following the application of certain identified microbial strains, and are not readily biodegradable in the natural environment [57, 60, 61, 577-579]. Most conventional PUs are resistant to biodegradation [60, 61]. For biomedical applications, PU elastomers having enhanced antimicrobial properties are needed, which can be achieved by incorporating antimicrobial ingredients such as chitosan [580], silver nanoparticles [581] and iodine [582].

Biodegradable PUs have recently attracted much attention due to concerns about environmental accumulation and the need to develop new materials for biomedical applications [583-585]. For such PUs, the macrodiols (polymers or copolymers) or ChExs used are based on ingredients that are inherently biodegradable, such as: PCL [456, 474, 478, 543, 586-615], PLA [598, 601, 605, 606, 608, 616-621], plant oils [58, 389, 476, 581, 586, 622-629], polyethylene butylene adipate (PEBA) [587, 608], lignin [623], gelatin [602], chitin/chitosan [630, 631], collagen [632], alginate [633] and heparin [634]. It is noteworthy that PUs with adequate biodegradability may still present excellent

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thermal stability, UV resistance, and chemical resistance [586]. However, more research is needed to understand the degradation and stability of these new PU materials under different ageing conditions.

11. Mechanical degradation and stabilization of polyurethane elastomers

11.1. Fatigue

11.1.1. General discussion

Mechanical energy in the form of applied stress can not only contribute to ozone-induced reactions, but could also lead to autoxidation. A high level of mechanical energy can cause the rupture of polymer bonds [126, 138, 139, 635, 636], and the formation of macroalkyl radicals. In the presence of oxygen, the alkyl radicals react rapidly to form peroxy radicals. Typical oxidative chain reactions then follow [126, 635, 636]. Cracks have been found to initiate at defects associated with sample geometry and sample processing, such as sharp corners [637-639]. The cracks propagate initially on the surface of the sample, followed by propagation through the sample thickness [638]. Crack orientation was found to depend not only on the type of loading (*e.g.*, tension and torsion) but also on the maximum level of loading [637]. It was also found that, in the presence of a low-viscosity fluid, the fatigue resistance of elastomers could be remarkably decreased, in proportion to the degree of swelling [640]. The variation of fatigue resistance of an elastomer in the swollen state being due to a reduction in viscoelastic energy loss and sharpening of crack tips [640]. For elastomers subject to cyclic deformation, the mechanooxidative degradation process is usually referred to as “fatigue” or “flex cracking”.

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Physical aspects of the fatigue of rubbers and elastomers have been extensively studied, especially regarding the rate and pattern of crack growth [637-639], related influencing factors such as the minimum stress and stress amplitude [641-643], and approaches for analysing the fatigue life [644, 645]. However, the understandings from studies of fatigue of other elastomers may not be readily applied to the mechanooxidative degradation of PU elastomers, which contain a segmented, phase-separated structure with the HS domains as a reinforcing filler. It has been found that the minimum value of tearing energy under which no fatigue failure occurs in the absence of chemical effects is far higher in PU elastomers than conventional elastomers [646]. This difference has been considered to be due to the segmented structure of the PU, which has highly hysteresial tensile properties [646].

It was found that for PEtUU elastomers, the immediate effect of a sinusoidal strain or cyclic compression was the destruction of the HSs [647, 648]. Shibayama et al. [648] suggested that the fatigue behavior of a PTMEG-based PEtUU elastomer under a sinusoidal strain first involved a dominant phase mixing process, followed by phase demixing related to the rearrangement and reorientation of the HSs, finally leading to fracture [648]. They also found that PEtUU elastomers that had longer SSs had a higher degree of phase separation, with spherulite formation and orientation behavior being less sensitive to fatigue time [649]. Yeh et al. [650] indicated that the immediate effect of cyclic elongation on segmented PUU elastomers with a low concentration of HSs results in a microstructure composed of lamellar hard domains and highly stressed nanofibrils consisting of alternating hard and crystalline soft domains [650]. However, when the strain is high enough, all the features related to the nanofibrillar morphology will be reduced [650].

Jimenez et al. [651] compared 4,4′-MDI-based PEtU elastomers with different SS structures (a linear PTMEG and an SS with a methyl group on the PTMG chain) during fatiguing (20% cyclic uniaxial extension, superimposed on 3% static strain). Compared to the PU with a linear PTMEG SS,

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the samples with methyl groups demonstrated better fatigue resistance (less phase mixing between the SS and HS), which could be related to the lack of crystallization of the SSs [651].

11.1.2. Antifatigue agents

Antifatigue agents, especially for rubbers and elastomers, have been extensively described in the literature [138, 370, 636, 652-655]. As mechanooxidative degradation is based on the same oxidative chain reactions as thermal degradation and photodegradation, the effect of stress is primarily to increase the rate of formation of radicals, which initiate the oxidation [656]. Given this, antifatigue agents are usually also antioxidants, although not all antioxidants are effective antifatigue agents [636]. Antifatigue agents generally fall into the diarylamine class, and the most widely used commercial agent is *N*-isopropyl-*N′*-phenyl-1,4-phenylenediamine (IPPD) [1-*N*-phenyl-4-*N*-propan-2-ylbenzene-1,4-diamine] (**Error! Reference source not found.**) [370, 636]. During fatiguing of elastomers, this compound, as a CB-D, can react with peroxy radicals to be converted to the corresponding stable aminoxyl radical [370, 410, 636, 654]. As discussed before, this aminoxyl radical is an effective CB-A, which can consume macroalkyl radicals and peroxy radicals in a reversible process [370, 410, 636]. Following the same mechanism as IPPD (shown in **Error! Reference source not found.**), hindered piperidines (**Error! Reference source not found.**) can also be used as antifatigue agents but are much less effective than IPPD, which is consistent with the lower efficiency of alkylamines as CB-D antioxidants [636, 653]. There are also many other aminoxyl generators that are effective antifatigue agents, such as phenolic nitrones, which have been discussed elsewhere [654]. Moreover, sulphoxides such as 3,3′-sulphinyldipropionate esters (**Error! Reference source not found.**) and phenolic thiols can also be effective antifatigue agents [636, 652, 655], via a hydroperoxide decomposing mechanism discussed previously.

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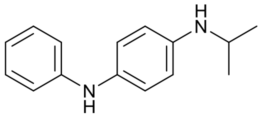
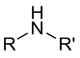
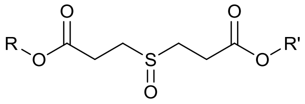


N-isopropyl-*N′*-phenyl-*p*-phenylenediamine (IPPD)
[1-*N*-phenyl-4-*N*-propan-2-ylbenzene-1,4-diamine]



Hindered piperidine



3,3'-Sulphinyldipropionate ester

Figure 44. Typical antifatigue agents.

It is noteworthy that internal friction during fatiguing will result in significant amounts of heat [647, 654]. Therefore, antioxidants could be useful for preventing thermal degradation during fatiguing.

11.2. Stress as a secondary/complementary effect on degradation

As discussed in Section 5.1, stress plays a significant role in ozonolytic degradation, but it can also affect other degradation processes in PU elastomers.

High shear during processing and stress during usage could lead to mechanical scission of polymer chains to give macroalkyl radicals. These radicals are a precursor to hydroperoxide formation, which is a key intermediate in the oxidative degradation of polymers [155, 370]. For photodegradation, the exposure of materials to stress may accelerate thermally activated processes, reduce the rate of recombination of radicals produced by photolysis, and increase the rate of oxygen diffusion [657]. Along with this, tensile stress accelerates molecular scission in polymers exposed to UV irradiation [657, 658], with local sites of disintegration formed in stressed polymers. These sites may be considered as submicrocracks, along which the fracture path progresses [155]. Therefore, all the above processes involving stress as a secondary effect will increase demand for stabilization

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[658]. It has been suggested that fibre reinforcement could reduce the sensitivity of materials to the application of tensile stress during UV irradiation [657].

The synergistic effects of oxidation and stress on the degradation of PU elastomers have frequently been observed in the form of crack formation and propagation. This phenomenon widely occurs in the areas of biomedical implants and tissue engineering materials where the stress level on the polymers is high [3, 537, 659]. Therefore, *in-vivo*/*in-vitro* oxidation studies of PU elastomers (discussed in Section 9) often require specimens to be under strain to take into account stress cracking (SC) of the materials [488, 552, 557, 564, 565, 570-573, 660-662].

SC is characterized by surface microcracking when the elastomer is elongated *in vivo* or *in vitro* [552, 564]. The degree of strain that is required to initiate microcracking varies from composition to composition. *In-vivo* studies have shown that harder compounds tend to have a higher strain threshold than corresponding softer ones [564]. Moreover, softer PEtU materials experienced greater SC than harder PEtU materials [564, 573].

Dynamic strain is also of interest as it occurs in specific biomedical applications such as pumping diaphragms. Implanted Pellethane® 2363-80A specimens have been shown to experience physical damage mainly in regions that were subjected to a higher hydrogen peroxide concentration from inflammatory cells and high degrees and rates of dynamic strain [557]. Wiggins et al. [662] found that the combination of dynamic loading and biaxial tensile strain (as low as 10%) accelerated oxidative degradation of a PEMEG-based PEtUU in $H_2O_2/CoCl_2$ solution. The rate of degradation increased with increasing strain rate but was not affected by strain magnitude [661]. In contrast, imposing a static or dynamic mechanical load did not affect the chemical stability of the PC SS in an $H_2O_2/CoCl_2$ solution [565]. Compared with PEtUs, PCUs were shown to be more resistant to such SC [564, 565].

Residual stress could be a major factor contributing to the *in-vivo* SC of PU materials [56]. Regarding this, there has been research focusing on the SC of prestressed PU samples [555, 570].

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The elimination of residual stress through annealing has been shown to prevent SC but not surface oxidation [3, 488, 537].

SC also occurs for PU elastomers in other strong oxidative environments. Faré et al. [502] found that an applied strain could increase the degradation rate of PEtUs and PCUUs in a NaClO solution (4% Cl_2 available, pH ≈ 13). Under such conditions, even PCUs experienced degradation as shown by the greatly increased surface roughness, with SEM analysis showing evidence of deep cracks and holes or ragged and stretched fractures perpendicular to the direction of stress.

Polymer blending, fibre reinforcement, and impact modification are areas where the industry has solved the SC issues [663], approaches which may then apply to PU elastomers. In addition, Jayabalan et al. [490] suggested that, for the synthesis of 4,4′-H_{12}MDI/HTBD-based PUs, replacing 1,4-BDO as the ChEx by *m*-phenylenediamine could result in highly ordered HSs due to increased hydrogen bonding among urea linkages, leading to increased resistance to SC.

Stress could also change the chemistry and structure of PU elastomers, which could alter the degradation in some way. For example, multiaxial, dynamic systems are frequently used in heart valve testing and they show increased calcification of PU. To overcome this, Khan et al. [488] found that static, uniaxial strain (stress) reduced the propensity of the PEtUs to calcify. Stress might have changed the concentration of the SS domains on the surface, which may have affected the level of calcification [488]. Additionally, an external force applied to PU elastomers could result in strain-induced phenomena such as crystallization [572]. The increased crystallinity may potentially enhance the stability of PU elastomers. However, information in this area is limited and more research is needed to understand the effect of stress on different forms of degradation.

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12. Summary

Due to the versatility of PU chemistry, a diverse range of building blocks, including macrodiols, isocyanates, and ChExs can be chosen for the synthesis of PU elastomers with desired properties. For many applications, the durability of the materials is crucial. Significant progress has been made in enhancing the stability of PU elastomers, mainly through the use of new macrodiols and ChExs, appropriate choice of isocyanates, and hybridization with more stable components. Previous research has also revealed the advantages and disadvantages of each strategy for enhancing PU stability. These aspects are summarised below.

Macrodiol components play a significant role in controlling the stability of PU elastomers:

- Due to the incorporation of polyestser diols, PEsUs have superior mechanical properties and oxidative stability, but poor resistance to hydrolysis (especially under acid conditions and higher temperatures) and enzymes (in particular esterases). The hydrophilicity/hydrophobicity of the polyester component plays a major role in the stability of PEsU elastomers against hydrolysis, calcification and enzymatic degradation. Lower hydrophilicity of the (polyester) SS could make PEsU elastomers, and PU elastomers more generally, less susceptible to these types of degradation.
- PEtUs, being based on polyether diols, have better hydrolysis and enzymatic resistance with moderate photo- and thermooxidative stability and mechanical properties. PEtUs are shown to be prone to oxidative degradation in *in-vivo*/*in-vitro* environments that contain reactive oxygen species, and also have a high propensity to calcify. Larger hydrocarbon segments between ether groups may provide better chemical and oxidative stability, but may reduce processibility. Biostability of PEtUs (typically against oxidation) could be enhanced by the incorporation of siloxane-based polymers into the SS and the modification of the material surface chemistry.

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- For biostability against oxidation and enzymatic degradation, a better alternative to PEtUs could be PCUs. However, PCUs are generally stiffer and may not be as suited to some biomedical applications as the more flexible PEtUs.
- PBUs have the worst oxidative and ozonolytic stability of all PU elastomers due to the unsaturated (alkene) character of the polybutadiene diol segments. However, they are resistant to hydrolysis (better than PEsUs but not as good as PEtUs). For PBUs, the weak link in their structures are the PB segments, which can undergo both chain scission and crosslinking degradation via oxidation or ozonolysis. Thus, blending and copolymerization of PB with another more stable polymer could be strategies to enhance the oxidative and ozonolytic stability of PBUs.
- In contrast, PIBUs, which are a hydrogenated version of PBUs, have outstanding oxidative and hydrolytic stability. However, further improvements in synthesis are needed for tailoring their T_g and mechanical properties, and this may not be readily achievable. The synthesis of PIB diols involves complex chemistry, which is also associated with higher cost. PUs that incorporate macrodiols with a linear aliphatic structure (such as PIB diol) are stable in oxidative, hydrolytic, enzymatic, and lipid solution environments.

The stability of PU elastomers also strongly depends on the structure of urethane/urea components and resulting HSs:

- The formation of HSs is favored when aromatic isocyanates are present, with these structures being resistant to hydrolytic and enzymatic degradation. However, aromatic components are known to be prone to photo- and thermooxidative degradation, which occurs via photo-Fries and chain scission reactions. Replacing aromatic isocyanates with aliphatic compounds generally improves oxidative stability, although leads to decreased mechanical properties.

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- HSs are usually more resistant to degradation than SSs due to their compact structure. In contrast, free urethane linkages (which do not form HSs) and HSs that contain labile structures may be less resistant than the macrodiol components of SSs during degradation by oxidative chemicals and reactive oxygen species *in vitro* or *in vivo*.
- The ability of a PU material to form HS microdomains may contribute to increased stability due to protection of hydrolysable HS linkages located within the microdomains. Highly ordered HSs, which can be formed using specific ChExs and show greater phase separation between the HSs and SSs, usually provide enhanced chemical and oxidative stability for PU elastomers.

There have been various strategies developed for enhancing the stability of PU elastomers:

- Replacing labile or photo- or thermally sensitive groups by less reactive groups, such as compounds with higher BDEs or non-chromophore groups, can lead to improvements in stability.
- Introduction of side chains into the PU backbone and chemical modification of the surface can enhance the hydrolytic stability of PUs.
- A greater extent of hydrogen bonding has been widely reported to improve the stability of PU elastomers against oxidative and enzymatic degradation. In particular, the high polarity of ester carbonyl groups can contribute to hydrogen bonding in PEsUs.
- A higher degree of crystallinity could result in better stability against photodegradation, ozonolysis, and *in-vitro*/*in-vivo* oxidation.
- Crosslinking, either physically or covalently, is effective in suppressing photo- and thermal oxidation, possibly due to restricted oxygen diffusion. Crosslinking has also been shown to be effective for improving the resistance of PU elastomers to ozonolysis, hydrolysis, enzymatic degradation, and organic solvents.

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13. Future perspectives

Despite the notable progress made during decades of research on PU elastomers, there remain gaps and challenges to address:

a) The mechanisms of different types of degradation for particular PU elastomers are still not deeply understood, which prevents the development of effective stabilization strategies. This lack of deep understanding may come from the limited amount of information obtained during the degradation process, where, in most cases, only the end degradation products are analysed. Advanced techniques could be employed to monitor the real-time evolution in chemical composition to assist with better understanding of the degradation processes. Additionally, much of the mechanistic understanding of PU elastomer degradation is based on the behavior of isolated components from the SSs of PUs, however, the overall material structural features (*e.g.*, segmentation, phase-separation, and hydrogen bonding) could significantly influence the degradability and stability of PU systems. Thus, the effects of overall structure should be more thoroughly investigated in the future.

b) For practical applications (*e.g.*, encapsulation materials for underwater devices), degradation occurs under complex conditions: combinations of multiple factors such as UV, heat, ozone, water, chemicals, and strain. The resulting degradation mechanism could be quite different from that with a single influencing factor. Many practical issues originating from this lack of understanding of complex processes are facing the industry and existing knowledge is not readily applicable to develop adequate solutions. A typical example is that while PU elastomer products are usually used under stress, the influence of stress on other types of degradation remains to be investigated.

c) The knowledge of degradation–structure–property relationships is rather limited and should be further examined in the future. Most work has focused on only the changes in

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bulk properties during degradation, whereas the causes of these changes are ambiguous. While most of the past work has been concerned with the analysis of the alteration in morphology, mechanical properties, thermal properties, and water swelling, there are many material characteristics for particular applications that remain to be studied. For example, acoustic properties for sonar applications. Structural features that contribute to such property changes should be fully characterized.

d) A significant challenge in developing stable PU elastomers is that almost any strategies that are proved to be effective could inevitably result in increases in the complexity of PU chemistry, processability and costs and/or compromise some material properties. Therefore, research efforts should be devoted to developing cost-effective solutions to the production of stable PU elastomers with appropriate material properties.

e) Currently, there is a trend to develop PUs based on renewable resources or those that are biodegradable. It is of interest to examine the stability of these PU systems under conditions that differ from their intended application (*i.e*, microbial, enzymatic and composting environments). For biomedical applications, for example, materials are required to be stable under the oxidative environment in the body but must be completely bioresorbable and biodegradable. Translating these materials into other usage environments may help to provide durable systems that are readily degradable after use into oligomers under other conditions.

f) We should also focus on the development of new, long-lasting stabilizers specifically designed for PU elastomers (which is lacking so far). There is a diversity of PUs and their structures are quite different to other polymers. New cost-effective methods for the dispersion of additives in PUs should be developed, which can not only produce homogeneous systems but also address current technical issues (*e.g.*, poor handleability

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due to high viscosity). Moreover, various nanoantioxidants should be tested in PU systems to help to achieve significantly improved oxidative stability.

For delivering truly stable PU elastomers, molecular design, new chemistry, and materials hybridization could be considered as key enablers in future research. For molecular design, we need to focus on the choice of macrodiols, isocyanates and ChExs to produce innovative PU materials. These materials should have the desired chain mobility, HS/SS phase separation, chemical and physical crosslinking including hydrogen bonding, and crystallinity. Along with these properties, appropriate balance of hydrophilicity/hydrophobicity should be achieved and specific groups for co-protection, self-protection or self-healing added to achieve outstanding stability, properties and function. PUs based on hydrogenated-PB or PIB are interesting in this regard, as long as alternative chemistry protocols will allow a significant reduction in costs and a greater control of the material properties. There are also a diverse range of chemical building blocks (including those from renewable resources such as vegetable oils, lignin, and chitosan/chitin) that can be used to form new macrodiols (including copolymers and grafted polymers), isocyanates and ChExs. New, preferably ‘green’, chemistry routes could be explored to produce new PU systems (including non-isocyanate PUs) cost-effectively, of which the stability against various external environmental factors should be carefully examined. Regarding materials hybridization, the effectiveness of polymer blending, copolymerization and interpenetrating networks should be further studied to produce new materials for desired structure, properties, functionality, hydrophobicity, and degradability (as required). In addition, nanotechnology and nanocomposites could be instrumental in the design of sophisticated material structures that could prevent the passage of peroxides, ozone, oxygen, free radicals and inorganic ions that lead to degradation.

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References

[1] Akindoyo JO, Beg MDH, Ghazali S, Islam MR, Jeyaratnam N, Yuvaraj AR. Polyurethane types, synthesis and applications – A review. RSC Adv 2016;6:114453-82.

[2] Engels HW, Pirkl HG, Albers R, Albach RW, Krause J, Hoffmann A, Casselmann H, Dormish J. Polyurethanes: Versatile Materials and Sustainable Problem Solvers for Today's Challenges. Angew Chem 2013;52:9422-41.

[3] Christenson EM, Anderson JM, Hiltner A. Biodegradation mechanisms of polyurethane elastomers. Corros Eng Sci Technol 2007;42:312-23.

[4] Gunatillake PA, Martin DJ, Meijs GF, McCarthy SJ, Adhikari R. Designing biostable polyurethane elastomers for biomedical implants. Aust J Chem 2003;56:545-57.

[5] Kanyanta V, Ivankovic A. Mechanical characterization of polyurethane elastomer for biomedical applications. J Mech Behav Biomed Mater 2010;3:51-62.

[6] Zdrahala RJ, Zdrahala IJ. Biomedical applications of polyurethanes: A review of past promises, present realities, and a vibrant future. J Biomater Appl 1999;14:67-90.

[7] Küting M, Roggenkamp J, Urban U, Schmitz-Rode T, Steinseifer U. Polyurethane heart valves: Past, present and future. Expert Rev Med Devices 2011;8:227-33.

[8] Ahmed N, Kausar A, Muhammad B. Advances in Shape Memory Polyurethanes and Composites: A Review. Polym Plast Technol Eng 2015;54:1410-23.

[9] Huang WM, Yang B, Zhao Y, Ding Z. Thermo-moisture responsive polyurethane shape-memory polymer and composites: A review. J Mater Chem 2010;20:3367-81.

[10] Liu Y, Lv H, Lan X, Leng J, Du S. Review of electro-active shape-memory polymer composite. Compos Sci Technol 2009;69:2064-8.

[11] Behl M, Lendlein A. Shape-memory polymers. Mater Today 2007;10:20-8.

[12] Leng J, Lan X, Liu Y, Du S. Shape-memory polymers and their composites: Stimulus methods and applications. Prog Mater Sci 2011;56:1077-135.

[13] Mather PT, Luo X, Rousseau IA. Shape Memory Polymer Research. Annu Rev Mater Res 2009;39:445-71.

ACCEPTED MANUSCRIPT

[14] Gurunathan T, Rao CRK, Narayan R, Raju KVSN. Polyurethane conductive blends and composites: synthesis and applications perspective. J Mater Sci 2013;48:67-80.

[15] Biggs J, Danielmeier K, Hitzbleck J, Krause J, Kridl T, Nowak S, Orselli E, Quan X, Schapeler D, Sutherland W, Wagner J. Electroactive Polymers: Developments of and Perspectives for Dielectric Elastomers. Angew Chem 2013;52:9409-21.

[16] Singh B, Sharma N. Mechanistic implications of plastic degradation. Polymer Degrad Stab 2008;93:561-84.

[17] Ramotowski T, Jenne K. NUWC XP-1 polyurethane-urea: a new, "acoustically transparent" encapsulant for underwater transducers and hydrophones. OCEANS 2003 Proc Vol 1 2003. p. 227-30.

[18] Ramotowski TS. Method for improving acoustic impedance of epoxy resins. US 8299187 B1, The United States of America as Represented by The Secretary of the Navy; 2012.

[19] Garu PK, Chaki TK. Acoustic & mechanical properties of neoprene rubber for encapsulation of underwater transducers. Int J Sci Eng Technol 2013;1:231-7.

[20] Chen Q, Liang S, Thouas GA. Elastomeric biomaterials for tissue engineering. Prog Polym Sci 2013;38:584-671.

[21] Szycher M. Biodurable polyurethanes. In: Szycher M, editor. Szycher's Handbook of Polyurethane. 2nd ed. Boca Raton: CRC Press; 2012. p. 711-38.

[22] Sonnenschein MF. Introduction to Polyurethane Chemistry. In: Sonnenschein MF, editor. Polyurethanes: Science, Technology, Markets, and Trends: John Wiley & Sons Inc; 2014. p. 105-26.

[23] Prisacariu C. Chemistry of polyurethane elastomers. In: Prisacariu C, editor. Polyurethane Elastomers: From Morphology to Mechanical Aspects. Vienna: Springer Vienna; 2011. p. 1-22.

[24] Hepburn C. Chemistry and Basic Intermediates. In: Hepburn C, editor. Polyurethane Elastomers. Dordrecht: Springer Netherlands; 1992. p. 1-28.

[25] Petrović ZS, Ferguson J. Polyurethane elastomers. Prog Polym Sci 1991;16:695-836.

[26] Król P. Synthesis methods, chemical structures and phase structures of linear polyurethanes. Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers. Prog Mater Sci 2007;52:915-1015.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[27] Thapliyal BP, Chandra R. Advances in photodegradation and stabilization of polyurethanes. Prog Polym Sci 1990;15:735-50.

[28] Szycher M.. Elastomers. In: Szycher M, editor. Szycher's Handbook of Polyurethane. 2nd ed. Boca Raton: CRC Press; 2012. p. 345-71.

[29] Prisacariu C. Structural studies on polyurethane elastomers. In: Prisacariu C, editor. Polyurethane Elastomers: From Morphology to Mechanical Aspects. Vienna: Springer Vienna; 2011. p. 23-60.

[30] Lee HF, Yu HH. Study of electroactive shape memory polyurethane-carbon nanotube hybrids. Soft Matter 2011;7:3801-7.

[31] Hepburn C. Property-Structure Relationships in Polyurethanes. In: Hepburn C, editor. Polyurethane Elastomers. Dordrecht: Springer Netherlands; 1992. p. 51-106.

[32] Gogolewski S. Selected topics in biomedical polyurethanes. A review. Colloid Polym Sci 1989;267:757-85.

[33] Špírková M, Pavličević J, Strachota A, Poreba R, Bera O, Kaprálková L, Baldrian J, Šlouf M, Lazić N, Budinski-Simendić J. Novel polycarbonate-based polyurethane elastomers: Composition–property relationship. Eur Polym J 2011;47:959-72.

[34] Hrdlička Z, Kuta A, Poręba R, Špírková M. Polycarbonate-based polyurethane elastomers: temperature-dependence of tensile properties. Chem Pap 2014;68:233-8.

[35] Fambri L, Penati A, Kolarik J. Modification of polycarbonate with miscible polyurethane elastomers. Polymer 1997;38:835-43.

[36] Labow RS, Meek E, Santerre JP. Hydrolytic degradation of poly(carbonate)-urethanes by monocyte-derived macrophages. Biomaterials 2001;22:3025-33.

[37] Tang YW, Labow RS, Santerre JP. Enzyme-induced biodegradation of polycarbonate polyurethanes: Dependence on hard-segment concentration. J Biomed Mater Res 2001;56:516-28.

[38] Tang YW, Labow RS, Santerre JP. Enzyme-induced biodegradation of polycarbonate-polyurethanes: Dependence on hard-segment chemistry. J Biomed Mater Res 2001;57:597-611.

[39] Eceiza A, Martin MD, Caba Kdl, Kortaberria G, Gabilondo N, Corcuera MA, Mondragon I. Thermoplastic Polyurethane Elastomers Based on Polycarbonate Diols With Different Soft

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Segment Molecular Weight and Chemical Structure: Mechanical and Thermal Properties. Polym Eng Sci 2008;48:297-306.

[40] Zhu R, Wang Y, Zhang Z, Ma D, Wang X. Synthesis of polycarbonate urethane elastomers and effects of the chemical structures on their thermal, mechanical and biocompatibility properties. Heliyon 2016;2:e00125/1-17.

[41] Collin S, Bussière PO, Thérias S, Lambert JM, Perdereau J, Gardette JL. Physicochemical and mechanical impacts of photo-ageing on bisphenol a polycarbonate. Polymer Degrad Stab 2012;97:2284-93.

[42] Diepens M, Gijsman P. Influence of light intensity on the photodegradation of bisphenol A polycarbonate. Polymer Degrad Stab 2009;94:34-8.

[43] Weibin G, Shimin H, Minjiao Y, long J, Yi D. The effects of hydrothermal aging on properties and structure of bisphenol A polycarbonate. Polymer Degrad Stab 2009;94:13-7.

[44] Yazdan Mehr M, van Driel WD, Udono H, Zhang GQ. Surface aspects of discolouration in Bisphenol A Polycarbonate (BPA-PC), used as lens in LED-based products. Opt Mater 2014;37:155-9.

[45] Artham T, Doble M. Fouling and Degradation of Polycarbonate in Seawater: Field and Lab Studies. J Polym Environ 2009;17:170-80.

[46] Banerjee S, Shah PN, Jeong Y, Chang T, Seethamraju K, Faust R. Structural characterization of telechelic polyisobutylene diol. J Chromatogr A 2015;1376:98-104.

[47] Motawie AM, Sadek EM, Awad MMB, Fakhr El-Din A. Coatings from epoxidized (polyurethane-polyester) resin system. J Appl Polym Sci 1998;67:577-81.

[48] Finelli AF, Marshall RA, Chung DA. Elastomers, synthetic. In: Kirk-Othmer, editor. Concise Encyclopedia of Chemical Technology. New York: John Wiley & Sons; 1985. p. 400-400.

[49] Govorčin Bajsić E, Rek V. Thermal stability of polyurethane elastomers before and after UV irradiation. J Appl Polym Sci 2001;79:864-73.

[50] Clough SB, Schneider NS, King AO. Small-angle X-Ray scattering from polyurethane elastomers. J Macromol Sci Part B Phys 1968;2:641-8.

[51] Kim BK, Lee YM. Structure-property relationship of polyurethane ionomer. Colloid Polym Sci 1992;270:956-61.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[52] Liaw DJ. The relative physical and thermal properties of polyurethane elastomers: Effect of chain extenders of bisphenols, diisocyanate, and polyol structures. J Appl Polym Sci 1997;66:1251-65.

[53] Bonk HW, Sardanopoli AA, Ulrich H, Sayigh AAR. Pellethane®: A New Generation of Polyurethane Thermoplastic Elastomers. J Elastoplast 1971;3:157-86.

[54] Rutkowska M, Krasowska K, Heimowska A, Steinka I, Janik H. Degradation of polyurethanes in sea water. Polymer Degrad Stab 2002;76:233-9.

[55] Martin DJ, Meijs GF, Renwick GM, Gunatillake PA, McCarthy SJ. Effect of soft-segment CH_2/O ratio on morphology and properties of a series of polyurethane elastomers. J Appl Polym Sci 1996;60:557-71.

[56] Stokes K, McVenes R, Anderson JM. Polyurethane elastomer biostability. J Biomater Appl 1995;9:321-54.

[57] Howard GT. Biodegradation of polyurethane: A review. Int Biodeterior Biodegradation 2002;49:245-52.

[58] Petrović ZS. Polyurethanes from vegetable oils. Polym Rev 2008;48:109-55.

[59] Cauich-Rodreguez JV, Chan-Chan LH, Hernandez-Sánchez F, Cervantes-Uc JM. Degradation of polyurethanes for cardiovascular applications. In: Pignatello R, editor. Advances in Biomaterials Science and Biomedical Applications. Rijeka: InTech; 2013. p. 51-82.

[60] Cregut M, Bedas M, Durand MJ, Thouand G. New insights into polyurethane biodegradation and realistic prospects for the development of a sustainable waste recycling process. Biotechnol Adv 2013;31:1634-47.

[61] Mahajan N, Gupta P. New insights into the microbial degradation of polyurethanes. RSC Adv 2015;5:41839-54.

[62] Sonnenschein MF. Polyurethane Building Blocks. In: Sonnenschein MF, editor. Polyurethanes: Science, Technology, Markets, and Trends: John Wiley & Sons Inc; 2014. p. 10-104.

[63] Chang VSC, Kennedy JP. Gas permeability, water absorption, hydrolytic stability and air-oven aging of polyisobutylene-based polyurethane networks. Polym Bull 1982;8:69-74.

ACCEPTED MANUSCRIPT

[64] Erdodi G, Kang J, Kennedy JP. Polyisobutylene-based polyurethanes. VI. Unprecedented combination of mechanical properties and oxidative/hydrolytic stability by H-bond acceptor chain extenders. J Polym Sci Part A Polym Chem 2010;48:2361-71.

[65] Kang J, Erdodi G, Brendel CM, Ely D, Kennedy JP. Polyisobutylene-based polyurethanes. V. Oxidative-hydrolytic stability and biocompatibility. J Polym Sci Part A Polym Chem 2010;48:2194-203.

[66] Ummadisetty S, Kennedy JP. Quantitative syntheses of novel polyisobutylenes fitted with terminal primary Br, OH, NH2, and methacrylate termini. J Polym Sci Part A Polym Chem 2008;46:4236-42.

[67] Erdodi G, Kang J, Kennedy JP, Yilgor E, Yilgor I. Polyisobutylene-based polyurethanes. III. Polyurethanes containing PIB/PTMO soft co-segments. J Polym Sci Part A Polym Chem 2009;47:5278-90.

[68] Jewrajka SK, Kang J, Erdodi G, Kennedy JP, Yilgor E, Yilgor I. Polyisobutylene-based polyurethanes. II. Polyureas containing mixed PIB/PTMO soft segments. J Polym Sci Part A Polym Chem 2009;47:2787-97.

[69] Jewrajka SK, Yilgor E, Yilgor I, Kennedy JP. Polyisobutylene-based segmented polyureas. I. Synthesis of hydrolytically and oxidatively stable polyureas. J Polym Sci Part A Polym Chem 2009;47:38-48.

[70] Ojha U, Kulkarni P, Faust R. Syntheses and characterization of novel biostable polyisobutylene based thermoplastic polyurethanes. Polymer 2009;50:3448-57.

[71] Kang J, Erdodi G, Kennedy JP. Polyisobutylene-based polyurethanes with unprecedented properties and how they came about. J Polym Sci, Part A Polym Chem 2011;49:3891-904.

[72] Wei X, Bagdi K, Ren L, Shah P, Seethamraju K, Faust R. Polyisobutylene-based thermoplastic polyurethanes exhibit significant phase mixing. Polymer 2013;54:1647-55.

[73] Kang J, Kennedy JP. Hydrolytically stable polyurethanes. J Polym Sci Part A Polym Chem 2015;53:1-4.

[74] Wang Y, Hillmyer MA. Hydroxy-telechelic poly(ethylene-co-isobutylene) as a soft segment for thermoplastic polyurethanes. Polym Chem 2015;6:6806-11.

[75] Toth K, Kekec NC, Nugay N, Kennedy JP. Polyisobutylene-based polyurethanes. VIII. Polyurethanes with -O-S-PIB-S-O- soft segments. J Polym Sci Part A Polym Chem 2016;54:1119-31.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[76] Toth K, Nugay N, Kennedy JP. Polyisobutylene-based polyurethanes. IX. synthesis, characterization, and properties of polyisobutylene-based poly(urethane-ureas). J Polym Sci Part A Polym Chem 2016;54:2361-9.

[77] Toth K, Nugay N, Kennedy JP. Polyisobutylene-based polyurethanes: VII. structure/property investigations for medical applications. J Polym Sci Part A Polym Chem 2016;54:532-43.

[78] Faust R, Ojha O. Polyisobutylene-based polyurethanes. US 8962785B2, Mass Lowell; 2017.

[79] Kennedy J, Nugay N, Nugay T. Polyisobutylene-based polyurethanes containing organically modified montmorillonite. US 9587069B2, University of Akron; 2017.

[80] Kennedy J, Nugay N, Nugay T. Photochemical preparation of hydroxyl-terminated polyisobutylenes and related methods and uses. US 9701781B2, University of Akron; 2017.

[81] Faust R, Wei X. High strength polyisobutylene polyurethanes. US 9926399B2, University of Massachusetts; 2018.

[82] Kennedy J, Kwon Y, Ummadisetty S. Polyisobutylenes and process for making same. US 10005852B2, University of Akron; 2018.

[83] Skarja GA, Woodhouse KA. Structure-property relationships of degradable polyurethane elastomers containing an amino acid-based chain extender. J Appl Polym Sci 2000;75:1522-34.

[84] Iqbal N, Tripathi M, Parthasarathy S, Kumar D, Roy PK. Aromatic versus Aliphatic: Hydrogen Bonding Pattern in Chain-Extended High-Performance Polyurea. ChemistrySelect 2018;3:1976-82.

[85] Na B, Lv R, Xu W, Tian N, Li J, Tan H, Fu Q. Enhanced hydrogen bonding and its dramatic impact on deformation behaviors in a biomedical poly(carbonate urethane) with fluorinated chain extender. J Polym Sci Part B Polym Phys 2009;47:2198-205.

[86] Frisch KC, Dieter JA. An Overview of Urethane Elastomers. Polym Plast Technol Eng 1975;4:1-21.

[87] Chiou BS, Schoen PE. Effects of crosslinking on thermal and mechanical properties of polyurethanes. J Appl Polym Sci 2002;83:212-23.

[88] Figovsky O, Shapovalov L, Buslov F. Ultraviolet and thermostable non-isocyanate polyurethane coatings. Surf Coat Int Part B 2005;88:67-71.

[89] Guan J, Song Y, Lin Y, Yin X, Zuo M, Zhao Y, Tao X, Zheng Q. Progress in Study of Non-Isocyanate Polyurethane. Ind Eng Chem Res 2011;50:6517-27.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[90] Diakoumakos CD, Kotzev DL. Non-isocyanate-based polyurethane and hybrid polyurethane-epoxy nanocomposite polymer compositions. US 8450413B2, Huntsman Advanced Materials Americas LLC; 2013.

[91] Kathalewar MS, Joshi PB, Sabnis AS, Malshe VC. Non-isocyanate polyurethanes: from chemistry to applications. RSC Adv 2013;3:4110-29.

[92] Pathak R, Kathalewar M, Wazarkar K, Sabnis A. Non-isocyanate polyurethane (NIPU) from tris-2-hydroxy ethyl isocyanurate modified fatty acid for coating applications. Prog Org Coat 2015;89:160-9.

[93] Rokicki G, Parzuchowski PG, Mazurek M. Non-isocyanate polyurethanes: synthesis, properties, and applications. Polym Adv Technol 2015;26:707-61.

[94] Beniah G, Fortman DJ, Heath WH, Dichtel WR, Torkelson JM. Non-Isocyanate Polyurethane Thermoplastic Elastomer: Amide-Based Chain Extender Yields Enhanced Nanophase Separation and Properties in Polyhydroxyurethane. Macromolecules 2017;50:4425-34.

[95] Bossion A, Jones GO, Taton D, Mecerreyes D, Hedrick JL, Ong ZY, Yang YY, Sardon H. Non-Isocyanate Polyurethane Soft Nanoparticles Obtained by Surfactant-Assisted Interfacial Polymerization. Langmuir 2017;33:1959-68.

[96] Brannigan RP, Walder A, Dove AP. Application of Modified Amino Acid-Derived Diols as Chain Extenders in the Synthesis of Novel Thermoplastic Polyester–Urethane Elastomers. ACS Sustainable Chem Eng 2017;5:6902-9.

[97] Cheng C, Li Y, Zhang X, Li J. Eugenol-based non-isocyanate polyurethane and polythiourethane. Iran Polym J 2017;26:821-31.

[98] Comí M, Lligadas G, Ronda JC, Galià M, Cádiz V. Adaptive bio-based polyurethane elastomers engineered by ionic hydrogen bonding interactions. Eur Polym J 2017;91:408-19.

[99] Cornille A, Auvergne R, Figovsky O, Boutevin B, Caillol S. A perspective approach to sustainable routes for non-isocyanate polyurethanes. Eur Polym J 2017;87:535-52.

[100] Cornille A, Ecochard Y, Blain M, Boutevin B, Caillol S. Synthesis of hybrid polyhydroxyurethanes by Michael addition. Eur Polym J 2017;96:370-82.

[101] Haniffa MACM, Ching YC, Chuah CH, Kuan YC, Liu DS, Liou NS. Synthesis, Characterization and the Solvent Effects on Interfacial Phenomena of Jatropha Curcas Oil Based Non-Isocyanate Polyurethane. Polymers 2017;9:162/1-18.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[102] He X, Xu X, Wan Q, Bo G, Yan Y. Synthesis and Characterization of Dimmer-Acid-Based Nonisocyanate Polyurethane and Epoxy Resin Composite. Polymers 2017;9:649/1-12.

[103] Heath W, Athey PS, Wilmot N, Shah HM, Vyakaranam KR, Knight N, Colson AC. Phase-segmented non-isocyanate elastomers. US 9758615B2, Dow Global Technologies LLC; 2017.

[104] Karami Z, Zohuriaan-Mehr MJ, Rostami A. Bio-based thermo-healable non-isocyanate polyurethane DA network in comparison with its epoxy counterpart. J CO_2 Util 2017;18:294-302.

[105] Ke J, Li X, Wang F, Jiang S, Kang M, Wang J, Li Q, Wang Z. Non-isocyanate polyurethane/epoxy hybrid materials with different and controlled architectures prepared from a CO_2-sourced monomer and epoxy via an environmentally-friendly route. RSC Adv 2017;7:28841-52.

[106] Liu G, Wu G, Huo S, Jin C, Kong Z. Synthesis and properties of non-isocyanate polyurethane coatings derived from cyclic carbonate-functionalized polysiloxanes. Prog Org Coat 2017;112:169-75.

[107] Schimpf V, Heck B, Reiter G, Mülhaupt R. Triple-Shape Memory Materials via Thermoresponsive Behavior of Nanocrystalline Non-Isocyanate Polyhydroxyurethanes. Macromolecules 2017;50:3598-606.

[108] Schimpf V, Ritter BS, Weis P, Parison K, Mülhaupt R. High Purity Limonene Dicarbonate as Versatile Building Block for Sustainable Non-Isocyanate Polyhydroxyurethane Thermosets and Thermoplastics. Macromolecules 2017;50:944-55.

[109] Schmidt S, Gatti FJ, Luitz M, Ritter BS, Bruchmann B, Mülhaupt R. Erythritol Dicarbonate as Intermediate for Solvent- and Isocyanate-Free Tailoring of Bio-Based Polyhydroxyurethane Thermoplastics and Thermoplastic Elastomers. Macromolecules 2017;50:2296-303.

[110] Schmidt S, Göppert NE, Bruchmann B, Mülhaupt R. Liquid sorbitol ether carbonate as intermediate for rigid and segmented non-isocyanate polyhydroxyurethane thermosets. Eur Polym J 2017;94:136-42.

[111] Yuan X, Sang Z, Zhao J, Zhang Z, Zhang J, Cheng J. Synthesis and properties of non-isocyanate aliphatic thermoplastic polyurethane elastomers with polycaprolactone soft segments. J Polym Res 2017;24:88/1-11.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[112] Zhang L, Luo X, Qin Y, Li Y. A novel 2,5-furandicarboxylic acid-based bis(cyclic carbonate) for the synthesis of biobased non-isocyanate polyurethanes. RSC Adv 2017;7:37-46.

[113] Aduba DC, Zhang K, Kanitkar A, Sirrine JM, Verbridge SS, Long TE. Electrospinning of plant oil-based, non-isocyanate polyurethanes for biomedical applications. J Appl Polym Sci 2018;135:46464/1-11.

[114] Doley S, Dolui SK. Solvent and catalyst-free synthesis of sunflower oil based polyurethane through non-isocyanate route and its coatings properties. Eur Polym J 2018;102:161-8.

[115] Doley S, Sarmah A, Sarkar C, Dolui SK. *In situ* development of bio-based polyurethane-blend-epoxy hybrid materials and their nanocomposites with modified graphene oxide via non-isocyanate route. Polym Int 2018;67:1062-9.

[116] Esmaeili N, Zohuriaan-Mehr MJ, Salimi A, Vafayan M, Meyer W. Tannic acid derived non-isocyanate polyurethane networks: Synthesis, curing kinetics, antioxidizing activity and cell viability. Thermochim Acta 2018;664:64-72.

[117] Farhadian A, Ahmadi A, Omrani I, Miyardan AB, Varfolomeev MA, Nabid MR. Synthesis of fully bio-based and solvent free non-isocyanate poly(ester amide/urethane) networks with improved thermal stability on the basis of vegetable oils. Polymer Degrad Stab 2018;155:111-21.

[118] Kébir N, Benoit M, Burel F. Elaboration of AA-BB and AB-type Non-Isocyanate Polyurethanes (NIPUs) using a cross metathesis polymerization between methyl carbamate and methyl carbonate groups. Eur Polym J 2018;107:155-163.

[119] Malik M, Kaur R. Synthesis of NIPU by the carbonation of canola oil using highly efficient 5,10,15-tris(pentafluorophenyl)corrolato-manganese(III) complex as novel catalyst. Polym Adv Technol 2018;29:1078-85.

[120] Pérez-Sena WY, Cai X, Kebir N, Verniéres-Hassimi L, Serra C, Salmi T, Leveneur S. Aminolysis of cyclic-carbonate vegetable oils as a non-isocyanate route for the synthesis of polyurethane: A kinetic and thermal study. Chem Eng J 2018;346:271-80.

[121] Pramanik SK, Sreedharan S, Singh H, Khan M, Tiwari K, Shiras A, Smythe C, Thomas JA, Das A. Mitochondria Targeting Non-Isocyanate-Based Polyurethane Nanocapsules for Enzyme-Triggered Drug Release. Bioconjugate Chem 2018;29:3532-3543.

[122] Shen Z, Zhang J, Zhu W, Zheng L, Li C, Xiao Y, Liu J, Wu S, Zhang B. A Solvent-free Route to Non-isocyanate Poly(carbonate urethane) with High Molecular Weight and Competitive Mechanical Properties. Eur Polym J 2018;107:258-266.

ACCEPTED MANUSCRIPT

[123] Wu Z, Cai W, Chen R, Qu J. Synthesis and properties of ambient-curable non-isocyanate polyurethanes. Prog Org Coat 2018;119:116-22.

[124] Xi X, Pizzi A, Delmotte L. Isocyanate-Free Polyurethane Coatings and Adhesives from Mono- and Di-Saccharides. Polymers 2018;10:402/1-21.

[125] Zhang K, Nelson AM, Long TE, Bertin PA, Beuhler A. Non-isocyanate polyurethanes and methods of making and using the same. US 9957356B2, Elevance Renewable Sciences Inc; 2018.

[126] Hawkins WL. Polymer degradation. In: Hawkins WL, editor. Polymer Degradation and Stabilization. Berlin, Heidelberg: Springer; 1984. p. 3-34.

[127] Rabek JF. Photochemical aspects of degradation of polymers. In: Rabek JF, editor. Polymer Photodegradation: Mechanisms and experimental methods. Dordrecht: Springer Netherlands; 1995. p. 24-66.

[128] Rabek JF. Photo-Oxidative Degradation. In: Rabek JF, editor. Photodegradation of Polymers: Physical Characteristics and Applications. Berlin, Heidelberg: Springer; 1996. p. 51-97.

[129] Wypych G. 7 - UV degradation & stabilization of polymers & rubbers. In: Wypych G, editor. Handbook of UV Degradation and Stabilization. 2nd ed. Toronto: ChemTec Publishing; 2015. p. 177-292.

[130] Grassie N, Scott G. Photo-degradation. In: Grassie N, Scott G, editors. Polymer Degradation and Stabilization. Cambridge UK: Cambridge University Press; 1988. p. 68-85.

[131] Scott G. Photodegradation and photostabilization of polymers. In: Scott G, editor. Atmospheric Oxidation and Antioxidants, Volume II. Amsterdam: Elsevier Ltd; 1993. p. 385-429.

[132] Rabek JF. Introduction to the Photo-oxidative Degradation Mechanisms of Polymers. In: Rabek JF, editor. Photostabilization of Polymers: Principles and Applications. Dordrecht: Springer Netherlands; 1990. p. 1-41.

[133] Zweifel H. Principles of stabilization. In: Zweifel H, editor. Stabilization of Polymeric Materials. Berlin, Heidelberg: Springer; 1998. p. 41-69.

[134] Scott G. Autoxidation and antioxidants: Historical perspective. In: Scott G, editor. Atmospheric Oxidation and Antioxidants, Volume I. Amsterdam: Elsevier Ltd; 1993. p. 1-44.

[135] Al-Malaika S. Autoxidation. In: Scott G, editor. Atmospheric Oxidation and Antioxidants, Volume I. Amsterdam: Elsevier Ltd; 1993. p. 45-82.

ACCEPTED MANUSCRIPT

[136] Denisov ET. A Theoretical Approach to the Optimisation of Antioxidant Action. In: Scott G, editor. Mechanisms of Polymer Degradation and Stabilization. Dordrecht: Springer Netherlands; 1990. p. 1-22.

[137] Grassie N, Scott G. Oxidation of polymers. In: Grassie N, Scott G, editors. Polymer Degradation and Stabilization. Cambridge UK: Cambridge University Press; 1988. p. 86-118.

[138] Ambelang JC, Kline RH, Lorenz OM, Parks CR, Wadelin C, Shelton JR. Antioxidants and Antiozonants for General Purpose Elastomers. Rubber Chem Technol 1963;36:1497-541.

[139] Scott G. Ageing, weathering and stabilization of polymers. Makromol Chem Macromol Symp 1988;22:225-35.

[140] Denisov ET, Denisova T. Kinetics of chain oxidation of organic compounds. Handbook of Antioxidants: Bond Dissociation Energies, Rate Constants, Activation Energies, and Enthalpies of Reactions. 2nd ed. Boca Raton: CRC Press; 1999. p. 17-64.

[141] Nangia PS, Benson SW. The kinetics of the interaction of peroxy radicals. II. Primary and secondary alkyl peroxy. Int J Chem Kinet 1980;12:43-53.

[142] Knap HC, Jørgensen S. Rapid Hydrogen Shift Reactions in Acyl Peroxy Radicals. J Phys Chem A 2017;121:1470-9.

[143] Gryn'ova G, Hodgson JL, Coote ML. Revising the mechanism of polymer autooxidation. Org Biomolecul Chem 2011;9:480-90.

[144] Roy PK, Surekha P, Raman R, Rajagopal C. Investigating the role of metal oxidation state on the degradation behaviour of LDPE. Polymer Degrad Stab 2009;94:1033-9.

[145] Roy PK, Surekha P, Rajagopal C, Chatterjee SN, Choudhary V. Studies on the photo-oxidative degradation of LDPE films in the presence of oxidised polyethylene. Polymer Degrad Stab 2007;92:1151-60.

[146] Dobashi Y, Ohkatsu Y. Dependence of ultraviolet absorbers' performance on ultraviolet wavelength. Polymer Degrad Stab 2008;93:436-47.

[147] Kijchavengkul T, Auras R, Rubino M, Alvarado E, Camacho Montero JR, Rosales JM. Atmospheric and soil degradation of aliphatic–aromatic polyester films. Polymer Degrad Stab 2010;95:99-107.

[148] Cui H, Hanus R, Kessler MR. Degradation of ROMP-based bio-renewable polymers by UV radiation. Polymer Degrad Stab 2013;98:2357-65.

ACCEPTED MANUSCRIPT

[149] Fernando SS, Christensen PA, Egerton TA, White JR. Carbon dioxide evolution and carbonyl group development during photodegradation of polyethylene and polypropylene. Polymer Degrad Stab 2007;92:2163-72.

[150] Fabiyi JS, McDonald AG, Wolcott MP, Griffiths PR. Wood plastic composites weathering: Visual appearance and chemical changes. Polymer Degrad Stab 2008;93:1405-14.

[151] Wang Z. Norrish Type I Reaction. In: Wang Z, editor. Comprehensive Organic Name Reactions and Reagents. New York: John Wiley & Sons Inc; 2010. p. 2062-66.

[152] Wang Z. Norrish Type II Reaction. In: Wang Z, editor. Comprehensive Organic Name Reactions and Reagents. New York: John Wiley & Sons Inc; 2010. p. 2067-71.

[153] Shemesh D, Lan Z, Gerber RB. Dynamics of Triplet-State Photochemistry of Pentanal: Mechanisms of Norrish I, Norrish II, and H Abstraction Reactions. J Phys Chem A 2013;117:11711-24.

[154] Wang Z. Photo-Fries Rearrangement. In: Wang Z, editor. Comprehensive Organic Name Reactions and Reagents. New York: John Wiley & Sons Inc; 2010. p. 2200-05.

[155] Rabek JF. Physical aspects of the photodegradation of polymers. In: Rabek JF, editor. Polymer Photodegradation: Mechanisms and experimental methods. Dordrecht: Springer Netherlands; 1995. p. 1-23.

[156] Rabek JF. Photodegradation and photo-oxidative degradation of heterochain polymers. In: Rabek JF, editor. Polymer Photodegradation: Mechanisms and experimental methods. Dordrecht: Springer Netherlands; 1995. p. 255-352.

[157] Wilhelm C, Gardette JL. Infrared analysis of the photochemical behaviour of segmented polyurethanes: 1. Aliphatic poly(ester-urethane). Polymer 1997;38:4019-31.

[158] Rek V, Bravar M. The effect of ultraviolet irradiation on polyurethane solution and on solid polymer. J Elastomers Plast 1980;12:245-55.

[159] Rek V, Bravar M. Ultraviolet degradation of polyester-based polyurethane. J Elastomers Plast 1983;15:33-42.

[160] Rek V, Bravar M, Jocić T. Ageing of solid polyester-based polyurethane. J Elastomers Plast 1984;16:256-64.

[161] Wilhelm C, Rivaton A, Gardette JL. Infrared analysis of the photochemical behaviour of segmented polyurethanes: 3. Aromatic diisocyanate based polymers. Polymer 1998;39:1223-32.

ACCEPTED MANUSCRIPT

[162] Wang LQ, Liang GZ, Dang GC, Wang F, Fan XP, Fu WB. Photochemical Degradation Study of Polyurethanes as Relic Protection Materials by FTIR-ATR. Chin J Chem 2005;23:1257-63.

[163] Rosu D, Ciobanu C, Rosu L, Teaca CA. The influence of polychromic light on the surface of MDI based polyurethane elastomer. Appl Surf Sci 2009;255:9453-7.

[164] Rosu D, Rosu L, Cascaval CN. IR-change and yellowing of polyurethane as a result of UV irradiation. Polymer Degrad Stab 2009;94:591-6.

[165] Gardette JL, Lemaire J. Photo-thermal oxidation of thermoplastic polyurethane elastomers: Part 3--Influence of the excitation wavelengths on the oxidative evolution of polyurethanes in the solid state. Polymer Degrad Stab 1984;6:135-48.

[166] Lee DK, Tsai HB. Properties of segmented polyurethanes derived from different diisocyanates. J Appl Polym Sci 2000;75:167-74.

[167] Rumon KA, Wilhelm WC, Damico DJ. Non-yellowing polyurethane adhesives. US 5166300 A, Lord Corp; 1992.

[168] Hoyle CE, Kim KJ, No YG, Nelson GL. Photolysis of segmented polyurethanes. The role of hard-segment content and hydrogen bonding. J Appl Polym Sci 1987;34:763-74.

[169] Hoyle CE, Kim KJ. Effect of crystallinity and flexibility on the photodegradation of polyurethanes. J Polym Sci Part A Polym Chem 1987;25:2631-42.

[170] Hoyle CE, Chawla CP, Kim KJ. The effect of flexibility on the photodegradation of aromatic diisocyanate-based polyurethanes. J Polym Sci Part A Polym Chem 1988;26:1295-306.

[171] Irusta L, Fernandez-Berridi MJ. Photooxidative behaviour of segmented aliphatic polyurethanes. Polymer Degrad Stab 1999;63:113-9.

[172] Wilhelm C, Gardette JL. Infrared analysis of the photochemical behaviour of segmented polyurethanes: aliphatic poly(ether-urethane)s. Polymer 1998;39:5973-80.

[173] Dannoux A, Esnouf S, Amekraz B, Dauvois V, Moulin C. Degradation mechanism of poly(ether-urethane) Estane® induced by high-energy radiation. II. Oxidation effects. J Polym Sci Part B Polym Phys 2008;46:861-78.

[174] Coquillat M, Verdu J, Colin X, Audouin L, Nevière R. Thermal oxidation of polybutadiene. Part 1: Effect of temperature, oxygen pressure and sample thickness on the thermal oxidation of hydroxyl-terminated polybutadiene. Polymer Degrad Stab 2007;92:1326-33.

ACCEPTED MANUSCRIPT

[175] Arrington KJ, Waugh JB, Radzinski SC, Matson JB. Photo- and Biodegradable Thermoplastic Elastomers: Combining Ketone-Containing Polybutadiene with Polylactide Using Ring-Opening Polymerization and Ring-Opening Metathesis Polymerization. Macromolecules 2017;50:4180-7.

[176] La Mantia FP, Morreale M, Botta L, Mistretta MC, Ceraulo M, Scaffaro R. Degradation of polymer blends: A brief review. Polymer Degrad Stab 2017;145:79-92.

[177] Lee J, Moon B. Synthesis of telechelic anthraquinone-functionalized polybutadiene via ROMP and study of its photo-oxidation and UV crosslinking behaviors. J Polym Sci Part A Polym Chem 2018;56:1249-58.

[178] Kamelian FS, Saljoughi E, Shojaee Nasirabadi P, Mousavi SM. Modifications and research potentials of acrylonitrile/butadiene/styrene (ABS) membranes: A review. Polym Compos 2018;39:2835-46.

[179] Beavan SW, Phillips D. Mechanistic studies on the photo-oxidation of commercial poly(butadiene). Eur Polym J 1974;10:593-603.

[180] Piton M, Rivaton A. Photooxidation of polybutadiene at long wavelengths ($\lambda > 300$ nm). Polymer Degrad Stab 1996;53:343-59.

[181] Adam C, Lacoste J, Lemaire J. Photo-oxidation of elastomeric materials: Part IV—Photo-oxidation of 1,2-polybutadiene. Polymer Degrad Stab 1990;29:305-20.

[182] Adam C, Lacoste J, Lemaire J. Photo-oxidation of elastomeric materials. Part 1—Photo-oxidation of polybutadienes. Polymer Degrad Stab 1989;24:185-200.

[183] Bussière PO, Gardette JL, Lacoste J, Baba M. Characterization of photodegradation of polybutadiene and polyisoprene: chronology of crosslinking and chain-scission. Polymer Degrad Stab 2005;88:182-8.

[184] Tan KT, White CC, Benatti DJ, Hunston DL. Evaluating aging of coatings and sealants: Mechanisms. Polymer Degrad Stab 2008;93:648-56.

[185] Speckhard TA, Strate GV, Gibson PE, Cooper SL. Properties of polyisobutylene-polyurethane block copolymers: I. Macroglycols from ozonolysis of isobutylene-isoprene copolymer. Polym Eng Sci 1983;23:337-49.

[186] Rabek JF. Photodegradation and photo-oxidative degradation of homochain polymers. In: Rabek JF, editor. Polymer Photodegradation: Mechanisms and experimental methods. Dordrecht: Springer Netherlands; 1995. p. 67-254.

ACCEPTED MANUSCRIPT

[187] Gonon L, Troquet M, Fanton E, Gardette JL.. Thermo and photo-oxidation of polyisobutylene—II. Influence of the temperature. Polymer Degrad Stab 1998;62:541-9.

[188] Lemaire J, Gardette JL, Rivaton A, Roger A. Dual photo-chemistries in aliphatic polyamides, bisphenol A polycarbonate and aromatic polyurethanes—A short review. Polymer Degrad Stab 1986;15:1-13.

[189] Andrady AL, Searle ND, Crewdson LFE. Wavelength sensitivity of unstabilized and UV stabilized polycarbonate to solar simulated radiation. Polymer Degrad Stab 1992;35:235-47.

[190] Pérez JM, Vilas JL, Laza JM, Arnáz S, Mijangos F, Bilbao E, Rodríguez M, León LM. Effect of reprocessing and accelerated ageing on thermal and mechanical polycarbonate properties. J Mater Process Technol 2010;210:727-33.

[191] Diepens M, Gijsman P. Photodegradation of bisphenol A polycarbonate. Polymer Degrad Stab 2007;92:397-406.

[192] Diepens M, Gijsman P. Photo-oxidative degradation of bisphenol A polycarbonate and its possible initiation processes. Polymer Degrad Stab 2008;93:1383-8.

[193] Diepens M, Gijsman P. Outdoor and accelerated weathering studies of bisphenol A polycarbonate. Polymer Degrad Stab 2011;96:649-52.

[194] Diepens M, Gijsman P. Photostabilizing of bisphenol A polycarbonate by using UV-absorbers and self protective block copolymers based on resorcinol polyarylate blocks. Polymer Degrad Stab 2009;94:1808-13.

[195] Pickett JE. Influence of photo-Fries reaction products on the photodegradation of bisphenol-A polycarbonate. Polymer Degrad Stab 2011;96:2253-65.

[196] Zhou W, Yang H, Zhou J. The thermal degradation of bisphenol: A polycarbonate containing methylphenyl–silicone additive. J Anal Appl Pyrolysis 2007;78:413-8.

[197] Diepens M, Gijsman P. Photodegradation of bisphenol A polycarbonate with different types of stabilizers. Polymer Degrad Stab 2010;95:811-7.

[198] Gomez CM, Gutierrez D, Asensio M, Costa V, Nohales A. Transparent thermoplastic polyurethanes based on aliphatic diisocyanates and polycarbonate diol. J Elastomers Plast 2017;49:77-95.

[199] Yang XF, Vang C, Tallman DE, Bierwagen GP, Croll SG, Rohlik S. Weathering degradation of a polyurethane coating. Polymer Degrad Stab 2001;74:341-51.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[200] Boubakri A, Guermazi N, Elleuch K, Ayedi HF. Study of UV-aging of thermoplastic polyurethane material. Mater Sci Eng A 2010;527:1649-54.

[201] Liu Y, Liu Y, Liu S, Tan H. Effect of accelerated xenon lamp aging on the mechanical properties and structure of thermoplastic polyurethane for stratospheric airship envelope. J Wuhan Univ Technol Mater Sci Ed 2014;29:1270-6.

[202] Bhargava S, Kubota M, Lewis RD, Advani SG, Prasad AK, Deitzel JM. Ultraviolet, water, and thermal aging studies of a waterborne polyurethane elastomer-based high reflectivity coating. Prog Org Coat 2015;79:75-82.

[203] Oprea S, Oprea V. Mechanical behavior during different weathering tests of the polyurethane elastomers films. Eur Polym J 2002;38:1205-10.

[204] Aglan H, Calhoun M, Allie L. Effect of UV and hygrothermal aging on the mechanical performance of polyurethane elastomers. J Appl Polym Sci 2008;108:558-64.

[205] Ludwick A, Aglan H, Abdalla MO, Calhoun M. Degradation behavior of an ultraviolet and hygrothermally aged polyurethane elastomer: Fourier transform infrared and differential scanning calorimetry studies. J Appl Polym Sci 2008;110:712-8.

[206] Nakatani H, Ooike H, Kishida T, Motokucho S. Photodegradation behavior of waterborne polyurethanes with different segment distributions and lengths. Prog Org Coat 2016;97:269-76.

[207] Hawkins WL. Stabilization Against Degradation by Radiation. In: Hawkins WL, editor. Polymer Degradation and Stabilization. Berlin, Heidelberg: Springer; 1984. p. 74-90.

[208] Ionescu M. Polybutadiene polyols. In: Ionescu M, editor. Chemistry and Technology of Polyols for Polyurethanes. Shawbury, Shrewsbury, Shropshire, UK: Rapra Technology Limited; 2005. p. 295-304.

[209] Doi Y, Yano A, Soga K, Burfield DR. Hydrogenation of polybutadienes. Microstructure and thermal properties of hydrogenated polybutadienes. Macromolecules 1986;19:2409-12.

[210] Dai L, Wang X, Bu Z, Li BG, Jie S. Facile access to carboxyl-terminated polybutadiene and polyethylene from *cis*-polybutadiene rubber. J Appl Polym Sci 2019 136:46934/1-9.

[211] Chiang CH, Tsai JC. Hydrogenation of polystyrene-*b*-polybutadiene-*b*-polystyrene mediated by group (IV) metal metallocene complexes. J Polym Sci Part A Polym Chem 2017;55:2141-9.

ACCEPTED MANUSCRIPT

[212] Ai C, Li J, Gong G, Zhao X, Liu P. Preparation of hydrogenated nitrile-butadiene rubber (H-NBR) with controllable molecular weight with heterogeneous catalytic hydrogenation after degradation via olefin cross metathesis. React Funct Polym 2018;129:53-7.

[213] Hashimoto H. Method for producing end-modified polybutadiene or end-modified hydrogenated polybutadiene and composition containing same. US 9815922B2, Nippon Soda Co Ltd; 2017.

[214] Hashimoto H. Method for producing (meth)acrylic-modified polybutadiene. US 9534094B2, Nippon Soda Co Ltd; 2017.

[215] Zou R, Tan J, Liu K, Liang L, Cheng X, Zhang X, Zhang L, Yue D. A hydrogenated hydroxy-terminated butadiene-acrylonitrile copolymer-based polyurethane elastomer with improved mechanical properties and aging resistance. RSC Adv 2016;6:20198-201.

[216] Rosu D, Rosu L, Mustata F, Varganici CD. Effect of UV radiation on some semi-interpenetrating polymer networks based on polyurethane and epoxy resin. Polymer Degrad Stab 2012;97:1261-9.

[217] Rabek JF. Physical Factors Which Influence Photodegradation. In: Rabek JF, editor. Photodegradation of Polymers: Physical Characteristics and Applications. Berlin, Heidelberg: Springer; 1996. p. 98-108.

[218] Malkappa K, Jana T. Simultaneous Improvement of Tensile Strength and Elongation: An Unprecedented Observation in the Case of Hydroxyl Terminated Polybutadiene Polyurethanes. Ind Eng Chem Res 2013;52:12887-96.

[219] Decker C, Moussa K, Bendaikha T. Photodegradation of UV-cured coatings II. Polyurethane– acrylate networks. J Polym Sci Part A Polym Chem 1991;29:739-47.

[220] Brunette CM, Hsu SL, MacKnight WJ. Hydrogen-bonding properties of hard-segment model compounds in polyurethane block copolymers. Macromolecules 1982;15:71-7.

[221] Miller JA, Lin SB, Hwang KKS, Wu KS, Gibson PE, Cooper SL. Properties of polyether-polyurethane block copolymers: effects of hard segment length distribution. Macromolecules 1985;18:32-44.

[222] Martin DJ, Meijs GF, Renwick GM, McCarthy SJ, Gunatillake PA. The effect of average soft segment length on morphology and properties of a series of polyurethane elastomers. I. Characterization of the series. J Appl Polym Sci 1996;62:1377-86.

[223] Hawkins WL. Stabilization Against Non-oxidative Thermal Degradation. In: Hawkins WL, editor. Polymer Degradation and Stabilization. Berlin, Heidelberg: Springer; 1984. p. 35-9.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[224] Hawkins WL. Stabilization against thermal oxidation. In: Hawkins WL, editor. Polymer Degradation and Stabilization. Berlin, Heidelberg: Springer; 1984. p. 40-73.

[225] Heller HJ, Blattmann HR. Some aspects of stabilization of polymers against light. Pure Appl Chem 1973;36:141-62.

[226] Wiles DM, Carlsson DJ. Photostabilization mechanisms in polymers: A review. Polymer Degrad Stab 1980;3:61-72.

[227] Scott G. Photodegradation and photostabilization of polymers. J Photochem 1984;25:83-90.

[228] Allen NS, Chirinis-Padron A, Henman TJ. The photo-stabilization of polypropylene: A review. Polymer Degrad Stab 1985;13:31-76.

[229] Scott G. Developments in the photo-oxidation and photo-stabilization of polymers. Polymer Degrad Stab 1985;10:97-125.

[230] Pospíšil J. Mechanistic action of phenolic antioxidants in polymers—A review. Polymer Degrad Stab 1988;20:181-202.

[231] Minagawa M. New developments in polymer stabilization. Polymer Degrad Stab. 1989;25:121-41.

[232] Pospíšil J. The key role of antioxidant transformation products in the stabilization mechanisms—A critical analysis. Polymer Degrad Stab 1991;34:85-109.

[233] Pospíšil J. Chemical and photochemical behaviour of phenolic antioxidants in polymer stabilization: A state of the art report, part II. Polymer Degrad Stab 1993;39:103-15.

[234] Yousif E, Haddad R. Photodegradation and photostabilization of polymers, especially polystyrene: review. SpringerPlus 2013;2:398/1-32.

[235] Wypych G. 3 - Mechanisms of UV stabilization. In: Wypych G, editor. Handbook of UV Degradation and Stabilization-2nd ed. Toronto: ChemTec Publishing 2015. p. 37-65.

[236] Al-Malaika S. Antioxidants — Preventive mechanisms. In: Scott G, editor. Atmospheric Oxidation and Antioxidants, Volume I. Amsterdam: Elsevier Ltd; 1993. p. 161-224.

[237] Scott G. Synergism and antagonism. In: Scott G, editor. Atmospheric Oxidation and Antioxidants, Volume II. Amsterdam: Elsevier Ltd; 1993. p. 431-59.

[238] Scott G. Antioxidants: Chain breaking mechanisms. In: Scott G, editor. Atmospheric Oxidation and Antioxidants, Volume I. Amsterdam: Elsevier Ltd; 1993. p. 121-60.

[239] Cicchetti O. Mechanisms of oxidative photodegradation and of UV stabilization of polyolefins. Adv Polym Sci 1970;7:70-112.

ACCEPTED MANUSCRIPT

[240] Rabek JF. Introduction to the Oxidative and Photo-Stabilization of Polymers. In: Rabek JF, editor. Photostabilization of Polymers: Principles and Applications. Dordrecht: Springer Netherlands; 1990. p. 42-79.

[241] Rabek JF. Antioxidants. In: Rabek JF, editor. Photostabilization of Polymers: Principles and Applications. Dordrecht: Springer Netherlands; 1990. p. 80-166.

[242] Rabek JF. Pigments. In: Rabek JF, editor. Photostabilization of Polymers: Principles and Applications. Dordrecht: Springer Netherlands; 1990. p. 167-201.

[243] Rabek JF. Photostabilizers. In: Rabek JF, editor. Photostabilization of Polymers: Principles and Applications. Dordrecht: Springer Netherlands; 1990. p. 202-78.

[244] Rabek JF. Hindered Amine Light Stabilizers (HALS). In: Rabek JF, editor. Photostabilization of Polymers: Principles and Applications. Dordrecht: Springer Netherlands; 1990. p. 279-356.

[245] Rabek JF. Polymer-Bound Additives. In: Rabek JF, editor. Photostabilization of Polymers: Principles and Applications. Dordrecht: Springer Netherlands; 1990. p. 357-95.

[246] Keller RW. Oxidation and Ozonation of Rubber. Rubber Chem Technol 1985;58:637-52.

[247] Grassie N, Scott G. Antioxidants and stabilizers. In: Grassie N, Scott G, editors. Polymer Degradation and Stabilization. Cambridge, UK: Cambridge University Press; 1988. p. 119-69.

[248] Saadat-Monfared A, Mohseni M. Polyurethane nanocomposite films containing nano-cerium oxide as UV absorber; Part 2: Structural and mechanical studies upon UV exposure. Colloids Surf A 2014;441:752-7.

[249] Valgimigli L, Baschieri A, Amorati R. Antioxidant activity of nanomaterials. J Mater Chem B 2018;6:2036-51.

[250] Wallder VT, Clarke WJ, DeCoste JB, Howard JB. Weathering Studies on Polyethylene. Ind Eng Chem Res 1950;42:2320-5.

[251] Van Bellingen C, Accorsi JV. The impact of carbon black morphology and dispersion on the weatherability of polyethylene. International Wire & Cable Symposium. Atlantic City, New Jersey 1999. p. 815-23.

[252] Accorsi JV. The Impact of Carbon Black Morphology and Dispersionon the Weatherability of Polyethylene. KGK Kautsch Gummi Kunstst 2001;54:321-6.

ACCEPTED MANUSCRIPT

[253] Horrocks AR, Mwila J, Miraftab M, Liu M, Chohan SS. The influence of carbon black on properties of orientated polypropylene 2. Thermal and photodegradation. Polymer Degrad Stab 1999;65:25-36.

[254] Funt JM, Sifleet WL, Tomme M. Carbon black in plastics. In: Donnet JB, Bansal RC, Wang MJ, editors. Carbon Black: Science and Technology. 2nd ed. New York: Marcel Dekker Inc; 1993. p. 389-408.

[255] Accorsi J, Yu M. Carbon black. In: Pritchard G, editor. Plastics Additives: An A-Z reference. Dordrecht: Springer Netherlands; 1998. p. 153-61.

[256] Bigger SW, Delatycki O. The effects of pigments on the photostability of polyethylene. J Mater Sci 1989;24:1946-52.

[257] Searle ND. Environmental Effects on Polymeric Materials. In: Andrady AL, editor. Plastics and the Environment: John Wiley & Sons Inc; 2005. p. 311-58.

[258] Osawa Z, Nagashima K, Ohshima H, Cheu EL. Study of the degradation of polyurethanes. VI. The effect of various additives on the photodegradation of polyurethanes. J Polym Sci Polym Lett Ed 1979;17:409-13.

[259] Lee BH, Kim HJ. Influence of isocyanate type of acrylated urethane oligomer and of additives on weathering of UV-cured films. Polymer Degrad Stab 2006;91:1025-35.

[260] Wang Y, Wang H, Li X, Liu D, Jiang Y, Sun Z. O_3/UV synergistic aging of polyester polyurethane film modified by composite uv absorber. J Nanomater 2013;2013:169405/1-7.

[261] Wang H, Wang Y, Liu D, Sun Z, Wang H. Effects of Additives on Weather-Resistance Properties of Polyurethane Films Exposed to Ultraviolet Radiation and Ozone Atmosphere. J Nanomater 2014;2014:487343/1-7.

[262] Saha S, Kocaefe D, Boluk Y, Pichette A. Enhancing exterior durability of jack pine by photo-stabilization of acrylic polyurethane coating using bark extract. Part 1: Effect of UV on color change and ATR–FT-IR analysis. Prog Org Coat 2011;70:376-82.

[263] Decker C, Masson F, Schwalm R. Weathering resistance of waterbased UV-cured polyurethane-acrylate coatings. Polymer Degrad Stab 2004;83:309-20.

[264] Seo J, Kim S, Lee YS, Kwon OH, Park KH, Choi SY, Chung YK, Jang DJ, Park SY. Enhanced solid-state fluorescence in the oxadiazole-based excited-state intramolecular proton-transfer (ESIPT) material: Synthesis, optical property, and crystal structure. J Photochem Photobiol A 2007;191:51-8.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[265] Kramer HEA. Tautomerism by Hydrogen Transfer in Salicylates, Triazoles and Oxazoles. In: Bouas-Laurent H, editor. Photochromism (Revised Edition). Amsterdam: Elsevier Ltd Science; 2003. p. 654-84.

[266] Schwalm R. Recent Developments. In: Schwalm R, editor. UV Coatings. Amsterdam: Elsevier Ltd; 2007. p. 206-51.

[267] Hayoz P, Peter W, Rogez D. A new innovative stabilization method for the protection of natural wood. Prog Org Coat 2003;48:297-309.

[268] Heller HJ. Protection of polymers against light irradiation. Eur Polym J 1969;5:105-32.

[269] Huang TK, Wang YC, Hsieh KH, Lin JJ. Molecular-level dispersion of phosphazene–clay hybrids in polyurethane and synergistic influences on thermal and UV resistance. Polymer 2012;53:4060-8.

[270] Yaneff PV, Adamsons K, Cliff N, Kanouni M. Migration of reactable UVAs and HALS in automotive plastic coatings. JCT Res 2004;1:201-12.

[271] Haacke G, Longordo E, Brinen JS, Andrawes FF, Campbell BH. Chemisorption and physical adsorption of light stabilizers on pigment and ultrafine particles in coatings. J Coat Technol 1999;71:87-94.

[272] Ávár L, Bechtold K. Studies on the interaction of photoreactive light stabilizers and UV-absorbers. Prog Org Coat 1999;35:11-7.

[273] Suits LD, Hsuan YG. Assessing the photo-degradation of geosynthetics by outdoor exposure and laboratory weatherometer. Geotext Geomembr 2003;21:111-22.

[274] Morlat-Therias S, Fanton E, Gardette JL, Peeterbroeck S, Alexandre M, Dubois P. Polymer/carbon nanotube nanocomposites: Influence of carbon nanotubes on EVA photodegradation. Polymer Degrad Stab 2007;92:1873-82.

[275] Mirabedini SM, Khodabakhshi K. Nanocomposites of PU Polymers Filled With Spherical Fillers. In: Thomas S, Datta J, Haponiuk JT, Reghunadhan A, editors. Polyurethane Polymers. Amsterdam: Elsevier Ltd; 2017. p. 135-72.

[276] Wen B, Wang F, Xu X, Ding Y, Zhang S, Yang M. The Effect of Encapsulation of Nano Zinc Oxide with Silica on the UV Resistance of Polypropylene. Polym Plast Technol Eng 2011;50:1375-82.

[277] Zhou S, Wu L, Sun J, Shen W. The change of the properties of acrylic-based polyurethane via addition of nano-silica. Prog Org Coat 2002;45:33-42.

ACCEPTED MANUSCRIPT

[278] Jalili MM, Moradian S. Deterministic performance parameters for an automotive polyurethane clearcoat loaded with hydrophilic or hydrophobic nano-silica. Prog Org Coat 2009;66:359-66.

[279] Saadat-Monfared A, Mohseni M, Tabatabaei MH. Polyurethane nanocomposite films containing nano-cerium oxide as UV absorber. Part 1. Static and dynamic light scattering, small angle neutron scattering and optical studies. Colloids Surf A 2012;408:64-70.

[280] Ammala A, Hill AJ, Meakin P, Pas SJ, Turney TW. Degradation Studies of Polyolefins Incorporating Transparent Nanoparticulate Zinc Oxide UV Stabilizers. J Nanopart Res 2002;4:167-74.

[281] Allen NS, Edge M, Ortega A, Sandoval G, Liauw CM, Verran J, Stratton J, McIntyre RB. Degradation and stabilization of polymers and coatings: nano versus pigmentary titania particles. Polymer Degrad Stab 2004;85:927-46.

[282] Allen NS, Edge M, Ortega A, Liauw CM, Stratton J, McIntyre RB. Behaviour of nanoparticle (ultrafine) titanium dioxide pigments and stabilizers on the photooxidative stability of water based acrylic and isocyanate based acrylic coatings. Polymer Degrad Stab 2002;78:467-78.

[283] Rashvand M, Ranjbar Z. Degradation and stabilization of an aromatic polyurethane coating during an artificial aging test via FTIR spectroscopy. Mater Corros 2014;65:76-81.

[284] Yang H, Zhu S, Pan N. Studying the mechanisms of titanium dioxide as ultraviolet-blocking additive for films and fabrics by an improved scheme. J Appl Polym Sci 2004;92:3201-10.

[285] Janotti A, Van De Walle CG. Fundamentals of zinc oxide as a semiconductor. Rep Prog Phys 2009;72:126501/1-29.

[286] Zhu T, Gao SP. The Stability, Electronic Structure, and Optical Property of TiO_2 Polymorphs. J Phys Chem C 2014;118:11385-96.

[287] Goh EG, Xu X, McCormick PG. Effect of particle size on the UV absorbance of zinc oxide nanoparticles. Scr Mater 2014;78–79:49-52.

[288] Chen XD, Wang Z, Liao ZF, Mai YL, Zhang MQ. Roles of anatase and rutile TiO_2 nanoparticles in photooxidation of polyurethane. Polym Test 2007;26:202-8.

[289] Xiong M, Gu G, You B, Wu L. Preparation and characterization of poly(styrene butylacrylate) latex/nano-ZnO nanocomposites. J Appl Polym Sci 2003;90:1923-31.

[290] Rashvand M, Ranjbar Z, Rastegar S. Nano zinc oxide as a UV-stabilizer for aromatic polyurethane coatings. Prog Org Coat 2011;71:362-8.

ACCEPTED MANUSCRIPT

[291] Zhao H, Li RKY. A study on the photo-degradation of zinc oxide (ZnO) filled polypropylene nanocomposites. Polymer 2006;47:3207-17.

[292] Rasouli D, Dintcheva NT, Faezipour M, La Mantia FP, Mastri Farahani MR, Tajvidi M. Effect of nano zinc oxide as UV stabilizer on the weathering performance of wood-polyethylene composite. Polymer Degrad Stab 2016;133:85-91.

[293] Dhoke SK, Khanna AS, Sinha TJM. Effect of nano-ZnO particles on the corrosion behavior of alkyd-based waterborne coatings. Prog Org Coat 2009;64:371-82.

[294] Salla J, Pandey KK, Srinivas K. Improvement of UV resistance of wood surfaces by using ZnO nanoparticles. Polymer Degrad Stab 2012;97:592-6.

[295] Bauer F, Mehnert R. UV Curable Acrylate Nanocomposites: Properties and Applications. J Polym Res 2005;12:483-91.

[296] Rashvand M, Ranjbar Z. Effect of nano-ZnO particles on the corrosion resistance of polyurethane-based waterborne coatings immersed in sodium chloride solution via EIS technique. Prog Org Coat 2013;76:1413-7.

[297] Vlad Cristea M, Riedl B, Blanchet P. Enhancing the performance of exterior waterborne coatings for wood by inorganic nanosized UV absorbers. Prog Org Coat 2010;69:432-41.

[298] Cristea MV, Riedl B, Blanchet P. Effect of addition of nanosized UV absorbers on the physico-mechanical and thermal properties of an exterior waterborne stain for wood. Prog Org Coat 2011;72:755-62.

[299] Mirabedini SM, Sabzi M, Zohuriaan-Mehr J, Atai M, Behzadnasab M. Weathering performance of the polyurethane nanocomposite coatings containing silane treated TiO_2 nanoparticles. Appl Surf Sci 2011;257:4196-203.

[300] Sabzi M, Mirabedini SM, Zohuriaan-Mehr J, Atai M. Surface modification of TiO_2 nano-particles with silane coupling agent and investigation of its effect on the properties of polyurethane composite coating. Prog Org Coat 2009;65:222-8.

[301] Jalili MM, Moradian S, Dastmalchian H, Karbasi A. Investigating the variations in properties of 2-pack polyurethane clear coat through separate incorporation of hydrophilic and hydrophobic nano-silica. Prog Org Coat 2007;59:81-7.

[302] Hang TTX, Dung NT, Truc TA, Duong NT, Van Truoc B, Vu PG, Hoang T, Thanh DTM, Olivier MG. Effect of silane modified nano ZnO on UV degradation of polyurethane coatings. Prog Org Coat 2015;79:68-74.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[303] Yates Jr JT. Photochemistry on TiO_2: Mechanisms behind the surface chemistry. Surf Sci 2009;603:1605-12.

[304] Yu J, Yu H, Cheng B, Zhou M, Zhao X. Enhanced photocatalytic activity of TiO_2 powder (P25) by hydrothermal treatment. J Mol Catal A Chem 2006;253:112-8.

[305] Kemmitt T, Al-Salim NI, Waterland M, Kennedy VJ, Markwitz A. Photocatalytic titania coatings. Curr Appl Phys 2004;4:189-92.

[306] Sclafani A, Palmisano L, Schiavello M. Influence of the preparation methods of titanium dioxide on the photocatalytic degradation of phenol in aqueous dispersion. J Phys Chem 1990;94:829-32.

[307] Christensen PA, Dilks A, Egerton TA, Temperley J. Infrared spectroscopic evaluation of the photodegradation of paint Part I The UV degradation of acrylic films pigmented with titanium dioxide. J Mater Sci 1999;34:5689-700.

[308] Zhou S, Xu Q, Xiao J, Zhong W, Yu N, Kirk SR, Shu T, Yin D. Consideration of roles of commercial TiO_2 pigments in aromatic polyurethane coating via the photodegradation of dimethyl toluene-2,4-dicarbamate in non-aqueous solution. Res Chem Intermed 2015;41:7785-97.

[309] Li S, Xu S, He L, Xu F, Wang Y, Zhang L. Photocatalytic Degradation of Polyethylene Plastic with Polypyrrole/TiO_2 Nanocomposite as Photocatalyst. Polym Plast Technol Eng 2010;49:400-6.

[310] Meng X, Wang H, Qian Z, Gao X, Yi Q, Zhang S, Yang M. Preparation of photodegradable polypropylene/clay composites based on nanoscaled TiO_2 immobilized organoclay. Polym Compos 2009;30:543-9.

[311] Cantrell A, McGarvey DJ, Truscott TG. Photochemical and photophysical properties of sunscreens. In: Paolo UG, editor. Comprehensive Series in Photosciences. Amsterdam: Elsevier Ltd; 2001. p. 495-519.

[312] Moustaghfir A, Tomasella E, Jacquet M, Rivaton A, Mailhot B, Gardette JL, Bêche E. ZnO/Al_2O_3 coatings for the photoprotection of polycarbonate. Thin Solid Films 2006;515:662-5.

[313] Siddiquey IA, Furusawa T, Sato M, Honda K, Suzuki N. Control of the photocatalytic activity of TiO_2 nanoparticles by silica coating with polydiethoxysiloxane. Dyes Pigm 2008;76:754-9.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[314] Klemchuk PP, Gande ME, Cordola E. Hindered Amine Mechanisms: Part III—Investigations using isotopic labelling. Polymer Degrad Stab 1990;27:65-74.

[315] Valet A. Outdoor applications of UV curable clearcoats - A real alternative to thermally cured clearcoats. Prog Org Coat 1999;35:223-33.

[316] Hodgson JL, Coote ML. Clarifying the Mechanism of the Denisov Cycle: How do Hindered Amine Light Stabilizers Protect Polymer Coatings from Photo-oxidative Degradation?. Macromolecules 2010;43:4573-83.

[317] Gryn’ova G, Ingold KU, Coote ML. New Insights into the Mechanism of Amine/Nitroxide Cycling during the Hindered Amine Light Stabilizer Inhibited Oxidative Degradation of Polymers. J Am Chem Soc 2012;134:12979-88.

[318] Son PN. Some mechanistic considerations of hindered amine uv stabilizers. Polymer Degrad Stab 1980;2:295-308.

[319] Voigt W, Todesco R. New approaches to the melt stabilization of polyolefins. Polymer Degrad Stab 2002;77:397-402.

[320] Yang L, Yee WA, Phua SL, Kong J, Ding H, Cheah JW, Lu X. A high throughput method for preparation of highly conductive functionalized graphene and conductive polymer nanocomposites. RSC Adv 2012;2:2208-10.

[321] Mendikute G, Irusta L, Fernández-Berridi M. Infrared study of the photochemical behaviour of aromatic poly(ether urethanes): effect of various stabilizers. e-Polym 2013;9:1489-98.

[322] Meredith P, Sarna T. The physical and chemical properties of eumelanin. Pigm Cell Res 2006;19:572-94.

[323] Shanmuganathan K, Cho JH, Iyer P, Baranowitz S, Ellison CJ. Thermooxidative Stabilization of Polymers Using Natural and Synthetic Melanins. Macromolecules 2011;44:9499-507.

[324] Ju KY, Lee Y, Lee S, Park SB, Lee JK. Bioinspired Polymerization of Dopamine to Generate Melanin-Like Nanoparticles Having an Excellent Free-Radical-Scavenging Property. Biomacromolecules 2011;12:625-32.

[325] Wang C, Wang D, Dai T, Xu P, Wu P, Zou Y, Yang P, Hu J, Li Y, Cheng Y. Skin Pigmentation-Inspired Polydopamine Sunscreens. Adv Funct Mater 2018;28:1802127/1-9.

[326] Wang Q, Zhang R, Lu M, You G, Wang Y, Chen G, Zhao C, Wang Z, Song X, Wu Y, Zhao L, Zhou H. Bioinspired Polydopamine-Coated Hemoglobin as Potential Oxygen Carrier with Antioxidant Properties. Biomacromolecules 2017;18:1333-41.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[327] Wang Z, Tang F, Fan H, Wang L, Jin Z. Polydopamine Generates Hydroxyl Free Radicals under Ultraviolet-Light Illumination. Langmuir 2017;33:5938-46.

[328] Yang X, Duan L, Ran X. Effect of polydopamine coating on improving photostability of polyphenylene sulfide fiber. Polym Bull 2017;74:641-56.

[329] Bao X, Zhao J, Sun J, Hu M, Yang X. Polydopamine Nanoparticles as Efficient Scavengers for Reactive Oxygen Species in Periodontal Disease. ACS Nano 2018;12:8882-92.

[330] Li S, Li Z, Pang J, Chen J, Wang H, Xie Q, Jiang Y. Polydopamine-Mediated Carrier with Stabilizing and Self-Antioxidative Properties for Polyphenol Delivery Systems. Ind Eng Chem Res 2018;57:590-9.

[331] Sutrisno L, Wang S, Li M, Luo Z, Wang C, Shen T, Chen P, Yang L, Hu Y, Cai K. Construction of three-dimensional net-like polyelectrolyte multilayered nanostructures onto titanium substrates for combined antibacterial and antioxidant applications. J Mater Chem B 2018;6:5290-302.

[332] Göçer H, Akıncıoğlu A, Öztaşkın N, Göksu S, Gülçin İ. Synthesis, Antioxidant, and Antiacetylcholinesterase Activities of Sulfonamide Derivatives of Dopamine-Related Compounds. Arch Pharm 2013;346:783-92.

[333] Gogoi S, Antonio T, Rajagopalan S, Reith M, Andersen J, Dutta AK. Dopamine D_2/D_3 Agonists with Potent Iron Chelation, Antioxidant and Neuroprotective Properties: Potential Implication in Symptomatic and Neuroprotective Treatment of Parkinson's Disease. ChemMedChem 2011;6:991-5.

[334] González-Montelongo R, Gloria Lobo M, González M. Antioxidant activity in banana peel extracts: Testing extraction conditions and related bioactive compounds. Food Chem 2010;119:1030-9.

[335] Wang D, Chen C, Ke X, Kang N, Shen Y, Liu Y, Zhou X, Wang H, Chen C, Ren L. Bioinspired Near-Infrared-Excited Sensing Platform for *In Vitro* Antioxidant Capacity Assay Based on Upconversion Nanoparticles and a Dopamine–Melanin Hybrid System. ACS Appl Mater Interfaces 2015;7:3030-40.

[336] Bobrov MY, Lizhin AA, Andrianova EL, Gretskaya NM, Frumkina LE, Khaspekov LG, Bezuglov VV. Antioxidant and neuroprotective properties of *N*-arachidonoyldopamine. Neurosci Lett 2008;431:6-11.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[337] Sellami M, Châari A, Aissa I, Bouaziz M, Gargouri Y, Miled N. Newly synthesized dopamine ester derivatives and assessment of their antioxidant, antimicrobial and hemolytic activities. Process Biochem 2013;48:1481-7.

[338] Sureshkumar M, Lee PN, Lee CK. Facile preparation of a robust and flexible antioxidant film based on self-polymerized dopamine in a microporous battery separator. RSC Adv 2012;2:5127-9.

[339] Wu Z, Zheng L, Li Y, Su F, Yue X, Tang W, Ma X, Nie J, Li H. Synthesis and structure–activity relationships and effects of phenylpropanoid amides of octopamine and dopamine on tyrosinase inhibition and antioxidation. Food Chem 2012;134:1128-31.

[340] Phua SL, Yang L, Toh CL, Guoqiang D, Lau SK, Dasari A, Lu X. Simultaneous Enhancements of UV Resistance and Mechanical Properties of Polypropylene by Incorporation of Dopamine-Modified Clay. ACS Appl Mater Interfaces 2013;5:1302-9.

[341] Yang L, Phua SL, Toh CL, Zhang L, Ling H, Chang M, Zhou D, Dong Y, Lu X. Polydopamine-coated graphene as multifunctional nanofillers in polyurethane. RSC Adv 2013;3:6377-85.

[342] Krishnamoorthy M, Sasikumar JM, Shamna R, Pandiarajan C, Sofia P, Nagarajan B. Antioxidant activities of bark extract from mangroves, *Bruguiera cylindrica* (L.) Blume and Ceriops decandra Perr. Indian J Pharmacol 2011;43:557-62.

[343] Chirinos Padrón AJ. Mechanistic aspects of polymer photostabilization. J Photochem Photobiol A 1989;49:1-39.

[344] Boehm HP. Funktionelle Gruppen an Festkörper-Oberflächen. Angew Chem 1966;78:617-28.

[345] Boehm HP. Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon 1994;32:759-69.

[346] Donnet JB, Custodero E. Reinforcement of Elastomers by Particulate Fillers. In: Mark JE, Erman B, Roland CM, editors. The Science and Technology of Rubber. 4th ed. Boston: Academic Press; 2013. p. 383-416.

[347] Schwetlick K, König T. Antioxidant action of phosphite, sulfite and borate esters—A comparison. Polymer Degrad Stab 1989;24:279-87.

[348] Schwetlick K. Mechanisms of Antioxidant Action of Phosphite and Phosphonite Esters. In: Scott G, editor. Mechanisms of Polymer Degradation and Stabilization. Dordrecht: Springer Netherlands; 1990. p. 23-60.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[349] Bauer I, Körner S, Pawelke B, Al-Malaika S, Habicher WD. Hydroperoxide decomposing ability and hydrolytic stability of organic phosphites containing hindered amine moieties (HALS-Phosphites). Polymer Degrad Stab 1998;62:175-86.

[350] Kovács E, Wolkober Z. The effect of the chemical and physical properties of carbon black on the thermal and photooxidation of polyethylene. J Polym Sci Polym Symp 1976;57:171-80.

[351] Gugumus F. Mechanisms and kinetics of photostabilization of polyolefins with *N*-methylated HALS. Polymer Degrad Stab 1991;34:205-41.

[352] Briggs PJ, McKellar JF. Mechanism of photostabilization of polypropylene by nickel oxime chelates. J Appl Polym Sci 1968;12:1825-33.

[353] Chien JCW, Conner WP. Quenching of excited states of diethyl ketone by paramagnetic metal chelates. J Am Chem Soc 1968;90:1001-6.

[354] Harper DJ, McKellar JF, Turner PH. Photostabilizing effect of Ni(II) chelates in polymers. II. Effect of diamagnetic chelates on polypropylene phosphorescence. J Appl Polym Sci 1974;18:2805-7.

[355] Carlsson DJ, Wiles DM. Photostabilization of Polypropylene. III. Stabilizers and Macro Ketones. Macromolecules 1974;7:259-62.

[356] Ranaweera RPR, Scott G. Mechanisms of antioxidant action: Metal complexes as u.v. stabilizers in polyethylene. Eur Polym J 1976;12:591-7.

[357] Carlsson DJ, Wiles DM. Photostabilization of polypropylene. II. Stabilizers and hydroperoxides. J Polym Sci Polym Chem Ed 1974;12:2217-33.

[358] Stumpe J, Schwetlick K. Deactivation of excited states in polyurethanes by energy transfer to salicylic acid derivatives and its application to the photo-stabilization of polyurethanes. Polymer Degrad Stab 1987;17:103-15.

[359] Heskins M, Guillet JE. Mechanism of Ultraviolet Stabilization of Polymers. Macromolecules 1968;1:97-8.

[360] Schonhorn H, Luongo JP. Effect of Fillers on the Photooxidative Stabilization of Polyethylene. Macromolecules 1969;2:364-6.

[361] Peña JM, Allen NS, Edge M, Liauw CM, Valange B. Studies of synergism between carbon black and stabilizers in LDPE photodegradation. Polymer Degrad Stab 2001;72:259-70.

[362] Pospíšil J, Pilař J, Nešpůrek S. Exploitation of the complex chemistry of hindered amine stabilizers in effective plastics stabilization. J Vinyl Add Tech 2007;13:119-32.

ACCEPTED MANUSCRIPT

[363] Takenaka H, Mizokawa S, Ohkatsu Y. Interaction of Hindered Amine Light Stabilizers and Ultraviolet Absorbers. J Jpn Pet Inst 2007;50:8-15.

[364] Prissok F, Scholz G. Stabilized polyurethanes. US 5900439 A, Basf Aktiengesellschaft; 1999.

[365] Wypych G. 5 - Stability of UV stabilizers. In: Wypych G, editor. Handbook of UV Degradation and Stabilization. 2nd ed. Toronto: ChemTec Publishing; 2015. p. 141-65.

[366] Pickett JE, Moore JE. Photodegradation of UV screeners. Polymer Degrad Stab 1993;42:231-44.

[367] Wypych G. 6 - Principles of stabilizer selection. In: Wypych G, editor. Handbook of UV Degradation and Stabilization. 2nd ed. Toronto: ChemTec Publishing; 2015. p. 167-76.

[368] Price DM, Hawkins M. Vapour pressures of hydroxybenzophenone UV absorbers. Thermochim Acta 1999;329:73-6.

[369] Shieh YT, Chen HT, Liu KH, Twu YK. Thermal degradation of MDI-based segmented polyurethanes. J Polym Sci, Part A Polym Chem 1999;37:4126-34.

[370] Scott G. Initiation processes in polymer degradation. Polymer Degrad Stab 1995;48:315-24.

[371] Gardette M, Perthue A, Gardette JL, Janecska T, Fóldes E, Pukánszky B, Therias S. Photo- and thermal-oxidation of polyethylene: Comparison of mechanisms and influence of unsaturation content. Polymer Degrad Stab 2013;98:2383-90.

[372] Hukins DWL, Mahomed A, Kukureka SN. Accelerated aging for testing polymeric biomaterials and medical devices. Med Eng Phys 2008;30:1270-4.

[373] Cao Z, Zhou Q, Jie S, Li BG. High *cis*-1,4 Hydroxyl-Terminated Polybutadiene-Based Polyurethanes with Extremely Low Glass Transition Temperature and Excellent Mechanical Properties. Ind Eng Chem Res 2016;55:1582-9.

[374] Sarkar S, Adhikari B. Thermal stability of lignin–hydroxy-terminated polybutadiene copolyurethanes. Polymer Degrad Stab 2001;73:169-75.

[375] Chen H, Lu H, Zhou Y, Zheng M, Ke C, Zeng D. Study on thermal properties of polyurethane nanocomposites based on organo-sepiolite. Polymer Degrad Stab 2012;97:242-7.

[376] Cai D, Jin J, Yusoh K, Rafiq R, Song M. High performance polyurethane/functionalized graphene nanocomposites with improved mechanical and thermal properties. Compos Sci Technol 2012;72:702-7.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[377] Wang Y, Ruan C, Sun J, Zhang M, Wu Y, Peng K. Degradation studies on segmented polyurethanes prepared with poly(D, L-lactic acid) diol, hexamethylene diisocyanate and different chain extenders. Polymer Degrad Stab 2011;96:1687-94.

[378] Trovati G, Sanches EA, Neto SC, Mascarenhas YP, Chierice GO. Characterization of polyurethane resins by FTIR, TGA, and XRD. J Appl Polym Sci 2010;115:263-8.

[379] Gite VV, Mahulikar PP, Hundiwale DG. Preparation and properties of polyurethane coatings based on acrylic polyols and trimer of isophorone diisocyanate. Prog Org Coat 2010;68:307-12.

[380] Król P, Pilch-Pitera B. Phase structure and thermal stability of crosslinked polyurethane elastomers based on well-defined prepolymers. J Appl Polym Sci 2007;104:1464-74.

[381] Cao Q, Liu P. Hyperbranched polyurethane as novel solid–solid phase change material for thermal energy storage. Eur Polym J 2006;42:2931-9.

[382] Ciobanu C, Ungureanu M, Ignat L, Ungureanu D, Popa VI. Properties of lignin–polyurethane films prepared by casting method. Ind Crops Prod 2004;20:231-41.

[383] Tien YI, Wei KH. The effect of nano-sized silicate layers from montmorillonite on glass transition, dynamic mechanical, and thermal degradation properties of segmented polyurethane. J Appl Polym Sci 2002;86:1741-8.

[384] Wang TL, Hsieh TH. Effect of polyol structure and molecular weight on the thermal stability of segmented poly(urethaneureas). Polymer Degrad Stab 1997;55:95-102.

[385] Petrović ZS, Zavargo Z, Flyn JH, Macknight WJ. Thermal degradation of segmented polyurethanes. J Appl Polym Sci 1994;51:1087-95.

[386] Senich GA, MacKnight WJ. Fourier Transform Infrared Thermal Analysis of a Segmented Polyurethane. Macromolecules 1980;13:106-10.

[387] Slade PE, Jenkins LT. Thermal analysis of polyurethane elastomers. J Polym Sci Part C Polym Symp 1964;6:27-32.

[388] Ferguson J, Petrovic Z. Thermal stability of segmented polyurethanes. Eur Polym J 1976;12:177-81.

[389] Malik M, Kaur R. Influence of aliphatic and aromatic isocyanates on the properties of poly(ether ester) polyol based PU adhesive system. Polym Eng Sci 2018;58:112-7.

[390] Chang WL. Decomposition behavior of polyurethanes via mathematical simulation. J Appl Polym Sci 1994;53:1759-69.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[391] Smith CP, Raes MC, Reisch JW, Chandalia KB, O'Connor JM. Thermoplastic polyurethane elastomers and polyurea elastomers made using low unsaturation level polyols prepared with double metal cyanide catalysts. US 5185420 A, Olin Corp; 1993.

[392] Nagle DJ, Celina M, Rintoul L, Fredericks PM. Infrared microspectroscopic study of the thermo-oxidative degradation of hydroxy-terminated polybutadiene/isophorone diisocyanate polyurethane rubber. Polymer Degrad Stab 2007;92:1446-54.

[393] Harris DJ, Assink RA, Celina M. NMR Analysis of Oxidatively Aged HTPB/IPDI Polyurethane Rubber: Degradation Products, Dynamics, and Heterogeneity. Macromolecules 2001;34:6695-700.

[394] Villar LD, Cicaglioni T, Diniz MF, Takahashi MFK, Rezende LC. Thermal aging of HTPB/IPDI-based polyurethane as a function of NCO/OH ratio. Mater Res 2011;14:372-5.

[395] Boubakri A, Haddar N, Elleuch K, Bienvenu Y. Influence of thermal aging on tensile and creep behavior of thermoplastic polyurethane. CR Acad Sci II 2011;339:666-73.

[396] Akbaş A, Aksoy S, Hasırcı N. Effects of thermal ageing on the properties and lifetime prediction of hydroxyl-terminated polybutadiene. Polymer 1994;35:2568-72.

[397] Assink RA, Lang DP, Celina M. Condition monitoring of a thermally aged hydroxy-terminated polybutadiene (HTPB)/isophorone diisocyanate (IPDI) elastomer by nuclear magnetic resonance cross-polarization recovery times. J Appl Polym Sci 2001;81:453-9.

[398] Trong-Ming D, Chiu WY, Hsieh KH. The thermal aging of filled polyurethane. J Appl Polym Sci 1991;43:2193-9.

[399] de la Fuente JL, Rodríguez O. Dynamic mechanical study on the thermal aging of a hydroxyl-terminated polybutadiene-based energetic composite. J Appl Polym Sci 2003;87:2397-405.

[400] Furukawa M. Hydrolytic and thermal stability of novel polyurethane elastomers. Angew Makromol Chem 1997;252:33-43.

[401] Flandrin FR, Widmaier JM, Flat JJ. Thermal ageing of polyurethane with hydrogenated polyisoprene soft segments. Polymer Degrad Stab 1997;57:59-67.

[402] Rische T, Meixner J, Pohl T, Feller T, Klippert U. Polyurethane-polyurea dispersions stable to thermal yellowing. US 5166300 A, Bayer Materialscience Ag; 2005.

[403] Calabrese RA, Boccuzzi RA. Stabilized polyether polyol and polyurethane foam obtained therefrom. USA 6348514 B1, Uniroyal Chemical Company Inc; 2002.

ACCEPTED MANUSCRIPT

[404] Drake WO, Pauquet JR, Zingg J, Zweifel H. Stabilization of polypropylene during melt processing - Influence on long-term thermal stability. Polym Prepr Am Chem Soc Div Polym Chem 1993;34:174-5.

[405] Hähner U, Habicher WD, Chmela S. Synthesis and antioxidative efficiency of organic phosphites and phosphonites with 2.2.6.6-tetramethylpiperidin-4-yl groups. Polymer Degrad Stab 1993;41:197-203.

[406] Chattopadhyay DK, Webster DC. Thermal stability and flame retardancy of polyurethanes. Prog Polym Sci 2009;34:1068-133.

[407] Liu X, Hao J, Gaan S.. Recent studies on the decomposition and strategies of smoke and toxicity suppression for polyurethane based materials. RSC Adv 2016;6:74742-56.

[408] Hawkins WL. Stabilization against degradation by ozone. In: Hawkins WL, editor. Polymer Degradation and Stabilization. Berlin, Heidelberg: Springer; 1984. p. 91-7.

[409] Lattimer RP, Layer RW, Rhee CK. Ozone degradation and antiozonants. In: Scott G, editor. Atmospheric Oxidation and Antioxidants, Volume II. Amsterdam: Elsevier Ltd; 1993. p. 363-84.

[410] Cataldo F. On the ozone protection of polymers having non-conjugated unsaturation. Polymer Degrad Stab 2001;72:287-96.

[411] Anonymous. Air Quality Criteria for Ozone and Related Photochemical Oxidants. Washington DC: US Environmental Protection Agency; 2006. 821 pp.

[412] Cataldo F. The action of ozone on polymers having unconjugated and cross- or linearly conjugated unsaturation: chemistry and technological aspects. Polymer Degrad Stab 2001;73:511-20.

[413] Coran AY. Chemistry of the vulcanization and protection of elastomers: A review of the achievements. J Appl Polym Sci 2003;87:24-30.

[414] Layer RW, Lattimer RP. Protection of Rubber against Ozone. Rubber Chem Technol 1990;63:426-50.

[415] Lewis PM. Effect of ozone on rubbers: Countermeasures and unsolved problems. Polymer Degrad Stab 1986;15:33-66.

[416] Qi CZ, Wang TM, Zhang XM. Protection Mechanisms of *p*-Phenylenediamine-Type Antiozonants. Rubber Chem Technol 1998;71:722-9.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[417] Anachkov MP, Rakovsky SK, Shopov DM, Razumovskii SD, Kefely AA, Zaikov GE. Study of the kinetics and mechanism of the increase in the molecular mass of EPDM-rubber during ozonolysis in solution. Polymer Degrad Stab 1986;14:189-98.

[418] Anachkov MP, Rakovsky SK, Stefanova RV, Shopov DM. Kinetics and mechanism of the ozone degradation of nitrile rubbers in solution. Polymer Degrad Stab 1987;19:293-305.

[419] Tucker H. The Reaction of Ozone with Rubber. Rubber Chem Technol 1959;32:269-77.

[420] Ho KW. Ozonation of hydrocarbon diene elastomers: A mechanistic study. J Polym Sci Part A Polym Chem 1986;24:2467-82.

[421] Stephens KE, Beatty CL. Effects of Ozone Exposure on the Physical Properties of Butadiene and Styrene/Butadiene Copolymers. ACS Symp Ser 1983;229:261-76.

[422] Ivan G, Giurginca M. Ozone destruction of some *trans*-polydienes. Polymer Degrad Stab 1998;62:441-6.

[423] Saunders KJ. Polyurethanes. In: Saunders KJ, editor. Organic Polymer Chemistry: An Introduction to the Organic Chemistry of Adhesives, Fibres, Paints, Plastics and Rubbers. Dordrecht: Springer Netherlands; 1988. p. 358-87.

[424] Schollenberger CS, Dinbergs K. A study of the weathering of an elastomeric polyurethane. Polym Eng Sci 1961;1:31-9.

[425] Holden G. Block copolymer blends with certain polyurethanes or ethylene-unsaturated ester copolymers. US 3562355 A, Shell Oil Co; 1971.

[426] Hiles MAF. Energy absorbing materials. US 4101704 A, National Research Development Corp UK; 1978.

[427] Hiles MAF. Energy absorbing polyurethane compositions. US 4476258 A, National Research Development Corp UK; 1984.

[428] Cottin A, Peyron G. Method for protecting a tire against ozone. US 20060127582 A1, Michelin Recherche Et Technique SA; 2006.

[429] Cottin A, Peyron G. Method for protecting a tire against ozone. US 20030127170 A1, Alain Cottin, Georges Peyron; 2003.

[430] Barth HJ. Process and articles involving codeposition of latex and polyurethane. US 3382138 A, Internat Latex & Chemical Corp; 1968.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[431] Domansky K, Leslie DC, McKinney J, Fraser JP, Sliz JD, Hamkins-Indik T, Hamilton GA, Bahinski A, Ingber DE. Clear castable polyurethane elastomer for fabrication of microfluidic devices. Lab Chip 2013;13:3956-64.

[432] De Nardo L, Moscatelli M, Silvi F, Tanzi MC, Yahia LH, FarèS. Chemico-physical modifications induced by plasma and ozone sterilizations on shape memory polyurethane foams. J Mater Sci Mater Med 2010;21:2067-78.

[433] Galante R, Ghisleni D, Paradiso P, Alves VD, Pinto TJA, Colaço R, Serro AP. Sterilization of silicone-based hydrogels for biomedical application using ozone gas: Comparison with conventional techniques. Mater Sci Eng C 2017;78:389-97.

[434] Rediguieri CF, De Bank PA, Zanin MHA, Leo P, Cerize NNP, de Oliveira AM, Pinto TdJA. The effect of ozone gas sterilization on the properties and cell compatibility of electrospun polycaprolactone scaffolds. J Biomater Sci Polym Ed 2017;28:1918-34.

[435] de Souza Botelho-Almeida T, Lourenço FR, Kikuchi IS, Awasthi R, Dua K, Pinto TdJA. Evaluating the Potential, Applicability, and Effectiveness of Ozone Sterilization Process for Medical Devices. J Pharm Innovation 2018;13:87-94.

[436] Galante R, Oliveira AS, Topete A, Ghisleni D, Braga M, Pinto TJA, Colaço R, Serro AP. Drug-eluting silicone hydrogel for therapeutic contact lenses: Impact of sterilization methods on the system performance. Colloids Surf B 2018;161:537-46.

[437] Tipnis NP, Burgess DJ. Sterilization of implantable polymer-based medical devices: A review. Int J Pharm 2018;544:455-60.

[438] Maity M, Das CK. Speciality polymer blends of polyurethane elastomers and chlorinated polyethylene rubber (peroxide cure). Polym Int 2000;49:757-62.

[439] Lake GJ, Mente PG. Ozone cracking and protection of elastomers at high and low temperatures. J Nat Rubber Res 1992;7:1-13.

[440] Torregrosa-Coque R, Álvarez- García S, Martín- Martínez JM. Migration of low molecular weight moiety at rubber–polyurethane interface: An ATR-IR spectroscopy study. Int J Adhes Adhes 2011;31:389-97.

[441] Lattimer RP, Rhee CK, Layer RW. Antiozonants. Kirk-Othmer Encyclopedia of Chemical Technology. New York: John Wiley & Sons Inc; 2000. 8 pp.

[442] Mise N, Nishino K, Yamada M. Polyurethanes stabilized with *p*-phenylenediamines. US 3637573 A, Takeda Chemical Industries Ltd; 1972.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[443] Popoff IC, Albert HE. Novel antioxidants and antiozonants. US 3035014 A, Pennsalt Chemicals Corp; 1962.

[444] Popoff IC. Antioxidants and antiozonants. US 3138571 A, Pennsalt Chemicals Corp; 1964.

[445] Clemitson IR. Properties. In: Clemitson IR, editor. Castable Polyurethane Elastomers. 2nd ed. Boca Raton: CRC Press; 2015. p. 161-92.

[446] Schollenberger CS, Stewart FD. Thermoplastic polyurethane hydrolysis stability. Angew Makromol Chem 1973;29:413-30.

[447] Macocinschi D, Filip D, Zaltariov MF, Varganici CD. Thermal and hydrolytic stability of silver nanoparticle polyurethane biocomposites for medical applications. Polymer Degrad Stab 2015;121:238-46.

[448] Brown DW, Lowry RE, Smith LE. Kinetics of Hydrolytic Aging of Polyester Urethane Elastomers. Macromolecules 1980;13:248-52.

[449] Schollenberger CS, Stewart FD. Thermoplastic Polyurethane Hydrolysis Stability. J Elastoplast 1971;3:28-56.

[450] Stevenson JS, Kusy RP. Structural degradation of polyurethane-based elastomeric modules. J Mater Sci Mater Med 1995;6:377-84.

[451] Pretsch T, Jakob I, Müller W. Hydrolytic degradation and functional stability of a segmented shape memory poly(ester urethane). Polymer Degrad Stab 2009;94:61-73.

[452] Kylmä J, Seppälä JV. Synthesis and Characterization of a Biodegradable Thermoplastic Poly(ester−urethane) Elastomer. Macromolecules 1997;30:2876-82.

[453] Ward RS, Jones RL. 1.26 Polyurethanes and Silicone Polyurethane Copolymers. In: Ducheyne P, editor. Comprehensive Biomaterials II. 2nd ed. Oxford: Elsevier Ltd; 2017. p. 570-619.

[454] Han J, Chen B, Ye L, Zhang AY, Zhang J, Feng ZG. Synthesis and characterization of biodegradable polyurethane based on poly(ε-caprolactone) and L-lysine ethyl ester diisocyanate. Front Mater Sci Chin 2009;3:25-32.

[455] Gunatillake PA, Meijs GF, Rizzardo E, Chatelier RC, McCarthy SJ, Brandwood A, Schindhelm K. Polyurethane elastomers based on novel polyether macrodiols and MDI: Synthesis, mechanical properties, and resistance to hydrolysis and oxidation. J Appl Polym Sci 1992;46:319-28.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[456] Kim YD, Kim SC. Effect of chemical structure on the biodegradation of polyurethanes under composting conditions. Polymer Degrad Stab 1998;62:343-52.

[457] Liu X, Xia Y, Liu L, Zhang D, Hou Z. Synthesis of a novel biomedical poly(ester urethane) based on aliphatic uniform-size diisocyanate and the blood compatibility of PEG-grafted surfaces. J Biomater Appl 2018;32:1329-42.

[458] Davies P, Evrard G. Accelerated ageing of polyurethanes for marine applications. Polymer Degrad Stab 2007;92:1455-64.

[459] Chaffin KA, Chen X, McNamara L, Bates FS, Hillmyer MA. Polyether Urethane Hydrolytic Stability after Exposure to Deoxygenated Water. Macromolecules 2014;47:5220-6.

[460] Loh XJ, Goh SH, Li J. Hydrolytic degradation and protein release studies of thermogelling polyurethane copolymers consisting of poly[(*R*)-3-hydroxybutyrate], poly(ethylene glycol), and poly(propylene glycol). Biomaterials 2007;28:4113-23.

[461] Simmons A, Hyvarinen J, Poole-Warren L. The effect of sterilisation on a poly(dimethylsiloxane)/poly(hexamethylene oxide) mixed macrodiol-based polyurethane elastomer. Biomaterials 2006;27:4484-97.

[462] Le Gac PY, Choqueuse D, Melot D. Description and modeling of polyurethane hydrolysis used as thermal insulation in oil offshore conditions. Polym Test 2013;32:1588-93.

[463] Yeganeh H, Jamshidi H, Jamshidi S. Synthesis and properties of novel biodegradable poly(ε-caprolactone)/ poly(ethylene glycol)-based polyurethane elastomers. Polym Int 2007;56:41-9.

[464] Yeganeh H, Lakouraj MM, Jamshidi S. Synthesis and properties of biodegradable elastomeric epoxy modified polyurethanes based on poly(ε-caprolactone) and poly(ethylene glycol). Eur Polym J 2005;41:2370-9.

[465] Gorna K, Gogolewski S. Biodegradable polyurethanes for implants. II. *In vitro* degradation and calcification of materials from poly(ϵ-caprolactone)–poly(ethylene oxide) diols and various chain extenders. J Biomed Mater Res 2002;60:592-606.

[466] Gorna K, Gogolewski S. *In vitro* degradation of novel medical biodegradable aliphatic polyurethanes based on ϵ-caprolactone and Pluronics® with various hydrophilicities. Polymer Degrad Stab 2002;75:113-22.

[467] Skarja GA, Woodhouse KA. Synthesis and characterization of degradable polyurethane elastomers containing an amino acid-based chain extender. J Biomater Sci Polym Ed 1998;9:271-95.

ACCEPTED MANUSCRIPT

[468] Guan J, Fujimoto KL, Sacks MS, Wagner WR. Preparation and characterization of highly porous, biodegradable polyurethane scaffolds for soft tissue applications. Biomaterials 2005;26:3961-71.

[469] Sonnenschein MF, Cox JM, van der Wal HR, Wendt BL. Thermoplastic Polyurethane Containing Structural Units of Polyester and Polyether Diols. US 20090149622 A1, Dow Global Technologies Inc; 2009.

[470] Fromstein JD, Woodhouse KA. Elastomeric biodegradable polyurethane blends for soft tissue applications. J Biomater Sci Polym Ed 2002;13:391-406.

[471] Gorna K, Gogolewski S. Preparation, degradation, and calcification of biodegradable polyurethane foams for bone graft substitutes. J Biomed Mater Res Part A 2003;67:813-27.

[472] Guan J, Sacks MS, Beckman EJ, Wagner WR. Biodegradable poly(ether ester urethane)urea elastomers based on poly(ether ester) triblock copolymers and putrescine: synthesis, characterization and cytocompatibility. Biomaterials 2004;25:85-96.

[473] Yin S, Xia Y, Jia Q, Hou ZS, Zhang N. Preparation and properties of biomedical segmented polyurethanes based on poly(ether ester) and uniform-size diurethane diisocyanates. J Biomater Sci Polym Ed 2017;28:119-38.

[474] Zhou L, Liang D, He X, Li J, Tan H, Li J, Fu Q, Gu Q. The degradation and biocompatibility of pH-sensitive biodegradable polyurethanes for intracellular multifunctional antitumor drug delivery. Biomaterials 2012;33:2734-45.

[475] Yeganeh H, Hojati-Talemi P. Preparation and properties of novel biodegradable polyurethane networks based on castor oil and poly(ethylene glycol). Polymer Degrad Stab 2007;92:480-9.

[476] Ibarra JC, Uscátegui YL, Arévalo FR, Díaz LE, Valero MF. Influence of Diisocyanate Chemical Structure on the Properties, Degradation and Cytotoxicity of Polyurethanes Obtained from Castor Oil. J Biomater Tissue Eng 2018;8:279-89.

[477] Jia Q, Xia Y, Yin S, Hou Z, Wu R. Influence of well-defined hard segment length on the properties of medical segmented polyesterurethanes based on poly(ε-caprolactone-*co*-L-lactide) and aliphatic urethane diisocyanates. Int J Polym Mater Polym Biomater 2017;66:388-97.

[478] Guan J, Sacks MS, Beckman EJ, Wagner WR. Synthesis, characterization, and cytocompatibility of elastomeric, biodegradable poly(ester-urethane)ureas based on poly(caprolactone) and putrescine. J Biomed Mater Res 2002;61:493-503.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[479] Moore TG, Adhikari R, Gunatillake PA. Biodegradable polyurethane and polyurethane ureas. US 9540478B2, Polynovo Biomaterials Pty Ltd; 2017.

[480] Gunatillake PA, Moore TG, Adhikari R. Chain extenders. US 9695268B2, Polynovo Biomaterials Pty Ltd; 2017.

[481] Tatai L, Moore TG, Adhikari R, Malherbe F, Jayasekara R, Griffiths I, Gunatillake PA. Thermoplastic biodegradable polyurethanes: The effect of chain extender structure on properties and in-vitro degradation. Biomaterials 2007;28:5407-17.

[482] Zia KM, Barikani M, Bhatti IA, Zuber M, Bhatti HN. Synthesis and characterization of novel, biodegradable, thermally stable chitin-based polyurethane elastomers. J Appl Polym Sci 2008;110:769-76.

[483] Slater C, Davis C, Strangwood M. Compression set of thermoplastic polyurethane under different thermal–mechanical-moisture conditions. Polymer Degrad Stab 2011;96:2139-44.

[484] Boubakri A, Haddar N, Elleuch K, Bienvenu Y. Impact of aging conditions on mechanical properties of thermoplastic polyurethane. Mater Des 2010;31:4194-201.

[485] Mondal S, Martin D. Hydrolytic degradation of segmented polyurethane copolymers for biomedical applications. Polymer Degrad Stab 2012;97:1553-61.

[486] Boubakri A, Elleuch K, Guermazi N, Ayedi HF. Investigations on hygrothermal aging of thermoplastic polyurethane material. Mater Des 2009;30:3958-65.

[487] Chapman TM, Rakiewicz-Nemeth DM, Swestock J, Benrashid R. Polyurethane elastomers with hydrolytic and thermooxidative stability. I. Polyurethanes with *N*-alkylated polyamide soft blocks. J Polym Sci Part A Polym Chem 1990;28:1473-82.

[488] Khan I, Smith N, Jones E, Finch DS, Cameron RE. Analysis and evaluation of a biomedical polycarbonate urethane tested in an *in vitro* study and an ovine arthroplasty model. Part I: materials selection and evaluation. Biomaterials 2005;26:621-31.

[489] Pilichowski JF, Liptaj T, Morel M, Terriac E, Baba M. Cross-linking of polybutadiene: correlation between solid-state ^{1}H NMR spectroscopy, thermoporosimetry, densimetry and crystallinity measurements. Polym Int 2003;52:1913-8.

[490] Jayabalan M, Lizymol PP, Thomas V. Synthesis of hydrolytically stable low elastic modulus polyurethane-urea for biomedical applications. Polym Int 2000;49:88-92.

[491] Furukawa M, Shiiba T, Murata S. Mechanical properties and hydrolytic stability of polyesterurethane elastomers with alkyl side groups. Polymer 1999;40:1791-8.

ACCEPTED MANUSCRIPT

[492] Kim BS, Kim BK. Enhancement of hydrolytic stability and adhesion of waterborne polyurethanes. J Appl Polym Sci 2005;97:1961-9.

[493] Park SH, Lee SK, Choi HY, Lee EM, Kim EY, Lim CH, Lee DW, Kim BK. Mechanical and surface properties and hydrolytic stability of cycloaliphatic polyester-based waterborne polyurethanes modified with fluoro oligomer. J Appl Polym Sci 2009;111:1828-34.

[494] Wolfram N, Hans H, Julius P, Peter F. Stabilization of polyesters with polycarbodiimide. US 3193522 A, Bayer Ag; 1965.

[495] Loew F. Elastomeric thermoplastic polyester polyurethane compositions stabilized against hydrolysis. US 3716502 A, Inmont Corp; 1973.

[496] Yang LH, Liu FC, Han EH. Effects of P/B on the properties of anticorrosive coatings with different particle size. Prog Org Coat 2005;53:91-8.

[497] Motokucho S, Nakayama Y, Morikawa H, Nakatani H. Environment-friendly chemical recycling of aliphatic polyurethanes by hydrolysis in a CO_2-water system. J Appl Polym Sci 2018;135:45897/1-7.

[498] Motokucho S, Yamaguchi A, Nakayama Y, Morikawa H, Nakatani H. Hydrolysis of aromatic polyurethane in water under high pressure of CO_2. J Polym Sci Part A Polym Chem 2017;55:2004-10.

[499] Meijs GF, McCarthy SJ, Rizzardo E, Chen YC, Chatelier RC, Brandwood A, Schindhelm K. Degradation of medical-grade polyurethane elastomers: The effect of hydrogen peroxide *in vitro*. J Biomed Mater Res 1993;27:345-56.

[500] Tanzi MC, Mantovani D, Petrini P, Guidoin R, Laroche G. Chemical stability of polyether urethanes versus polycarbonate urethanes. J Biomed Mater Res 1997;36:550-9.

[501] Chan-Chan LH, Solis-Correa R, Vargas-Coronado RF, Cervantes-Uc JM, Cauich-Rodriguez JV, Quintana P, Bartolo-Pérez P. Degradation studies on segmented polyurethanes prepared with HMDI, PCL and different chain extenders. Acta Biomater 2010;6:2035-44.

[502] Faré S, Petrini P, Motta A, Cigada A, Tanzi MC. Synergistic effects of oxidative environments and mechanical stress on *in vitro* stability of polyetherurethanes and polycarbonateurethanes. J Biomed Mater Res 1999;45:62-74.

[503] Tanzi MC, Faré S, Petrini P. *In vitro* stability of polyether and polycarbonate urethanes. J Biomater Appl 2000;14:325-48.

ACCEPTED MANUSCRIPT

[504] Kannan RY, Salacinski HJ, Odlyha M, Butler PE, Seifalian AM. The degradative resistance of polyhedral oligomeric silsesquioxane nanocore integrated polyurethanes: An *in vitro* study. Biomaterials 2006;27:1971-9.

[505] Takahara A, Hergenrother RW, Coury AJ, Cooper SL. Effect of polyol chemistry on the *in vitro* biostability of segmented polyurethanes. In: Akutsu T, Koyanagi H, Anderson JM, Cohn LH, Frommer PL, Hachida M, Kataoka K, Nitta SI, Nojiri C, Olsen DB, Pennington DG, Takatani S, Yozu R, editors. Artificial Heart 3: Proceedings of the 3rd International Symposium on Artificial Heart and Assist Devices. Tokyo: Springer Japan; 1991. p. 77-83.

[506] Takahara A, Coury AJ, Hergenrother RW, Cooper SL. Effect of soft segment chemistry on the biostability of segmented polyurethanes. I. *In vitro* oxidation. J Biomed Mater Res 1991;25:341-56.

[507] Tetsufumi T, Hitoshi S, Hiroshi U, Shiro K. Lipase-catalyzed hydrolytic degradation of polyurethane in organic solvent. Chem Lett 2001;30:492-3.

[508] Troev K. Study of the reactions of dimethyl hydrogen phosphonate with urethane and acetanilide. Heteroat Chem 2000;11:205-8.

[509] Troev K, Atanasov VI, Tsevi R, Grancharov G, Tsekova A. Chemical degradation of polyurethanes. Degradation of microporous polyurethane elastomer by dimethyl phosphonate. Polymer Degrad Stab 2000;67:159-65.

[510] Troev K, Tsekova A, Tsevi R. Chemical degradation of polyurethanes: Degradation of flexible polyester polyurethane foam by phosphonic acid dialkyl esters. J Appl Polym Sci 2000;78:2565-73.

[511] Troev K, Tsekova A, Tsevi R. Chemical degradation of polyurethanes 2. Degradation of flexible polyether foam by dimethyl phosphonate. Polymer Degrad Stab 2000;67:397-405.

[512] Troev K, Grancharov G, Tsevi R. Chemical degradation of polyurethanes 3. Degradation of microporous polyurethane elastomer by diethyl phosphonate and tris(1-methyl-2-chloroethyl) phosphate. Polymer Degrad Stab 2000;70:43-8.

[513] Troev K, Grancharov G, Tsevi R, Tsekova A. A novel approach to recycling of polyurethanes: chemical degradation of flexible polyurethane foams by triethyl phosphate. Polymer 2000;41:7017-22.

[514] Troev K, Atanassov V, Tzevi R. Chemical degradation of polyurethanes. II. Degradation of microporous polyurethane elastomer by phosphoric acid esters. J Appl Polym Sci 2000;76:886-93.

ACCEPTED MANUSCRIPT

[515] Seneker SD, Born L, Schmelzer HG, Eisenbach CD, Fischer K. Diisocyanato dicyclohexylmethane: Structure/property relationships of its geometrical isomers in polyurethane elastomers. Colloid Polym Sci 1992;270:543-8.

[516] Fittipaldi M, Grace LR. Lipid-induced degradation in biocompatible poly(Styrene-Isobutylene-Styrene) (SIBS) thermoplastic elastomer. J Mech Behav Biomed Mater 2017;68:80-7.

[517] Fittipaldi M, Grace LR. Modeling the effects of lipid contamination in poly(styrene-isobutylene-styrene) (SIBS). J Mech Behav Biomed Mater 2018;80:97-103.

[518] Takahara A, Hergenrother RW, Coury AJ, Cooper SL. Effect of soft segment chemistry on the biostability of segmented polyurethanes. II. *In vitro* hydrolytic degradation and lipod sorption. J Biomed Mater Res 1992;26:801-18.

[519] Gostev AA, Karpenko AA, Laktionov PPJPB.$$$. Polyurethanes in cardiovascular prosthetics. Polym Bull 2018;75:4311-25.

[520] Wang S, Gu Z, Wang Z, Chen X, Cao L, Cai L, Li Q, Wei J, Shin JW, Su J. Influences of mesoporous magnesium calcium silicate on mineralization, degradability, cell responses, curcumin release from macro-mesoporous scaffolds of gliadin based biocomposites. Sci Rep 2018;8:174/1-12.

[521] Onuki Y, Bhardwaj U, Papadimitrakopoulos F, Burgess DJ. A Review of the Biocompatibility of Implantable Devices: Current Challenges to Overcome Foreign Body Response. J Diabetes Sci Technol 2008;2:1003-15.

[522] Boloori_Zadeh P, Corbett SC, NayebHashemi H. Effects of fluid flow shear rate and surface roughness on the calcification of polymeric heart valve leaflet. Mater Sci Eng C 2013;33:2770-5.

[523] Schoen FJ, Levy RJ. Chapter II.4.5 - Pathological Calcification of Biomaterials. In: Ratner BD, Hoffman AS, Schoen FJ, Lemons JE, editors. Biomaterials Science. 3rd ed. Amsterdam: Academic Press; 2013. p. 739-54.

[524] Munnelly A, Schoen F, Vyavahare N. Biomaterial Calcification: Mechanisms and Prevention. In: Eliaz N, editor. Degradation of Implant Materials. New York: Springer New York; 2012. p. 359-92.

[525] Schoen FJ, Harasaki H, Kim KM, Anderson HC, Levy RJ. Biomaterial-associated calcification: pathology, mechanisms, and strategies for prevention. J Biomed Mater Res 1988;22:11-36.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[526] Boloori Zadeh P, Corbett SC, NayebHashemi H. In-vitro calcification study of polyurethane heart valves. Mater Sci Eng C 2014;35:335-40.

[527] Bernacca GM, Mackay TG, Wilkinson R, Wheatley DJ. Polyurethane heart valves: Fatigue failure, calcification, and polyurethane structure. J Biomed Mater Res 1997;34:371-9.

[528] Kokubo T, Kushitani H, Sakka S, Kitsugi T, Yamamuro T. Solutions able to reproduce *in vivo* surface-structure changes in bioactive glass-ceramic A-W3. J Biomed Mater Res 1990;24:721-34.

[529] Golomb G, Wagner D. Development of a new *in vitro* model for studying implantable polyurethane calcification. Biomaterials 1991;12:397-405.

[530] Tanahashi M, Yao T, Kokubo T, Minoda M, Miyamoto T, Nakamura T, Yamamuro T. Apatite coated on organic polymers by biomimetic process: improvement in adhesion to substrate by HCl treatment. J Mater Sci Mater Med 1995;6:319-26.

[531] Yang M, Zhang Z, Hahn C, King MW, Guidoin R. Assessing the resistance to calcification of polyurethane membranes used in the manufacture of ventricles for a totally implantable artificial heart. J Biomed Mater Res 1999;48:648-59.

[532] Thomas V, Jayabalan M. A new generation of high flex life polyurethane urea for polymer heart valve—Studies on *in vivo* biocompatibility and biodurability. J Biomed Mater Res Part A 2009;89:192-205.

[533] Singh C, Wang X. Metal Ion-Loaded Nanofibre Matrices for Calcification Inhibition in Polyurethane Implants. J Funct Biomater 2017;8:22/1-16.

[534] Shimada K, Higuchi A, Kubo R, Murakami T, Nakazawa Y, Tanaka R. The effect of a silk Fibroin/Polyurethane blend patch on rat Vessels. Organogenesis 2017;13:115-24.

[535] Labow RS, Meek E, Santerre JP. Differential synthesis of cholesterol esterase by monocyte-derived macrophages cultured on poly(ether or ester)-based poly(urethane)s. J Biomed Mater Res 1998;39:469-77.

[536] Labow RS, Meek E, Santerre JP. The biodegradation of poly(urethane)s by the esterolytic activity of serine proteases and oxidative enzyme systems. J Biomater Sci-Polym Ed 1999;10:699-713.

[537] Santerre JP, Woodhouse K, Laroche G, Labow RS. Understanding the biodegradation of polyurethanes: From classical implants to tissue engineering materials. Biomaterials 2005;26:7457-70.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[538] Phua SK, Castillo E, Anderson JM, Hiltner A. Biodegradation of a polyurethane *in vitro*. J Biomed Mater Res 1987;21:231-46.

[539] Santerre JP, Duguay DG, Labow RS, Brash JL. Interactions of Hydrolytic Enzymes at an Aqueous—Polyurethane Interface. ACS Symp Ser 1995;602:352-70.

[540] Chiono V, Sartori S, Calzone S, Boffito M, Tonda-Turo C, Mattu C, Gentile P, Ciardelli G. Synthetic biodegradable medical polyurethanes. In: Zhang X, editor. Science and Principles of Biodegradable and Bioresorbable Medical Polymers. Cambridge UK: Woodhead Publishing; 2017. p. 189-216.

[541] Kay MJ, McCabe RW, Morton LHG. Chemical and physical changes occurring in polyester polyurethane during biodegradation. Int Biodeterior Biodegrad 1993;31:209-25.

[542] Labow RS, Erfle DJ, Santerre JP. Neutrophil-mediated degradation of segmented polyurethanes. Biomaterials 1995;16:51-9.

[543] Jiang X, Li J, Ding M, Tan H, Ling Q, Zhong Y, Fu Q. Synthesis and degradation of nontoxic biodegradable waterborne polyurethanes elastomer with poly(ε-caprolactone) and poly(ethylene glycol) as soft segment. Eur Polym J 2007;43:1838-46.

[544] Hong Y, Guan J, Fujimoto KL, Hashizume R, Pelinescu AL, Wagner WR. Tailoring the degradation kinetics of poly(ester carbonate urethane)urea thermoplastic elastomers for tissue engineering scaffolds. Biomaterials 2010;31:4249-58.

[545] Kulkarni A, Reiche J, Kratz K, Kamusewitz H, Sokolov IM, Lendlein A. Enzymatic chain scission kinetics of poly(ε-caprolactone) monolayers. Langmuir 2007;23:12202-7.

[546] Santerre JP, Labow RS, Adams GA. Enzyme–biomaterial interactions: Effect of biosystems on degradation of polyurethanes. J Biomed Mater Res 1993;27:97-109.

[547] Labow RS, Duguay DG, Santerre JP. The enzymatic hydrolysis of a synthetic biomembrane: A new substrate for cholesterol and carboxyl esterases. J Biomater Sci Polym Ed 1995;6:169-79.

[548] Santerre JP, Labow RS, Duguay DG, Erfle D, Adams GA. Biodegradation evaluation of polyether and polyester-urethanes with oxidative and hydrolytic enzymes. J Biomed Mater Res 1994;28:1187-99.

[549] Christenson EM, Patel S, Anderson JM, Hiltner A. Enzymatic degradation of poly(ether urethane) and poly(carbonate urethane) by cholesterol esterase. Biomaterials 2006;27:3920-6.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[550] Marchant RE, Zhao Q, Anderson JM, Hiltner A. Degradation of a poly(ether urethane urea) elastomer: infra-red and XPS studies. Polymer 1987;28:2032-9.

[551] Santerre JP, Labow RS. The effect of hard segment size on the hydrolytic stability of polyether-urea-urethanes when exposed to cholesterol esterase. J Biomed Mater Res 1997;36:223-32.

[552] Schubert MA, Wiggins MJ, Schaefer MP, Hiltner A, Anderson JM. Oxidative biodegradation mechanisms of biaxially strained poly(etherurethane urea) elastomers. J Biomed Mater Res 1995;29:337-47.

[553] Schubert MA, Wiggins MJ, Anderson JM, Hiltner A. Role of oxygen in biodegradation of poly(etherurethane urea) elastomers. J Biomed Mater Res 1997;34:519-30.

[554] Simmons A, Hyvarinen J, Odell RA, Martin DJ, Gunatillake PA, Noble KR, Poole-Warren LA. Long-term *in vivo* biostability of poly(dimethylsiloxane)/poly(hexamethylene oxide) mixed macrodiol-based polyurethane elastomers. Biomaterials 2004;25:4887-900.

[555] Zhao Q, Agger MP, Fitzpatrick M, Anderson JM, Hiltner A, Stokes K, Urbanski P. Cellular interactions with biomaterials: *In vivo* cracking of pre-stressed pellethane 2363-80A. J Biomed Mater Res 1990;24:621-37.

[556] Zhao Q, Topham N, Anderson JM, Hiltner A, Lodoen G, Payet CR. Foreign-body giant cells and polyurethane biostability: *In vivo* correlation of cell adhesion and surface cracking. J Biomed Mater Res 1991;25:177-83.

[557] Wiggins MJ, Wilkoff B, Anderson JM, Hiltner A. Biodegradation of polyether polyurethane inner insulation in bipolar pacemaker leads. J Biomed Mater Res 2001;58:302-7.

[558] Anderson JM. Mechanisms of inflammation and infection with implanted devices. Cardiovasc Pathol 1993;2:33-41.

[559] Stokes K, Coury A, Urbanski P. Autooxidative Degradation of Implanted Polyether Polyurethane Devices. J Biomater Appl 1986;1:411-48.

[560] Stokes K, Urbanski P, Upton J. The *in vivo* auto-oxidation of polyether polyurethane by metal ions. J Biomater Sci Polym Ed 1989;1:207-30.

[561] Christenson EM, Anderson JM, Hiltner A. Oxidative mechanisms of poly(carbonate urethane) and poly(ether urethane) biodegradation: *In vivo* and *in vitro* correlations. J Biomed Mater Res Part A 2004;70:245-55.

ACCEPTED MANUSCRIPT

[562] Wu Y, Sellitti C, Anderson JM, Hiltner A, Lodoen GA, Payet CR. An FTIR–ATR investigation of *in vivo* poly(ether urethane) degradation. J Appl Polym Sci 1992;46:201-11.

[563] McCarthy SJ, Meijs GF, Mitchell N, Gunatillake PA, Heath G, Brandwood A, Schindhelm K. *In-vivo* degradation of polyurethanes: transmission-FTIR microscopic characterization of polyurethanes sectioned by cryomicrotomy. Biomaterials 1997;18:1387-409.

[564] Szycher M, Reed AM, Siciliano AA. *In vivo* testing of a biostable polyurethane. J Biomater Appl 1991;6:110-30.

[565] Wiggins MJ, MacEwan M, Anderson JM, Hiltner A. Effect of soft-segment chemistry on polyurethane biostability during *in vitro* fatigue loading. J Biomed Mater Res Part A 2004;68:668-83.

[566] Christenson EM, Anderson JM, Hiltner A. Antioxidant inhibition of poly(carbonate urethane) *in vivo* biodegradation. J Biomed Mater Res Part A 2006;76:480-90.

[567] Christenson EM, Dadsetan M, Wiggins M, Anderson JM, Hiltner A. Poly(carbonate urethane) and poly(ether urethane) biodegradation: *In vivo* studies. J Biomed Mater Res Part A 2004;69:407-16.

[568] Mathur AB, Collier TO, Kao WJ, Wiggins M, Schubert MA, Hiltner A, Anderson JM. *In vivo* biocompatibility and biostability of modified polyurethanes. J Biomed Mater Res 1997;36:246-57.

[569] Zhao Q, Casas-Bejar J, Urbanski P, Stokes K. Glass Wool–H_2O_2/$CoCl_2$ test system for *in vitro* evaluation of biodegradative stress cracking in polyurethane elastomers. J Biomed Mater Res 1995;29:467-75.

[570] Zhao QH, McNally AK, Rubin KR, Renier M, Wu Y, Rose-Caprara V, Anderson JM, Hiltner A, Urbanski P, Stokes K. Human plasma α2-macroglobulin promotes *in vitro* oxidative stress cracking of pellethane 2363-80A: *In vivo* and *in vitro* correlations. J Biomed Mater Res 1993;27:379-88.

[571] Schubert MA, Wiggins MJ, Anderson JM, Hiltner A. The effect of strain state on the biostability of a poly(etherurethane urea) elastomer. J Biomed Mater Res 1997;35:319-29.

[572] Hergenrother RW, Wabers HD, Cooper SL. Effect of hard segment chemistry and strain on the stability of polyurethanes: *in vivo* biostability. Biomaterials 1993;14:449-58.

[573] Pinchuk L, Martin JB, Esquivel MC, Macgregor DC. The Use of Silicone/Polyurethane Graft Polymers as a Means of Eliminating Surface Cracking of Polyurethane Prostheses. J Biomater Appl 1988;3:260-96.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[574] Martin DJ, Poole Warren LA, Gunatillake PA, McCarthy SJ, Meijs GF, Schindhelm K. Polydimethylsiloxane/polyether-mixed macrodiol-based polyurethane elastomers: biostability. Biomaterials 2000;21:1021-9.

[575] Schubert MA, Wiggins MJ, Anderson JM, Hiltner A. Comparison of two antioxidants for poly(etherurethane urea) in an accelerated *in vitro* biodegradation system. J Biomed Mater Res 1997;34:493-505.

[576] Stachelek SJ, Alferiev I, Choi H, Chan CW, Zubiate B, Sacks M, Composto R, Chen IW, Levy RJ. Prevention of oxidative degradation of polyurethane by covalent attachment of di-*tert*-butylphenol residues. J Biomed Mater Res Part A 2006;78:653-61.

[577] Osman M, Satti SM, Luqman A, Hasan F, Shah Z, Shah AA. Degradation of Polyester Polyurethane by Aspergillus sp. Strain S45 Isolated from Soil. J Polym Environ 2018;26:301-10.

[578] Wilkes RA, Aristilde L. Degradation and metabolism of synthetic plastics and associated products by Pseudomonas sp.: capabilities and challenges. J Appl Microbiol 2017;123:582-93.

[579] Lucas N, Bienaime C, Belloy C, Queneudec M, Silvestre F, Nava-Saucedo JE. Polymer biodegradation: Mechanisms and estimation techniques – A review. Chemosphere 2008;73:429-42.

[580] Javaid MA, Khera RA, Zia KM, Saito K, Bhatti IA, Asghar M. Synthesis and characterization of chitosan modified polyurethane bio-nanocomposites with biomedical potential. Int J Biol Macromol 2018;115:375-84.

[581] Deka H, Karak N, Kalita RD, Buragohain AK. Bio-based thermostable, biodegradable and biocompatible hyperbranched polyurethane/Ag nanocomposites with antimicrobial activity. Polymer Degrad Stab 2010;95:1509-17.

[582] Luo J, Deng Y, Sun Y. Antimicrobial Activity and Biocompatibility of Polyurethane—Iodine Complexes. J Bioact Compat Polym 2010;25:185-206.

[583] Guo B, Ma PXJSCC. Synthetic biodegradable functional polymers for tissue engineering: a brief review. Sci China Chem 2014;57:490-500.

[584] Noreen A, Zia KM, Zuber M, Tabasum S, Zahoor AF. Bio-based polyurethane: An efficient and environment friendly coating systems: A review. Prog Org Coat 2016;91:25-32.

[585] Rahimi A, Mashak A. Review on rubbers in medicine: natural, silicone and polyurethane rubbers. Plast Rubber Compos 2013;42:223-30.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[586] Bayan R, Karak N. Renewable resource modified polyol derived aliphatic hyperbranched polyurethane as a biodegradable and UV-resistant smart material. Polym Int 2017;66:839-50.

[587] Cheng KW, Hsu SH. A facile method to prepare superparamagnetic iron oxide and hydrophobic drug-encapsulated biodegradable polyurethane nanoparticles. Int J Nanomed 2017;12:1775-89.

[588] Chen YP, Hsu SH. Preparation and characterization of novel water-based biodegradable polyurethane nanoparticles encapsulating superparamagnetic iron oxide and hydrophobic drugs. J Mater Chem B 2014;2:3391-401.

[589] Gurusamy Thangavelu SA, Murali A, Sharanya M, Jaisankar SN, Mandal AB. Studies on biodegradable polyurethane-SWCNTs nanocomposite films by covalent approach: Physicochemical, electric and mechanical properties. Appl Surf Sci 2018;449:745-54.

[590] Guan Y, Su Y, Zhao L, Meng F, Wang Q, Yao Y, Luo J. Biodegradable polyurethane micelles with pH and reduction responsive properties for intracellular drug delivery. Mater Sci Eng C 2017;75:1221-30.

[591] Wei Q, Jin J, Wang X, Shen Q, Zhou M, Bu S, Zhu Y. The growth and pluripotency of mesenchymal stem cell on the biodegradable polyurethane synthesized with ferric catalyst. J Biomater Sci Polym Ed 2018;29:1095-108.

[592] Hsu SH, Chang WC, Yen CT. Novel flexible nerve conduits made of water-based biodegradable polyurethane for peripheral nerve regeneration. J Biomed Mater Res Part A 2017;105:1383-92.

[593] Xu C, Huang Y, Tang L, Hong Y. Low-Initial-Modulus Biodegradable Polyurethane Elastomers for Soft Tissue Regeneration. ACS Appl Mater Interfaces 2017;9:2169-80.

[594] Huang YJ, Hung KC, Hung HS, Hsu SH. Modulation of Macrophage Phenotype by Biodegradable Polyurethane Nanoparticles: Possible Relation between Macrophage Polarization and Immune Response of Nanoparticles. ACS Appl Mater Interfaces 2018;10:19436-48.

[595] Mu Y, Xue S, Pei D, Jiang W, Wan X. One-Step Synthesis of Biodegradable Polyurethane Prepolymer and Its Rapid Gelation Behavior at High Water Content. Macromol Chem Phys 2017;218:1600369/1-8.

[596] Lee HT, Tsou CH, Li CL, Gu JH, Wu CL, Hwang JJ, et al. Preparation and Characterization of Biodegradable Polyurethane Composites Containing Attapulgite Nanorods. Adv Polym Tech 2018;37:208-20.

ACCEPTED MANUSCRIPT

[597] Zhu Q, Li X, Fan Z, Xu Y, Niu H, Li C, Dang Y, Huang Z, Wang Y, Guan J. Biomimetic polyurethane/TiO_2 nanocomposite scaffolds capable of promoting biomineralization and mesenchymal stem cell proliferation. Mater Sci Eng C 2018;85:79-87.

[598] Chien YC, Chuang WT, Jeng US, Hsu SH. Preparation, Characterization, and Mechanism for Biodegradable and Biocompatible Polyurethane Shape Memory Elastomers. ACS Appl Mater Interfaces 2017;9:5419-29.

[599] Wu Y, Lin W, Hao H, Li J, Luo F, Tan H. Nanofibrous scaffold from electrospinning biodegradable waterborne polyurethane/poly(vinyl alcohol) for tissue engineering application. J Biomater Sci Polym Ed 2017;28:648-63.

[600] Xu C, Kuriakose AE, Truong D, Punnakitikashem P, Nguyen KT, Hong Y. Enhancing anti-thrombogenicity of biodegradable polyurethanes through drug molecule incorporation. J Mater Chem B 2018;6:7288-7297.

[601] Gu SY, Chang K, Jin SP. A dual-induced self-expandable stent based on biodegradable shape memory polyurethane nanocomposites (PCLAU/Fe_3O_4) triggered around body temperature. J Appl Polym Sci 2018;135:45686/1-10.

[602] Vieira T, Silva JC, Borges JP, Henriques C. Synthesis, electrospinning and *in vitro* test of a new biodegradable gelatin-based poly(ester urethane urea) for soft tissue engineering. Eur Polym J 2018;103:271-81.

[603] Shahrousvand E, Shahrousvand M, Ghollasi M, Seyedjafari E, Jouibari IS, babaei A, Salimi A. Preparation and evaluation of polyurethane/cellulose nanowhisker bimodal foam nanocomposites for osteogenic differentiation of hMSCs. Carbohydr Polym 2017;171:281-91.

[604] Kucińska-Lipka J. Polyurethanes Crosslinked with Poly(vinyl alcohol) as a Slowly-Degradable and Hydrophilic Materials of Potential Use in Regenerative Medicine. Materials 2018;11:352/1-19.

[605] Wang YJ, Jeng US, Hsu SH. Biodegradable Water-Based Polyurethane Shape Memory Elastomers for Bone Tissue Engineering. ACS Biomater Sci Eng 2018;4:1397-406.

[606] Laube T, Weisser J, Berger S, Börner S, Bischoff S, Schubert H, Gajda M, Bräuer R, Schnabelrauch M. *In situ* foamable, degradable polyurethane as biomaterial for soft tissue repair. Mater Sci Eng C 2017;78:163-74.

[607] Kishan AP, Wilems T, Mohiuddin S, CosgriffHernandez EM. Synthesis and Characterization of Plug-and-Play Polyurethane Urea Elastomers as Biodegradable Matrixes for Tissue Engineering Applications. ACS Biomater Sci Eng 2017;3:3493-502.

[608] Hsu SH, Hung KC, Dai SA, Lu CY. Biocompatible and biodegradable elastomer. US 15/195578,

National Taiwan University; 2017.

[609] Singhal P, Wilson TS, CosgriffHernandez E, Maitland DJ. Ultra low density biodegradable shape memory polymer foams with tunable physical properties. US 9840577B2, Texas A&M University System, Lawrence Livermore National Security LLC; 2017.

[610] Pereira IHL, Ayres E, Patrício PS, Góes AM, Gomide VS, Junior EP, Oréfice RL. Photopolymerizable and injectable polyurethanes for biomedical applications: Synthesis and biocompatibility. Acta Biomater 2010;6:3056-66.

[611] Zhang C, Zhang N, Wen X. Synthesis and characterization of biocompatible, degradable, light-curable, polyurethane-based elastic hydrogels. J Biomed Mater Res Part A 2007;82:637-50.

[612] Zhou L, Yu L, Ding M, Li J, Tan H, Wang Z, Fu Q. Synthesis and Characterization of pH-Sensitive Biodegradable Polyurethane for Potential Drug Delivery Applications. Macromolecules 2011;44:857-64.

[613] Kiran S, James NR, Jayakrishnan A, Joseph R. Polyurethane thermoplastic elastomers with inherent radiopacity for biomedical applications. J Biomed Mater Res Part A 2012;100:3472-9.

[614] Sarkar D, Yang JC, Gupta AS, Lopina ST. Synthesis and characterization of L-tyrosine based polyurethanes for biomaterial applications. J Biomed Mater Res Part A 2009;90:263-71.

[615] Barrioni BR, de Carvalho SM, Oréfice RL, de Oliveira AAR, Pereira MdM. Synthesis and characterization of biodegradable polyurethane films based on HDI with hydrolyzable crosslinked bonds and a homogeneous structure for biomedical applications. Mater Sci Eng C 2015;52:22-30.

[616] Bruin P, Veenstra GJ, Nijenhuis AJ, Pennings AJ. Design and synthesis of biodegradable poly(ester-urethane) elastomer networks composed of non-toxic building blocks. Makromol Chem Rapid Commun 1988;9:589-94.

[617] Zhang J, Wu M, Yang J, Wu Q, Jin Z. Anionic poly(lactic acid)-polyurethane micelles as potential biodegradable drug delivery carriers. Colloids Surf A 2009;337:200-4.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[618] Wang H, Yu J, Fang H, Wei H, Wang X, Ding Y. Largely improved mechanical properties of a biodegradable polyurethane elastomer via polylactide stereocomplexation. Polymer 2018;137:1-12.

[619] Barrioni BR, de Carvalho SM, de Oliveira AAR, Pereira MdM. Improved biocompatibility of polyurethane film by association with bioactive glass through ultrasonic implantation. Mater Lett 2018;223:53-6.

[620] Chen J, Dong R, Ge J, Guo B, Ma PX. Biocompatible, Biodegradable, and Electroactive Polyurethane-Urea Elastomers with Tunable Hydrophilicity for Skeletal Muscle Tissue Engineering. ACS Appl Mater Interfaces 2015;7:28273-85.

[621] Ma Z, Hong Y, Nelson DM, Pichamuthu JE, Leeson CE, Wagner WR. Biodegradable Polyurethane Ureas with Variable Polyester or Polycarbonate Soft Segments: Effects of Crystallinity, Molecular Weight, and Composition on Mechanical Properties. Biomacromolecules 2011;12:3265-74.

[622] Ng WS, Lee CS, Chuah CH, Cheng SF. Preparation and modification of water-blown porous biodegradable polyurethane foams with palm oil-based polyester polyol. Ind Crops Prod 2017;97:65-78.

[623] Luo X, Xiao Y, Wu Q, Zeng J. Development of high-performance biodegradable rigid polyurethane foams using all bioresource-based polyols: Lignin and soy oil-derived polyols. Int J Biol Macromol 2018;115:786-91.

[624] Acik G, Kamaci M, Altinkok C, Karabulut HRF, Tasdelen MA. Synthesis and properties of soybean oil-based biodegradable polyurethane films. Prog Org Coat 2018;123:261-6.

[625] Gao Z, Peng J, Zhong T, Sun J, Wang X, Yue C. Biocompatible elastomer of waterborne polyurethane based on castor oil and polyethylene glycol with cellulose nanocrystals. Carbohydr Polym 2012;87:2068-75.

[626] Sonnenschein MF, Ginzburg VV, Schiller KS, Wendt BL. Design, polymerization, and properties of high performance thermoplastic polyurethane elastomers from seed-oil derived soft segments. Polymer 2013;54:1350-60.

[627] Miao S, Sun L, Wang P, Liu R, Su Z, Zhang S. Soybean oil-based polyurethane networks as candidate biomaterials: Synthesis and biocompatibility. Eur J Lipid Sci Technol 2012;114:1165-74.

ACCEPTED MANUSCRIPT

[628] Dutta S, Karak N, Saikia JP, Konwar BK. Biocompatible epoxy modified bio-based polyurethane nanocomposites: Mechanical property, cytotoxicity and biodegradation. Bioresour Technol 2009;100:6391-7.

[629] Xia Y, Larock RC. Vegetable oil-based polymeric materials: synthesis, properties, and applications. Green Chem 2010;12:1893-909.

[630] Usman A, Zia KM, Zuber M, Tabasum S, Rehman S, Zia F. Chitin and chitosan based polyurethanes: A review of recent advances and prospective biomedical applications. Int J Biol Macromol 2016;86:630-45.

[631] Zia KM, Barikani M, Zuber M, Bhatti IA, Sheikh MA. Molecular engineering of chitin based polyurethane elastomers. Carbohydr Polym 2008;74:149-58.

[632] Zuber M, Zia F, Zia KM, Tabasum S, Salman M, Sultan N. Collagen based polyurethanes—A review of recent advances and perspective. Int J Biol Macromol 2015;80:366-74.

[633] Zia KM, Zia F, Zuber M, Rehman S, Ahmad MN. Alginate based polyurethanes: A review of recent advances and perspective. Int J Biol Macromol 2015;79:377-87.

[634] Zia F, Zia KM, Zuber M, Tabasum S, Rehman S. Heparin based polyurethanes: A state-of-the-art review. Int J Biol Macromol 2016;84:101-11.

[635] Costa L, Luda MP, Trossarelli L. Ultra-high molecular weight polyethylene: I. Mechano-oxidative degradation. Polymer Degrad Stab 1997;55:329-38.

[636] Scott G. Recent trends in the stabilization of polymers. Br Polym J 1983;15:208-23.

[637] Papadopoulos IC, Thomas AG, Busfield JJC. Rate transitions in the fatigue crack growth of elastomers. J Appl Polym Sci 2008;109:1900-10.

[638] Hainsworth SV. An environmental scanning electron microscopy investigation of fatigue crack initiation and propagation in elastomers. Polym Test 2007;26:60-70.

[639] Saintier N, Cailletaud G, Piques R. Crack initiation and propagation under multiaxial fatigue in a natural rubber. Int J Fatigue 2006;28:61-72.

[640] Cho K, Jang WJ, Lee D, Chun H, Chang YW. Fatigue crack growth of elastomers in the swollen state. Polymer 2000;41:179-83.

[641] Abraham F, Alshuth T, Jerrams S. The effect of minimum stress and stress amplitude on the fatigue life of non strain crystallising elastomers. Mater Des 2005;26:239-45.

[642] Alshuth T, Abraham F, Jerrams S. Parameter Dependence and Prediction of Fatigue Properties of Elastomer Products. Rubber Chem Technol 2002;75:635-42.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[643] Abraham F, Alshuth T, Jerrams S. Dependence on mean stress and stress amplitude of fatigue life of EPDM elastomers. Plast Rubber Compos 2001;30:421-5.

[644] Mars WV, Fatemi A. A literature survey on fatigue analysis approaches for rubber. Int J Fatigue 2002;24:949-61.

[645] Wang B, Lu H, Kim GH. A damage model for the fatigue life of elastomeric materials. Mech Mater 2002;34:475-83.

[646] Whittaker RE. Cut growth and fatigue properties of cellular polyurethane elastomers. J Appl Polym Sci 1974;18:2339-53.

[647] Mead JL. Mechanical degradation of a polyurethane elastomer. PhD Thesis, Massachusetts Institute of Technology; 1986. 126 pp.

[648] Shibayama M, Kawauchi T, Kotani T, Nomura S, Matsuda T. Structure and properties of fatigued segmented poly(urethaneurea) i. Segment orientation mechanism due to fatigue. Polym J 1986;18:719-33.

[649] Shibayama M, Ohki Y, Kotani T, Nomura S. Structure and properties of fatigued segmented poly(urethaneurea)s ii. Structural analyses of fatigue mechanism. Polym J 1987;19:1067-80.

[650] Yeh F, Hsiao BS, Sauer BB, Michel S, Siesler HW. In-situ studies of structure development during deformation of a segmented poly(urethane−urea) elastomer. Macromolecules 2003;36:1940-54.

[651] Jimenez G, Asai S, Shishido A, Sumita M. Effect of the soft segment on the fatigue behavior of segmented polyurethanes. Eur Polym J 2000;36:2039-50.

[652] Coker MSS, Scott G, Sweis HAA. Mechanisms of antioxidant action: Sulphur compounds as inhibitors of mechanochemical degradation of rubber. Polymer Degrad Stab 1982;4:333-41.

[653] Nethsinghe LP, Scott G. Mechanisms of antioxidant action. The role of nitroxyl radicals as chain-breaking acceptor antioxidants in the mechanodegradation of rubber. Eur Polym J 1984;20:213-7.

[654] Scott G. A review of recent developments in the mechanisms of antifatigue agents. Rubber Chem Technol 1985;58:269-83.

[655] Scott G, Suharto R. Mechanisms of antioxidant action. Antifatigue activity of polymer-bound phenolic sulphides in SBR. Eur Polym J 1985;21:765-8.

[656] Potter WD, Scott G. Mechano-chemical reactions of polymers. Formation of free radicals in stressed rubber. Eur Polym J 1971;7:489-97.

ACCEPTED MANUSCRIPT

[657] O'Donnell B, White JR. Stress-accelerated photo-oxidation of polypropylene and glass-fibre-reinforced polypropylene. Polymer Degrad Stab 1994;44:211-22.

[658] O'Donnell B, White JR. Photo-oxidation of polystyrene under load. J Mater Sci 1994;29:3955-63.

[659] Phillips RE, Smith MC, Thoma RJ. Biomedical Applications of Polyurethanes: Implications of Failure Mechanisms. J Biomater Appl 1988;3:207-27.

[660] Martin DJ, Poole Warren LA, Gunatillake PA, McCarthy SJ, Meijs GF, Schindhelm K. New methods for the assessment of *in vitro* and *in vivo* stress cracking in biomedical polyurethanes. Biomaterials 2001;22:973-8.

[661] Wiggins MJ, Anderson JM, Hiltner A. Effect of strain and strain rate on fatigue-accelerated biodegradation of polyurethane. J Biomed Mater Res Part A 2003;66:463-75.

[662] Wiggins MJ, Anderson JM, Hiltner A. Biodegradation of polyurethane under fatigue loading. J Biomed Mater Res Part A 2003;65:524-35.

[663] Robeson LM. Environmental stress cracking: A review. Polym Eng Sci 2013;53:453-67.

[664] Pinchuk L. A review of the biostability and carcinogenicity of polyurethanes in medicine and the new generation of 'biostable' polyurethanes. J Biomater SciPolym Ed 1995;6:225-67.

ACCEPTED MANUSCRIPT