

Plant Oil-Based Waterborne Polyurethanes: A Brief Review

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Abstract: The increasing pressure from consumers and policy makers to reduce the use of synthetic polymers, whose production contributes to the depletion of non-renewable resources and are usually non-biodegradable, has prompted the efforts to find suitable bio-based sources for the production of polymers. Vegetable oils have been a frequently spotted in this search because they are versatile, highly available and a low cost liquid biosource, which can be used in the synthesis of a wide plethora of different polymers and reactive monomers. Following the same idea of reducing the environmental stress, the traditional polyurethanes that are soluble in organic solvents have been targeted for replacement, particularly in applications such as adhesives and coatings, in which the solvent is released to the atmosphere increasing the air pollution. Instead, waterborne polyurethanes (WBPU), which are polyurethane dispersions (PUD) prepared in aqueous media, release benign water to the atmosphere during use as supported or self-standing films for different applications. In this brief review, the contributions to the development of WBPUs based on vegetable oils are discussed, focusing mainly on the contributions of the last decade. The synthesis of ionic and non-ionic PUDs, their characterization and the properties of the resulting dried materials, as well as derived composite materials are considered.

Keywords: Vegetable oils; polyurethane dispersions (PUD); waterborne polyurethane (WBPU); biopolyols; biopolyurethanes; coatings; adhesives; ink binders

Abbreviations

¹ H-NMR	proton nuclear magnetic resonance
AESO	acrylated epoxidized soybean oil
Ag-HNT	silver-halloysite nanoparticles
APTES	3-aminopropyltriethoxy silane
a-PUD	anionic polyurethane dispersions
AT	attapulgitite (AT)



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a-WBPU	anionic WBPU
bio-PU	bio based polyurethanes
bio-WBPU	bio based waterborne polyurethanes
CNC	cellulose nanocrystals
CO	castor oil
CSO	cottonseed oil
c-WBPU	cationic WBPU
DBTDL	dibutyltin dilaurate
DLS	dynamic light scattering
DMA	Dynamic Mechanical Analysis
DMBA	dimethylolbutanoic acid
DMPA	dimethylol propionic acid
DSC	Differential Scanning Calorimetry
FT	halloysite nanotubes (FT)
FTIR	Fourier-transform infrared spectroscopy
GPC	Gel Permeation Chromatography
HDI	hexamethylen diisocyanate
HEMA	hydroxyethylmethacrylate,
IPDI	isophorone diisocyanate
MDI	4,4'-di-p-phenylmethane diisocyanate
MEK	Methyl Ethyl Ketone
MFFT	minimum film forming temperature
MSOLs	methoxylated soybean oil polyols
MT	montmorillonite
NIPUs	non-isocyanate polyurethanes
N-MDEA	N-methyl diethanolamine
n-WBPU	nonionic waterborne polyurethane
PCL	polycaprolactone diol
PEG	Polyethylene glycol
PET	polyethylene terephthalate
SiWPU	polyurethane/silica
PPG	Poly(propylene glycol)
PU	polyurethane
PUA	c-WBPU-acrylate dispersion
PUD	polyurethane dispersions
SEM	scanning electronic microscopy
SPI	soy protein isolates
TA	tartaric acid
TDI	toluene diisocyanate
TEA	Triethylamine
T _g	glass transition temperature
TGA	thermal gravimetric analysis
VOC	volatile organic compounds
WBPU	waterborne polyurethanes

1 Introduction

Since their appearance, polyurethanes (PUs) have been highly appreciated because their versatility makes them useful in a large number of very different applications, from varnishes, coatings and paints to materials for biomedical devices, from footwear materials to thermal and acoustic insulators, from sealants to furniture, bedding and automotive applications [1–7]. Accordingly, the global market for PUs is estimated to keep growing from about USD 65.5 billions in 2018 [8] to USD 91 billions by 2026 [9].

Because of the increasing global concern about the preservation of the environment, the development of waterborne polyurethanes (WBPU) has received a constantly increasing interest due to the beneficial replacement of organic solvents (volatile organic compounds, VOC) by water, an ecofriendly solvent [10]. The advantages of the use of these polymers have up to now outperform the disadvantages of utilizing a non-ecofriendly component in the synthesis such as isocyanate. Additionally, the interest in working with materials that may have lower environmental impact has led researchers and industry to try to replace petroleum-based reactants. The road to the use of non-isocyanate polyurethanes (NIPUs) is being paved by relatively recent research efforts [11–14] and it is only to be expected that this path will lead to the commercial competitiveness of these materials in the future. On the other hand, the development and production of bio-based polyols has been simpler and of more rapid development [15]. The use of vegetable oils as source for numerous and different types of chemicals has been targeted, and achieved a large success for the production of polyols with different molecular structures that can be utilized in the synthesis of PUs [16,17]. In particular, WBPU can be applied in the production of fibers, adhesives, metal primers, sealants, paint additives, textile dyes, biomaterials, etc., which explains the growing interest in the continuous development of these materials [16,18].

Traditional PUs are the result of the reaction between a diisocyanate (or a polyisocyanate) with a macrodiol (or polyol) [19]. However, to produce PU aqueous dispersions (PUD) is necessary to add an emulsifier to prevent the coagulation of the organic soluble PU in the aqueous media [18,20]. This goal can be achieved by addition of an external agent. Moreover, the use of an internal emulsifier (a co-reactant) offers the advantage of avoiding its exudation from the material once the solvent has been evaporated and the PU piece has been consolidated.

Thus, an internal emulsifier should provide the means to allow for a stable suspension to be formed. Usually, this is achieved by co-reaction of the isocyanate with a diol containing an ionic group in its molecular structure. Anionic WBPU are synthesized by using diols with a carboxylic or a carboxylate group (such as the most frequently used dimethylol propionic acid, DMPA), while cationic WBPU are produced by adding a diol that usually contains an amine group. The synthesized WBPU requires the addition of a counter-ion to be stably dispersed in water. Non-ionic internal emulsifiers (for example, molecules containing polyether segments) have also been considered, although they result in dispersions of less stability than in the case of the use of ionic emulsifiers [6]. The synthesis of these polyurethanes and their further dispersion in water results in aqueous suspensions of nanoparticles that are stable when the particle size is in the range of 20–200 nm [18].

This review focuses on the recent contributions to the development of WBPU based on vegetable oils. The synthesis and characterization of ionic and non-ionic PUDs, as well as the properties of the resulting dried materials, and derived composite materials were considered for the preparation of this article.

2 Chemistry of Plant Oil Based PUDs

2.1 Biopolyols

The synthesis of bio-based polyurethanes has gained interest in recent decades, because of the need to find alternative raw materials, such as renewable monomers and promote sustainable development. Following this objective, the use of polyols of biological origin from renewable resources, such as

vegetable oil, sugar, chitosan, natural rubber, chitin, glucan, and heparin for the synthesis of polyurethane has been proposed [21,22].

Most natural vegetable oils, with the exception of castor and lesquerella oils, do not contain hydroxyl groups. Therefore, to be used as raw material in the production of polyurethanes, the vegetable oils are often chemically modified to introduce hydroxyl groups into their structures. Ester groups and double carbon-carbon bonds are the two main functionalities present in triglycerides. Therefore, various synthetic routes can be used for the production of polyols from these molecules introducing or adding hydroxyls in their structure. These synthetic routes involve epoxidation reactions followed by oxirane ring opening, hydroformylation followed by hydrogenation, thiol-ene coupling, transesterification and amidation, among the most cited ones in the literature [5,23–28].

The fatty acids and esters also have the functionalities mentioned above. Therefore, the synthetic routes mentioned can also be used to produce polyols from fatty acids or fatty acid esters. In addition to these methods, other methods, such as dimerization of fatty acids, followed by reduction, have been developed to produce polyols, as well as polycondensation with glycols, to obtain fatty acid esters [27].

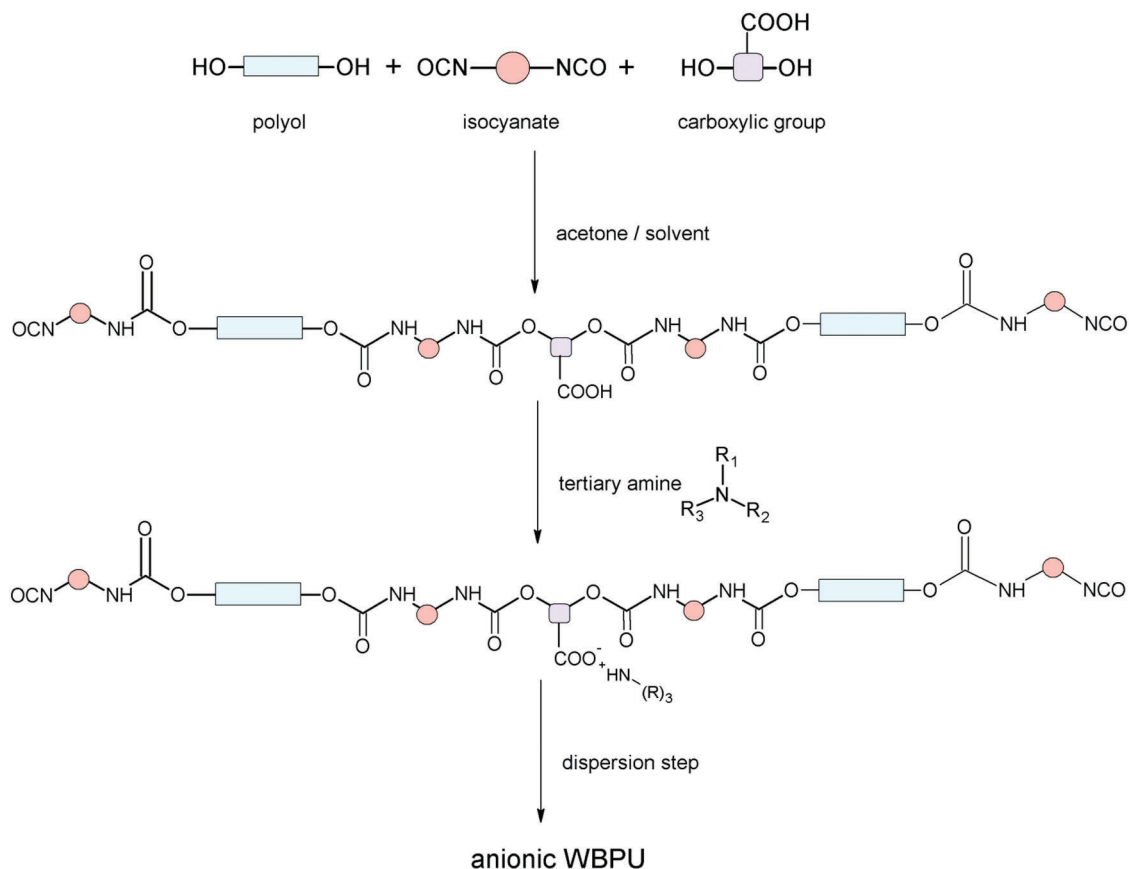
As mentioned above, castor oil (CO) is one of the few oils from biomass that contains natural hydroxyl groups. In its composition, approximately 90% of the fatty acids consist of ricinoleic acid, a monounsaturated 18-carbon fatty acid with a hydroxyl group at carbon 12. The structural analysis of this oil shows that it has an average hydroxyl functionality of 2.7, resulting from the contributions of 70% of triols (triricinoleate of glycerol) and 30% of diols (triacylglycerol having only two ricinoleyl groups). Due to the presence of its natural hydroxyl groups and its wide availability, castor oil results in a very versatile and valuable raw material for direct use in the manufacture of PU [5]. With the aim of using diols from vegetable oils, other authors have used very interesting strategies to include hydroxyl groups in the structure of oil, for example, Sashivinay Kumar Gaddam and co-workers [29], synthesized phosphorylated polyols (phospols) derived from cottonseed oil (CSO) through the ring-opening hydrolysis of epoxy groups in the presence of ortho-phosphoric acid.

2.2 Synthesis of PUDs

It is well known that for the synthesis of polyurethanes, polyols, and a diisocyanate are the starting materials. If the source of polyols is a bio-based polyol, the hydroxyls groups are less reactive, and a catalyst is used, such as dibutyltin dilaurate (DBTDL). In traditional PU synthesis, depending on the desired pre-polymer, chain extenders are often used. One of the most widely used extenders is 1,4-butanediol, however, some authors have used other hydroxyl-containing extenders. For example, Xia et al. [30] used d-isosorbide, a non-toxic diol derived from carbohydrates with a rigid molecular structure and chirality, to prepare polymers with high glass transition temperature (T_g) and special optical properties.

However, the synthesis of aqueous-based polyurethanes, prepared with or without chain extenders also requires the use of emulsifying agents. As already mentioned in the introduction, the use of internal emulsifiers is preferred since it avoids any possible migration of this component after the film consolidation. The emulsifying agents used will define whether the WBPU is cationic, anionic or non-ionic.

In the works reviewed in this article, the polymerization is carried in bulk and, in many cases, with the addition of a co-solvent to complete the reaction followed by the addition of water. In general, the synthesis reaction of WBPU could be divided into two steps. The first one is the formation of NCO-terminated prepolymer in which a solvent (usually acetone) and high temperature, is used, for the control of the viscosity of the medium. The second step is the addition and co-reaction with the internal emulsifying agents that incorporate ionic centers into the polymer chemical structure. This reaction is followed by the dispersion of the polyurethane in water, at room temperature using a high shear device [31–33]. [Scheme 1](#) shows the general reaction for a simple synthesis of a WBPU.



Scheme 1: Synthetic route of a-WBPU

2.2.1 Aliphatic or Aromatic Isocyanates

A large number of publications on WBPU synthesis with different diisocyanates are found in the literature [34]. In most of them, aliphatic diisocyanates, such as isophorone diisocyanate (IPDI) are preferred over aromatic ones, such as 4,4'-di-p-phenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI) since the latter ones present higher reactivity towards water [6]. Additionally, IPDI is frequently selected because of the transparency of the resulting films.

2.2.2 Biopolyols Chemistry and Size of WBPU Particles

The functionality of the polyols utilized and their hydrophobicity/hydrophilicity have an effect on the size of the particles dispersed. Li et al. [35] prepared UV-curable WBPU based on polycaprolactone diol (PCL) and IPDI with contents of acrylated epoxidized soybean oil (AESO) (as source of both OH and C=C groups) from 0 to 20% and hydroxyethyl methacrylate (HEMA) as co-monomer further participating of the UV crosslinking of the formed film. They found that increasing the percentage of the AESO in the formulation, the size of the particles in suspension increased from 26.8 to 43.6 nm for HEMA at 0 to 20%, respectively. The effect of adding the triglyceride based molecules of the AESO (functionality higher than 2 and more hydrophobic than PCL) lead to higher viscosity of the dispersions (at a given solids content) and to lower dispersibility in water, thus to an increase of the size of the particles. The dispersions were stable up to 10% content of AESO.

2.2.3 Internal Emulsifiers. Anionic, Cationic and Non-Ionic WBPU

The most commonly used diacid in the anionic WBPU (a-WBPU) formulation is DMPA, the ionic centers that provide this acid are located in the hard segments of the polyurethane, increasing its hydrophilicity. Since these ionic centers are responsible for the dispersion of the micelles in the aqueous medium, the hydrophilic hard domains are preferably located on the surface of the particle [36,37]. Nevertheless, some authors avoided the addition of acid to introduce ionic centers, reacting the double bonds present in the triacylglycerides with maleic anhydride as a strategy. In this way, the carboxylic acid group, which provides the ionic center, is located in the starting polyol [38]. Other such approach proposed [29] the synthesis of a WBPU from a cottonseed-oil-based phosphorylated polyol which supplied the ionic center and was part of the structure of the soft segments (flexible polyol).

The content of the emulsifier in the formulation strongly affects the size of the polyurethane nanoparticles formed, with smaller particles resulting from the use of a higher concentration of emulsifier. Because of this result, the viscosity of the PUDs also increased (larger hydrodynamic volume of particles due to the comparatively larger double layer) [16,20,39–47].

Although not many ionic diols have been reported, Hormaiztegui et al. [33] used another carboxylic acid, tartaric acid (TA) as internal emulsifier. The use of this acid in the production of a castor oil-based a-WBPU allowed the synthesis of stable PUDs. Because of the replacement of the more usual DMPA with TA, the WBPU had a relatively higher bio-carbon content (38 wt.% and 43 wt.% bio carbon in DMPA and TA-based formulations, respectively). The authors showed that TA reacts with the isocyanate through the hydroxyl groups of the alcoholic and the acid groups, which resulted in films that are more fragile. On the other hand, the films obtained from this acid were transparent with a glass transition temperature, T_g , above room temperature as it was also the case of the analogous WBPU prepared with DMPA.

An interesting work was presented by Liu et al., who synthesized an anionic emulsifier from soybean oil and glutaric acid through a self-catalysis and solvent-free method [48]. Synthetic and vegetable oil-based polyols were used to synthesize a series of WBPU, to test the effectiveness of the bio-based emulsifier. As in the case of Hormaiztegui et al. [33] the emulsifier also reacted with the isocyanate through the hydroxyl groups corresponding to the alcoholic and acid groups (12–17% of the -COOH groups were consumed by reaction with the diisocyanate), but the long and flexible fatty acid chain improved the phase compatibility between hard and soft segments, leading to the increase of the elongation at break and toughness of the PU films. In addition, this bio-based emulsifier provided an excellent dispersion stability (centrifugation at 3000 rpm for 30 min does not produce precipitation or stratification). As observed by other researchers, the increase in the content of the emulsifier lead to higher electrostatic repulsion and WBPU dispersions with smaller particles.

Although at present, investigations are mainly directed to the synthesis of a-WBPU, research work has also been extended to the synthesis of cationic-WBPU (c-WBPU). These polymers offer the characteristic advantage of being stable under acidic conditions. They also offer good compatibility with softeners and fixing agents, show good wear resistance, and are widely used for applications such as dyeing, leather, coating, adhesives, textiles and paper, etc. [49,50]. However, they also present some disadvantages such as low solid content during synthesis, lower flexibility and water resistance than the a-WBPU. Probably, their greatest advantage is that they show antibacterial, antistatic and adhesive capabilities, particularly suitable for the treatment of anionic leathers and glass surfaces. The cationic emulsifiers used in the synthesis of c-WBPU are quaternary ammonium salts or amine salts, with N-methyl diethanolamine (N-MDEA) being the most widely used [51].

As in the case of a-WBPU, in the synthesis of c-WBPU, the higher concentration of the cationic internal emulsifier, the smaller the nanoparticles of the PUD to be obtained. Lu et al. [39] reported this effect on PUD prepared from methoxylated soybean oil polyols (MSOLs). In their case, they also studied

the effect of the hydroxyl functionalities of the MSOLs and saw that as the functionality increased the crosslinking also increased (evidenced by the increasing T_g in the amorphous PUs measured by DSC and DMA techniques) and the particles size grew. However, a higher OH functionality requires a larger amount of isocyanate and consequently more N-methyl diethanolamine, the internal cationic emulsifier used in the formulation, and as a result, the size of the particles is reduced. Thus, the size of the nanoparticles in the dispersions can be tailored by the functionality of the biopolyol and the addition of the emulsifier.

Few works in the literature refer to the synthesis of aqueous dispersions of non-ionic polyurethanes, in which no emulsifier is added to generate the dispersion. Baixia Ren et al. synthesized a series of nonionic waterborne polyurethane (n-WBPU) using different proportions of isocyanate (diphenyl methane diisocyanate-50 MDI-50), hydroxylated tung oil (HTO) and PEG as main materials. Without an emulsifying agent, the authors regulated the formation of the emulsion through the oil content in the formulation. The surface tension of the micelles decreased with the increase of the HTO content, since the micelles became less hydrophilic, turning the emulsion more unstable [52].

3 Characterization of the PUDs

The dispersions of WBPU have been characterized by several techniques. During the synthesis, the amount of free isocyanate can be followed by FTIR or by n-dibutylamine titration [41,53]. For the determination of the particle size distributions in the dispersions, dynamic light scattering (DLS) is frequently utilized. The electrolytic stability of dispersions can be determined by placing the PUD in a beaker and slowly adding an aqueous solution of NaCl 2 M by means of a burette until coagulation is observed. The stability can also be assessed by centrifugation of the suspensions, starting from low rpm and repeating the test at increasing speeds, for two minutes in each step until the suspension is seen to sediment [32] or with an assay of 30 min centrifugation at 3000 rpm without observed sedimentation [54]. Additionally, the pH of the polyurethane aqueous dispersions is frequently reported as part of the PUD characterization. The structure of the polymers can be investigated by FTIR and proton nuclear magnetic resonance ($^1\text{H-NMR}$) and the molecular weight and molecular weight distributions of the polyurethane can be obtained by Gel Permeation Chromatography (GPC) [33].

3.1 Viscosity of the PUDs

Considering the potential use as coatings and adhesives, the viscosity of the dispersions is an important property to consider. The application of the thin film (or any processing step, in general) requires a low enough viscosity during the dispersion deposition and spreading onto the substrate, but high enough at rest to prevent dripping. On the other hand, too high viscosities at rest can lead to rough surfaces because of the inability of a highly viscous liquid to smooth the surface level after deposition, which affects the gloss of the surface of the resulting film.

Madbouly et al. [18] presented an interesting study of the rheology of the waterborne PUD (size of the nanodroplets about 30 nm), that investigates the effect of the solid content as well as the temperature on the viscosity and viscoelastic properties of the suspensions. The WBPU was synthesized from castor oil and isophorone diisocyanate, using DMPA as internal emulsifier. The study showed that for dispersions with concentrations below 18 wt.% of the nanodroplets, the complex viscosity of the PUD at room temperature (20°C) followed a Newtonian behavior, but at higher concentrations pseudoplasticity became increasingly more evident and for concentrations above 25 wt.%, it extended to the whole range of shear rates observed. The strong dependency of the viscosity with the concentration was related to the obvious variation in the solids content, but also to the water bound as a thin layer to the surface of the PU particles. A rather interesting observation of the authors was that for the case of bio-PU the size of the PU particles was much smaller than for a similarly prepared synthetic dispersion. Because of the size

reduction, the surface/volume ratio was higher and the surface bounded water was also higher, which led to a lower amount of free water and consequently to a much higher viscosity of the suspensions (about 5 orders of magnitude higher). Fitting the zero shear viscosity to the Krieger–Dougherty equation [55] allowed to find that the concentration at maximum packing corresponded to 35 wt.% in these dispersions. The study of the evolution during drying and heating at temperatures above and close to 60°C showed that there is a “gelation-like” event that occurs via the formation of fractal structures by contact among the PU particles and increasing intermeshing as the process continues.

Pseudoplastic behavior was also reported for PUD prepared from jatropha oil [56]. In that case, the viscosity was also used as a tool to assess the stability of the dispersions for about one and half year after the preparation. A slight increase in the viscosity of the suspensions was considered minor and an acceptable stability was assumed for the intended use of the PUDs.

Fig. 1a shows the example of the viscosity of an a-WBPU based on castor oil and PCL [32]. It illustrates the pseudoplastic behavior also observed by other authors. Fig. 1b (different scale) displays the comparison of the behavior of composite dispersions prepared with the same WBPU and two different concentrations of cellulose nanocrystals (CNC), 5 and 10 wt.%. As expected, the pseudoplastic behavior of the aqueous dispersions was intensified due to the presence of the nanoparticles.

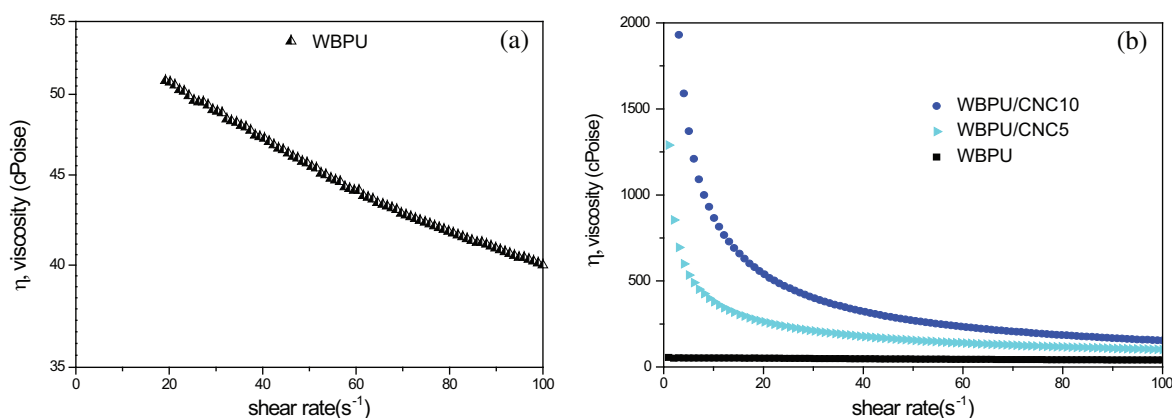


Figure 1: (a) Viscosity vs. shear rate for a-WBPU dispersion based on castor oil and PCL at low solids content (PUD at 15 wt.%), and (b) nanocomposite dispersions prepared from the same WBPU containing CNC (0, 5 and 10 wt.%)

The shear rate dependence of the viscosity has been also expressed according to the Herschel-Bulkley fluid model, which represents a shear-thinning behavior with yield stress. Yong et al. [57] used this model to fit the flow behavior of dispersions of a poly(propylene glycol)-WBPU (PPG-WBPU) containing CO or CO and epoxy resins of high functionality that increased the viscosity of the material. The authors correlated the appearance of a yield stress with the behavior of the applied coating. If the viscosity is too high, the rugosities formed during application do not disappear by the flow of the material and thus, the resulting roughness led to lower gloss of the surface.

The size of the WBPU nanoparticles, their size distribution and the colloidal state, are related to the charged surface, neutralization and certainly, the nature, functionality and reactivity of the chemicals used in the formulation, as well as the solids content have a direct effect on the rheological behavior of the dispersions and in the resulting properties of the dried films. Such rheological behavior has a direct effect on the reproducibility of the performance of these systems.

3.2 Particle Size and Optical Properties of the PUDs

Additionally, for several applications of these WBPU, the optical properties of the PUDs are also important, for example, when transparency is a requirement or when pigments are going to be added to the formulation to achieve a particular colour.

The optical transparency of the dispersion is related to the size of the WBPU particles and to the chemical nature of the reagents used in the synthesis. As indicated in the previous section, if transparency is required, the most frequently used isocyanate is IPDI. On the other hand, the hydrophobicity/hydrophilicity of the biopolyol and the selection of the internal emulsifier are the variables to consider to produce a stable dispersion with small particles [35,36,39,41,44,47].

As an example of this effect, the work of Liang et al. [58] shows that by using different ratios of two bio-based polyols in a blend, it is possible to vary the size of the nanoparticles in the PUD from 615 to 23 nm. As the size of the nanoparticles in the PUD was reduced, the dispersion became more transparent. The resulting films also showed the same trend, which was the result of the effect of the hydroxyl functionality of the polyols and the content of emulsifier.

4 Films from WBPU Dispersions

Generally, the films are prepared by casting of the PUDs into a mould and drying at temperature 30–45°C for 24 h. The characterization techniques used depend on the application for which it was formulated, but the most common are: scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), static contact angle in water or non-polar solvents, dynamic mechanical analysis (DMA), thermal transitions of the samples (DSC), thermal gravimetric analysis (TGA), mechanical testing [57,59]. An interest property is the hydrolysis resistance of the WBPU films, which can be followed during time under controlled environmental conditions by the changes observed in the samples, for example in their mechanical properties [6].

4.1 Mechanical and Thermal Properties of the Dried Films

Tensile tests of self-standing films produced from casting and drying of the PUDs is one of the most frequent methods of characterization reported for these materials. The effect of the biopolyol functionality has been addressed by several authors. Thus, Lu et al. measured and compared tensile mechanical properties of cationic polyurethane films prepared from methoxylated soybean oil polyols [39]. By varying the hydroxyl number of the polyols (135 to 200 mg KOH/g polyol) they were able to change the properties from those of an elastomer when the hydroxyl functionality was low to a plastic behavior at high functionality. Consequently, the Young's modulus was increased from 33.6 MPa to 554 MPa; at the same time the elongation at break was reduced from 291 to 235%. According to their results, the toughness of the materials (as the area under the stress-strain curves) was also largely increased as the hydroxyl functionality increased, from 12.4 MPa (low OH number) to 45.9 MPa (high OH number), which correlated with the increased crosslinked density and hard segment content on these c-WBPUs.

Similarly, Liang et al. [60] prepared a series of c-WBPU synthesized from different bio-based polyols prepared from olive, castor, corn, canola, rice bran, grape seed and linseed oil by thiol-ene photo-click reaction and analyzed the relation between the hydroxyl number of the polyols and the properties of the WBPU. The OH numbers of the polyols increase from 190 to 305 mg KOH/g, depending of the source. As in the previous case, the properties of the WBPU varied from those of a flexible film with an elongation at break of 204%, Young's modulus of 9 MPa (polyol with low OH number) to a hard PU film with Young's modulus of 301 MPa and a low elongation at break of 3% (polyol with high OH number). The toughness of this series of WBPU decreased from 2.22 to 0.17 MPa (increased brittleness) with the increase of the OH number and related cross-linking density. The properties reported depend, among other variables, on the glass transition temperature, T_g , of the materials and as it could be

expected, the T_g was higher in the WBPU formulated with polyols with high OH content as result of the restricted movement of the polymer chains due to the high cross-linked density, and increased hard segment content.

The presence of crystalline phases also affects the mechanical properties of the films, acting as effective crosslinking points and thus stiffening the material. A comparison between two a-WBPU made from a PCL-diol and another one including a bio-based diol, both of similar molecular weight, was used to illustrate this point [32,40]. The PCL based WBPU was amorphous in the conditions of the test, while the bio-polyol rapidly crystallized. While the first one showed elastomeric behavior, the bio-based one showed the behavior of a tough plastic material. Fig. 2 shows this mentioned difference for the neat films described and related microfibrillar cellulose nanocomposites, which will be discussed in Section 5. This structural difference due to the presence of amorphous or crystalline phases in the soft segment region affected also the thermal resistance of the PUs as it can be seen in the Fig. 3, where the biopolyol shows two regions of thermal degradation (seen as two drops of weight loss in the TGA curves and two peaks in the corresponding derivative signals). The first weight loss of the bio-based material appears in the same region that the PCL-based material and the second one occurs in a higher temperature range [32].

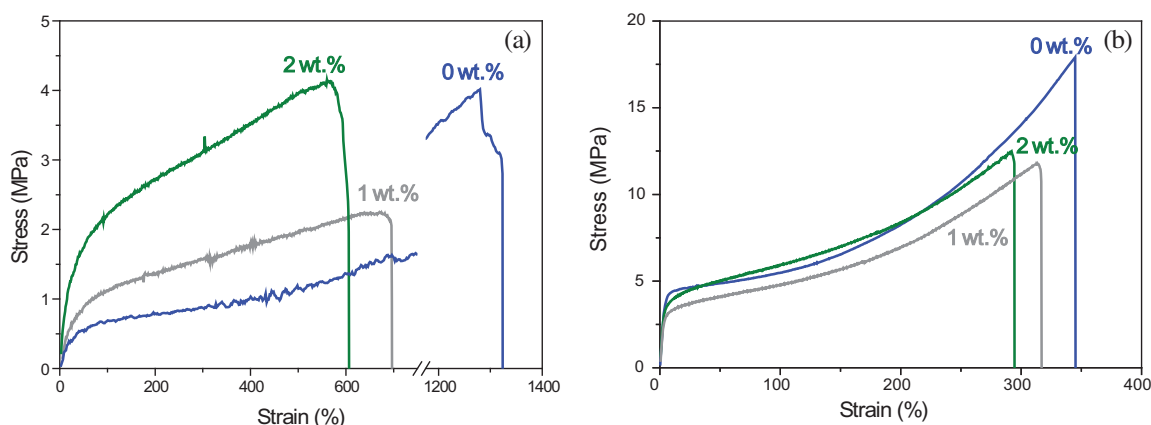


Figure 2: Tensile curves for (a) a series of PCL-based WBPU (WBPU-PCL) and (b) a bio-based diol WBPU series (WBPU-bio based) containing microfibrillar cellulose (MFC) at different concentrations (0, 1 and 2 wt.%)

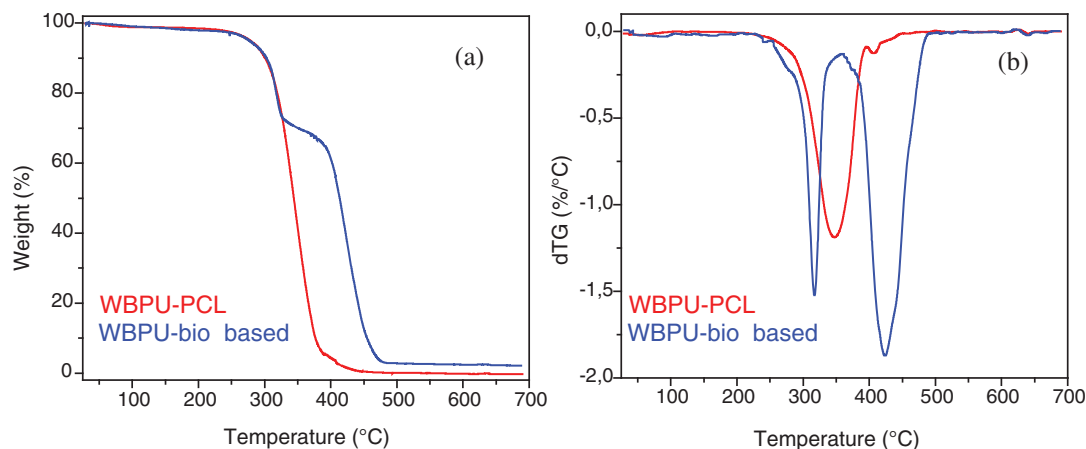


Figure 3: TG (a) and dTG (b) for PCL-based WBPU (WBPU-PCL) and bio-based diol WBPU (WBPU-bio based)

Man et al. [61] developed a series of c-WBPU coatings from a tung oil based polyol, varying the concentration of the polyol in the formulation. They used IPDI as isocyanate source, PEG as chain extender and N-MDEA as internal cationic emulsifier. The increase of the concentration of the tung oil based polyol led to dispersions with larger particle size (the hydrophobicity of the polyol made more difficult the dispersion), higher gel content, lower water absorption and higher surface contact angle. The authors analyzed the adhesion and chemical resistance properties of the cured films. All samples showed strong adhesion to different substrates (glass plate, silica gel, wood and sheet metal) due to the presence of hydrogen bonds in the cured films. They also possessed good chemical resistance, with the films showing no changes after being submerged in tetrahydrofuran or chloroform for 3 days at room temperature. The incorporation of increasing quantities of the tung oil based polyol also greatly affected the mechanical properties of the films, which became more rigid materials. The authors observed that the unsaturations of tung oil (three conjugated double bonds in the eleostearic acid, which is the major fatty acid contained in the oil) are preserved during the preparation of the WBPU. However, after one month of applying the coating essentially all the $-C=C-$ have disappeared due to oxidative polymerization. This reaction is also a reason for the improved mechanical properties of these coatings.

Xia et al. [30] used soybean oil-based amide diol, hexamethylene diisocyanate (HDI) and DMPA as well as d-isosorbide (a diol derived from carbohydrates with a rigid molecular structure) as chain extender and triethylamine (TEA) as counter-ion to prepare a waterborne polyurethane-urea dispersion. The addition of different amounts of isosorbide resulted in increasing glass transition temperature and improved mechanical properties: Young's modulus increased from 2.34 to 63 MPa, tensile strength from 0.69 to 8.15 MPa and tensile toughness from 3.76 MPa to 21.2 MPa when the concentration was increased from 0 to 20 wt.% of isosorbide in the polyol mixture.

Other authors considered the possibility of improving the properties of the final materials by combining the properties of different polymers. For example, Wang et al. [62] prepared anionic PUD from castor oil and 2 dimethyl butanoic acid as internal emulsifier. The authors produced blends with Na alginate that were then casted and dried. Then, all the samples were soaked into $CaCl_2$ (5 wt.% aqueous solution) for 24 hs followed by drying at 60°C for more than 12 hs. The preparation produced films with increased modulus and tensile strength, while the elongation at break decreased. Additionally, surface hydrophobicity and thermal resistance also increased with increased alginate content due to intermolecular H-bonding between alginate and WBPU and the crosslinked network structure generated by calcification in the presence of alginate.

Very recently, Liang et al. [58] worked also with the idea of using polyols blends to tailor final properties. They formulated a bio-based PUDs using castor oil and octahydro-2,5-pentalenediol (OPD) synthesized from naturally occurring citric acid, as the polyol components, dimethylol butanoic acid (DMBA) as the internal emulsifier and isophorone diisocyanate (IPDI). The authors varied the OPD:CO ratio, obtaining from elastomeric to rigid polymers. As ratio was increased from 0:10 to 5:5, the Young's modulus and tensile strength increased from 32.1 MPa to 382.1 MPa and from 9.5 MPa to 22.3 MPa, respectively, and the elongation at break significantly decreased from 192% to 12%, as expected due to the addition of a rigid molecule in the backbone chain of the WBPU.

Combination of PUs with acrylic monomers has also been investigated, as in the work of Lu et al., who prepared latexes of a-WBPU from acrylated epoxydated soybean oil (AESO) and acrylic monomers [63]. The vinyl containing copolymers showed increase of their glass transition temperature and improved thermal stability and mechanical properties (intermediate between those of the acrylic neat polymer and the unmodified WBPU). Depending on the proportion of the acrylic in the latex formulation, the properties could vary from those of soft and tough elastomers to rigid and tough plastics.

Analogously to previous results reported by Lu et al. [39,63], the results from the work of Zhang et al. [64] confirmed the effect of crosslinking on the structure of WBPU particles and the resulting films. In this

case, the authors prepared an a-WBPU based on castor oil and a polycarbonate diol, but they added to the formulation, a small percentage of 2 amino 2-(hydroxymethyl) 1,3 propanediol as crosslinker, which lead to the increase of the particle size from 50.28 nm to 124.4 nm (0 and 1.5% of the crosslinker in the hard segments, respectively) with the dispersions being stable over time. Related to the changes introduced in the formulations, the properties of the films were also affected, resulting in: increased glass transition temperature and tensile strength and reduced elongation at break, improved thermal stability and increased surface hydrophobicity.

Modification of the crosslinking density as a means of improving properties was also considered by Xia et al. [65], who prepared an a-PUD from castor oil, which was self-crosslinked by the addition of aziridine (a curing agent) that reacted with carboxylate groups of the DMPA present in the WBPU as internal emulsifier. As reported by other authors, the Young's modulus and tensile strength were increased (from 14.5 to 125 MPa and from 13.1 to 18.1 MPa, respectively) with the addition of the aziridine varying from 0 to the stoichiometric ratio of aziridine to carboxylate groups.

5 Nanocomposite Formulations

Addition of organic and inorganic filler particles to WBPU dispersions has been investigated in order to improve the final properties of the films. The ones more frequently considered have been: silica to increase hardness, nanoclays to modify thermal and barrier properties, silver to improve microbiological resistance and nanocellulose to improve mechanical properties and thermal stability without reducing the percentage of bio-based components and to take advantage of the well-known compatibility of polyurethanes and cellulose. Compatibility polymer-filler is highly important in the formulation of composite dispersions. Besides, when the polymer and the particles can be dispersed in the same medium the preparation of the nanocomposite dispersions is greatly facilitated [34,46,66–68].

Xia et al. [69] prepared a typical a-WBPU from castor oil, but after neutralization they added 3-aminopropyltriethoxy silane (APTES), which co-reacted with the remaining isocyanate. Water and strong stirring led to the formation of aqueous dispersions prepared with different amounts of silica (0 to 2 wt.% of the Si element per total solids). As it could be expected, the addition of the inorganic rigid nanoparticles improved the thermal resistance as well as the mechanical properties of the films: Young's modulus increased from 32 MPa to 116 MPa, tensile strength from 15 to 20 MPa, while elongation at break was reduced from 379 to 91% and tensile toughness from 31 to 11 MPa.

Fu et al. [70] developed a bio-based WPU organic-inorganic hybrid material by chemically incorporating nano-silica in the structure of the polyurethane. Castor oil was used as bio precursor of a thiol-ene coupling reaction in order to obtain an alkoxy silane castor oil and a carboxyl castor oil, to develop finally a castor oil-based polyurethane/silica (SiWPU) nanocomposite. Nanocomposite suspensions exhibited an apparent core shell structure because the nano-silica was encapsulated by WBPU. As the silica content increased, so it did the hydrophobicity and thermal stability of the nanocomposite films. Additionally, the roughness of the films also increased as assessed by AFM.

The effects of the addition of nanoclays through in situ polymerization to a jatropha oil-based WBPU were investigated [71]. The oil derived polyol was prepared by epoxidation and ring opening, achieving an OH number of 184 mg KOH/g polyol. The authors prepared an a-WBPU using dimethylolbutanoic acid (DMBA) as internal emulsifier. They used montmorillonite (MT), halloysite nanotubes (FT) and attapulgite (AT) at concentrations of 2 wt.% in the PU, as well as the nanoclays modified with APTES. The incorporation of the nanoclays improved the surface roughness and hydrophobicity of the nanocomposite films prepared. Due to its layered structure and good dispersion in the WBPU, the modified MT proved to be the best clay for improving the thermal stability of the material, thus, acting as a heat insulator. The T_g of the PUs was also increased because of the additional H bonding and the

confinement of the polymer chains. These changes had a correlation with the improved mechanical properties found in the composites.

Panda et al. [72] also prepared composites with a nanoclay. For this study, they obtained a castor oil-based a-WBPU and used organically modified nanoclay cloisite as a filler. The nanoclay was added after the synthesis of the WBPU, and it was observed that the filler participated in hydrogen bond formation with the PU, affecting the films properties. Incorporation of 3 wt.% of clay increased the Young's modulus from 19.7 MPa to 108.1 MPa and the tensile strength from 11.3 MPa to 20.8 MPa in comparison to the neat film.

The addition of silver nanoparticles to the formulation of WBPU was considered in order to incorporate antibacterial properties to the material. For example, Fu et al. [53] synthesized a series of antibacterial castor oil based WBPU by modification of silver nanoparticles. The nanofiller were silver-halloysite nanoparticles (Ag-HNT), that could be well dispersed in the WBPU. As in the case of other inorganic fillers addition, the films showed improved mechanical and thermal properties.

Gao et al. [68] presented results on WBPU based on castor oil and polyethylene glycol filled with eucalyptus CNC. Because of the good compatibility between polyurethane and cellulose, the distribution of the CNC was uniform. On the other hand, the size polydispersion of the CNC was very wide in this work, although the aspect ratio (L/D) was in the order of 23. The high aspect ratio, good compatibility and uniform distribution led to a large improvement on the mechanical properties of the elastomeric polyurethane (4 wt.% addition of CNC resulted in a value of the Young modulus of more than four times higher that of the PU, while the addition of just 1 wt.% of CNC led to a value of tensile strength more than twice the value measured for the neat polymer). The occurrence of a maximum in the mechanical properties as the CNC concentration was varied was explained by the formation of agglomerates as the concentration increases above a critical value related to the percolation threshold. In this particular case, the matrix was a segmented PU and interestingly, there was very little reduction of the tensile elongation at break, which was related to the formation of H-bonding mainly between the nanoparticles and the hard segments of the nanocomposite films, thus little affecting the stretching of the soft segments of the PUs.

Because of the small size of the WBPU particles in the aqueous dispersions and the nanosize of the organic or inorganic particles added to the nanocomposite formulations, the films usually remain transparent or slightly translucent. Fig. 4 illustrates this point by showing a film made from a neat castor oil-based a-WBPU and two composite films containing 5 and 10 wt.% of CNC [32].

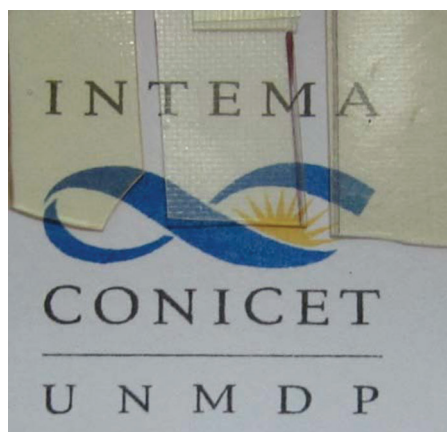


Figure 4: Digital photography of castor oil-based a-WBPU films containing 0, 5 and 10 wt.% of CNC (left to right)

Other nanocomposites were also obtained from an a-WBPU prepared from a castor oil-based macrodiol (poly(2,2-dimethylpropylene sebacate) diol with 70% of carbon coming from renewable sources, and OH number of 80 mg KOH/g) [34]. Hexamethylene diisocyanate (HDI) was the isocyanate monomer and CNCs from sisal were the nanoparticles used to provide nanoreinforcement to the PU. These materials showed the classical result observed when rigid particles are added to a polymeric composite: increased Young's modulus and decreased strain at break, although even at the highest concentration the material was very extensible. The stress at break depends on the larger stress supported by the composites and the lower elongations at break (compared with the neat polymer) and in this case, it was affected mostly by the elongation at break (Fig. 5). Overall the stress at break decreased from 11.66 MPa to 7.21 MPa, for the neat and the 5 wt.% CNC-composite, respectively [34].

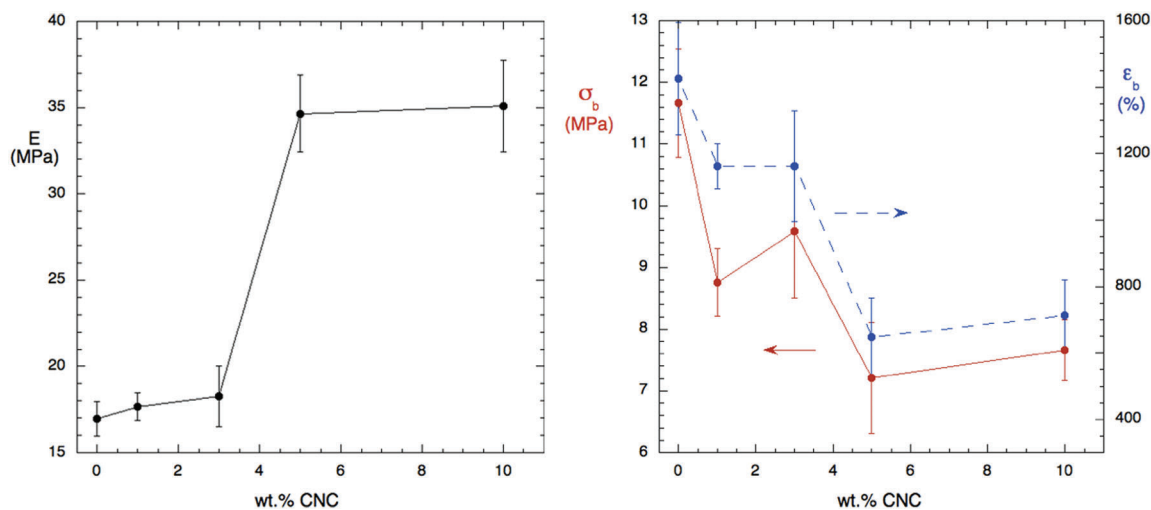


Figure 5: Effect of the addition of CNC on the tensile properties of an a-WBPU

The Fig. 5 also shows that for this system, percolation appears between 3 and 5wt.% (where a large and drastic increase of the modulus is seen).

Similar observations (increase of the modulus and decrease of the elongation at break) can be inferred from Fig. 2 that included microfibrillar cellulose (MFC) nanocomposites, in that particular case comparing an a-WBPU based on PCL and another one bio-based. The authors demonstrated that in their case interactions filler-matrix were more intense in the case of the PCL based materials and thus, the properties were correspondingly more dependent on the MFC addition in that series of nanocomposites [40].

6 Applications

The selection and optimization of the WBPU for their final applications require of specific characterizations depending on the intended use. Some of those applications and particular characterization methods are reported in this section.

6.1 Coatings

As already mentioned, WBPU are growingly being considered as a valuable green alternative to solvent based systems and so, they are particularly appreciated for coating formulations. Besides general characterizations, such as the viscosity of the PUDs and the mechanical and thermal properties of the films, the application of coatings also rely on the knowledge of the minimum film forming temperature (MFFT) and the T_g of the materials. The first one must be lower than the temperature of drying, for the

film to be formed. Actually, the transition from opaque to transparent/clear is taken as a measure of the complete coalescence of the suspended particles. On the other hand, the T_g must be low enough to allow for the coalescence of the particles, but high enough to obtain adequate hardness and toughness of the film [73].

In many cases, additional means of curing have been considered such as blending or copolymerization of the WBPU in order to tailor mechanical properties, hardness, thermal and chemical resistance as well as gloss. For similar reasons, some nanocomposite formulations have also been considered.

Patel et al. [74] prepared PUD from cardanol that was further crosslinked by autooxidation at room temperature, and was proposed as a good candidate for the formulation of industrial protective primers. Cardanol is a phenolic lipid and the main component of cashew nutshell liquid, it has a highly unsaturated chain attached to a phenolic ring. The authors prepared an anionic PUD from an epoxy derivative of the oil with a ~36 wt.% solids content and average particle size of 61.5 nm, that was visually translucent. The effect of adding an oxidative catalyst drier was investigated with the coatings being dried for about a week before testing. Oxidative crosslinking showed to increase significantly the hardness and solvent resistance, while reducing the water uptake of the coating films. It also resulted in an improved barrier behavior during exposure to the action of a NaCl solution. The corrosion resistance of the coating applied onto a steel substrate was also studied by using electrochemical impedance spectroscopy and the results showed again the beneficial effect of the oxidative crosslinking.

Mishra et al. [75] prepared an a-WBPU based on castor oil, endcapping the excess isocyanate with HEMA and neutralizing later with TEA before adding water under vigorous stirring. Hydroquinone was added to inhibit the reaction of the $-C=C-$ during synthesis and storage and acetone was evaporated after preparation. The UV formulations were mixed with reactive diluents at constant weight ratio (50:50) consisting in different acrylate monomers. They were prepared as self-standing films and also applied onto glass, wood and mild steel to be cured later on, by UV irradiation. After UV curing, the crosslinking density increased, which resulted in higher thermal stability, higher tensile strength and reduced elongation at break. All coatings showed good resistance to salt water and acid solutions, although were slightly more affected by alkaline solutions. They also showed improved behavior in rubbing test (more than 100 passes with MEK). According to the authors, because of the presence of the castor oil chains in the PU, the water resistance of all the formulations was good compared to the traditional WBPU (2.65 wt.% water absorption for the trimethylol propane triacrylate crosslinked sample). Samples prepared with this particular monomer also showed increased pencil and scratch hardness and lower impact resistance.

Recently, Cakić et al. [76] developed a series of WBPU based on a castor oil-based polyol prepared by transesterification with an oligoester obtained by glycolysis of recycled PET. The a-WBPU was prepared and then reacted with APTES, which formed nanosilica particles (silicon content in the composite solid fraction: 0.5 to 2 wt.%) by an in-situ sol gel process. The hybrid WBPU composites showed an increase in thermal stability with increasing silica concentration, because of the strong network structure that was formed between PU and nanofiller (good compatibility) as assessed by SEM. Optical clarity was obtained at low silica concentration, while rigidity/stiffness increased with increased filler addition. However, the gloss of the samples decreased by increasing the crosslinking and nanofiller content, probably because of the high viscosity that may have been reached in these systems, as it was discussed in previous sections. In spite of this, the values of gloss and adherence were acceptable for coating applications.

Coating obtained from a cottonseed oil-based phosphorylated polyol a-WBPU, which also contained silica nanoparticles formed by in situ formation with co-reacted APTES, led to increased Young's modulus and tensile strength [29]. On the other hand, potentiodynamic polarization studies showed the beneficial effects of the siloxane cross-link density on the corrosion protection of the developed coatings (3.5 wt.% NaCl solution at room temperature). It was reported that the corrosion protection performance depended of the combination of different effects: the barrier properties of the siloxane cross-linking

network and the strong chemical bonding between the substrate and the phosphoryl groups present in the modified cottonseed oil polyol, which resulted in the good corrosion protection observed.

Improved corrosion protection was also reported in the work of Liang et al. [58] due to the modified chemical structure of the a-WBPU in which a rigid molecule (OPD) was incorporated. The formation of a complex cross-linked network due to the cyclic rings of the OPD, which restricts the penetration of corrosive species, was the explanation offered for the improved performance.

Nanoclays have also been used to increase the hardness of coating films. Panda et al. [72] showed that the incorporation of nanoclay improves the hardness of WBPU nanocomposites, from 3B to 4H for a castor oil-based a-WBPU loaded with 0 and 3 wt.% cloisite, respectively. Abrasion resistance also was improved by the addition of the filler, the weight loss per 1000 cycle reduced from 9 mg to 4 mg for neat WBPU and the composite with 3 wt.% of nanoclay, due to the strong interfacial interaction between the well dispersed clay and the polyurethane surrounding the particles.

The surface hydrophobicity of a wood coating was increased by the use of a jatropha oil-based polyol with different OH numbers ranging (138 to 217 mgKOH/g) [77]. As the OH number was increased, the percentage of hard segments increased and the hydrophobicity increased. Thereby, the water contact angle increased significantly from 66° to 90° for WBPUs having 34.2% and 45.0% of hard segment content, respectively.

An interesting work was presented by Zhang et al. [78] in which a castor oil based WBPU was mixed with sodium lignosulfonate (NaLS) in order to develop a composite with UV absorption capacity. Mechanical properties, thermal stability, thermo-physical performance and hydrophobicity were improved by addition of the NaLS, due to: increasing crosslink density and consequent decreased free volume, stronger interfacial interactions between filler and PU matrix, nano-enhancement of sodium lignosulfonate and the contribution of the presence of strong hydrophobic groups from the NaLS. This material was shown to be suitable for UV absorption coatings and sunscreen creams, and this was corroborated by optical absorbance measured by UV/visible spectrophotometry, offering a complete barrier for 280-320 nm. The transmittance of visible and ultraviolet light could be regulated by controlling the content of NaLS.

6.2 Adhesives

Traditionally, PUs have developed a well-earned reputation of high performance as adhesives, in particular as wood adhesives. The strength of such adhesion can be traced back to the formation of covalent bonding to the substrate, van der Waals forces and hydrogen bonding as well as mechanical interlocking [5]. Polyurethanes have a long history as adhesives, but with the revival of bio-based chemicals, they have become an active field of research and innovation, because of the interest in replacing petroleum based chemicals and the necessity of reducing environmental impact, while keeping low cost and biodegradability. In particular, vegetable oils (palm, linseed, tung, castor, jatropha, soybean oils, etc.) have been considered as sources for the synthesis of polyols to formulate adhesives more environmentally amiable.

Different methods have been considered to improve the low water resistance of adhesives made from soy protein isolates (SPI) including the addition of WBPUs, and in some cases using PUD from synthetic sources [79]. The improvement obtained in the mechanical behavior in dry and wet states, prompted other researchers to investigate the effect of using bio-WBPU. Thus, Liu et al. [80] studied a bio WBPU derived from soy oil to improve the wet strength of a soy protein adhesive. Although soy protein adhesives are more ecofriendly than phenolic ones and so they have been considered as potential replacements, their poor water resistance is a disadvantage. The goal of these authors was to modify the hydrophilic nature of the proteins that leads to low wet strength, by mixing them with soy oil-based WBPU and developing covalent and non-covalent bonds that lead to the increase of the adhesive's water resistance. An optimum concentration of about 50% WBPU was observed, at which the surface became

more hydrophobic, showing also better water resistance, higher viscosity (although still with good flowability during application). Additionally, at this concentration the wet adhesion strength onto wood was also good, being ~ 3.8 MPa, a clear improvement over the slightly above 2 MPa measured for the neat SPI adhesive. The improvement was explained by the good penetration and developed adhesion of the small molecules of the protein to wood and the beneficial effect of the PUs preventing the penetration of water in the interphase region between the adhesive and wood. All the tests showed cohesive failure of the adhered surfaces.

6.3 Textile Ink Binders and Synthetic Leather Finishings

The glossy-matte characteristics of finishing could be tailored in PPG-WBPU prepared using castor oil (CO) in a proportion below 5 wt.% and adding multifunctional epoxy resins into the formulation [57]. While the film containing CO showed a rather smooth and glossy surface, the ones that included epoxy resins presented higher nanoroughness on the surface, which led to low-gloss films. Actually, PUDs purposely prepared to perform as matte surfaces are preferred for applications in the vehicle interior parts or in leather surfaces [57].

UV-curable WBPU based on PCL and AESO were reported to form stable dispersions up to 10 wt.% content of AESO with a transparent bluish aspect, while higher contents of the oil-derived component produced translucent and slightly yellow dispersions with some micro-precipitation [35]. Increased hydrophobicity was also reported and further demonstrated by the reduction of water absorption (from 21.73 % to 8.49% at 0 and 20% AESO) and the change of the contact angle using water as the probe liquid (from 65.26 to 91.04°, also for 0–20% AESO). Both effects were the result of the hydrophobicity of the oil chains and the increased crosslinking density obtained during the UV-curing. The authors also verified that the strength color on printed fabrics (measured at the wavelength 520 nm) increased with the increase of AESO in the formulation, and so it did the fastness, although these benefits were not as important for concentrations above 10 wt.%. High concentrations of AESO in the formulations lead to reduced strength of the color with respect to the other oil-derived containing formulations because of high crosslinking on this particular sample resulted in microphase separation and consequently reduced cohesive strength of the WBPU and weaker adhesion.

6.4 Antibacterial Properties

Another important property for some coating applications is the biocide capacity that can offer protection against microorganisms to different solid substrates. Liang et al. [10] studied the biocide capacity of films prepared from a castor oil based c-WBPU. As it might be expected the films showed enhanced antibacterial activity when the content of the cation-center molecule, N-MDEA, was increased, but also when the polyol functionality was lowered. The activity was proven to be effective against *Vibrio parahaemolyticus*, but rarely so against *Listeria monocytogenes*.

Recently, Man et al. [61] also developed a series of c-WBPU coatings from a tung oil based polyol, and in this case they varied the OH content of the polyol. Also, they analyze the adhesion and chemical resistance properties of the cured films. All samples showed strong adhesion to different substrates (glass plate, silica gel, wood and sheet metal) due to the presence of hydrogen bonds in the cured films. They also possessed good chemical resistance, with the films showing no changes after being submerged in tetrahydrofuran or chloroform for 3 days at room temperature. They found that all WBPU formulations exhibit inhibition effect toward *Escherichia coli* and *Staphylococcus aureus* due to the quaternary ammonium groups from the structure of the polyurethanes.

A castor oil-based WBPU containing silver-halloysite nanoparticles presented also antibacterial properties [53]. A sample containing a small amount of silver, only 0.351 wt.%, presented an antibacterial ratio for *Escherichia coli* and *Staphylococcus aureus* of 99.99 and 91.82, respectively.

An interesting approach in the use of WBPU in the field of antibacterial materials is as supporting surface. Liu and co-workers [81], developed a coating using UV-curable castor oil-based c-WBPU-acrylate dispersion (PUA) with a modified lysozyme. UV curing at room temperature was used to avoid denaturing the enzymes, and producing a covalent bond between the enzyme and the WBPU-acrylate. Thus, the lysozyme was fixed and the bacterial killing efficiency of the coating remained at 68.3% after six continuous uses. On the other hand, due to the interaction between ammonium cations in the PUA molecular chain and the bacterial cells, the neat coating without enzymes also showed a killing efficiency of 23.1% and 35.5% for *S. aureus* and *E. coli*, respectively. The killing efficiency increased up to 91.3% for *S. aureus* and 62.9% for *E. coli* when enzyme content was 2.5 wt.%.

7 Final Comments

The aim of this review was to illustrate, with several representative examples, the many contributions in the open literature to the development of vegetable oil-based waterborne polyurethanes. It is clear that important advantages are obtained by using this type of materials: the reduction of the release of organic volatiles during the application and the reduction of the dependence on non-renewable sources, in addition to the well-known versatility of polyurethanes, which allows to make contributions to widely different fields of application. In this article, some of the most frequent applications were reviewed: coatings, adhesives, binders, and surface modifiers.

The use of vegetable oils as source of polyols for WBPU is a relatively recent field of work, but undoubtedly one of very rapid growth. This is not surprising because during the last years, vegetable oils have consolidated their position as renewable, valuable, viable and competitive source of raw materials for the production of monomers and polymers. The present work has shown the important role of the polyols on the final properties of the dispersions and the resulting films. They are the main component used to tailor the PUDs, the one offering the greatest possibilities for this task. Nature itself offers many different plant oils with different chemical structures, while organic synthesis adds many different routes of chemical modification that expands the offer of different reagents to be used in the synthesis of polyurethanes: epoxidation, ring opening, hydroxylation, grafting by reaction of double bonds (attaching moieties with different functional groups), transesterification, etc.

The supply of isocyanate containing molecules is more limited, since essentially, only aliphatic molecules are considered, due to their better behavior in aqueous media (as compared to aromatic isocyanates) and to the transparency of the produced materials, which is a requirement for several applications. Similarly, there are not many options for the selection of the ionic diols used in these formulations, but some have been proposed including bio-based molecules and their chemical modifications. The possibility of not using ionic emulsifiers has also been considered, but prolonged stability of the resulting dispersions is still a challenge.

Finally, examples have been presented of the multiple possibilities of combining the WBPU formulations with other polymers and nanoparticles, widening even more the range of possible applications and largely improving, in a rather simple way, their final properties.

It is only to be expected that the development of these materials continues witnessing a growth in the number of alternative and new formulations as well as applications. The tailoring of specific materials fitting specific needs is extremely interesting and these ecofriendly polymers will be able to meet those needs, judging from the steadily growing number of contributions to the field.

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