Electronic Thesis and Dissertation Repository

8-24-2017 1:30 PM

Effects of lignin as a stabilizer or antioxidant in polyolefins

Afsana S. Kabir
The University of Western Ontario

Supervisor
Dr. Chunbao (Charles) Xu
The University of Western Ontario Joint Supervisor
Dr. Takashi Kuboki
The University of Western Ontario

Follow this and additional works at: https://ir.lib.uwo.ca/etd

⊙ Part of the Chemical Engineering Commons, and the Polymer and Organic Materials Commons

Abstract

Lignin, a major component of biomass, is an attractive alternative to hindered phenol-based antioxidants for polymers due to its renewable nature and naturally occurring hindered phenolic structure. In this study, for the first time, lignin de-polymerization was explored as a promising approach to improve the reactivity of the lignin-based antioxidants for polymers (polyethylene, PE and polypropylene, PP). A proprietary hydrolytic de-polymerization process was utilized to increase the antioxidant activity of two types of technical lignin: kraft lignin, KL (a by-product from the pulp and paper industry) and hydrolysis lignin, HL (a by-product from the pre-treatment processes in cellulosic ethanol plants). The de-polymerized lignins had up to five times more antioxidant activity compared to the crude lignins, a result of their higher phenolic content, improved hydrophobicity, and lower molecular weight. The results also revealed that the addition of 2.5 wt% DKL or 5 wt% DHL attained the same level of antioxidant activity as the addition of 0.5 wt% commercial antioxidant. Owing to the lower price of DKL or DHL compared with that of the commercial antioxidant or the neat PE, the addition of the larger amount of DKL and DHL did not increase the cost of the PE blends. Instead, the material cost of a PE blend that contains a larger amount of DKL (2.5 wt%) or DHL (5 wt%) is actually lower than that of a PE blend with a smaller amount of commercial antioxidant (0.5 wt%).

Keywords

Co-Authorship Statement

Chapter 3: De-polymerization of crude lignins to improve the thermo-oxidative stability of polyolefins

Authors: Afsana S. Kabir, Zhongshun Yuan, Takashi Kuboki, and Chunbao (Charles) Xu

Status: Ready for submission to a journal, such as Journal of Materials Science.

Experimental work and data analysis were performed by Afsana S. Kabir. Chunbao (Charles) Xu, Takashi Kuboki, and Zhongshun Yuan also provided consultation regarding experimental work and interpretation of results. The manuscript was written and revised by Afsana S. Kabir, and reviewed by Chunbao (Charles) Xu, Takashi Kuboki, and Zhongshun Yuan.

Chapter 4: Effects of de-polymerized lignin content on thermo-oxidative stability of polyethylene

Authors: Afsana S. Kabir, Zhongshun Yuan, Takashi Kuboki, and Chunbao (Charles) Xu
Status: Ready for submission to a journal, such as Polymer Degradation and Stability.

Experimental work and data analysis were performed by Afsana S. Kabir. Chunbao (Charles) Xu, Takashi Kuboki, and Zhongshun Yuan also provided consultation regarding experimental work and interpretation of results. The manuscript was written and revised by Afsana S. Kabir, and reviewed by Chunbao (Charles) Xu, Takashi Kuboki, and Zhongshun Yuan.

Acknowledgments

Table of Contents

List of Tables

List of Figures

List of Schemes

Chapter 1

1 Introduction

1.1 Background

The growing interest in researching lignin as a potential source for biofuels and bio-chemicals is driven by multiple factors: 1) the abundance of lignin, 2) absence of competition between food and fuel, and 3) recent legislations and mandates promoting a green economy. Lignin, one of the primary constituents of plant cell walls, constitutes about 10-40 wt% of plant biomass [1,2]. The pulp and paper mills are the largest commercial source of lignin in the form of kraft lignin in "black liquor". As of 2013, the global production of kraft lignin was approximately 50 million tons per annum, most of which is used as a low-value fuel, with less than 5% of it being utilized as chemicals or other products [3]. According to the estimate by Ragauskas et al., the second generation of biorefineries will produce additional 62 million tons of lignin annually, which is a 60% surplus after meeting the refineries' internal energy requirement [4].

The depletion of fossil fuels and increasing concern about climate changes have motivated the governments to initiate mandates towards having a carbon neutral green economy. The U.S. Department of Agriculture and U.S. Department of Energy have aimed to derive 20% of transportation fuels and 25% of U.S. chemical commodities from biomass by 2030 [5]. Similarly, in Europe, the Dutch Ministry of Economic Affairs have set ambitious goals to substitute 30% of transportation fuels by biofuel and 20-45% of fossil-based raw materials by biomass-based chemicals by 2040 [5]. As a result, there is an up-and-coming need to develop value-added bio-products from lignin.

Lignin is the largest renewable resource for aromatic compounds [4]. It is an amorphous polymer of three main phenyl propanoid units, i.e., p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, derived from p-coumaryl, coniferyl and sinapyl alcohols [6,7]. The bonding pattern in lignin is dominated by ether linkages (45-50% β-O-4 and 6-8% α-O-

4); the rest being β-5, β-β, 5-5 and such linkages [6,7]. Due to its high aliphatic hydroxyl, aromatic hydroxyl and carboxyl content, lignin has been researched as an alternative to commercial reactants in the production of polyurethane foam, phenolic adhesive, epoxy resins and adipic acid [8–11].

Antioxidants being exploited are the additives for retarding oxidation or bio- or photo-degradation of polymer blends. They are commonly synthetic compounds in hindered phenolic structure. Exploiting renewable antioxidant from natural sources have been extensively investigated. For instance, renewable and sustainable lignocellulosic materials, such as agricultural residues, forestry, and industrial wastes, represent an attractive source of antioxidants compounds owing to their content of lignin in polyphenolic structure. A number of studies have suggested that lignin could be a promising resource for bio-based antioxidants due to its structural similarity with the commercial hindered phenolic antioxidants widely used in polymer stabilization [12–15].

Lignin as a bio-antioxidant has attracted lots of attention for providing resistance against thermo-oxidative degradation and photodegradation in polyolefins. Many past studies [16–27] researched on the addition of lignin in polyolefins, where the lignins used were mainly extracted from plants using organic solvents or steam explosion, or might have been modified using esterification or grafting techniques to improve their compatibility with the polymer matrix. Whereas, esterification decreases the phenolic content of lignin and grafting adds additional cost to the process. There is a scarcity of literature addressing the effect of adding technical lignin (i.e., kraft lignin from pulp and paper mills and hydrolysis lignin from biorefineries) in polyolefins. Moreover, since the phenyl propanoid units in lignin are connected by ether linkages, the breakdown of these ether linkages could increase the phenol content, thus potentially improving the antioxidant property.

Past researches, comparing the antioxidant activity of lignin from various sources, indicated that the antioxidant activity of the lignin increased with decreasing molecular weight and increasing phenol content [28,29]. To the best of our knowledge, effects of

depolymerized technical lignin as a thermo-oxidative stabilizer in polyolefins, are yet to be explored. Hence, this thesis aims at researching the prospect of depolymerized lignin as an antioxidant in polyolefins.

1.2   Thesis Objectives

The overall objective of this thesis project is to research the prospect of depolymerized lignin as an antioxidant in polyolefins. Specifically, this thesis work aimed to:

i.   Investigate the effects of 5 wt% addition of commercial kraft lignin (KL) and hydrolytic lignin (HL) on thermo-oxidative stability of polyolefins (polypropylene and polyethylene);

ii.   Explore the effects of 5 wt% addition of hydrolytically de-polymerized lignins on thermo-oxidative stability of polyolefins (polypropylene and polyethylene);

iii.   Examine the impact of varying contents of de-polymerized kraft lignin (DKL) and de-polymerized hydrolysis lignin (DHL) in polyethylene on its thermo-oxidative stability;

1.3   Thesis Structure

This thesis consists of five chapters organized in the following manner:

Chapter 1 briefly describes the motivation behind academic and industrial interest in researching lignin as a potential source of bio-based chemical and the scientific background behind how lignin performs as an antioxidant. Finally, the research objectives and thesis structure are outlined.

Chapter 2 provides a detailed literature review related to polymer degradation and lignin. In this chapter, the importance of antioxidant, the mechanism of polymer degradation and stabilization, how lignin fits into the growing market for the antioxidant and bioeconomy, and previous studies on lignin as a bio-based chemical, especially in polyolefins are discussed.

Chapter 3 compares the effects of hydrolytic depolymerization of both KL and HL on the thermo-oxidative performance of polyethylene and polypropylene with 5 wt% addition of KL, DKL, HL and DHL. The thermo-oxidative stabilization of the resulted polymer blends was evaluated in terms of oxidation induction Time, DSC activation energy and TGA thermal degradation behavior.

Chapter 4 analyzes the effect of different level of DKL and DHL in Polyethylene to find what cost-effective optimum percent of DKL and DHL can give the same level of performance of 0.5 wt% of commercial antioxidant.

Chapter 5 presents the overall conclusions of the thesis work and recommendations for future studies.

1.4   References

[1]   P. Harmsen, W. Huijgen, L. López, R. Bakker, Literature Review of Physical and Chemical Pretreatment Processes for Lignocellulosic Biomass, Food Biobased Res. (2010) 1–49. http://www.ecn.nl/docs/library/report/2010/e10013.pdf.

[2]   Y. Sun, J. Cheng, Hydrolysis of lignocellulosic materials for ethanol production : a review q, Bioresour. Technol. 83 (2002) 1–11. doi:10.1016/S0960-8524(01)00212-7.

[3]   S. Laurichesse, L. Avérous, Chemical modification of lignins: Towards biobased polymers, Prog. Polym. Sci. 39 (2014) 1266–1290. doi:10.1016/j.progpolymsci.2013.11.004.

[4]   A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R. a Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T.J. Tschaplinski, G. a Tuskan, C.E. Wyman, Lignin valorization: improving lignin processing in the biorefinery., Science. 344 (2014) 1246843. doi:10.1126/science.1246843.

[5]   J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, The catalytic valorization of lignin for the production of renewable chemicals, Chem. Rev. 110 (2010) 3552–3599. doi:10.1021/cr900354u.

[6]   C. Xu, R. Arneil, D. Arancon, J. Labidi, R. Luque, Lignin depolymerisation strategies: towards valuable chemicals and fuels, Chem. Soc. Rev. Chem. Soc. Rev. 43 (2014) 7485–7500. doi:10.1039/c4cs00235k.

[7]   F.S. Chakar, A.J. Ragauskas, Review of current and future softwood kraft lignin process chemistry, Ind. Crops Prod. 20 (2004) 131–141. doi:10.1016/j.indcrop.2004.04.016.

[8]   S. Huang, N. Mahmood, M. Tymchyshyn, Z. Yuan, C.C. Xu, Reductive de-polymerization of kraft lignin for chemicals and fuels using formic acid as an in-situ hydrogen source, Bioresour. Technol. 171 (2014) 95–102. doi:10.1016/j.biortech.2014.08.045.

[9]   N. Mahmood, Z. Yuan, J. Schmidt, C. Xu, Preparation of bio-based rigid polyurethane foam using hydrolytically depolymerized Kraft lignin via direct replacement or oxypropylation, Eur. Polym. J. 68 (2015) 1–9. doi:10.1016/j.eurpolymj.2015.04.030.

[10]   F. Ferdosian, Z.S. Yuan, M. Anderson, C. (Charles) Xu, Synthesis of lignin-based epoxy resins: optimization of reaction parameters using response surface methodology, RSC Adv. 4 (2014) 31745. doi:10.1039/C4RA03978E.

[11]   D.R. Vardon, M.A. Franden, C.W. Johnson, E.M. Karp, M.T. Guarnieri, J.G. Linger, M.J. Salm, T.J. Strathmann, G.T. Beckham, Adipic acid production from lignin, Energy Environ. Sci. 8 (2015) 617–628. doi:10.1039/C4EE03230F.

[12]   A. García, A. Toledano, M.Á. Andrés, J. Labidi, Study of the antioxidant capacity of Miscanthus sinensis lignins, Process Biochem. 45 (2010) 935–940. doi:10.1016/j.procbio.2010.02.015.

[13]	I. Egüés, C. Sanchez, I. Mondragon, J. Labidi, Antioxidant activity of phenolic compounds obtained by autohydrolysis of corn residues, Ind. Crops Prod. 36 (2012) 164–171. doi:10.1016/j.indcrop.2011.08.017.

[14]	Q. Lu, W. Liu, L. Yang, Y. Zu, B. Zu, M. Zhu, Y. Zhang, X. Zhang, R. Zhang, Z. Sun, J. Huang, X. Zhang, W. Li, Investigation of the effects of different organosolv pulping methods on antioxidant capacity and extraction efficiency of lignin, Food Chem. 131 (2012) 313–317. doi:10.1016/j.foodchem.2011.07.116.

[15]	T. Dizhbite, G. Telysheva, V. Jurkjane, U. Viesturs, Characterization of the radical scavenging activity of lignins - Natural antioxidants, Bioresour. Technol. 95 (2004) 309–317. doi:10.1016/j.biortech.2004.02.024.

[16]	C.A. Johnson, P.J. Szalay, Method of improving heat stability of vinyl chloride polymers US 3484397 A ABSTRACT available in, (n.d.) 4–7.

[17]	K. Levon, J. Huhtala, B. Malm, J.J. Lindberg, Improvement of the thermal stabilization of polyethylene with lignosulphonate, Polymer (Guildf). 28 (1987) 745–750. doi:10.1016/0032-3861(87)90223-0.

[18]	P. Alexy, B. Košíková, G. Podstránska, The effect of blending lignin with polyethylene and polypropylene on physical properties, Polymer (Guildf). 41 (2000) 4901–4908. doi:10.1016/S0032-3861(99)00714-4.

[19]	R. Pucciariello, V. Villani, C. Bonini, M. D'Auria, T. Vetere, Physical properties of straw lignin-based polymer blends, Polymer (Guildf). 45 (2004) 4159–4169. doi:10.1016/j.polymer.2004.03.098.

[20]	C. Pouteau, P. Dole, B. Cathala, L. Averous, N. Boquillon, Antioxidant properties of lignin in polypropylene, Polym. Degrad. Stab. 81 (2003) 9–18. doi:10.1016/S0141-3910(03)00057-0.

[21]   M. Canetti, F. Bertini, A. De Chirico, G. Audisio, Thermal degradation behaviour of isotactic polypropylene blended with lignin, Polym. Degrad. Stab. 91 (2006) 494–498. doi:10.1016/j.polymdegradstab.2005.01.052.

[22]   A. Gregorová, Z. Cibulková, B. Košíková, P. Šimon, Stabilization effect of lignin in polypropylene and recycled polypropylene, Polym. Degrad. Stab. 89 (2005) 553–558. doi:10.1016/j.polymdegradstab.2005.02.007.

[23]   X. Yue, F. Chen, X. Zhou, G. He, Preparation and Characterization of Poly (vinyl chloride) Polyblends with Fractionated Lignin, Int. J. Polym. Mater. 61 (2012) 214–228. doi:10.1080/00914037.2011.574659.

[24]   L. Dehne, C. Vila Babarro, B. Saake, K.U. Schwarz, Influence of lignin source and esterification on properties of lignin-polyethylene blends, Ind. Crops Prod. 86 (2016) 320–328. doi:10.1016/j.indcrop.2016.04.005.

[25]   D. Ye, S. Li, X. Lu, X. Zhang, O.J. Rojas, Antioxidant and Thermal Stabilization of Polypropylene by Addition of Butylated Lignin at Low Loadings, ACS Sustain. Chem. Eng. 4 (2016) 5248–5257. doi:10.1021/acssuschemeng.6b01241.

[26]   R.R.N. Sailaja, M. V. Deepthi, Mechanical and thermal properties of compatibilized composites of polyethylene and esterified lignin, Mater. Des. 31 (2010) 4369–4379. doi:10.1016/j.matdes.2010.03.046.

[27]   R.R.N. Sailaja, Low density polyethylene and grafted lignin polyblends using epoxy-functionalized compatibilizer: Mechanical and thermal properties, Polym. Int. 54 (2005) 1589–1598. doi:10.1002/pi.1864.

[28]   Pan X, Kadla J, Ehara K, et al (2006) Organosolv Ethanol Lignin from Hybrid Poplar as a Radical Scavenger : Relationship between Lignin Structure , Extraction Conditions , and Antioxidant Activity. J Agric Food Chem 54:5806–5813. doi: 10.1021/jf0605392

[29]   V. Ugartondo, M. Mitjans, M.P. Vinardell, Comparative antioxidant and cytotoxic effects of lignins from different sources, Bioresour. Technol. 99 (2008) 6683–6687. doi:10.1016/j.biortech.2007.11.038.

Chapter 2

2   Literature Review

2.1   Polymers and polymer degradation

Polymers are a broad class of materials that are composed of repeating units of smaller molecules called monomers. Polymers are useful in many applications because of their strength and durability. They can be natural in origin, such as cellulose and lignin, while other polymers (e.g. polyethylene and polypropylene) are termed synthetic polymers, and are synthesized with petroleum-based monomers [1,2].

One of the challenges of working with polymers is their degradability when used in high-temperature conditions or in outdoor applications, which can result in the breaking of polymer chains, the production of free radicals and the subsequent reduction in molecular weight, thereby deteriorating mechanical properties and rendering materials useless for their end use purposes. Therefore, almost all synthetic polymers require stabilization against adverse environmental effects. It is necessary to find methods to reduce or prevent damage induced by environmental components such as heat, light, and oxygen. The stabilization of polymers may be achieved in many ways, including addition of some additives such as hindered phenolic antioxidants, phosphite antioxidants, thiosynergists, hindered amine stabilizers, and UV light absorbers, etc. The additive used depends on the extent of the stabilization needed, and the adverse environmental conditions for the end use product of the polymer [1,3].

2.2   Stabilization of Polymers

Polymer degradation is the change in molecular weight/chain length of a polymeric material leading to loss of desired properties in the end-use product. The weak sites inherent in the polymer are affected by various thermal and chemical factors, such as, heat, light (UV), and mechanical stress, all of which initiate the degradation of a polymer, leading to eventual major mass loss through chain scission, crosslinking, and branching.

Thermal degradation is usually accelerated by the presence of oxygen. For example, in Polyethylene, thermo-oxidative degradation starts at 423K in air, whereas in the inert atmosphere it is delayed until the temperature reaches 565K [4]. Antioxidants have been exploited to retard thermo-oxidative degradation of many polymers.

The mechanism of thermo-oxidative degradation involves a series of chain reactions. The first step in the degradation process is usually the loss of a hydrogen atom from the polymer chain. The initiation can happen in two ways: either high energy input can abstract an H from the polymer chain (RH) and create alkyl radicals (R.) and hydrogen radicals (H.), or O_2 can react with the molecule (RH) to create two free radicals (R. and .OOH). In propagation, the free radicals then can react with O_2 and extract a hydrogen from another polymer molecule (RH), giving rise to peroxy radicals (ROO.), or more free alkyl radicals (R.). The peroxy radicals can extract another hydrogen atom from the polymer chain to form hydroperoxide species (ROOH) that could undergo homolytic cleavage to create secondary initiators RO. and OH., which continue to propagate the reaction to other chains. Some of the free radicals created could self-terminate themselves, and the whole process can be described below [5]:

Initiation:

RH- energy $\rightarrow$ R. + H.

RH + O_2 $\rightarrow$ R. + .OOH

Propagation:

R. + O_2 $\rightarrow$ ROO.

ROO. + RH $\rightarrow$ ROOH + R.

RH + H. $\rightarrow$ H_2 + R.
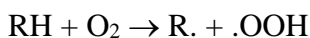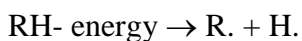
Chain transfer or branching:

ROOH → RO. + OH.

Self-termination:

RO. + H. → ROH

ROO. + H. → ROOH

RO. + R. → ROR
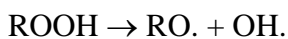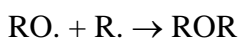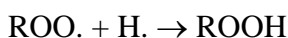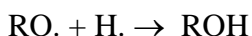
The amount of propagation eventually exhausts the amount of self-termination, leading to degradation of the polymer through chain scission or crosslinking [5]. For certain polymers, such as polypropylene (PP), the degradation happens through the beta scission of the polymer chain containing a free radical, whereas, for polyethylene (PE), the free radical often causes one chain to graft onto another chain, leading to crosslinking and thus furthering the degradation phenomenon [5,6].

Peterson, et al. proposed the following bimolecular decomposition mechanism for hydroperoxide decomposition: ROOH + RH → RO. + R. + HOH, and suggested that it is the rate limiting step of thermo-oxidative degradation. In thermal degradation under inert conditions, random scission is the rate-limiting step, and it has a higher activation energy. Whereas, due to the switch of the rate-limiting step from random scission to decomposition of hydroperoxide radical, the polymers degrade earlier under thermo-oxidative conditions compared to inert environment [7].

The mechanism of UV degradation is quite similar to thermo-oxidative degradation. UV radiation causes photooxidative degradation, which results in breaking of the polymer chains, produces free radicals and reduces molecular weight, causing deterioration of mechanical properties and leading to useless materials [1,3,8]. Similar to the thermo-oxidative degradation, photodegradation also goes through the steps of initiation, propagation, chain branching and termination [1,8].

Even though it accounts for only 4% of total radiation reaching the earth, the energy of the radiation of the UV spectrum is enough to break down the C-H and C-C bonds in polyolefins. Although polyolefins do not have any functional groups that can absorb the UV rays, during the processing stage, the polyolefins become oxidized to create various compounds containing C=O groups, which can absorb the UV rays and create an unstable, excited state. The excited molecules can transfer their energy through a variety of mechanisms, including decomposition of hydroperoxides, formed in the early stages of oxidation, that are unstable and provide a source of free radicals for further initiation; chain scission; and crosslinking. Decomposition of hydroperoxides produces the carbonyl-containing structures-aldehydes, ketones, acids, etc.- similar to the compounds formed during thermos-oxidative degradation of polyolefins. With increasing degradation, the carbonyl content increases with the decrease in tensile strength and elongation. There are various factors that affect this photodegradation, including the UV energy, the temperature, the orientation and the thickness of the sample [8].

Polymer degradation reduces the product's lifetime and deteriorates the characteristics necessary for the end-use purposes, such as tensile strength, aesthetic appeal, electrical conductivity and melt flow instability, and thus necessitates stabilization additives. There are many kinds of additives used in the polymer blend depending on the stage and extent of stabilization needed. Industrial antioxidants are the additives used during polymer processing to prevent oxidative degradation during the lifetime of the end-use product [3,8,9].

The primary antioxidants, such as hindered phenol compounds, are free *radical scavengers* designed to react with the initial free radicals that are formed by donating a hydrogen atom [10,11].. Hindered phenol are called hindered because the reactive hydroxyl group in the benzene ring is sterically shielded by hydrocarbon units connected to each neighboring atom. The electron donating large groups weaken the OH bond by pushing it to donate the hydrogen atom. This hydrogen atom can then react with the free radicals in the polymer and *scavenge the free radicals and stabilize the polymer.* The

antioxidant turns itself into a stable, inactive phenoxy radical that will prevent the initiation of new radicals in the polymer. Some of the popular commercially-used hindered phenolic antioxidants are BHT (2,6-di-tbutyl-4-methylphenol), Irganox 1076, and Irganox 1010 (Figure 2-1). BHT is the first generation antioxidant, and the latter ones are advanced versions of BHT that improve the secondary structure of the BHT molecule. Incorporation of the secondary structure into BHT's 2,6-di-t-butyl phenol moiety helps to increase the molecular weight of the antioxidant. Lower molecular weight poses the problem of getting volatilized easily whereas too high of a molecular weight has the difficulty of diffusing in the polymer matrix. New generations of antioxidants aim at optimizing the molecular weight without sacrificing phenol concentration [12,13]. The secondary antioxidants, such as phosphite compounds, interrupt the degradation cycle by taking the oxygen from the hydroperoxides and transforming them into more stable alcohol (ROH) forms, and make the processes cost-effective by lowering the amount of primary antioxidants needed [9].

AO-1   BHT

AO-2   Irganox® 1076

AO-3   Irganox® 1010
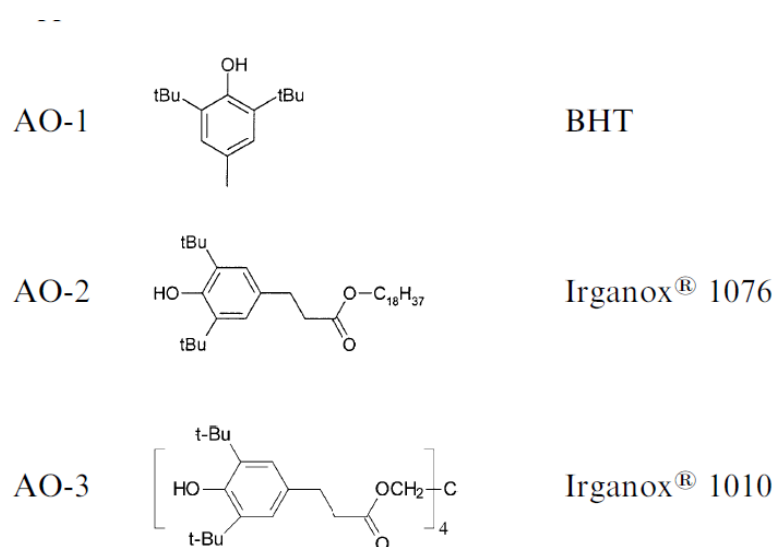
Figure 2-1. First generation, second generation, and third generation hindered phenolic antioxidants [12]

Photo stabilization of polymers may be achieved in many ways. The following stabilizing systems have been developed based on the action of a stabilizer: (1) light screeners, (2) UV absorbers, (3) excited-state quenchers, (4) peroxide decomposers, and (5) free radical scavengers. Usually, a combination of antioxidant and UV absorbers are used to extend the lifetime of the polymer [1].

Many natural compounds with polyphenolic structure (such as flavonoids, vitamin E) could also have antioxidant properties and have been studied as a stabilizer, especially in the food industry [14,15]. In this context, the hindered phenolic structure inherent in lignin, a major component of lignocellulosic biomass, have been studied in many literature studies as a free radical scavenging antioxidant for polymers [16–21].

2.3   What is Lignin?

Lignocellulosic biomass is composed of cellulose, hemicellulose, lignin and some minor components. The cellulose crystals are embedded in a matrix of hemicellulose and lignin [22]. Cellulose and Hemicellulose are polymers of sugar and can be converted to produce biofuels (e.g., bio-ethanol, bio-butanol, etc.) and platform chemicals such 5-hydromethyl furfural (5-HMF) [23].

Lignin is the second most abundant natural polymer, just after cellulose. Depending on the type of the wood, the lignin content varies from 10-40 wt% (on dry basis) [24,25]. It is an amorphous polymer of phenylpropanoid monomer structures, and acts as a thermoplastic material. It affects the transportation of water and different nutrients in a plant and creates a binder between the plant cells to provide resistance to sunlight, frost, fungi and other such biological attacks [22,25].

The structure of lignin is extremely complex. It is a three-dimensional polymer with three major phenyl propane derived alcohols: p-coumaryl alcohol (4-hydroxyl phenyl, H), coniferyl alcohol (guaiacyl, G) and sinapyl alcohol (syringyl, S) as the primary building blocks [Figure 2-2]. The structure includes a variety of functional groups, namely hydroxyl, methoxyl, carbonyl and carboxyl moieties [22,25]. Hydroxyl groups and the

aromatic/phenolic rings are the characteristic functional groups in lignin, and determine its reactivity and constitute the reactive sites to be exploited in macromolecular chemistry [26].
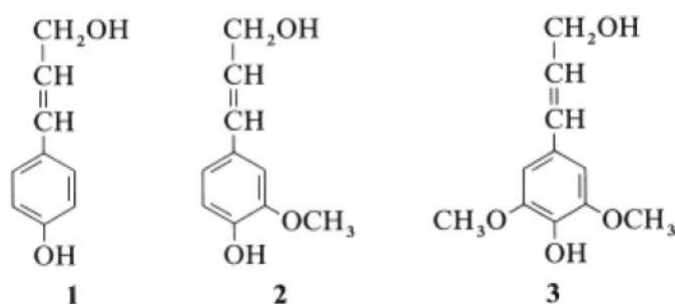
Figure 2-2. 1) P-coumaryl-, 2) coniferyl- and 3) sinapyl alcohol [25]

Woody plants can be divided into two categories: hardwood (angiosperm) and softwood (gymnosperm) [25]. It has been identified that more than 90% of the lignin contained in softwood is made up of coniferyl alcohol (G), with the remaining being mainly p-coumaryl alcohol units. In contrast, hardwood lignin is formed of varying ratios of coniferyl (G) and sinapyl (S) alcohol types of units and grass lignin is made up of mostly p-coumaryl alcohol units (H) [22,25].

2.4   Lignin Sources

The main source of technical lignin is the pulp and paper industry with a lignin production capacity of about 50 million tonnes (mainly kraft lignin) per year [27]. There are two main pulping processes: mechanical and chemical pulping. The mechanical process, mainly for the production of newsprint and paperboards, keeps both cellulose and lignin intact in the fibers, resulting in papers weaker in strength. However, mechanical pulping results in larger pulp yields than chemical pulping. In chemical pulping, wood chips are treated with chemicals to remove lignin and hemicellulose, thus yielding purer and cleaner fibers. Delignification gives the pulp and papers greater flexibility and strength at the expense of fiber yield [28].

Chemical pulping processes treat lignocellulosic material with chemicals so that the lignin can be dissolved and separated from the fibers. There are two major commercial routes for producing chemical pulps: kraft (sulfate) pulping and sulfite pulping. Kraft pulping involves treating the wood chips and sawdust with a sodium sulfide and sodium hydroxide solution. Most of the lignin and hemicellulose are dissolved and separated in the black liquor stream, which is routed to a chemical recovery plant [28]. Most of the waste liquor is burned in the recovery boiler to produce energy for the plant, while a not very significant amount of commodity chemicals (e.g., turpentine, tall oil, and resin) is extracted [28,29].

In North America 60-70% of Kraft pulping mills have a production bottleneck due to the thermal capacity of their recovery boilers. Thus, there is an opportunity to isolate lignin from the black liquor using acid precipitation and then use it as a valuable chemical resource, which would also diversify the product portfolios of the pulp and paper mills [28,29].

The second route of chemical pulping is sulfite pulping, where almost pure cellulose fibers are produced by using various salts of sulfurous acids to extract the lignin from wood chips. The major by-product from sulfite pulping is lignosulfonates. There are also some newer pulping methods in the market, including organosolv, alkaline and soda pulping processes. All of these processes produce lignin as a by-product [28].

Several processes exist for the recovery of lignin from black liquor, including Westvaco, LignoBoost, and LignoForce System. The uniqueness of LignoForce System, developed by FPInnovations, is that the black liquor is oxidized under controlled conditions before the acidification step of the conventional lignin recovery process takes place. This improves the filterability of lignin, along with reducing the TRS (totally reduced sulfur compounds) and/or SO_2 emissions [29]. This thesis utilizes the KL supplied by FPInnovations.

Another prospective commercial source of lignin could be the many modern third generation biorefineries, producing cellulosic sugar-based ethanol/butanol or chemicals and a large amount of hydrolysis lignin (HL). FPInnovation has patented a biomass conversion process, producing sugars from the cellulose and hemicellulose components of a hardwood, while generating a significant amount of solid residue containing HL (56-57 wt%), cellulose, and mono and oligosaccharides. HL can also be used for production of valuable products after proper modification [26].

2.5 Summary of previous studies on lignin in polymer

Traditionally, lignin is used as a low-cost fuel, and for production of leather tanning [26]. Nevertheless, a wide variety of bulk and fine chemicals, particularly aromatic compounds, and bio-based materials can be obtained from lignin [22,26,30,31]. Table 2-1 summarizes the usages of lignins in polymer-lignin blends:

Table 2-1. Applications of lignins in polymer-lignin blends

Polymer matrix	Main function of lignin	References
Protein-lignin blends	Reduced water absorption and improved mechanical properties	[22]
Starch-lignin blends	Reduced water absorption and improved mechanical properties	[22]
Polyhydroxyalkanoates	Improved recyclability, T_g, melting point, and Young's modulus	[22]
Polylactides and Polyglycolides	Reduced flammability, improved thermal degradation, improved processing performance	[22]
Epoxy-lignin composites	Substitution of bis phenol-A as the raw material in preparing epoxy based adhesives	[22,30,31]
Phenol-formaldehyde resin	Substitute of phenol for preparing phenol-formaldehyde resin for adhesive and foam	[22,30,31]
Polyolefin-lignin blend	UV and thermal stabilizer, plasticizers, filler, fire retardant	[27,30]
Vinyl polymer-lignin blend	UV and thermal stabilizer	[22]
Lignin-polyester blend	Improved mechanical properties and processability	[22]

Lignin in polyurethanes	Replacement for polyols. Increased crosslinking of the polyurethane networks, (b) increased T_g, (c) increased tensile strength, (d) increased curing rates and, (e) increased thermal stability	[22,26,31]
Synthetic rubber–lignin blends	Filler	[22]

Besides the bio-based materials presented above, Isikgor and Remzi Becer presented a collection of 200 lignocellulose derived value-added compounds and suggested that how the combination of new and current technologies can lead to the realization of commodity polymers from lignin [32]. A few examples of the compounds mentioned in this refernce incldue polyethylene terephthalate (PET), polystyrene, Kevlar, unsaturated polyesters, polyaniline, benzene, toluene, xylene, phenols, hydroxybenzoic acids as well as coniferyl, sinapyl, and p-coumaryl compounds [32]. Ragauskas et al. suggested the potential use of lignin-derived carbon fiber for light weight vehicles [33]. Radical scavenging activity of lignin and the addition of lignin in polyolefin blends are discussed in details in the following Section 2.6 and 2.7, respectively.

2.6   Lignin as a radical scavenger

As discussed in section 2.2, hindered phenols are primary antioxidants that function by scavenging the peroxy radicals created in the oxidation process. The growing interest in the substitution of synthetic antioxidants by natural ones has fostered research in exploiting forestry and agricultural residues as a stabilizer in food industry, cosmetics, pharmaceuticals and plastics [14,15,34–36]. Similar to the commercial hindered phenol-based antioxidants, the hindered phenolic structure inherent in lignin enables it to work as a free radical scavenging antioxidant. As summarized below, several researchers have analyzed the antioxidant activity of lignin regarding its ability to scavenge free radicals. They have also related the antioxidant activity of the lignin samples to their structural features (molecular weight, polydispersity, functional groups) and purity (hemicelluloses and other components content), resulting from different processing parameters.

Dizhbite et al. [37] reported the antioxidant activity of lignins extracted from coniferous and deciduous wood species using various processes and concluded that non-etherified

phenolic hydroxyl groups, aliphatic hydroxyl groups in the side chain, high molecular weight, enhanced heterogeneity, and polydispersity are the main factors decreasing the radical scavenging activity of the lignin. The radical scavenging ability of phenolic compounds depended not only on the capacity to form a phenoxyl radical but also on the stability of the phenoxyl radical. They postulated that phenolic structures with substituents that can stabilize the phenoxyl radicals have higher antioxidant activity than those that do not. Methoxyl groups at the ortho position stabilized phenoxyl radicals by resonance as well as by hindering their propagation, thereby increasing the antioxidant activity. Also, the purity (presence of hemicellulose or other non-lignin compounds) and heterogeneity of lignin also diminished the antioxidant capacity since carbohydrates can generate hydrogen bonding with lignin phenolic groups, thereby interfering with the antioxidant properties of the lignin.

Addler [18] also analyzed twenty-one organosolv ethanol lignin samples from hybrid poplar trees and concluded that lignins with more phenolic hydroxyl groups, fewer aliphatic hydroxyl groups, lower molecular weight, and narrow polydispersity showed high antioxidant activity. It was explained that the low molecular weight fraction of the lignin possessed more aromatic hydroxyl than the high molecular weight fraction and thus had higher antioxidant activity.

García et al. [16] investigated effects of different fractionation processes on the antioxidant activity of *Miscanthus sinensis*. They established that the organosolv fractionation process of *Miscanthus sinensis* presented the highest radical scavenging activity, followed by autohydrolysis and alkaline samples. These results were in agreement with Dizhbite et al. [37], where alkaline processes produced lignins with higher hemicellulose contamination than organosolv treatments, generating hydrogen bonding between carbohydrates and lignin phenolic groups and resulting in lower antioxidant activity. The authors also inferred that lignin with a lower hydroxyl content would lead to higher compatibility with the thermoplastic matrix and thus act as a better thermal stabilizer for polymers in practice.

Further, García et al. [38,39] studied effects of processing parameters on the lignins' antioxidant activity by analyzing the capacity of various lignins from apple tree pruning to reduce the ABTS radical. In these studies, it was concluded that the source and purification affect antioxidant activity and radical scavenging is directly related to total phenolic content. It was also shown that lignin, though at higher amounts, could attain the same level of antiradical activity as those of some powerful and well-known commercial antioxidants [38,39].

Kaur and Uppal [40] investigated the capacity of lignin derived from sugarcane bagasse in reduction of DPPH radicals. The lignin was found to exhibit greater antioxidant activity than its oxidized derivative. They attributed this finding to the higher content of phenolic hydroxyl groups in lignin than oxidized lignin. By comparing the antioxidant activity of the lignin with some commercial antioxidants, they found that the antioxidant activity of both lignin and oxidized lignin was higher than that of BHT (3,5-di-tert-butyl-4-hydroxytoluene) whereas lower than that of BHA (3-tert-butyl-4- hydroxyanisole), and concluded that the sugarcane bagasse lignin has the potential to be used as an antioxidant for food oils and fats [40].

2.7 Blending lignin with polyolefins: performance and trends

The addition of lignin in polyolefins, such as Low-Density Polyethylene (LDPE) and High-Density Polyethylene (HDPE), has attracted growing attention since as early as 1978 [22]. The presence of lignin in the lignin-polyolefin blends could provide the polymer resistance against UV radiation and elevated temperatures. Levon et al. monitored the stabilization effects of three kinds of lignin: lignosulfonate, KL, and desulphonated lignin in LDPE and HDPE, and reported that among these three kinds of lignin, only lignosulfonate worked as a thermal stabilizer, but for LDPE, while the other two lignin did not perform well due to their poor compatibility with the polymer matrixes [41].

Alexy et al. [21] blended lignin from prehydrolysis of beech wood, with PE and PP as a stabilizer at 10-30 wt% addition level. They measured the tensile strength of the composite samples after 113 h exposure in UV in a QUV tester, and 500h exposure in an oven at 130° C. With PE, lignin addition up to 10 wt% retained the mechanical properties during the UV exposure, while the tensile strength of the PE-lignin composites (after 20 wt% lignin addition) increased after heat-exposure. With PP, however, the additon of lignin did not affect the resistance of the composites to UV radiation, but deterioriated the mechanical properties of the composites after exposition to heat [21].

Pouteau et al. [19] utilized industrial KL from wood and lignin samples from various botanical sources in PP and reported that lignin with a low molecular weight and low phenolic content had better compatibility and antioxidant activity, which was however in contradiction to many literature as discussed previously on the radical scavenging activity of lignin.

Pucciariello et al. [42] investigated blends of a straw-lignin with LDPE, LLDPE (Linear Low-Density Polyethylene), HDPE and PS (Polystyrene). Although the modulus of most lignin-polymer blends slightly increased, both the tensile stress and elongation reduced, which was likely due to the poor compatibility between lignin and the synthetic polymers leading to non-uniform distribution of the lignin particles in the matrix. This problem may be resolved by employing efficient mixing techniques and compatibilizing agents. On the other hand, this research demonstrated that lignin could be an effective antioxidant to increase the resistance of PS, LLDPE and LDPE to UV radiation, although adverse effects was observed when blending lignin with HDPE due to the poor compatibility of lignin in HDPE matrix.

Gregorová et al. reported the antioxidant property of a sulfur free lignin from beech wood prehydrolysis, when blended with both neat and recycled PP [43]. Similarly, Canetti et al. confirmed the enhancement of the thermal stability of an isotactic PP by addition of lignin in particular under the oxidative condition [20].

However, Piña et al. [44] investigated the antioxidant effect of kraft lignin in HDPE, compared against a commercial antioxidant. They concluded that although kraft lignin could act as an antioxidant, it had much less effectiveness than the commercial antioxidant mainly due to its larger molecular weight and poorer compatibility with the polymer. Chemical modification of lignin to either reduce its molecular weight or enhance its compatibility with other polymers is thus beneficial for improving the effectiveness of lignin as an antioxidant. For instance, Sailaja [45] blended lignin grafted Poly (methyl methacrylate) (LPMMA) with LDPE in the presence of a small amount of compatibilizer. The grafting modification of lignin contributed to increasing the hydrophobicity and thermal stability of the lignin compared to the untreated lignin, resulting in improvement in mechanical and thermal stability of the LPMMA-LDPE composite compared to the untreated lignin-LDPE blend. Sailaja and Deepthi [46] blended esterified lignin with LDPE with the addition of maleic anhydride grafted LDPE as a compatibilizer. The results revealed that the esterification modification of lignin and the usage of the compatibilizer improved the dispersion of the lignin particles in the polymer matrix, resulting in better mechanical properties and thermo-oxidative stability of the blend.

Ye et al. [47] investigated the thermo-oxidative performance of blends of esterified lignin with PP in terms of oxidation induction time and induction aging time. Despite the decrease in phenolic content due to the esterification of the lignin, it improved the compatibility of the lignin with the polymer and increased the thermos-oxidative stability of the composites. Dehne et al. [48] evaluated the effects of lignin types (kraft lignin, soda lignin, hydrolysis lignin and organosolv lignin) and esterification on the properties of the PE-lignin blends, and concluded that the type of lignin did not noticeably affect the mechanical properties blend, while esterification of the lignins greatly improved the mechanical strength of the blends.

The antioxidant market is expected to grow with the expanding of the plastic industry owing to the growing demand to replace metal parts in the automotive and aerospace

industries with lightweight engineering plastics [49], and the growing demand for plastic in packaging, durable goods, automotive and other industrial applications [50]. Polyolefins (e.g., PE and PP) represent around 60% of the thermoplastics market, and the global demand for PE and PP reached 150 million tons in 2015. Asia is the largest consumer of polyolefins, seconded by North America and Europe (with around 34% of the market share) [50]. As a result, there would be a steep demand for antioxidants to ensure processing stability and protect the finished products. The segment revenue from antioxidants in European and North American markets was $1.02B in 2014, which is projected to be $1.62B in the next few years [49].

As discussed above, lignins after modifications can be effective antioxidants to substitute the petroleum-based antioxidants in polyolefins (e.g., PE and PP). Compared with the commercial petroleum-based antioxidants, lignin-based antioxidants are not only renewable, but also inexpensive and widely available.

As per a study by Oak Ridge National Laboratory, the available biomass resoruces in the forms of forest and agricultural residues will amount to 1.5 billion tons in 2030 in the United States alone [51]. As described previoulsy, about 50 million tons of lignin (mainly kraft lignin in "black liquor") are genreated as a pulping side product in the pulp and paper mills alone [27], and it was estimated that additional 62 million tons of lignin would be produced from the second generation biorefineries [33]. The amount of lignin produced far exceeds the amount needed to fulfill the internal energy necessity of the pulp and paper mills and the biorefineries. Currently, only 2% of the technical lignin is being commercialized as a specialized chemical [27]. Considering the growing market for polyolefins and thus antioxidants, and the surplus amount of lignin being produced, lignin has a great potential of occupying a significant portion of the antioxidants market [30].

2.8   Lignin modification techniques

As discussed in the previous section, chemical modification of lignin to either reduce its molecular weight or enhance its compatibility with other polymers is beneficial for

improving the effectiveness of lignin as an antioxidant. Typical lignin modification techniques involving functionalization of hydroxyl groups in lignin by esterification, etherification, phenolation, and urethanization [27].

There are various approaches for lignin de-polymerization, including thermochemical depolymerization and conversion, catalytic depolymerization, and biological depolymerization. Pandey and Kim [52] published a comprehensive review on different thermochemical methods for lignin de-polymerization and conversion, including three major thermochemical routes: pyrolysis, oxidation, and gasification. Pyrolysis refers to the process of heating an organic substance in the absence of air so that the molecular structure is broken down into smaller units, while the limited oxygen available for the reaction ensures that there is no further combustion to carbon dioxide. When pyrolysis is performed in the presence of hydrogen, the process is called hydrogenation or hydrogenolysis. In oxidative processes, oxidative cracking is done in order to cleave the lignin rings, aryl ether bonds, or other linkages within the lignin. Ragauskas et al. [33] published a review concerning oxidative processes for lignin de-polymerization, involving catalytic side-chain oxidation and fragmentation reactions. The main products from lignin oxidation include aromatic acids and aldehydes with smaller market volumes.

Catalytic hydro-treatment has been considered as an important approach for lignin de-polymerization (or call reductive de-polymerization). Suitable catalysts and solvents can speed up this process. Catalysts used in reducitve de-polymerization of lignin, such as Ni-Mo or Co-Mo/Al_2O_3, promote high lignin conversion, and suppress char formation and condensation, while keeping the reaction severity under a permissible limit [53].

Recently Mahmood et al. [26] reviewed different chemical strategies for lignin depolymerization, based on solvent and catalyst selection: 1) acid catalysis, 2) metallic catalysis, 3) base catalysis, 4) ionic liquid assisted, 4) sub or supercritical fluids assisted, 5) oxidative route, and 6) de-polymerization under low pressure. A novel low-T/low-P lignin de-polymerization process was developed in our group in collaboration with FPInnovations, to convert kraft lignin (Mw ~ 10,000 g/mol) and hydrolysis lignin (Mw >

20,0000 g/mol) into de-polymerized lignin (DL) of a lower molecular weight (Mw ~ 1,000-2,000 g/mol) at a high yield (>70-90 %). This lignin de-polymerization technology has been licensed to FPInnovations for commercialization, and a US patent for technology has been filed. The DLs and liquefied lignocellulosic biomass were used as bio-substitutes for phenols or polyols for the production of bio-based phenol formaldehyde (PF) and polyurethane (PU) resins/foams, or as a bisphenol-A replacement for the synthesis of lignin-based epoxy resins.

As discussed previously, there had been researches on increasing the compatibility of lignin in the polymer matrix by esterifying or grafting of the lignin. However, to the best of our knowledge, there does not exist a published work by far utilizing the de-polymerized lignin as an antioxidant in polyolefins. Hence, this thesis is dedicated to exploring this particular area of research.

2.9   Knowledge gaps and research opportunities

Lignin as a radical scavenger has attracted lots of attention for application in polyolefins as bio-antioxidant to provide resistance against thermo-oxidative degradation and photodegradation. It has been demonstrated in literature work that lignins can act as effective radical scavenger and can be added to polyolefins for improving their thermo-oxidative resistance. There had also work conducted on improving the compatibility of lignin in polymer matrix by modifying lignin using esterification or grafting techniques. Whereas, esterification decreases the phenolic content of lignin and grafting adds additional cost to the process. There is not much literature work by far addressing the effects of adding technical lignin (i.e., kraft lignin from pulp and paper mills and hydrolysis lignin from biorefineries) and their de-polymerized format in polyolefins on their antioxidant property. Effects of depolymerized technical lignin as a thermo-oxidative stabilizer in polyolefins, are yet to be explored.

2.10   References

[1]   E. Yousif, R. Haddad, Photodegradation and photostabilization of polymers,

especially polystyrene: review, Springerplus. 2 (2013) 398. doi:10.1186/2193-1801-2-398.

[2]   Dow-Corning, Degradation of polymers in nature, (n.d.). http://www.dowcorning.com/content/publishedlit/01-1112-01.pdf (accessed June 12, 2017).

[3]   C.H. Bamford, C.F.H. Tipper, Degradation of polymers, Elsevier Scientific Pub. Co., Amsterdam ; New York, 1975.

[4]   C.L. Beyler, M.M. Hirschler, Thermal Decomposition of Polymers, SPE Handb. Fire Prot. Eng. (2001) 110–131. doi:10.1021/cm200949v.

[5]   N. Pasquini, A. Addeo, Polypropylene handbook, Hanser Munich, 2005.

[6]   A.A. Mendes, A.M. Cunha, C.A. Bernardo, Study of the degradation mechanisms of polyethylene during reprocessing, Polym. Degrad. Stab. 96 (2011) 1125–1133. doi:10.1016/j.polymdegradstab.2011.02.015.

[7]   J.D. Peterson, S. Vyazovkin, C.A. Wight, Kinetics of the thermal and thermo-oxidative degradation of polystyrene, polyethylene and poly(propylene), Macromol. Chem. Phys. 202 (2001) 775–784. doi:10.1002/1521-3935(20010301)202:6<775::AID-MACP775>3.0.CO;2-G.

[8]   B. Baum, The weathering degradation of polyolefins, Polym. Eng. Sci. 14 (1974) 206–211. doi:10.1002/pen.760140309.

[9]   Phlip Jacoby, The Effect of Hindered Phenol Stabilizers on Oxygen Induction Time (OIT) Measurements , and The Use of OIT Measurements to Predict Long Term Thermal Stability – Philip Jacoby , Vice President of Technology , Mayzo Inc ., Norcross , GA, 1230 (1975) 268–271.

[10]   M. Tolinski, Additives for polyolefins: getting the most out of polypropylene,

polyethylene and TPO, William Andrew, 2015.

[11]   V.R. Preedy, R.R. Watson, The encyclopedia of vitamin E, CABI, 2007.

[12]   I. Vulic, G. Vitarelli, J.M. Zenner, Structure-property relationships: Phenolic antioxidants with high efficiency and low colour contribution, Polym. Degrad. Stab. 78 (2002) 27–34. doi:10.1016/S0141-3910(02)00115-5.

[13]   J. Tocháček, Effect of secondary structure on physical behaviour and performance of hindered phenolic antioxidants in polypropylene, Polym. Degrad. Stab. 86 (2004) 385–389. doi:10.1016/j.polymdegradstab.2004.05.010.

[14]   J. Pokorný, Natural antioxidants for food use, Trends Food Sci. Technol. 2 (1991) 223–227. doi:10.1016/0924-2244(91)90695-F.

[15]   M.S. Brewer, Natural Antioxidants: Sources, Compounds, Mechanisms of Action, and Potential Applications, Compr. Rev. Food Sci. Food Saf. 10 (2011) 221–247. doi:10.1111/j.1541-4337.2011.00156.x.

[16]   A. García, A. Toledano, M.Á. Andrés, J. Labidi, Study of the antioxidant capacity of Miscanthus sinensis lignins, Process Biochem. 45 (2010) 935–940. doi:10.1016/j.procbio.2010.02.015.

[17]   A. García, M. González Alriols, G. Spigno, J. Labidi, Lignin as natural radical scavenger. Effect of the obtaining and purification processes on the antioxidant behaviour of lignin, Biochem. Eng. J. 67 (2012) 173–185. doi:10.1016/j.bej.2012.06.013.

[18]   Pan X, Kadla J, Ehara K, et al (2006) Organosolv Ethanol Lignin from Hybrid Poplar as a Radical Scavenger : Relationship between Lignin Structure , Extraction Conditions , and Antioxidant Activity. J Agric Food Chem 54:5806–5813. doi: 10.1021/jf0605392

[19] C. Pouteau, P. Dole, B. Cathala, L. Averous, N. Boquillon, Antioxidant properties of lignin in polypropylene, Polym. Degrad. Stab. 81 (2003) 9–18. doi:10.1016/S0141-3910(03)00057-0.

[20] M. Canetti, F. Bertini, A. De Chirico, G. Audisio, Thermal degradation behaviour of isotactic polypropylene blended with lignin, Polym. Degrad. Stab. 91 (2006) 494–498. doi:10.1016/j.polymdegradstab.2005.01.052.

[21] P. Alexy, B. Košíková, G. Podstránska, The effect of blending lignin with polyethylene and polypropylene on physical properties, Polymer (Guildf). 41 (2000) 4901–4908. doi:10.1016/S0032-3861(99)00714-4.

[22] W.O.S. Doherty, P. Mousavioun, C.M. Fellows, Value-adding to cellulosic ethanol : Lignin polymers, Ind. Crop. Prod. 33 (2011) 259–276. doi:10.1016/j.indcrop.2010.10.022.

[23] C. Xu, R. Arneil, D. Arancon, J. Labidi, R. Luque, Lignin depolymerisation strategies: towards valuable chemicals and fuels, Chem. Soc. Rev. Chem. Soc. Rev. 43 (2014) 7485–7500. doi:10.1039/c4cs00235k.

[24] Y. Sun, J. Cheng, Hydrolysis of lignocellulosic materials for ethanol production : a review q, Bioresour. Technol. 83 (2002) 1–11. doi:10.1016/S0960-8524(01)00212-7.

[25] P. Harmsen, W. Huijgen, L. López, R. Bakker, Literature Review of Physical and Chemical Pretreatment Processes for Lignocellulosic Biomass, Food Biobased Res. (2010) 1–49. http://www.ecn.nl/docs/library/report/2010/e10013.pdf.

[26] N. Mahmood, Z. Yuan, J. Schmidt, C. (Charles) Xu, Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: A review, Renew. Sustain. Energy Rev. 60 (2016) 317–329. doi:10.1016/j.rser.2016.01.037.

[27]   S. Laurichesse, L. Avérous, Chemical modification of lignins: Towards biobased polymers, Prog. Polym. Sci. 39 (2014) 1266–1290. doi:10.1016/j.progpolymsci.2013.11.004.

[28]   Office of technology assessment, The pulp and paper making processes, Technol. Reducing Dioxin Manuf. Bleach. Wood Pulp. (1989) 17–26.

[29]   L. Kouisni, A. Gagne, K. Maki, P. Holt-Hindle, M. Paleologou, LignoForce System for the Recovery of Lignin from Black Liquor: Feedstock Options, Odor Profile, and Product Characterization, ACS Sustain. Chem. Eng. 4 (2016) 5152–5159. doi:10.1021/acssuschemeng.6b00907.

[30]   D. Stewart, Lignin as a base material for materials applications: Chemistry, application and economics, Ind. Crops Prod. 27 (2008) 202–207. doi:10.1016/j.indcrop.2007.07.008.

[31]   L. Dessbesell, C.C. Xu, R. Pulkki, M. Leitch, N. Mahmood, Forest biomass supply chain optimization for a biorefinery aiming to produce high-value bio-based materials and chemicals from lignin and forestry residues : a review of literature, 288 (2017) 277–288.

[32]   F.H. Isikgor, C. Remzi Becer, Lignocellulosic Biomass: a sustainable platform for production of bio-based chemicals and polymers, Polym. Chem. 6 (2015) 4497–4559. doi:10.1039/c3py00085k.

[33]   A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R. a Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T.J. Tschaplinski, G. a Tuskan, C.E. Wyman, Lignin valorization: improving lignin processing in the biorefinery., Science. 344 (2014) 1246843. doi:10.1126/science.1246843.

[34]   A. Masek, Flavonoids as natural stabilizers and color indicators of ageing for polymeric materials, Polymers (Basel). 7 (2015) 1125–1144.

doi:10.3390/polym7061125.

[35]   P. Cerruti, M. Malinconico, J. Rychly, L. Matisova-Rychla, C. Carfagna, Effect of natural antioxidants on the stability of polypropylene films, Polym. Degrad. Stab. 94 (2009) 2095–2100. doi:10.1016/j.polymdegradstab.2009.07.023.

[36]   M.D. Samper, E. Fages, O. Fenollar, T. Boronat, R. Balart, The potential of flavonoids as natural antioxidants and UV light stabilizers for polypropylene, J. Appl. Polym. Sci. 129 (2013) 1707–1716. doi:10.1002/app.38871.

[37]   T. Dizhbite, G. Telysheva, V. Jurkjane, U. Viesturs, Characterization of the radical scavenging activity of lignins - Natural antioxidants, Bioresour. Technol. 95 (2004) 309–317. doi:10.1016/j.biortech.2004.02.024.

[38]   A. García, M. González, G. Spigno, J. Labidi, Lignin as natural radical scavenger . Effect of the obtaining and purification processes on the antioxidant behaviour of lignin, Biochem. Eng. J. 67 (2012) 173–185. doi:10.1016/j.bej.2012.06.013.

[39]   A. Garcia, D. Amendola, M. González, G. Spigno, J. Labidi, Lignin as natural radical scavenger. Study of the antioxidant capacity of apple tree pruning lignin obtained by different methods, Chem. Eng. Trans. 24 (2011) 925–931.

[40]   R. Kaur, S.K. Uppal, Structural characterization and antioxidant activity of lignin from sugarcane bagasse, Colloid Polym. Sci. 293 (2015) 2585–2592. doi:10.1007/s00396-015-3653-1.

[41]   K. Levon, J. Huhtala, B. Malm, J.J. Lindberg, Improvement of the thermal stabilization of polyethylene with lignosulphonate, Polymer (Guildf). 28 (1987) 745–750. doi:10.1016/0032-3861(87)90223-0.

[42]   R. Pucciariello, V. Villani, C. Bonini, M. D'Auria, T. Vetere, Physical properties of straw lignin-based polymer blends, Polymer (Guildf). 45 (2004) 4159–4169. doi:10.1016/j.polymer.2004.03.098.

[43] A. Gregorová, Z. Cibulková, B. Košíková, P. Šimon, Stabilization effect of lignin in polypropylene and recycled polypropylene, Polym. Degrad. Stab. 89 (2005) 553–558. doi:10.1016/j.polymdegradstab.2005.02.007.

[44] I. Piña, F. Ysambertt, D. Perez, K. Lopez, Study of Antioxidant Effectiveness of Kraft Lignin in HDPE, J. Polym. 2015 (2015).

[45] R.R.N. Sailaja, Low density polyethylene and grafted lignin polyblends using epoxy-functionalized compatibilizer: Mechanical and thermal properties, Polym. Int. 54 (2005) 1589–1598. doi:10.1002/pi.1864.

[46] R.R.N. Sailaja, M. V. Deepthi, Mechanical and thermal properties of compatibilized composites of polyethylene and esterified lignin, Mater. Des. 31 (2010) 4369–4379. doi:10.1016/j.matdes.2010.03.046.

[47] D. Ye, S. Li, X. Lu, X. Zhang, O.J. Rojas, Antioxidant and Thermal Stabilization of Polypropylene by Addition of Butylated Lignin at Low Loadings, ACS Sustain. Chem. Eng. 4 (2016) 5248–5257. doi:10.1021/acssuschemeng.6b01241.

[48] L. Dehne, C. Vila Babarro, B. Saake, K.U. Schwarz, Influence of lignin source and esterification on properties of lignin-polyethylene blends, Ind. Crops Prod. 86 (2016) 320–328. doi:10.1016/j.indcrop.2016.04.005.

[49] Frost & Sullivan, Strategic Analysis of the European and North American Plastics Additives Market, (2015). http://cds.frost.com (accessed May 12, 2017).

[50] G. Fabrizio, GLOBAL MARKET TRENDS AND INVESTMENTS IN POLYETHYLENE AND POLYPROPYLENE, (2016). https://www.icis.com/globalassets/documents/forms/ppf-pdf/global_trends_whitepaper_pp_pe.pdf (accessed June 22, 2017).

[51] R.D. Perlack, B.J. Stokes, U.S. Billion-Ton Update:Biomass Supply for a Bioenergy and Bioproducts Industry, Oak Ridge, TN, 2011.

[52]   M.P. Pandey, C.S. Kim, Lignin Depolymerization and Conversion: A Review of Thermochemical Methods, Chem. Eng. Technol. 34 (2011) 29–41. doi:10.1002/ceat.201000270.

[53]   J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, The Catalytic Valorization of Lignin for the Production of Renewable Chemicals The Catalytic Valorization of Lignin for the Production of Renewable Chemicals, (2010). doi:10.1021/cr900354u.

Chapter 3

3 De-polymerization of crude lignins to improve the thermo-oxidative stability of polyolefins

3.1 Introduction

Lignin, one of the primary constituents of plant cell walls, is the largest renewable resource for aromatic compounds [1]. It is an amorphous polymer of three main phenyl propanoid units connected dominantly by ether linkages [2,3]. As of 2013, global production of lignin, mainly kraft lignin (KL) in black liquor – a waste stream from kraft pulping process, was approximately 50 million tonnes per annum, most of which is used as a low-cost fuel for pulping chemicals recovery and heat generation utilized within the pulp mills, with less than 5% of it being utilized as chemicals or other products [4]. On the other hand, hydrolysis of lignocellulosic biomass for cellulosic ethanol production also generate lignin, commonly denoted as hydrolysis lignin (HL), as a side-product, mainly utilized as a low-cost fuel for heat generation. With the advance in pulp and paper mills, and biorefineries for biomass derived fuels and chemicals, the production of lignin in downstream will further increase [1]. As a result, there is a growing need to develop value-added products from lignin, to diversify the product portfolios of the pulp and paper mills, cellulosic ethanol plants and biorefineries, which in return will also help make the processes more economically competitive. Due to its high aliphatic hydroxyl, aromatic hydroxyl and carboxyl content, lignin has been researched as an alternative to commercial reactants in the production of polyurethane foam, adhesive, epoxy resins and adipic acid [5–8]. A number of studies have suggested that lignin could be a promising resource for bio-based antioxidants due to its structural similarity with the traditionally used hindered phenolic antioxidants used in polymer stabilization [9–12].

Industrial antioxidants are the additives used for polymer to prevent the thermo-oxidative degradation during processing and life time. Commercial stabilizing package includes a combination of hindered phenol based antioxidant and phosphorous based melt stabilizer. The hindered phenolic antioxidants are called "hindered" because the reactive hydroxyl

group is shielded by hydrocarbon units connected to each neighboring atom in the benzene ring. The bulky groups on ortho positions push the OH group to donate the H to trap the initial free radicals derived from the oxidation reactions. The antioxidant molecule resonance stabilizes itself into stable phenoxy radicals; thus preventing the initiation of new radicals [13,14]. Likewise, as shown in Scheme 3-1, the hindered phenolic structure inherent in lignin, enables it to work as a free radical scavenging antioxidant, which has been proved by the 2, 2-diphenyl-1-picrylhydrazyl (DPPH) method [9–12].
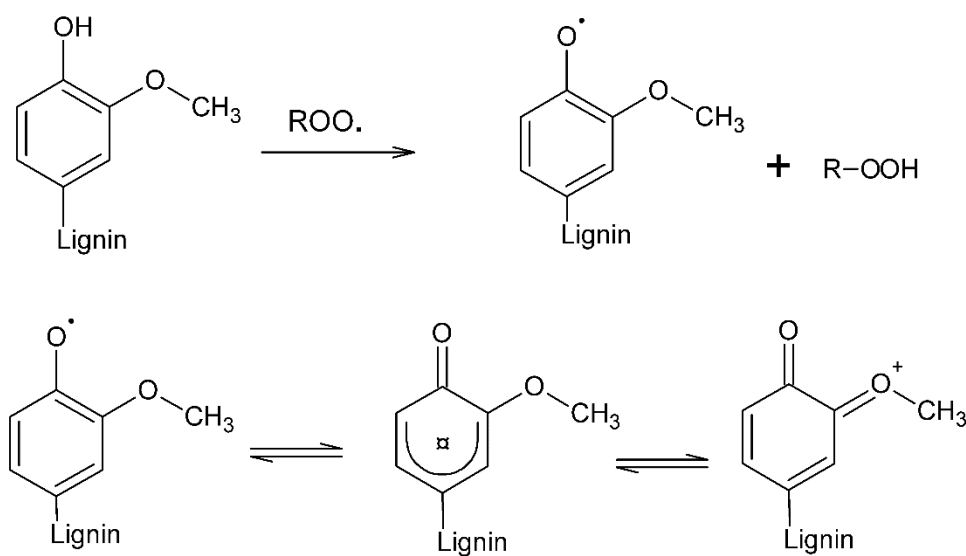
Scheme 3-1. Trapping of peroxy radicals by lignin and eventual delocalized stabilization of the phenoxy radical created from the lignin

The property and structure of lignin vary vastly depending on the source. Most of the previous works [15–22], concerning the effects of lignin on polymer stabilization, utilized high purity lignin extracted from the plants using organic solvents or steam explosion. There is a scarcity of literature addressing the effects of technical lignins, particularly at a low level. Moreover, normally technical lignin has a large molecular weight and hence low reactivity and compatibility with other polymers. Since the phenyl

propanoid units in lignin are connected by ether linkages, breakdown of these ether linkages could also increase the phenolic content, thus potentially improving the antioxidant property. De-polymerization also has the potential of reducing the hydrophilicity of crude lignins by decreasing the aliphatic hydroxyl content. Past researches, comparing the antioxidant activity of lignin from various sources, indicated that with decreasing molecular weight, increasing phenolic content, and decreasing aliphatic hydroxyl content the antioxidant activity of the lignin increased [23, 24]. Hence, there is potential for improving the antioxidant activity of lignin by de-polymerizing it. To verify the above hypothesis, this work investigated (i) antioxidant performance of two technical lignins, commercial kraft lignin (KL) and hydrolytic lignin (HL) as an additive in polyolefins and (ii) effects of de-polymerization of KL/HL on their performance as additives in polyolefins with respect to thermo-oxidative stability.

3.2   Experimental

3.2.1   Materials and compounding

Kraft lignin (KL) and hydrolysis lignin (HL) were supplied by FPInnovations. The former is a product from their proprietary LignoForce process [25] in its pilot plant in Thunder Bay, Ontario, and the latter is a by-product of their proprietary hardwood fractionation process for bioproducts, called "TMP-bio process" [26]. The HL contained 50-60 wt% lignin balanced by the residual cellulose and hemicellulose. The molecular weight of the KL is approx.10000 g/mol and the molecular weight of the HL was not measurable due to its insolubility in a suitable solvent.

De-polymerization of the KL and HL was realized by a low-temperature/low-pressure process developed by the authors' group (currently patent pending). Briefly, KL de-polymerization was carried out in a Parr autoclave reactor (500 mL) at 250°C, 1 h, with 20 wt.% KL substrate concentration in poly-alcohol-water co-solvent in the presence of an alkaline catalyst (NaOH/KL mass ratio of 0.28), producing de-polymerized KL (DKL) at a yield of ~90 wt.%. De-polymerized hydrolysis lignin (DHL) was obtained by acid

catalyzed de-polymerization at 200°C, 1 h with 20 wt.% HL substrate concentration in the same solvent in the presence of an acid catalyst (H2SO4/HL mass ratio of 2% w/w), leading to ~70 wt.% yield of DHL.

Low density polyethylene (LDPE) with the density of 0.93 g/mL and melt flow index of 2.5 g/min and isotactic polypropylene (PP) with the density of 0.90 g/mL and melt flow index of 1.2 g/min were supplied by Sigma Aldrich. PE and PP were extruded in neat form and with addition of 5 wt% of KL, HL, DKL and DHL, respectively, at 140°C and 190°C using a HAAKE MiniLab II Micro Compounder. The screw speed was set at 100 rpm and the residence time was 10 min.

3.2.2   Characterization of lignin and de-polymerized lignin

3.2.2.1   Gel permeation chromatography (GPC)

Molecular weights and their distributions of the lignins were measured using Waters Breeze GPC-HPLC (1525 binary pump, UV detector set at 270 nm, Waters styragel HR1 column at 40°C). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 ml/min. Linear polystyrene standards were used for the molecular weight calibration curve.

3.2.2.2   Fourier transform infrared spectroscopy (FT-IR)

The lignins and their depolymerized counterparts were analyzed on Nicolet 6700 Fourier Transform Infrared Spectroscopy (FT-IR) with smart iTR/ATR accessory to verify the presence of functional groups such as hydroxyl groups in the structure. The FT-IR spectra were measured in the range of 500–4000 cm-1 in attenuated total reflectance (ATR) mode.

3.2.2.3   Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy

^{1}H NMR spectroscopy was performed only for KL, DKL, and DHL because a suitable solvent for HL was not available (in other words, HL is not soluble in any common

solvent). In order to increase the solubility of KL, DKL and DHL in d-chloroform for the quantitative analysis of ^{1}H NMR, the samples were acetylated first. The details of the acetylation process and ^{1}H NMR process was described elsewhere [27].

3.3 Characterization of antioxidant activity

3.3.1 Differential scanning calorimetry (DSC)

The oxidation induction time (OIT) is an accelerated thermoanalytical measurement often used in industries to predict the thermo-oxidative stability of polymers. The OIT tests were carried out according to ASTM D3895 using a differential scanning calorimeter (DSC1, Mettler Toledo) with a STARe software. A sample of 5-6 mg was placed in an open standard 40 μL aluminum pan and an empty pan was used as reference. First, the sample was heated from 50°C to 220°C at a heating rate of 10°C/min under a nitrogen flow of 50 mL/min. After the temperature reached 220°C, the sample was maintained at the temperature for 1 minute and then the purge nitrogen gas was switched to air with a flow rate of 50 ml/min. Air was selected since this environment would represent a similar situation during polymer processing and/or shelf life. The sample was held at 220°C until the sample went through oxidative degradation, where an exotherm appeared in the DSC curve. The time interval between the switch of gas and the onset of the thermo-oxidation exotherm was reported as the OIT time. A typical DSC curve obtained from an OIT test for a PE-KL sample is illustrated in Scheme 3-2.
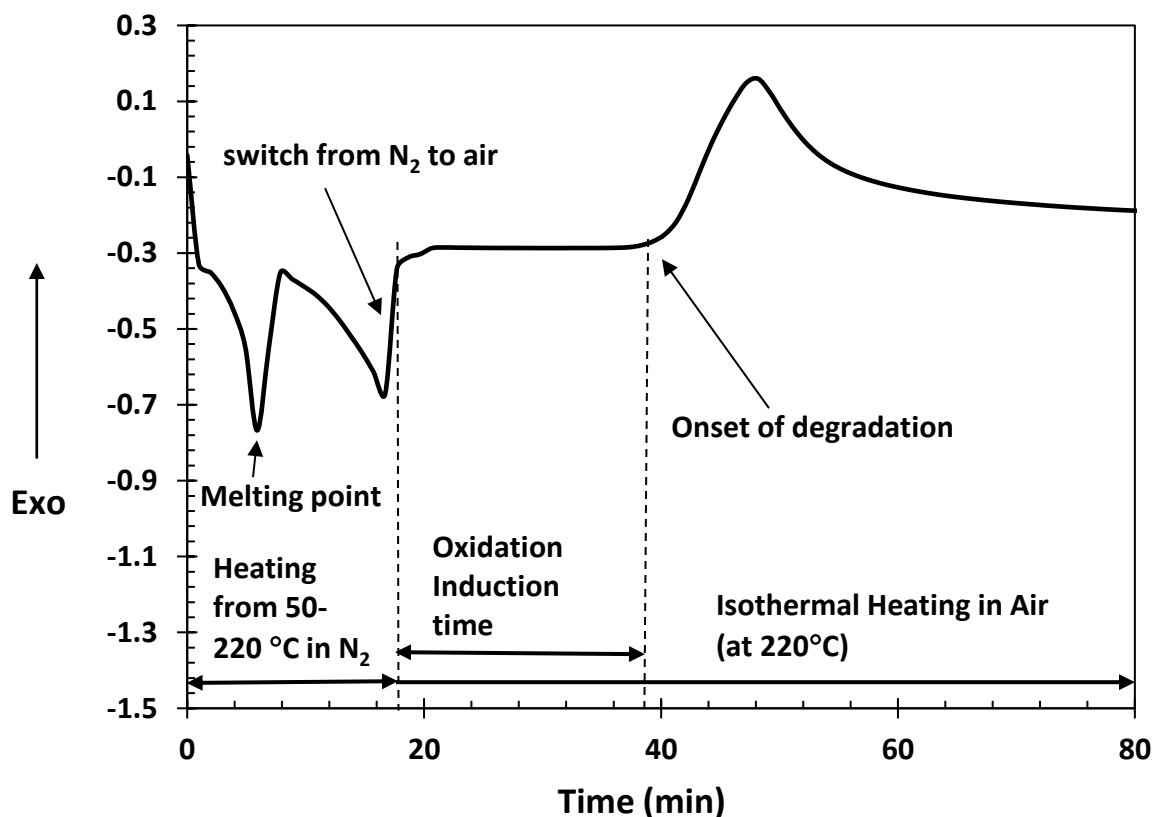
Scheme 3-2. Schematic illustration of a typical DSC curve of oxidation induction time

measurement of polymer-lignin samples

Activation energy for oxidative degradation was also measured using DSC by following the Flynn/Wall/Ozawa method described in ASTM E698-16. A sample of 5-6 mg was introduced in an open standard 40 µL aluminum pan and heated from 50 to 450°C at 4 different heating rates (7.5, 10, 12.5, and 15°C/min) under an air flow of 50 mL/min.

3.3.2   Thermo-gravimetric analysis (TGA)

Thermal degradation behavior was examined on a thermogravimetric analyzer (Q500, TA Instrument) with a Universal TA analysis software. A sample of 5 mg was loaded in a

furnace constantly purged with air at flow rate of 20 mL/min. TGA traces were recorded from 50 to 800°C at a heating rate of 10°C/min.

3.4   RESULTS AND DISCUSSION

3.4.1   De-polymerization of lignins

Table 3-1 summarizes results obtained from GPC measurements for the two de-polymerized lignins, DKL and DHL. Weight-average molecular weight of KL was reduced from 10,000 g/mol to 1,164 g/mol after the de-polymerization. The HL with molecular weight being too large to be measurable was reduced to 1413 g/mol after de-polymerization.

Table 3-1. Molecular weight and polydispersity index (PDI) of DKL and DHL

Type of lignin	M_W (g/mol)	M_n (g/mol)	PDI
DKL	1,164	557	2.09
DHL	1,413	651	2.17

Figure 3-1 shows FTIR spectra of the 4 types of lignins to examine changes in hydroxyl groups, ether linkages and other functional groups within the lignin structure after de-polymerization. The broad band between 3200 to 3550 cm−1 corresponds to the vibration of hydroxyl groups [28]. The adsorption at 1060–1160 cm-1 corresponds to the C-O in ethers and alcohols [28]. Comparing between the spectra of KL and DKL, the intensities of C-O remain the same, but that of OH became slightly stronger. However, in DHL, even though the intensities of C-O and OH are weaker, the intensities of aromatic adsorption in 1400-1700 cm-1 became stronger, likely due to the removal of sugars (or cellulose/hemicellulose derivatives) in HL during the de-polymerization operation.
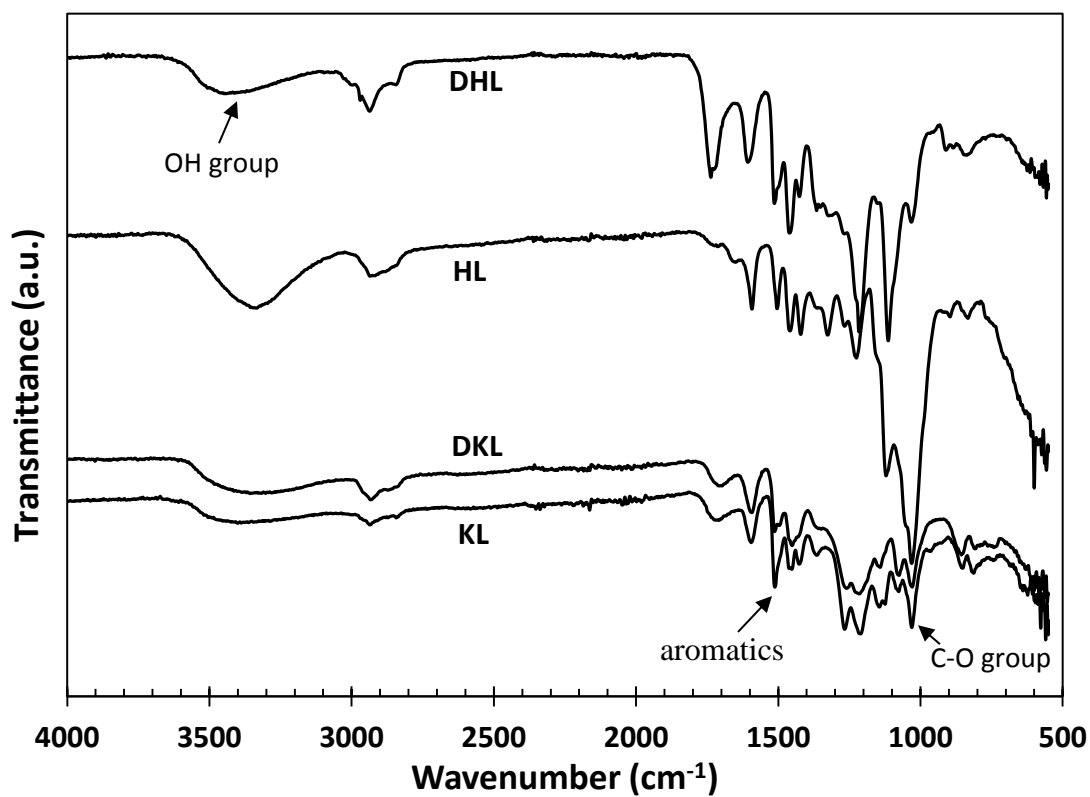
Figure 3-1. FTIR spectra of 4 kinds of lignins

^{1}H NMR spectra of acetylated KL, DKL and DHL are illustrated in Figure 3-2.
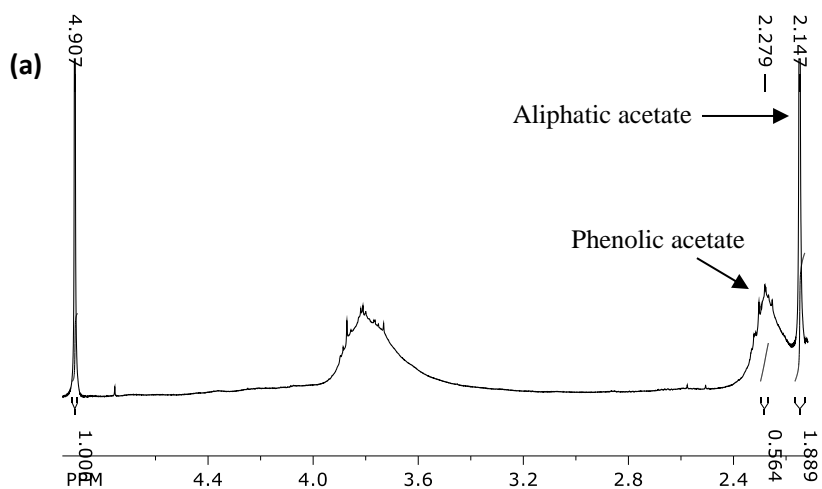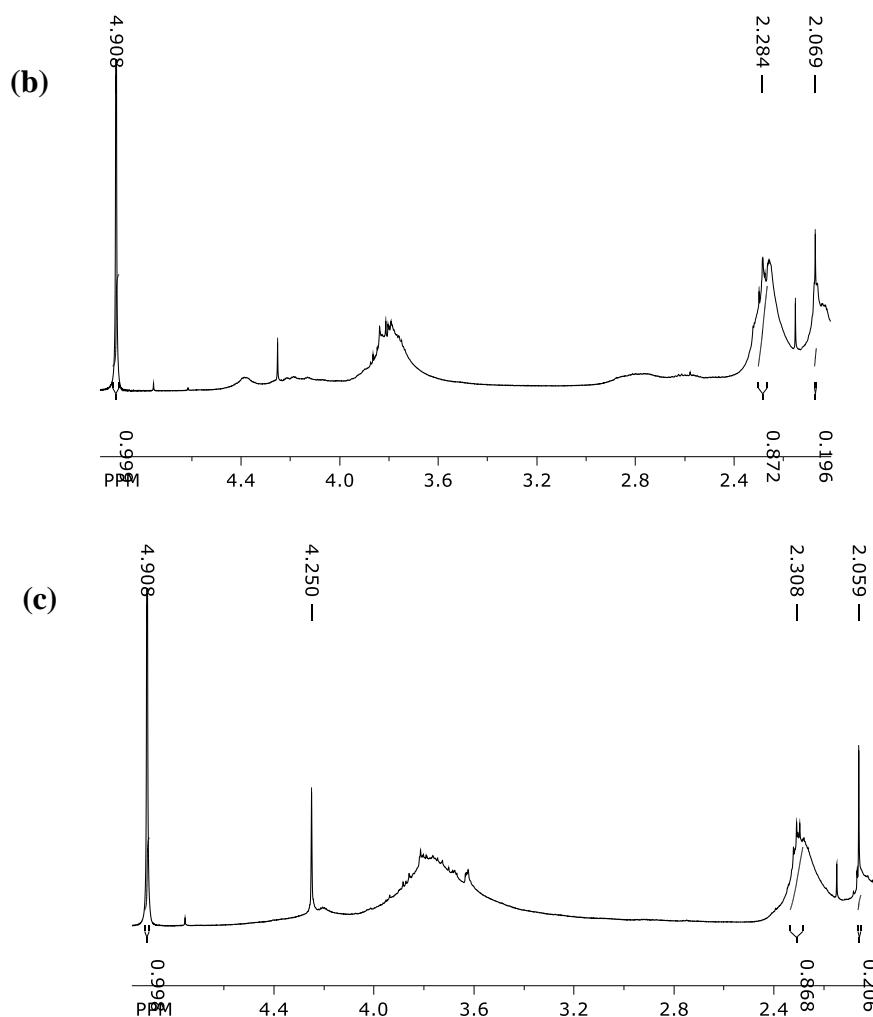
Figure 3-2. ^{1}H NMR spectra of the acetylated a) KL, b) DKL, and c) DHL

In the ^{1}H NMR spectra of the acetylated KL, DKL and DHL with dibromomethane as internal standard (Figure 3-2), the signals at 4.9 ppm, 2.2-2.6 ppm, and 1.8-2.2 ppm correspond to dibromomethane, phenolic and aliphatic acetates, respectively [29]. The phenolic acetate protons and aliphatic acetate protons in the ^{1}H NMR spectra represent phenolic hydroxyls and aliphatic hydroxyls in their acetylated samples, respectively. The signal area corresponding to internal standard was initially calibrated and then integrated to 1.0, followed by the integration of the regions related to phenolic acetate peaks. The phenolic content was calculated as follows [29]:

$$M_{P,OH} = \frac{\frac{2}{3} \times I_{P,AC} \times M_{DBM} \times 180}{W_{AC} - \left(\frac{2}{3} \times I_{P,AC} + \frac{2}{3} \times I_{A,AC}\right) \times M_{DBM} \times 42} \tag{1}$$

The aliphatic hydroxyl content was calculated as follows [29]:

$$M_{P,OH} = \frac{\frac{2}{3} \times I_{P,AC} \times M_{DBM} \times 180}{W_{AC} - \left(\frac{2}{3} \times I_{P,AC} + \frac{2}{3} \times I_{A,AC}\right) \times M_{DBM} \times 42} \tag{2}$$

where $M_{P,OH}$ are the moles of phenolic OH per lignin unit (with an average molecular weight of 180 g/mol); 2 and 3 are the number of protons of internal standard (dibromomethane) and acetyl groups, respectively; $I_{P,AC}$ is the integration of peaks of phenolic acetates; MDBM are the moles of internal standard $= W_{DBM}/173.83$ (weight of internal standard in relation to its molecular weight); W_{AC} is the weight of the acetylated samples of the KL or DKL or DHL; 42 is the formula weight of acetyl group minus one $=$ (43 - 1).

With the above Eq. (1), the phenolic content of KL, DKL, and DHL was obtained to be 0.24, 0.5 and 0.34 moles per lignin unit, respectively. And with the above Eq. (2), the aliphatic hydroxyl content of KL, DKL and DHL was obtained to be 0.814, 0.125, and 0.084 moles per lignin unit, respectively. As revealed by the results of FTIR and GPC measurements, the de-polymerization process cleaved ether linkages of the lignin units to significantly reduce the molecular weights of the lignins, which resulted in a higher phenolic content and lower aliphatic hydroxyl content in the de-polymerized lignins, as evidenced by the above calculated values of moles of phenolics per lignin unit and moles of aliphatic hydroxyls per lignin unit based on the ^{1}H NMR spectra of KL, DKL, and DHL.

3.4.2 Thermo-oxidative stability of PE and PP with addition of various lignins

3.4.2.1 Oxidation induction time (OIT)
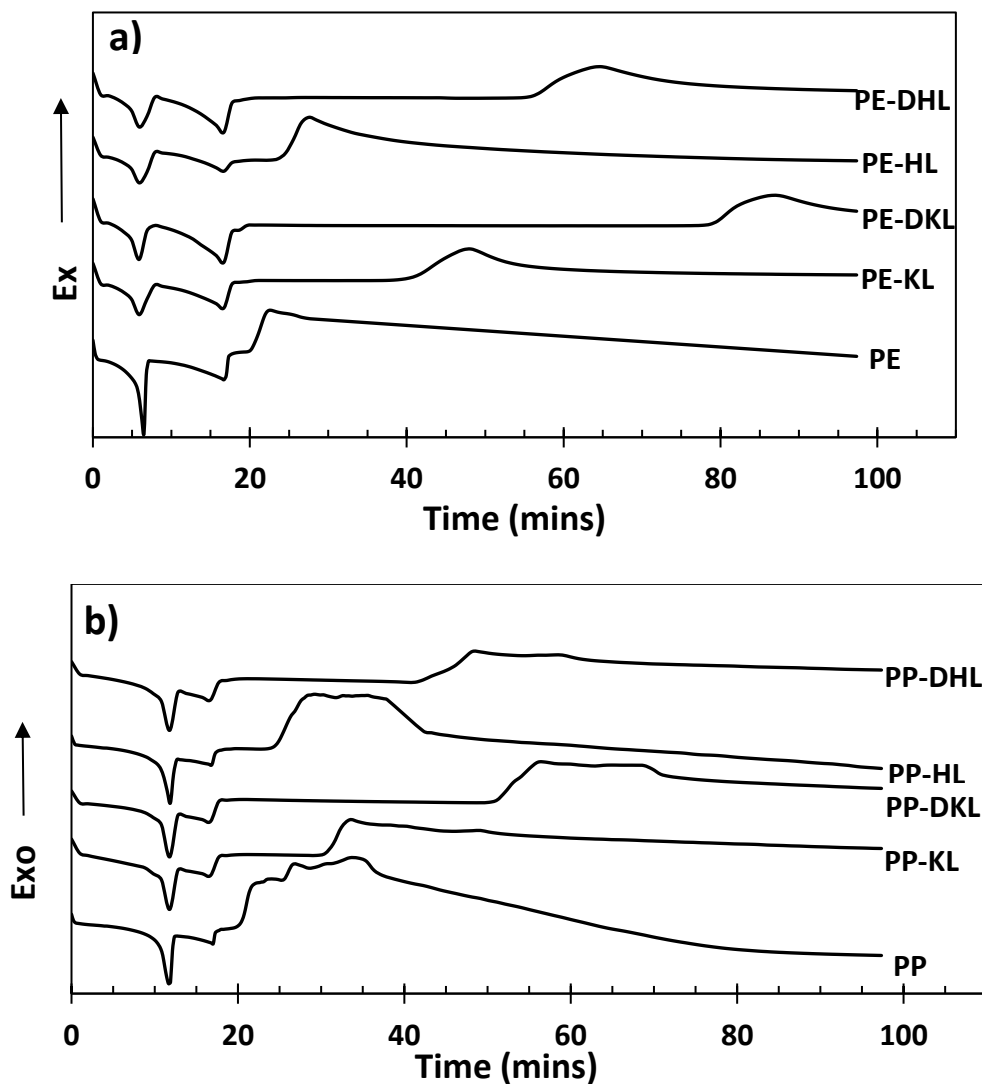
Figure 3-3. DSC OIT curves obtained from a) PE-lignins and b) PP-lignins samples

DSC curves obtained from OIT tests for PE-lignins and PP-lignins (containing 5 wt% of KL, HL, DKL and DHL, respectively). As illustrated in the previous Scheme 3-2 and Figure 3-3, thermo-oxidative degradation of a polymer can be divided into several stages. The onset of exotherm is the initiation point of oxidation. The first exotherm peak

denotes formation of free radicals (i.e., peroxy radicals). The later peaks indicate the degradation of the peroxy radicals and further oxidation or degradation stages [30]. If an antioxidant is incorporated in a polymer, it scavenges the free radicals generated in the oxidation process. Once all the antioxidants are consumed, the reaction proceeds at a much faster rate and presents a detectable exotherm in the DSC output. Thus, the oxidation induction time (OIT) can be prolonged by introducing an antioxidant in the polymer, and the value of OIT can be used as a measure of effectiveness of an antioxidant.

In accordance to the method as described in Scheme 2 and the DSC results presented in Figure 3-3, OIT values of PE-lignins and PP-lignins were obtained and summarized in Table 3-2, in comparison with the values of neat PE and neat PP. The results as presented in Table 3-2 clearly show that DKL is the most effective lignin as an antioxidant, increasing the OIT from 2.0 min (neat PE) or 1.8 min (neat PP) to 56 min (PE-DKL) or 33 min (PP-DKL), followed by DHL, KL and HL. It is noted that this order is in a good agreement to the order of phenolic content in lignins: DKL > DHL > KL > HL (as evidenced by the ^{1}H NMR results discussed previously in section 3.4.1). Thus, it may be concluded that the de-polymerization process could effectively improve the antioxidant activity of lignin by increasing its phenolic content. The de-polymerization process also improved the hydrophobicity of lignin molecules by decreasing the aliphatic hydroxyl content. As a result, the de-polymerized lignins had a better compatibility with the hydrophobic polymer matrix compared to the crude lignins.

In addition, due to the difference in structure, the degradation phenomena of the polymers are different. Polyolefins have the weakest bond at their tertiary carbons. As every other carbon in PP is a tertiary carbon, it is more susceptible to oxidative degradation compared to PE [31], i.e., PP produces free radicals more quickly than PE, which is reflected in its early consumption of the antioxidants and shorter OIT. As to be discussed later in the section of TGA (Section 3.4.2.3.), this is also the reason why PP-lignins had earlier onset temperatures for mass loss upon heating than PE-lignins.

Table 3-2. Oxidation Induction Time (OIT) of PE-lignins and PP-lignins

Sample	OIT (min)
Neat PE	2.0
PE-KL	22
PE-DKL	56
PE-HL	6.1
PE-DHL	35
Neat PP	1.8
PP-KL	14
PP-DKL	33
PP-HL	5.8
PP-DHL	25

3.4.2.2   Activation energy for oxidative degradation

For studies of the kinetics of the thermo-oxidative degradation process of the PE and PP with/without lignin additives, DSC thermograms were collected in 50 mL/min air at various heating rates, 7.5°C/min, 10°C/min, 12.5°C/min, and 15°C/min. Figures 4 and 5 illustrate the DSC curves of neat PE and PE-lignins, and PP and PP-lignins respectively, at various heating rates.
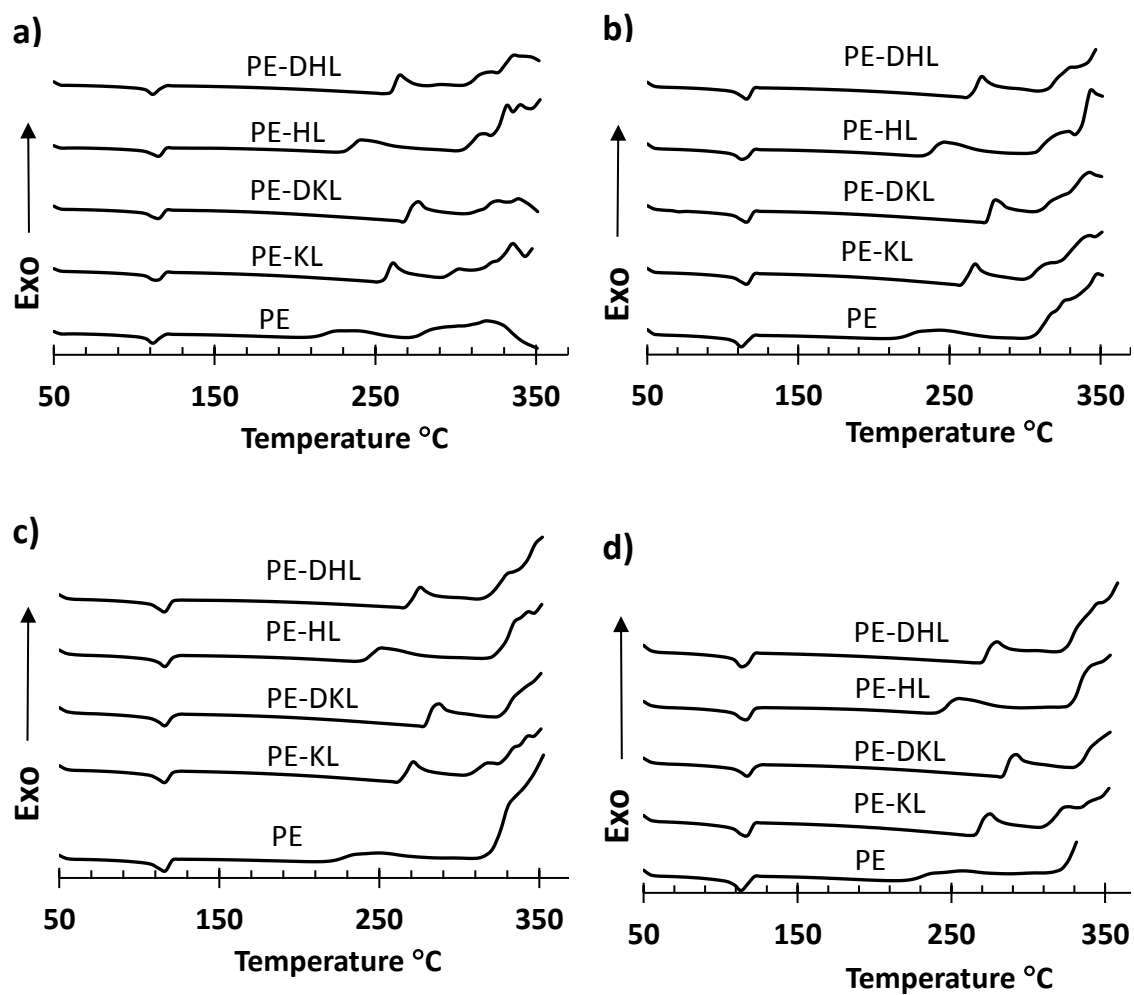
Figure 3-4. DSC curves of neat PE and PE-lignins in 50 mL/min air flow heated at various heating rates: (a) 7.5°C/min, (b) 10°C/min, (c) 12.5°C/min, and (d) 15°C/min
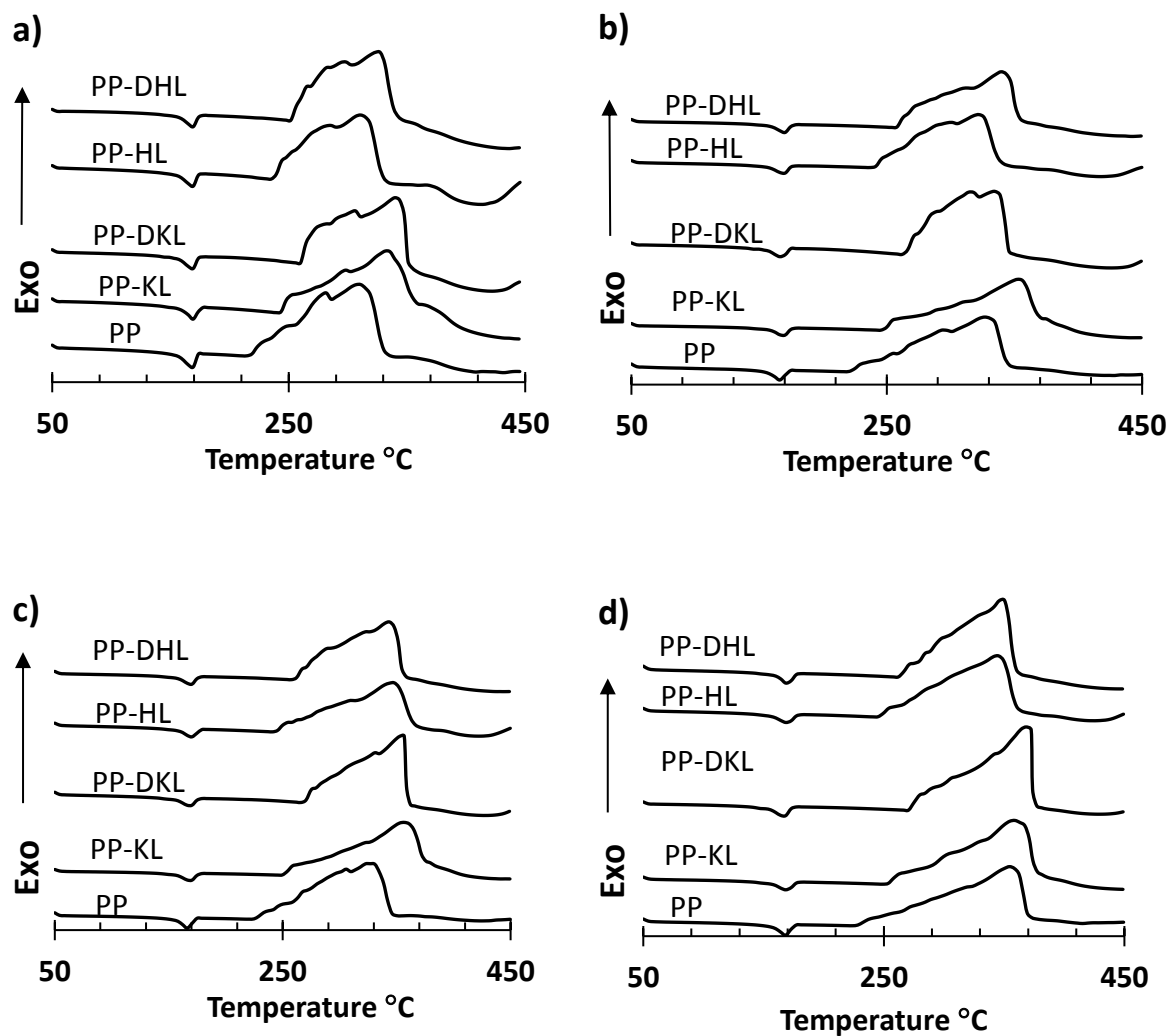
Figure 3-5. DSC curves of neat PP and PP-lignins in 50 mL/min air flow heated at various heating rates: (a) 7.5°C/min, (b) 10°C/min, (c) 12.5°C/min, and (d) 15°C/min

PE-lignins exhibited multiple peaks and valleys on the DSC curves after the initial exotherm peak (Figure 3-4), whereas PP-lignins had only one large exotherm peak (Figure 3-5), which are in a good agreement to the reported results in the literature for neat PE and neat PP [30]. It is widely accepted that the degradation process in PP is governed by only chain scission, whereas PE undergoes branching and crosslinking along

with the chain scission. Hence, the multiple peaks observed in PE could be related to the crosslinking and branching reactions [30,32].

According to the Flynn/Wall/Ozawa method described in ASTM E698-16, the activation energy (E) for oxidative degradation of a polymer can be written as:

$$E = -2.19\,R\,\frac{\mathrm{d}\log\beta}{\mathrm{d}\,T_{\mathrm{p}}^{-1}} \qquad (3)$$

where R is the gas constant, β is the heating rate, and Tp is the temperature at the maximum of the first peak of exotherm.

By plotting log β vs. 1/ T_{p} (as shown in Figure 3-6), the slope is used for calculating the activation energy. As mentioned above, the Flynn/Wall/Ozawa method calculates the activation energy employing the peak temperature of exotherm on the DSC heating curves. However, in order to effectively comprehend the activation energy of thermo-oxidative degradation of a polymer before and after incorporating an antioxidant, in this work we employed temperature at the onset of exotherm (T_{o}) instead of the peak temperature for calculation of E in accordance to Eq. 3. As is known, the primary role of an antioxidant (lignins in this study) are scavenging peroxy radicals, thus delaying the propagation reactions. Hence, antioxidants are active only during the induction period, resulting in an increase in onset of the exotherm, and sometimes the peak temperature of the exotherm, while the latter peaks are not normally correlated with the activity of the antioxidant [33,34].
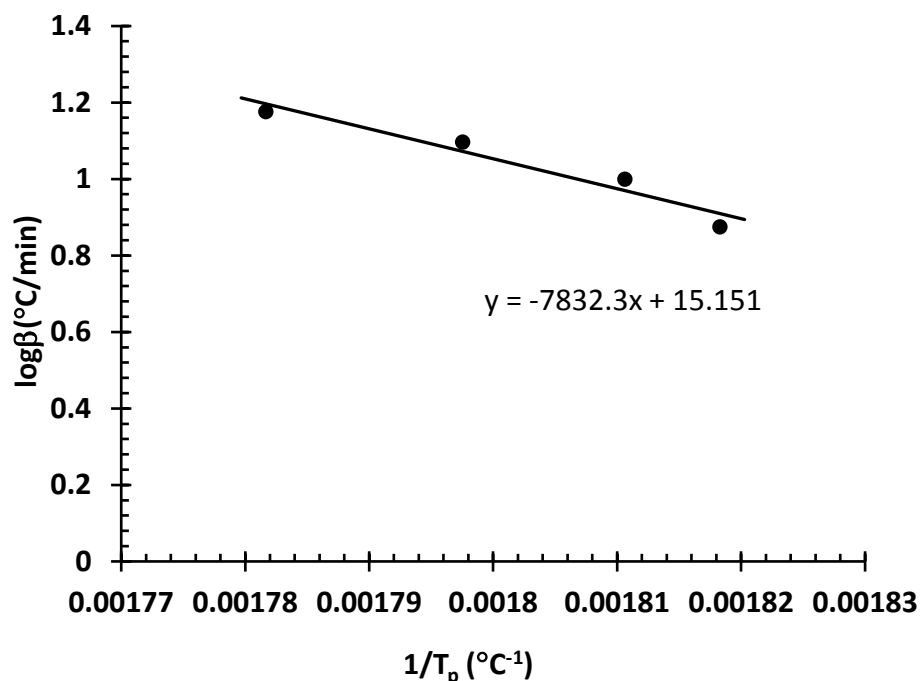
Figure 3-6. Sample curve of PE-DKL for measuring activation energy for the oxidation of degradation using flynn/wall/ozawa method

Table 3-3 summarizes the activation energies of thermo-oxidative degradation of PE-lignins and PP-lignins. As clearly shown in the Table 3-3, the addition of any of the four lignins to PE or PP increased the activation energy of the thermo-oxidative degradation process, e.g., the E of PE-DHL reached 125 kJ/mol compared with 34.2 kJ/mol for neat PE, which confirms the effectiveness of lignins as active antioxidants. Among all four lignins, DKL exhibited the highest activation energy while HL had the lowest activation energy, and the order of the activation energy is as follows: DKL > DHL > KL > HL. Such order is in a good agreement with those of their phenolic content and OIT as discussed previously. As well known, an antioxidant hinders the overall oxidative degradation by consuming free radicals and producing stabilized phenoxy radicals, which hence increases the energy barrier (i.e., activation energy) that the polymer has to overcome to initiate the oxidation.

Table 3-3. Activation energies of PE and PP with and without lignin

Sample	Activation energy (kJ/mol)
PE	34.2
PE-KL	95.8
PE-DKL	142
PE-HL	87.9
PE-DHL	125
PP	100.2
PP-KL	112.5
PP-DKL	217.2
PP-HL	103.2
PP-DHL	145.4

3.4.2.3   Thermal degradation

Table 3-4 summarizes temperature at the onset of thermal degradation, temperature at 10% weight loss, and temperature at the maximum degradation rate, based on the TGA thermograms of PE, PP, KL, DKL, HL, DHL, PE-lignins, and PP-lignins (Figures 3-7, 3-8, 3-9). With all samples except DKL prior to the onset degradation tempeature, there was a small increase (~1%) in the mass due to the formation of peroxy and hydroperoxide radicals although it is not visible in the TGA curves by naked eyes [32]. Later these free radicals initiated degradation of the PE or PP forming volatile products as indicated by the rapid mass loss step in the TGA curves. In PE and PE-lignins, there was another small mass loss near to completion, which signifies ignition of the char [30]. By contrast, the TGA curves of PP and PP-lignins exhibit one single degradation step as similarly reported in the literature data [30].

The TGA curves of the lignins and depolymerized lignins suggest that these lignins lose weight through multiple steps: the first step is likely related to release of volatiles and the second step degradation of lignins. The TGA curves of PE-lignins and PP-lignins clearly show that the addition of the lignins increased the onset degradation temperature and the maximum degradation temperature of PE and PP, suggesting that the lignins acted as free radical scavengers for PE and PP upon thermo-oxidative heating.

Table 3-4. Thermal degradation temperature of PE-lignins and PP-lignins

Sample	Temperature at the onset of degradation	Temperature at 10% weight loss	Temperature at the maximum degradation rate
KL	175	265	560
DKL	95	233	551
HL	164	190	293
DHL	47	300	556
PE	266	340	349
PE-KL	288	390	446
PE-DKL	302	404	450
PE-HL	190	343	405
PE-DHL	270	393	446
PP	250	318	380
PP-KL	267	330	389
PP-DKL	272	332	393
PP-HL	218	316	376
PP-DHL	260	333	399
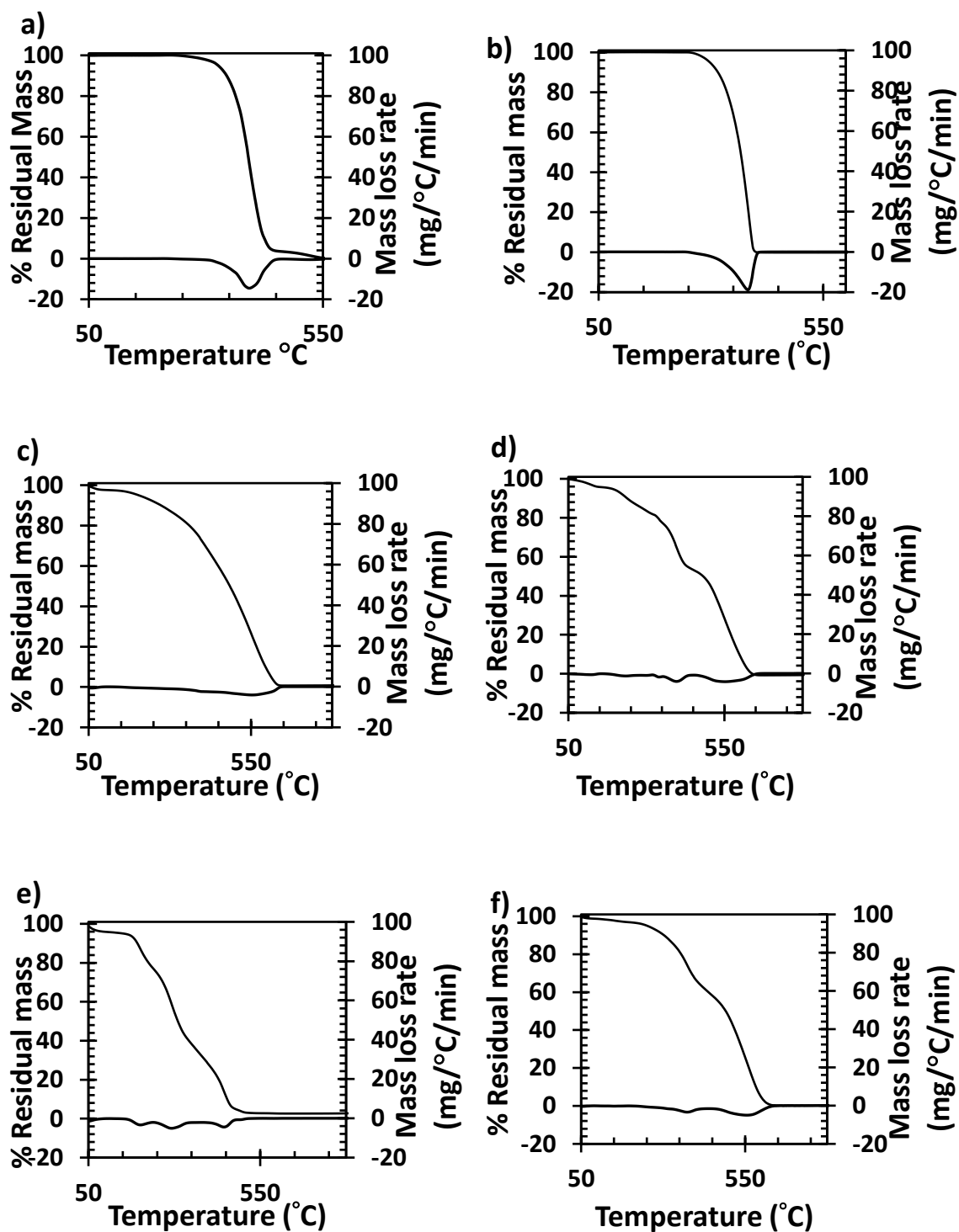
Figure 3-7. Typical TGA curves of a) PE, b) PP, c) KL, d) DKL, e) HL, and f) DHL
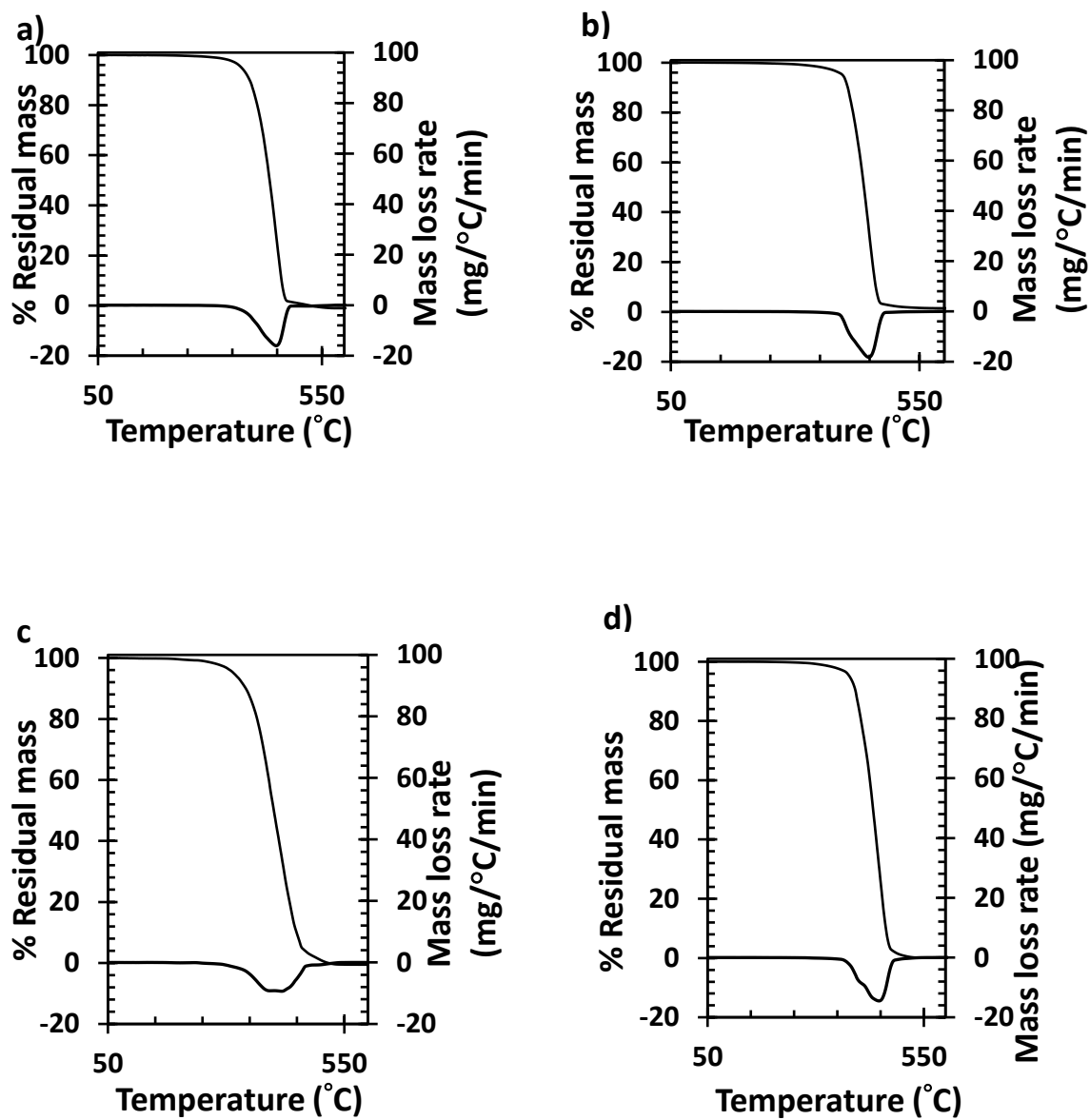
Figure 3-8. Typical TGA curves of a) PE-KL, b) PE-DKL, c) PE-HL, and d) PE-DHL
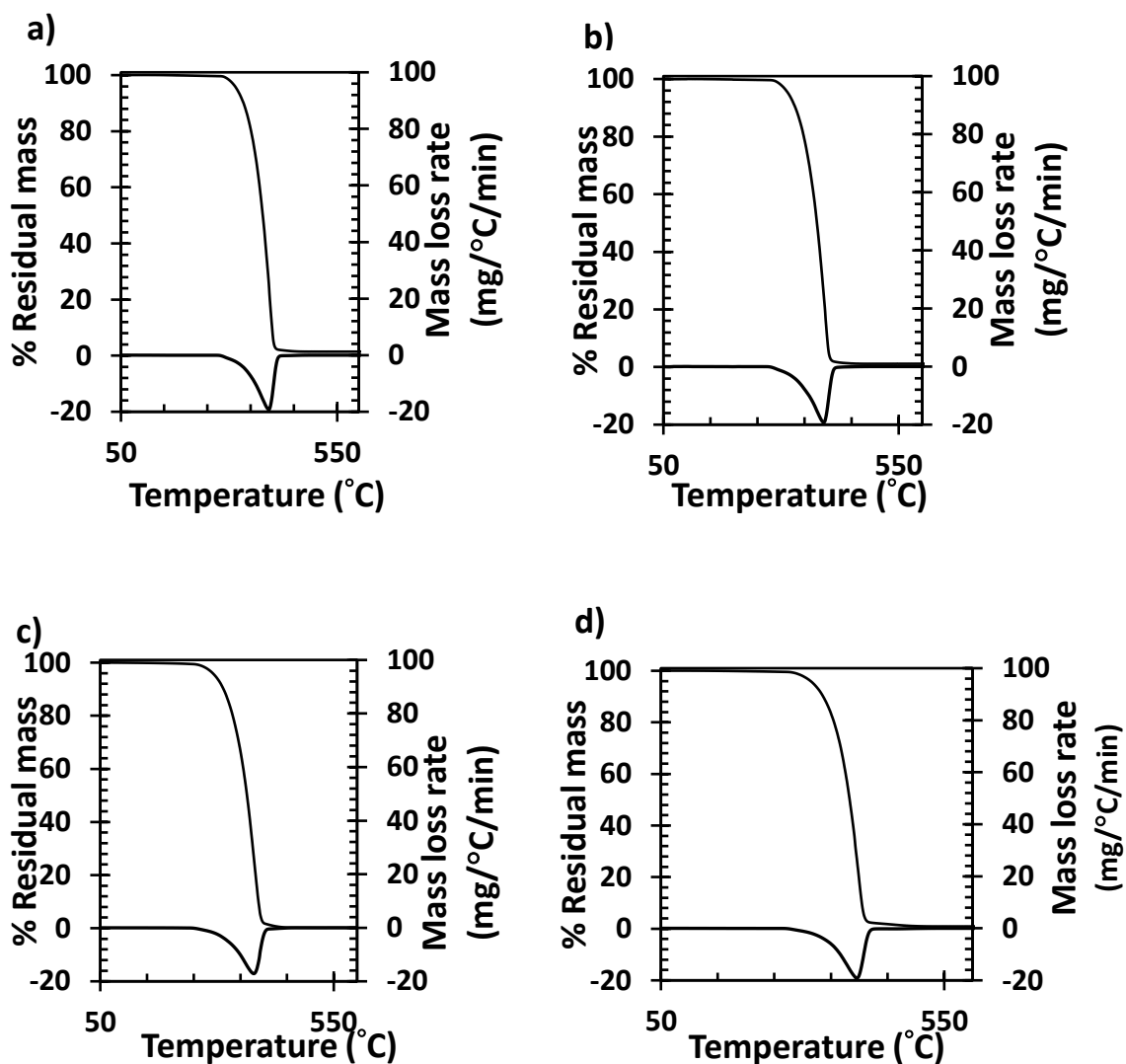
Figure 3-9. Typical TGA curves of a) PP-KL, b) PP-DKL, c) PP-HL, and d) PP-DHL

KL was less effective in thermal stabilization than DKL. It is expected that the aryl ether linkages in KL were broken and unstable free radicals were formed during de-polymerization at elevated temperatures. Moreover, DKL has a higher phenolic content than KL, which would contribute to increasing the thermal stability of the polyolefin too. Similarly, HL proved to be less effective for thermal stabilization of PE/PP than DHL. Since HL has a high percentage of cellulose and hemicellulose, it would decompose at a lower temperature than other lignins. As a result, PE-HL and PP-HL exhibited even

poorer thermal stability than neat PE and PP. However, the addition of DHL enhanced the thermal stability of the polymers with increased degradation temperature of PE and PP, acting as a thermo-oxidative stabilizer. The superior performance of DHL than HL is likely owing to of the fact that most cellulose and hemicellulose in HL could be removed during the hydrolytic de-polymerization process.

3.5   Conclusions

(1) Kraft lignin (a waste product from the pulp and paper industry) and hydrolysis lignin (a by-product from the pre-treatment processes in cellulosic ethanol plants) were utilized as an antioxidant for polyethylene (PE) and polypropylene (PP).

(2) KL and HL were modified by a de-polymerization process. The obtained de-polymerized KL (DKL) and de-polymerized HL (DHL) have a much lower molecular weight (less than 1500 g/mol) but increased aromatic hydroxyl content.

(3) The addition of all four lignins to PE and PP increased the oxidation induction time (OIT) activation energy for oxidative degradation, and thermal degradation temperature (except HL) of PE and PP. The antioxidant effects of the lignin follow the order of: de-polymerized KL (DKL) or de-polymerized HL (DHL), KL and HL, which was the same order as their phenolic content.

(4) De-polymerization also improved the compatibility of the lignins with the non-polar polymer matrix by decreasing the aliphatic hydroxyl content and improving the hydrophobicity.

(5) De-polymerization proved to be an effective strategy to improve the antioxidant activity of technical lignins.

3.6   References

[1]   A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R. a Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N.

Saddler, T.J. Tschaplinski, G. a Tuskan, C.E. Wyman, Lignin valorization: improving lignin processing in the biorefinery., Science. 344 (2014) 1246843. doi:10.1126/science.1246843.

[2]   C. Xu, R. Arneil, D. Arancon, J. Labidi, R. Luque, Lignin depolymerisation strategies: towards valuable chemicals and fuels, Chem. Soc. Rev. Chem. Soc. Rev. 43 (2014) 7485–7500. doi:10.1039/c4cs00235k.

[3]   F.S. Chakar, A.J. Ragauskas, Review of current and future softwood kraft lignin process chemistry, Ind. Crops Prod. 20 (2004) 131–141. doi:10.1016/j.indcrop.2004.04.016.

[4]   S. Laurichesse, L. Avérous, Chemical modification of lignins: Towards biobased polymers, Prog. Polym. Sci. 39 (2014) 1266–1290. doi:10.1016/j.progpolymsci.2013.11.004.

[5]   S. Huang, N. Mahmood, M. Tymchyshyn, Z. Yuan, C.C. Xu, Reductive de-polymerization of kraft lignin for chemicals and fuels using formic acid as an in-situ hydrogen source, Bioresour. Technol. 171 (2014) 95–102. doi:10.1016/j.biortech.2014.08.045.

[6]   N. Mahmood, Z. Yuan, J. Schmidt, C. Xu, Preparation of bio-based rigid polyurethane foam using hydrolytically depolymerized Kraft lignin via direct replacement or oxypropylation, Eur. Polym. J. 68 (2015) 1–9. doi:10.1016/j.eurpolymj.2015.04.030.

[7]   F. Ferdosian, Z.S. Yuan, M. Anderson, C. (Charles) Xu, Synthesis of lignin-based epoxy resins: optimization of reaction parameters using response surface methodology, RSC Adv. 4 (2014) 31745. doi:10.1039/C4RA03978E.

[8]   D.R. Vardon, M.A. Franden, C.W. Johnson, E.M. Karp, M.T. Guarnieri, J.G. Linger, M.J. Salm, T.J. Strathmann, G.T. Beckham, Adipic acid production from lignin, Energy Environ. Sci. 8 (2015) 617–628. doi:10.1039/C4EE03230F.

[9]   A. García, A. Toledano, M.Á. Andrés, J. Labidi, Study of the antioxidant capacity of Miscanthus sinensis lignins, Process Biochem. 45 (2010) 935–940. doi:10.1016/j.procbio.2010.02.015.

[10]   I. Egüés, C. Sanchez, I. Mondragon, J. Labidi, Antioxidant activity of phenolic compounds obtained by autohydrolysis of corn residues, Ind. Crops Prod. 36 (2012) 164–171. doi:10.1016/j.indcrop.2011.08.017.

[11]   Q. Lu, W. Liu, L. Yang, Y. Zu, B. Zu, M. Zhu, Y. Zhang, X. Zhang, R. Zhang, Z. Sun, J. Huang, X. Zhang, W. Li, Investigation of the effects of different organosolv pulping methods on antioxidant capacity and extraction efficiency of lignin, Food Chem. 131 (2012) 313–317. doi:10.1016/j.foodchem.2011.07.116.

[12]   T. Dizhbite, G. Telysheva, V. Jurkjane, U. Viesturs, Characterization of the radical scavenging activity of lignins - Natural antioxidants, Bioresour. Technol. 95 (2004) 309–317. doi:10.1016/j.biortech.2004.02.024.

[13]   V.R. Preedy, R.R. Watson, The encyclopedia of vitamin E, CABI, 2007.

[14]   M. Tolinski, Additives for polyolefins: getting the most out of polypropylene, polyethylene and TPO, William Andrew, 2015.

[15]   C.A. Johnson, P.J. Szalay, Method of improving heat stability of vinyl chloride polymers US 3484397 A ABSTRACT available in, (n.d.) 4–7.

[16]   K. Levon, J. Huhtala, B. Malm, J.J. Lindberg, Improvement of the thermal stabilization of polyethylene with lignosulphonate, Polymer (Guildf). 28 (1987) 745–750. doi:10.1016/0032-3861(87)90223-0.

[17]   P. Alexy, B. Košíková, G. Podstránska, The effect of blending lignin with polyethylene and polypropylene on physical properties, Polymer (Guildf). 41 (2000) 4901–4908. doi:10.1016/S0032-3861(99)00714-4.

[18] R. Pucciariello, V. Villani, C. Bonini, M. D'Auria, T. Vetere, Physical properties of straw lignin-based polymer blends, Polymer (Guildf). 45 (2004) 4159–4169. doi:10.1016/j.polymer.2004.03.098.

[19] C. Pouteau, P. Dole, B. Cathala, L. Averous, N. Boquillon, Antioxidant properties of lignin in polypropylene, Polym. Degrad. Stab. 81 (2003) 9–18. doi:10.1016/S0141-3910(03)00057-0.

[20] M. Canetti, F. Bertini, A. De Chirico, G. Audisio, Thermal degradation behaviour of isotactic polypropylene blended with lignin, Polym. Degrad. Stab. 91 (2006) 494–498. doi:10.1016/j.polymdegradstab.2005.01.052.

[21] A. Gregorová, Z. Cibulková, B. Košíková, P. Šimon, Stabilization effect of lignin in polypropylene and recycled polypropylene, Polym. Degrad. Stab. 89 (2005) 553–558. doi:10.1016/j.polymdegradstab.2005.02.007.

[22] X. Yue, F. Chen, X. Zhou, G. He, Preparation and Characterization of Poly (vinyl chloride) Polyblends with Fractionated Lignin, Int. J. Polym. Mater. 61 (2012) 214–228. doi:10.1080/00914037.2011.574659.

[23] Pan X, Kadla J, Ehara K, et al (2006) Organosolv Ethanol Lignin from Hybrid Poplar as a Radical Scavenger : Relationship between Lignin Structure , Extraction Conditions , and Antioxidant Activity. J Agric Food Chem 54:5806–5813. doi: 10.1021/jf0605392

[24] V. Ugartondo, M. Mitjans, M.P. Vinardell, Comparative antioxidant and cytotoxic effects of lignins from different sources, Bioresour. Technol. 99 (2008) 6683–6687. doi:10.1016/j.biortech.2007.11.038.

[25] L. Kouisni, A. Gagne, K. Maki, P. Holt-Hindle, M. Paleologou, LignoForce System for the Recovery of Lignin from Black Liquor: Feedstock Options, Odor Profile, and Product Characterization, ACS Sustain. Chem. Eng. 4 (2016) 5152–5159. doi:10.1021/acssuschemeng.6b00907.

[26] Z. Yuan, T.C. Browne, X. Zhang, Biomass fractionation process for bioproducts, (2011). https://www.google.com/patents/US20110143411.

[27] N. Mahmood, Z. Yuan, J. Schmidt, C. Xu, Production of polyols via direct hydrolysis of kraft lignin: Effect of process parameters, Bioresour. Technol. 139 (2013) 13–20. doi:10.1016/j.biortech.2013.03.199.

[28] F. Ferdosian, Z. Yuan, M. Anderson, C. Xu, Sustainable lignin-based epoxy resins cured with aromatic and aliphatic amine curing agents: Curing kinetics and thermal properties, Thermochim. Acta. 618 (2015) 48–55. doi:10.1016/j.tca.2015.09.012.

[29] N. Mahmood, Z. Yuan, J. Schmidt, C. Xu, Production of polyols via direct hydrolysis of kraft lignin: Effect of process parameters, Bioresour. Technol. 139 (2013) 13–20. doi:10.1016/j.biortech.2013.03.199.

[30] J.D. Peterson, S. Vyazovkin, C.A. Wight, Kinetics of the thermal and thermo-oxidative degradation of polystyrene, polyethylene and poly(propylene), Macromol. Chem. Phys. 202 (2001) 775–784. doi:10.1002/1521-3935(20010301)202:6<775::AID-MACP775>3.0.CO;2-G.

[31] C.L. Beyler, M.M. Hirschler, Thermal Decomposition of Polymers, SPE Handb. Fire Prot. Eng. (2001) 110–131. doi:10.1021/cm200949v.

[32] W. Camacho, S. Karlsson, Assessment of thermal and thermo-oxidative stability of multi-extruded recycled PP, HDPE and a blend thereof, Polym. Degrad. Stab. 78 (2002) 385–391. doi:10.1016/S0141-3910(02)00192-1.

[33] G. Litwinienko, T. Kasprzycka-Guttman, A DSC study on thermoxidation kinetics of mustard oil, Thermochim. Acta. 319 (1998) 185–191. doi:10.1016/S0040-6031(98)00410-9.

[34] G. Litwinienko, K. Jodko-Piórecka, Recent Developments in DSC Analysis to

Evaluate Thermooxidation and Efficacy of Antioxidants in Vegetable Oils, in: Differ. Scanning Calorim., CRC Press, 2014: pp. 49–74. doi:doi:10.1201/b17739-5.

Chapter 4

4 Effects of de-polymerized lignin content on thermo-oxidative stability of polyethylene

4.1 Introduction

Polymers are subjected to degradation in all stages of their lifecycle, starting from processing, shelf life to end use. There are three types of degradation: thermal, thermo-oxidative, and photo-oxidative degradation, depending on the environment. In the case of thermal degradation, thermal scission in the weak sites of the polymer produces primary radicals. Later the polymer undergoes degradation through various pathways including radical transfer, random scission, chain scission, cross-linking and branching. In the case of thermo-oxidative degradation and photo-oxidative degradation, initiation is induced by temperature and UV radiation or chemical initiators like oxygen or peroxides to create free radicals, which later form peroxy radicals by reacting with oxygen. The degradation happens through the chain reactions of these initiators and propagators with oxygen, and the events similar to the thermal degradation occur in the later stages. Due to the nature of the reactions with oxygen, thermo-oxidative and photo-oxidative degradation are more severe and propagate much faster than the thermal degradation in an inert atmosphere. Commercially, hindered phenolic antioxidants are employed to retard the thermo-oxidative degradation process [1–3]. Recently, initiatives have been taken to employ lignin, a biomass component, as a green alternative to traditional petroleum-based hindered phenolic antioxidants in polymer processing [4–9].

Lignin is a natural phenolic polymer comprised of phenylpropane building blocks, as one of three major components of lignocellulosic biomass [10,11]. In wood, lignin contributes in the nutrient transportation and protection of the cells from adverse environmental conditions [12,13]. Currently, lignin is used mainly as a low-value fuel, but due to its aromatic structure, lignin has potential to be utilized as a chemical [14]. A number of studies have suggested that lignin could be employed as a stabilizer or antioxidant for plastics and rubbers [4,7,8,15,16].

The antioxidant behavior of lignin stems from its inherent hindered phenolic structure, which facilitates lignin to work as a free radical scavenger. As demonstrated by previous researchers [17,18], the scavenging activity of lignin depends on its origin, and the antioxidant activity of the lignin increases with decreasing molecular weight and increasing phenolic content [18,19]. Our recent study (as discussed in Chapter 3) showed that de-polymerization of crude lignins (kraft lignin and hydrolysis lignin) decreased the molecular weight and increased the phenolic content of the respective lignins and led to an increased thermo-oxidative stability of polypropylene (PP) and polyethylene (PE).

According to Frost and Sullivan [20], the antioxidant market is rapidly increasing with a projected growth of $1.62B in the next few years. Simultaneously, the production of lignin is rapidly growing owing to the fact that most of the kraft pulping mills in North America has a bottle-neck in their recovery boilers and hence extracting kraft lignin out of the pulping process would lead to production capacity improvement in pulp and paper mills, and the development of bio-refineries technologies. As of 2013, the global production of kraft lignin was approximately 50 million tons per annum [14]. Ragauskas et al. estimated that the second generation of biorefineries are going to add additional 62 million tons of lignin per year in the market [21]. Due to the growing markets for polyolefins and antioxidants, as well as the production of surplus amount of lignin, lignin has a great potential to become widespread in the antioxidant market. In this study, we examine effects of addition amounts of de-polymerized kraft lignin (DKL) and de-polymerized hydrolysis lignin (DHL) in PE on its thermo-oxidative stability, and find the appropriate content to achieve the performance comparable to that of a PE blend with 0.5 wt% commercial antioxidant.

4.2 Experimental

4.2.1 Materials

The materials used in preparing the binary blends were low-density polyethylene (LDPE), de-polymerized kraft lignin (DKL), de-polymerized hydrolysis Lignin (DHL), and Irganox 1010. LDPE with the density of 0.925 g/mL and melt flow index of 2.5

g/min was supplied by Sigma-Aldrich. Kraft lignin (KL) and hydrolysis lignin (HL) were obtained from FPInnovation, which are products of their proprietary LignoForce process [22] in its pilot plant in Thunder Bay, Ontario and "TMP-bio process" [23], respectively. De-polymerization of the KL and HL were realized by a low-temperature/low-pressure process developed by the authors' group (currently patent pending). Briefly, KL de-polymerization was carried out in a Parr autoclave reactor (500 mL) at 250°C, 1 h, with 20 wt.% KL substrate concentration in poly-alcohol-water co-solvent in the presence of an alkaline catalyst (NaOH/KL mass ratio of 0.28), producing de-polymerized KL (DKL) at a yield of ~90 wt.%. De-polymerized hydrolysis lignin (DHL) was obtained by acid catalyzed de-polymerization at 200°C, 1 h with 20 wt.% HL substrate concentration in the same solvent in the presence of an acid catalyst (H_2SO4/HL mass ratio of 2% w/w), leading to ~70 wt.% yield of DHL. The DKL and DHL had a molecular weight of 1164 g/mol and 1413 g/mol, respectively. The phenolic content of the DKL and DHL was 2.7 mol phenol/kg and 1.9 mol phenol/kg, respectively. The aliphatic hydroxyl content of the DKL and DHL was 0.7 mol/kg and 0.46 mol/kg respectively.

The commercial antioxidant (Irganox 1010) was supplied by Sigma-Aldrich. Irganox 1010 is the trade name of Pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), which is a third-generation antioxidant with the phenolic content of 3.6 mol phenol/kg and volatility as measured in terms of 10% weight loss measured from thermogravimetric analysis at 287°C [24].

Eight samples, whose compositions are summarized in Table 4-1, were prepared using a HAAKE MiniLab II Micro Compounder. The PE and antioxidants were compounded at 140°C for 10 min at 100 rpm.

Table 4-1. Compositions of PE blends

Sample name	PE (wt%)	Irganox 1010 (wt%)	DKL (wt%)	DHL (wt%)
PE	100	0	0	0
PE-0.5irg	99.5	0.5	0	0
PE-0.5DKL	99.5	0	0.5	0
PE-2.5DKL	97.5	0	2.5	0

PE-5DKL	95	0	5	0
PE-0.5DHL	99.5	0	0	0.5
PE-2.5DHL	97.5	0	0	2.5
PE-5DHL	95	0	0	5

4.2.2   Scanning electron microscopy (SEM)

The compounded samples were fractured in liquid Nitrogen and observed in a scanning electron microscope (LEO (Zeiss) 1540XB FIB/SEM) at 1 keV. Prior to imaging, the samples were coated with 10 nm osmium using Osmium Plasma Coater (Filgen OPC80T).

4.2.3   Differential scanning calorimetry (DSC)

The isothermal DSC (differential scanning calorimetry) method of measuring Oxidation Induction Time (OIT) was employed in accordance to the ASTM standard [ASTM D-3895] for quality control of polyolefins containing primary (chain-breaking) antioxidants. A sample of 5-6 mg was heated in an open aluminum pan in a differential scanning calorimeter (DSC1, Mettler Toledo) with a STARe software, from 50°C to 220°C at a heating rate of 10°C/min under a nitrogen flow of 50 mL/min. After the temperature reached 220°C, the sample was maintained at the temperature for 1 minute and then the purge nitrogen gas was switched to air with a flow rate of 50 ml/min. The sample was heated in air at 220°C until the time at which oxidation begins, and the heat flow was recorded. The time interval between the switch of gas and the onset of the thermo-oxidation exotherm was reported as the OIT time.

The activation energy for thermo-oxidative degradation was also measured using DSC by following the Flynn/Wall/Ozawa Method as described in ASTM E698-16. A sample of 5-6 mg was heated from 50°C to 450°C at four different heating rates (7.5, 10, 12.5, and 15°C/min) under an air flow of 50 mL/min.

4.2.4   Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was conducted in a Q-500, TA Instrument apparatus with a Universal TA analysis software. A sample with a mass of 5-6 mg was heated in an air atmosphere (20 mL/min) at a heating rate of 10°C/min from 50°C to 600°C and the TGA traces were recorded.

4.2.5   Mechanical Testing

Tensile tests were performed on Type V specimens as per ASTM D638, on an ADMET Expert7600 computerized universal testing machine, at ambient conditions and at a crosshead speed of 5 mm/min. Some PE blends were selected for the tensile tests. In order to produce Type V specimens, the samples were compounded using the HAAKE MiniLab II Micro Compounder at 140°C for 10 min at 100 rpm. The resulting molten polymer from the compounder was transferred to a preheated mini-injection molding machine (HAAKE MiniJet), which then injected the melt into a mold with a 240 bar injection pressure. Injection cylinder and mold temperatures were set at 140°C and 40°C, respectively.

Long-term thermo-oxidative stability was evaluated in terms of change in tensile properties after 200 h exposure in the oven at 100°C. Long-term UV stability was evaluated in terms of change in tensile properties after 200 h exposure in fluorescent UV light in an accelerated weathering tester (LUV-2) according to ASTM D4329−13 at 100% humidity at 40 °C.

4.3 Results and Discussions

4.3.1 Morphology
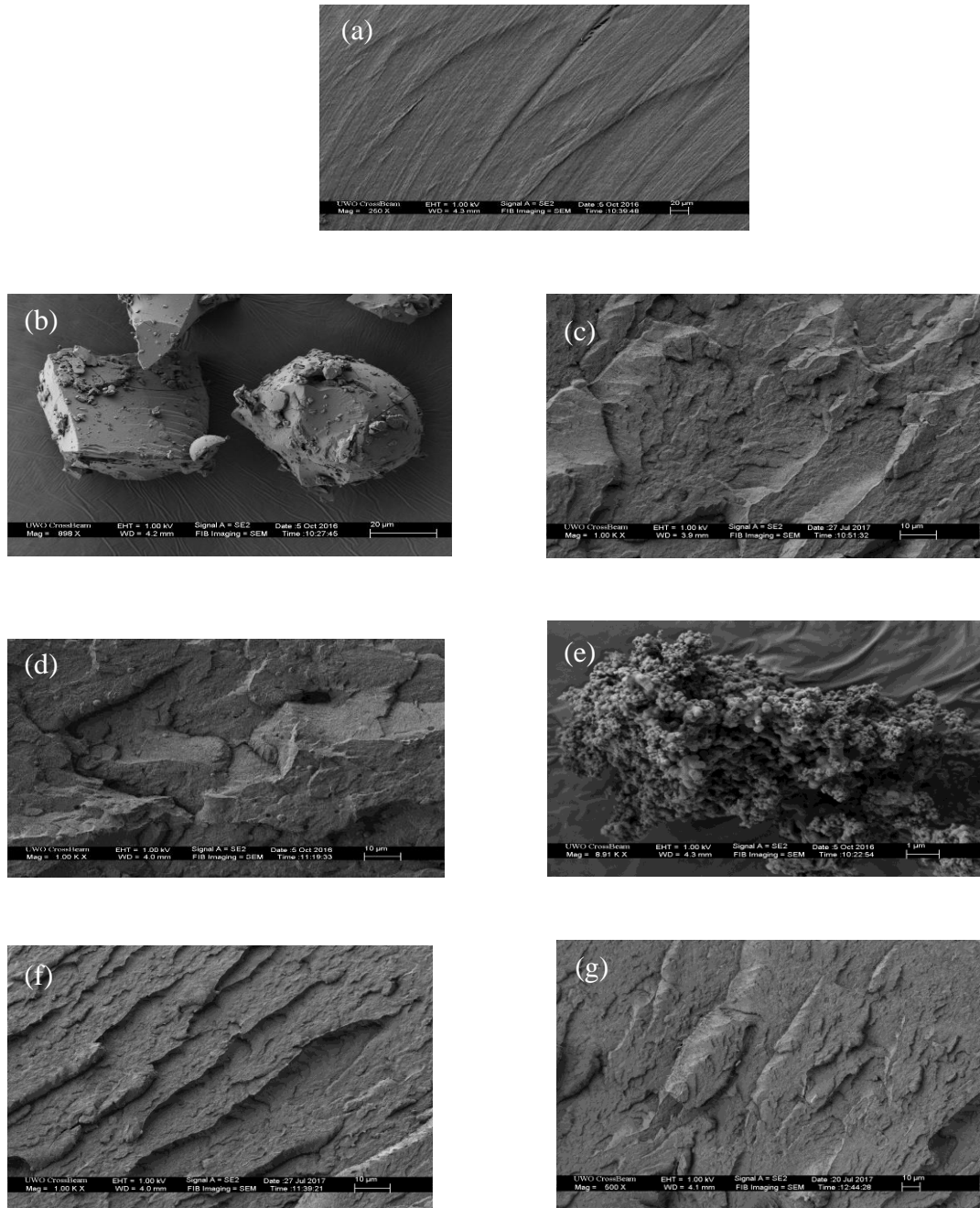
Figure 4-1. SEM micrographs of a) PE, b) DKL, c) PE-0.5DKL blend, d) PE-5DKL blend, e) DHL, f) PE-0.5DHL blend and g) PE-5DHL blend

Figure 4-1 shows representative SEM micrographs of some typical samples. The fracture surface of the neat PE did not show any particles (Figure 4-1a) as expected. When the DKL, whose original size is around 20 μm (Figure 4-1b), was added to PE at 0.5 wt% addition, no particles were visible (Figure 4-1c), but many particles of 1-2 μm were observed in the PE-DKL blend at the 5 wt% DKL addition (Figure 4-1d). This may suggest that the DKL in the PE at the 0.5 wt% addition is highly dispersed or soluble. However, with further addition, DKL reached its solubility limit in PE and precipitated out or was less dispersed, and thus the DKL particles were visible by SEM. When the DHL, whose original size is less than 1 μm (Figure 4.1e), was added to PE, no particles were visible in the PE-DHL blends at the 0.5 wt% (Figure 4-1f) and 5 wt% addition (Figure 4-1g). Hence, this result may suggest that DHL is soluble or has good dispersity in the PE up to the 5 wt% addition. The improved solubility or dispersity of DHL compared to DKL in PE might be owe to DHL's less aliphatic hydroxyl content (0.46 mol/kg), compared to DKL (0.7 mol/kg), which led to the increased compatibility of DHL with the non-polar PE matrix.

4.3.2   Oxidation induction time (OIT)

Figure 4-2 presents the OIT graphs of various PE blends and Figure 4-3 summarizes the OIT values dervied from Figure 4-2.
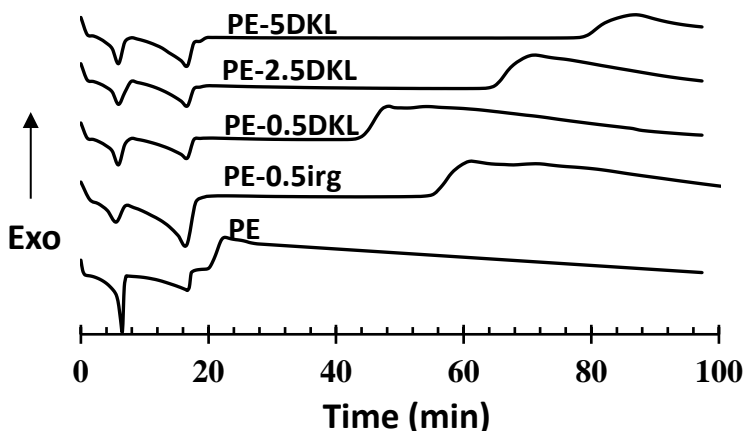
Figure 4-2. DSC curves obtained from OIT tests for various PE blends
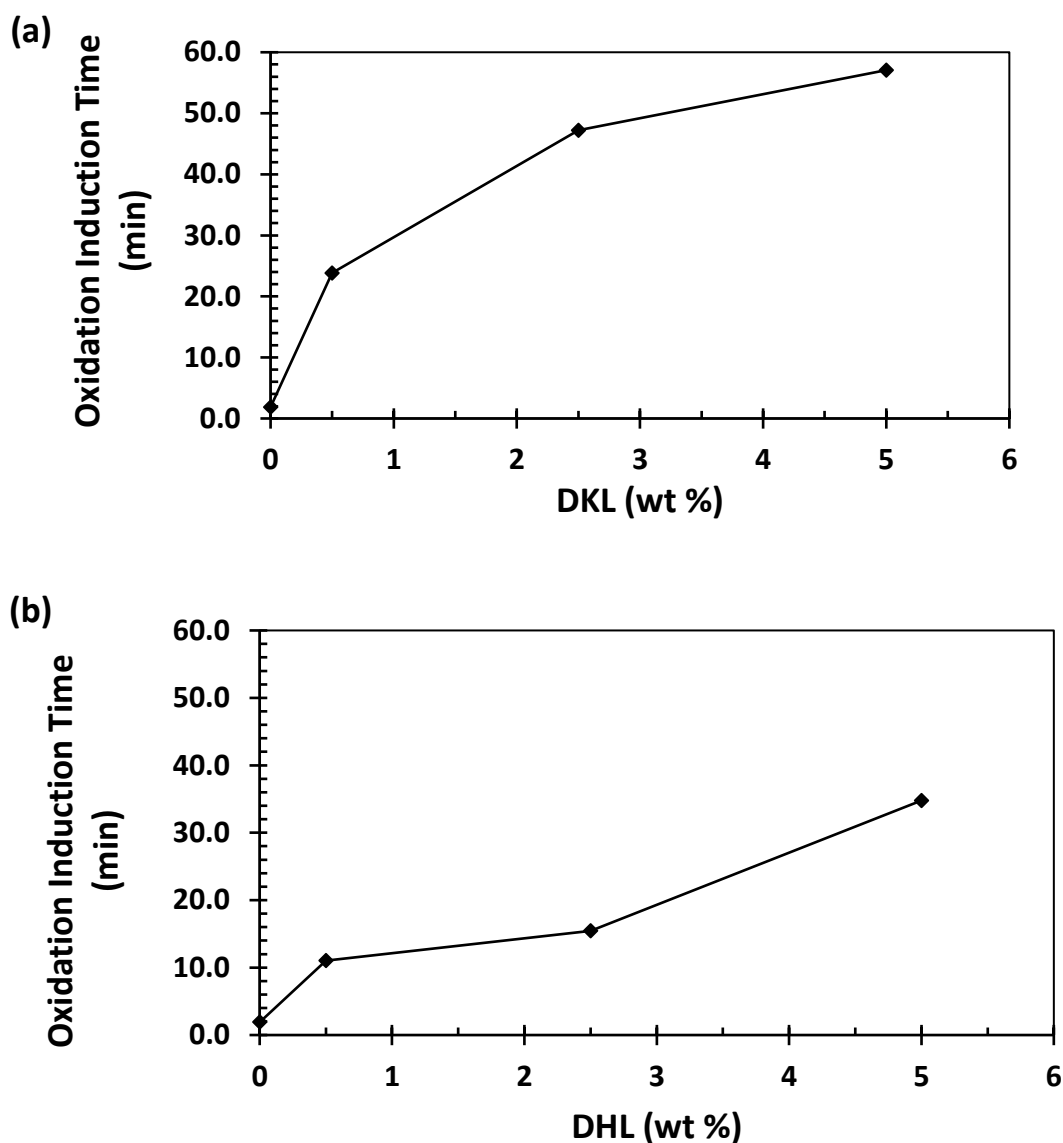
Figure 4-3. Oxidation induction time of PE with (a) DKL and (b) DHL

The OIT measures thermo-oxidative stability of polymeric materials. PE blends containing lignin displayed a longer OIT compared to that of neat PE, indicating the enhanced stability to thermo-oxidative degradation rendered by the lignin molecules. Compared with that of neat PE (OIT ~ 2 min), OIT of PE-DKL increased to ~25 min with the addition of only 0.5 wt% of DKL, and OIT of PE-DHL rose to 11.5 min with only 0.5 wt% addition of DHL. The improvement in the thermo-oxidative stability of the

PE blends can be explained by the aromatic hydroxyl groups (or phenolics) present in DKL (2.7 mol phenol/kg) and DHL (1.9 mol phenol/kg) which are effective for scavenging the radicals generated in the thermo-oxidative degradation process, similar to the effects of hindered phenolic antioxidants.

As presented by Figure 4-3a, after the addition of 2.5 wt% of DKL, the increase in OIT is less pronounced than that from 0 to 0.5 wt% addition. On the other hand, as presented by Figure 4-3b, the OIT increases with the increase of DHL content in an almost linear manner. These different phenomena may be a result of difference in DKL's and DHL's solubility or dispersity in PE. As suggested previously from Figure 4-1, PE-DKL had the precipitation of DKL below the 5 wt% addition. Due to the precipitation, the interaction between DKL and PE was less effective, hence the OIT values level off after 2.5 wt% DKL addition. However, since the DHL has better solubility or dispersity in PE up to the 5 wt% addition (Figure 4-1), the interaction between DHL and PE was more effective and the OIT values increased almost linearly with the DHL addition amount.

As demonstrated in Figure 4.3, the addition of 2.5 wt% DKL and 5 wt% DHL can reach the same level of OIT achieved by the addition of 0.5 wt% Irganox 1010 (~35.9 mins). According to Pouteau et al., antioxidants with low molecular weight have the benefit of diffusing in the polymer matrix easily, which leads to better antioxidant activity [5]. However, the studies on commercial antioxidants by Vulic et al. [24] and Tocháček et al. [25] suggested that antioxidants with low molecular weight has a problem of quick volatilization. Tocháček et al. [25] demonstrated that stabilizer performance of antioxidants falls drastically when the molecular weight decreased below 300-400 g/mol. Multiple studies [24,25] attributed the stability rendered by Irganox 1010 to its higher molecular weight (compared to first generation antioxidants) without sacrificing the phenolic concentration. After the de-polymerization, DKL and DHL had the weight-average molecular weight (M_w) of 1164 g/mol and 1413 g/mol, respectively, which are close to the molecular weight of Irganox 1010 (1178 g/mol). Hence, DKL and DHL are expected to provide similar level of antioxidant activity of Irganox 1010. However, as

demonstrated in Figure 4-3, it takes five times more DKL and 10 times more DHL to provide the same level of efficacy of Irganox 1010. This can be attributed to the lower phenolic content of DKL and DHL as compared to Irganox 1010. According to the literature, the structure of Irganox 1010 is composed of multiple hindered phenols tethered together, which have improved the phenolic concentration without sacrificing the molecular weight [24]. The phenolic content of Irganox 1010 is 3.6 mol phenol/kg [24]; whereas even after de-polymerization, DKL had the phenolic content of 2.7 mol phenol/kg and DHL had the phenolic content of 1.9 mol phenol/kg. Moreover, even after de-polymerization, DKL and DHL had polar polyol components in their side chains whereas Irganox 1010 had nonpolar components in its secondary structure. Hence, the hydrophilicity of DKL and DHL also contributed to the reduced compatibility with hydrophobic PE, as compared to commercial antioxidant.

4.3.3 Activation energy for oxidative degradation

Figure 4-4 illustrates the DSC curves of neat PE, PE-DKL, PE-DHL, and PE-Irganox blends at various heating rates. PE-DKL and PE-DHL exhibited multiple peaks and valleys on the DSC curves after the initial exotherm peak. It is widely accepted PE undergoes branching and crosslinking along with the chain scission during the degradation phenomenon. Hence, the multiple peaks observed in PE could be related to the crosslinking and branching reactions [3,26].
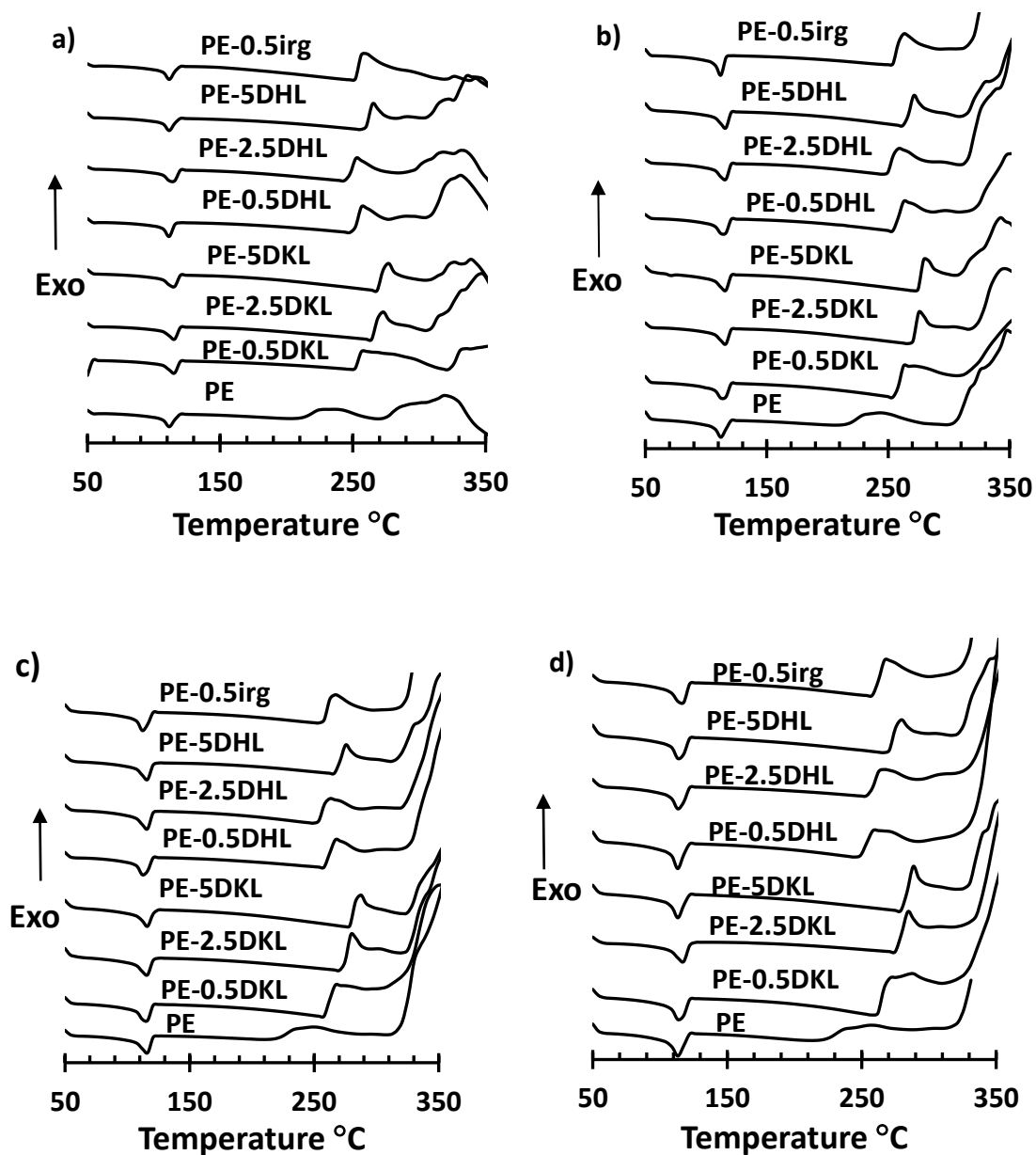
Figure 4-4. DSC curves of various PE blends at different heating rates: (a) 7.5°C/min, (b) 10°C/min, (c) 12.5°C/min, and (d) 15°C/min.

According to the Flynn/Wall/Ozawa method described in ASTM E698-16, the activation energy (E) for oxidative degradation of a polymer can be written as:

$$E = -2.19\, R\, \frac{\text{dlog}\,\beta}{\text{d}\, T_{\text{p}}^{-1}} \tag{1}$$

where R is the gas constant, β is the heating rate, and T_p is the temperature at the maximum of the first peak of exotherm.

Thus, by plotting $\log \beta$ vs. $1/\, T_p$, as shown previously (Figure 3-6), the slope ($= E/(-2.19R)$) can be used for calculating the activation energy. As mentioned above, the Flynn/Wall/Ozawa method calculates the activation energy employing the peak temperature of exotherm on the DSC heating curves. However, in order to effectively comprehend the activation energy of thermo-oxidative degradation of a polymer before and after incorporating an antioxidant, we employed temperature at the onset of exotherm (T_o) instead of the peak temperature for calculation of E in accordance to Eq. 1. As is known, the primary role of an antioxidant (de-polymerized lignins in this study) is scavenging peroxy radicals, thus retarding the propagation reactions. Hence, antioxidants are active only during the induction period, resulting in an increase in onset of the exotherm, and sometimes the peak temperature of the exotherm, while the latter peaks are not normally correlated with the activity of the antioxidant [27,28].

Figure 4-5 shows the activation energy of PE blends, which were calculated using the DSC thermograms obtained at different heating rates (Figure 4-4). An antioxidant hinders the overall oxidative degradation by consuming free radicals and producing stabilized phenoxy radicals, which hence increases the energy barrier (activation energy) that the PE has to overcome to initiate the oxidation reaction.

Both Figures 4-5a and 4-5b indicate that the activation energy of the PE blends increased with increasing the de-polymerized lignin content. The relationship is similar to that of OIT vs. the depolymerized lignin content (Figure 4-3): the activation energy increased with the DKL content but leveled off at 2.5 wt% DKL addition (Figure 4-5a). On the

other hand, the activation energy increased with the increase of DHL content in an almost linear manner (Figure 4-5b). These different phenomena might be a result of difference in DKL's and DHL's solubility in PE, as similarly discussed previously for the relationship of OIT vs. the depolymerized lignin content (Figure 4-3).
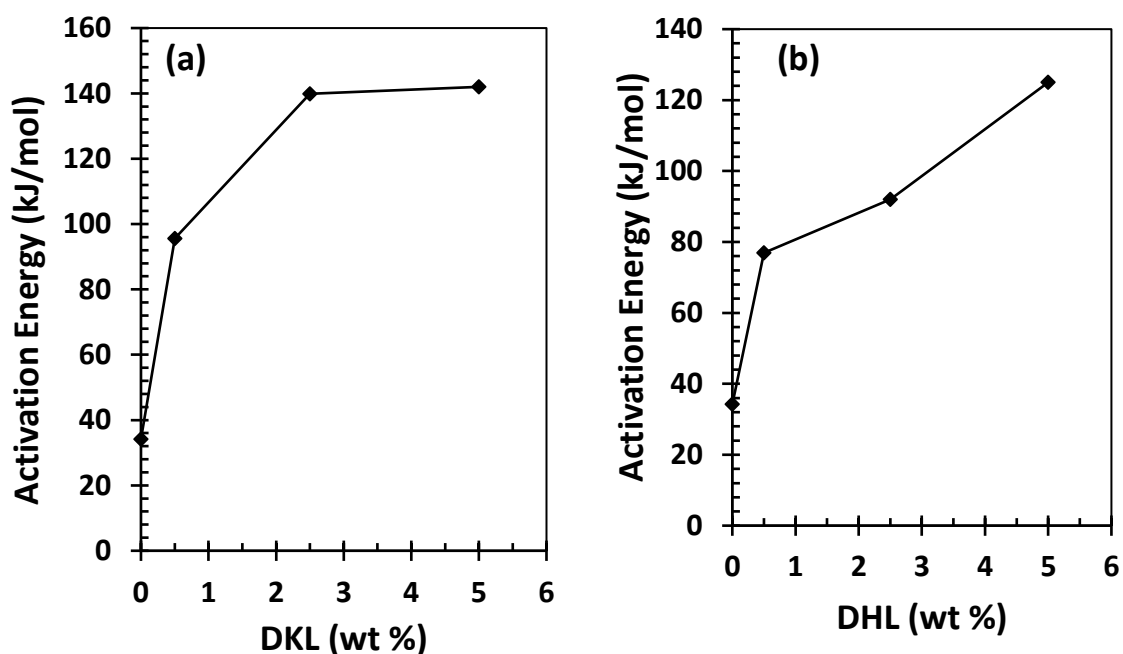
Figure 4-5. Activation Energy of PE blends with (a) DKL and (b) DHL

4.3.4   Temperatures at mass loss

Typical TGA and differential TGA (DTGA) curves of various PE blends are shown in Figure 4-6. Table 4-2 summarizes the temperature at the onset of mass loss, the temperature at 10% mass loss, and the temperature at the maximum mass loss rate, which were determined from the TGA and DTGA thermograms.

74
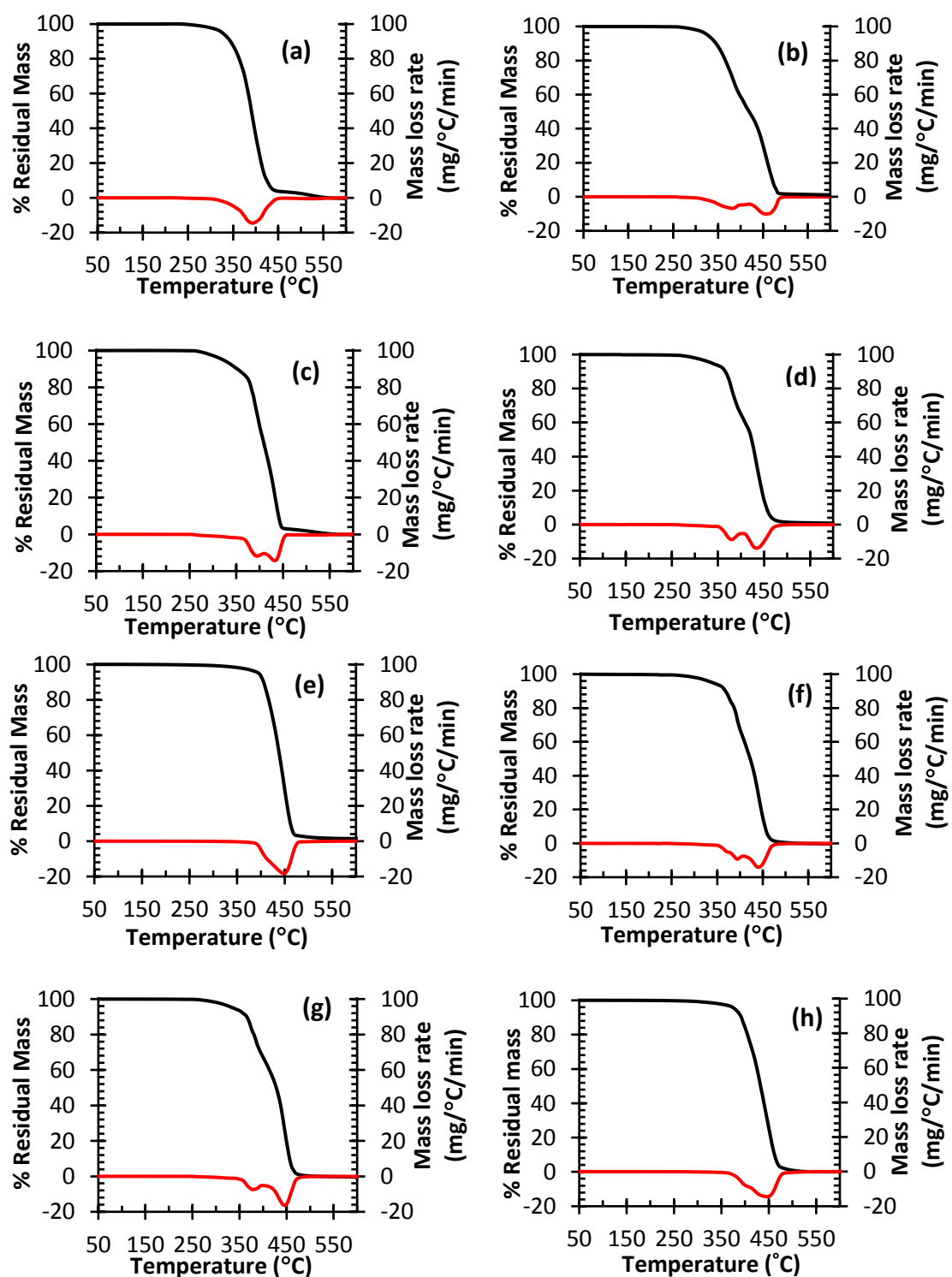
Figure 4-6. Typical TGA and DTGA curves of (a) PE, (b) PE-0.5irg, (c) PE-0.5DKL, (d) PE-2.5DKL, (e) PE-5DKL, (f) PE-0.5DHL, (g) PE-2.5DHL, and (h) PE-5DHL

Table 4-2. Temperatures at mass loss for PE blends

Sample	Temperature at the onset of mass loss (°C)	Temperature at 10% mass loss (°C)	Temperature at the maximum mass loss rate (°C)
PE	266	343	390
PE-0.5irg	271	346	457
PE-0.5DKL	268	349	430
PE-2.5DKL	273	365	434
PE-5DKL	302	404	450
PE-0.5DHL	266	365	441
PE-2.5DHL	270	365	445
PE-5DHL	270	393	446

The increase of DKL and DHL contents in the PE blends progressively shifted the TGA and DTGA curves toward higher temperature. Incorporation of DKL and DHL into PE increased the temperatures at onset, 10% and maximum mass loss by about 5-30°C, demonstrating that thermal-oxidative stability of PE was improved by the addition of the de-polymerized lignins.

4.3.5   Mechanical properties

Tensile tests were conducted for selected samples (PE, PE-2.5DKL and PE-0.5irg) before and after 200 h thermo-oxidative or UV exposure.
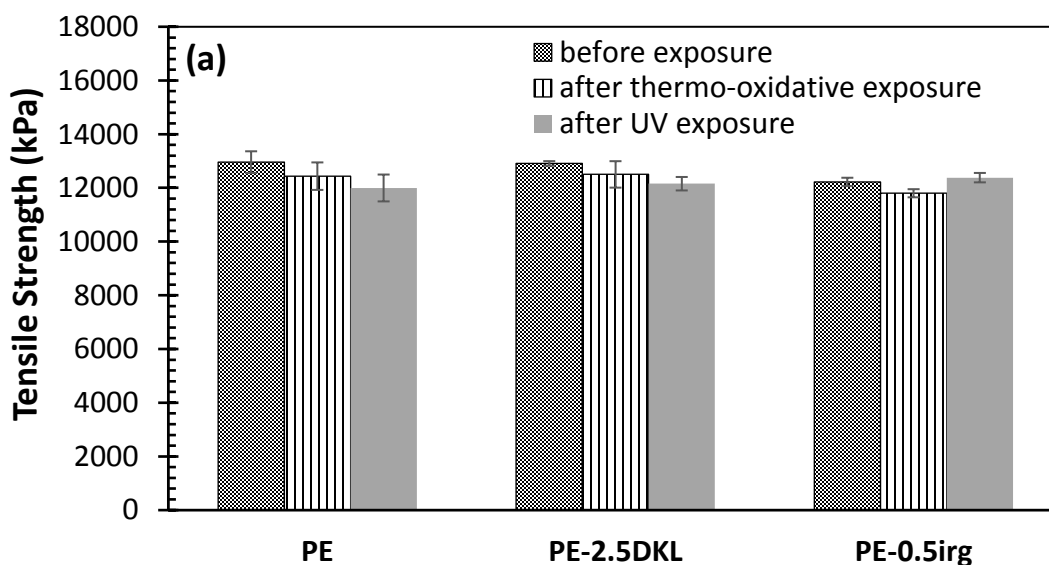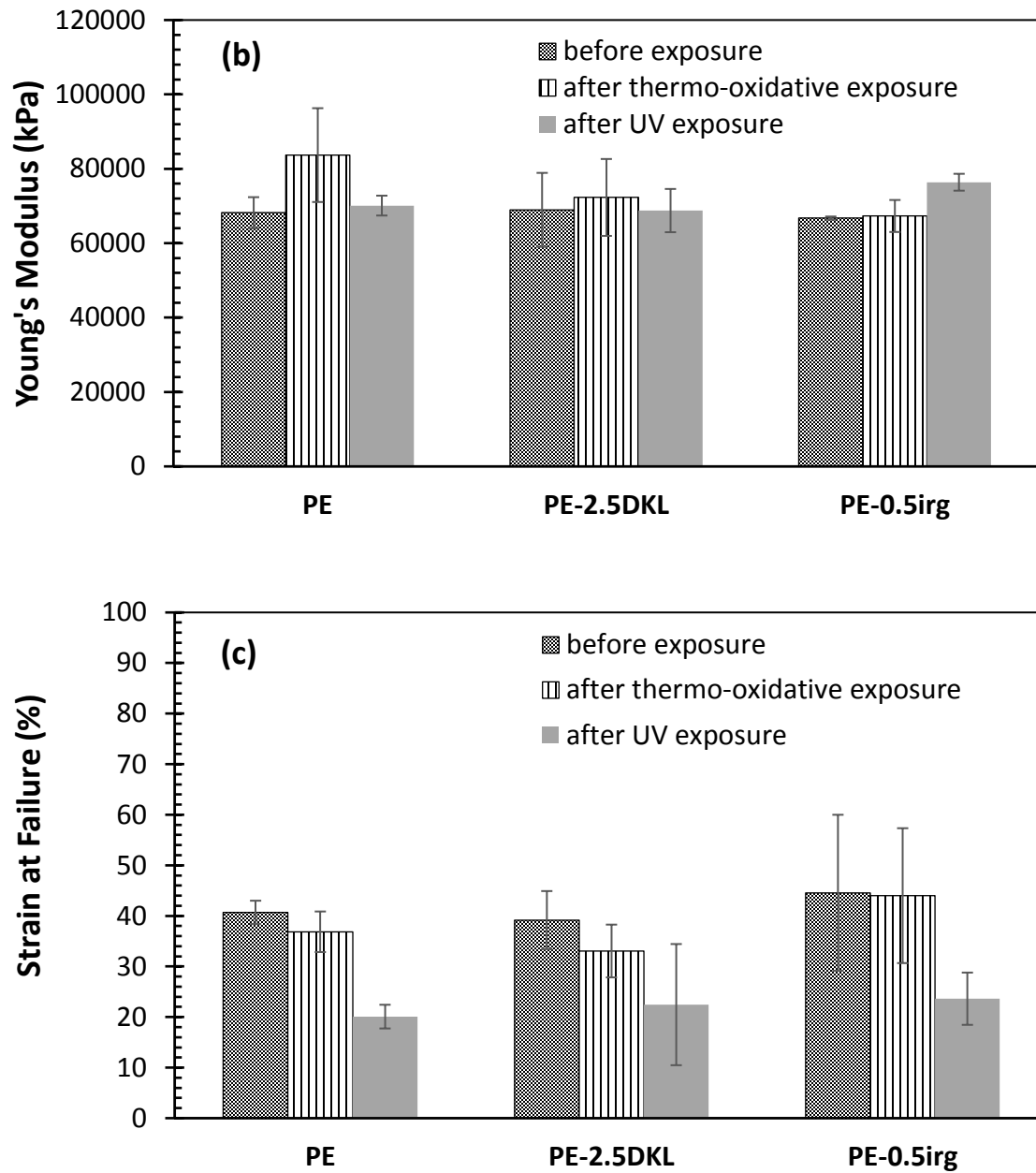
Figure 4-7. Mechanical properties of PE blends: (a) tensile strength, (b) Young's modulus, and (c) strain at failure

Figure 4-7a shows tensile strength of PE blends. Although the standard deviation of the results was large, the results suggested that the addition of DKL did not affect the tensile strength of the PE before exposing to the weathering conditions. It should be noted that these results are better than what reported in literature. Many literature studies on a high level of addition of a crude (or unmodified) lignin in a polyolefin observed decrease in tensile strength due to the poor compatibility between polar lignin and the non-polar polymer matrix [4,29,30]. In this work, the addition of 2.5 wt% DKL did not alter the tensile strength of PE may be owe to the improved compatibility between PE and DKL that has a low molecular weight and decreased aliphatic hydroxyl content. After 200h thermo-oxidative exposure, the tensile strength of all the samples including the PE and the two blends decreased. After UV exposure, however, PE-2.5DKL and PE-0.5irg blends had better tensile strength than neat PE. The PE-2.5DKL blend has better tensile strength than that of either the neat PE or the PE-0.5irg after 200h thermo-oxidative exposure.

Figures 4-7 b and 4-7c shows Young's modulus and strain at failure of the neat PE and the PE blends. Addition of Irganox or DKL did not change Young's modulus and strain at failure of the PE significantly before or after the thermo-oxidative or UV exposure. The similar results of mechanical properties of all these samples (PE, PE-DKL and PE-irg) after thermo-oxidative and UV exposure might be due to short time exposure (200h) to heat and UV. Given a longer time of exposure, some differences in the mechanical properties between these samples would be observed, which will be further investigated in future work.

The benefits of adding DKL or DHL to PE are two folds: (1) economic benefit as DKL or DHL is less expensive than the commercial antioxidant and the neat PE (as demonstrated in Section 4.4), and (2) environmental benefit as it is expected that the PE-DKL or PE-DHL bio-blend would be more biodegradable than neat PE [16,31,32].

4.4   Analysis of Material Costs of PE Blends

As discussed in the previous sections, PE blend with 2.5 wt% of DKL or 5 wt% of DHL addition could attain the same level of thermo-oxidative stability as the PE blend with 0.5 wt% of Irganox 1010 does. The material costs of these PE blends are simply estimated here and summarized in Table 4-3, based on 1 ton of each blend and assuming the prices of the raw materials are: 1200 USD/t-PE, 1000 USD/t-DKL or DHL, and 4000 USD/t-Irganox. The prices of PE and commercial antioxidant (Irganox 1010) were obtained from commercial products listed on www.alibaba.com in July, 2017, and the prices of DKL and DHL were estimated by our own research group based on a techno-economic study of our proprietary lignin de-polymerization process.

Table 4-3. Material costs of 1 ton PE or PE blends

Blend name	Antioxidant	Amount of antioxidant (t)	Amount of PE (t)	Cost of antioxidant (USD)	Cost of PE (USD)	Cost of PE blend (USD)
PE		0	1	0	1,200	1,200
PE-0.5irg	Irganox 1010	0.005	0.995	20	1,194	1,214
PE-2.5DKL	DKL	0.025	0.975	25	1,170	1,195
PE-5DHL	DHL	0.05	0.95	50	1,140	1,190

Table 4-3 demonstrates that the addition of the larger amount of DKL and DHL did not increase the cost of the PE blends. Instead, the material cost of the PE blend that contains a larger amount of DKL (2.5 wt%) or DHL (5 wt%) is actually lower than that of the PE blend with a smaller amount of the commercial antioxidant (0.5 wt%).

4.5   Conclusions

Effects of addition amounts of de-polymerized kraft lignin (DKL) and de-polymerized hydrolysis lignin (DHL) in PE on their thermo-oxidative stability were examined in this study, compared with a PE blend with 0.5 wt% commercial antioxidant (Irganox 1010). The OIT and activation energy for thermo-oxidative degradation of the PE blend increased with the increase of DKL or DHL content: the increase leveled off after the addition of 2.5 wt% of DKL, but increased in an almost linear manner for DHL up to 5

wt% addition. It is postulated that the difference in the way to increase between DKL and DHL were caused by that in the solubility of DKL and DHL in PE matrix, as suggested by the SEM micrographs. The results also revealed that the addition of 2.5 wt% DKL or 5 wt% DHL attained the same level of antioxidant activity as the addition of 0.5 wt% Irganox 1010. The lower phenolic concentration, complex molecular feature, and higher hydrophilicity of the de-polymerized lignins might account for their lower antioxidant activity than the commercial antioxidant at a given content. However, owing to the lower price of DKL or DHL compared with that of the commercial antioxidant or the neat PE, the addition of the larger amount of DKL and DHL did not increase the cost of the PE blends. Instead, the material cost of a PE blend that contains a larger amount of DKL (2.5 wt%) or DHL (5 wt%) is actually lower than that of a PE blend with a smaller amount of commercial antioxidant (0.5 wt%).

Mechanical testing showed that DKL addition to PE did not alter the tensile properties of PE. Mechanical properties of all samples (PE, PE-2.5 DKL and PE-0.5irg) after 200h thermo-oxidative and UV exposure are similar likely due to short exposure time to heat and UV. Mechanical properties of the PE blend after longer time exposure to heat and UV will be further investigated in future work.

4.6　　　References

[1]　　E. Yousif, R. Haddad, Photodegradation and photostabilization of polymers, especially polystyrene: review, Springerplus. 2 (2013) 398. doi:10.1186/2193-1801-2-398.

[2]　　B. Baum, The weathering degradation of polyolefins, Polym. Eng. Sci. 14 (1974) 206–211. doi:10.1002/pen.760140309.

[3]　　J.D. Peterson, S. Vyazovkin, C.A. Wight, Kinetics of the thermal and thermo-oxidative degradation of polystyrene, polyethylene and poly(propylene),

Macromol. Chem. Phys. 202 (2001) 775–784. doi:10.1002/1521-3935(20010301)202:6<775::AID-MACP775>3.0.CO;2-G.

[4]   P. Alexy, B. Košíková, G. Podstránska, The effect of blending lignin with polyethylene and polypropylene on physical properties, Polymer (Guildf). 41 (2000) 4901–4908. doi:10.1016/S0032-3861(99)00714-4.

[5]   C. Pouteau, P. Dole, B. Cathala, L. Averous, N. Boquillon, Antioxidant properties of lignin in polypropylene, Polym. Degrad. Stab. 81 (2003) 9–18. doi:10.1016/S0141-3910(03)00057-0.

[6]   D. Feldman, V. Forge, Rigid Poly (viny1 chloride) -Organosolv Lignin Blends for Applications in Building, J. Appl. Polym. Sci. 61 (1996). doi:10.1002/(SICI)1097-4628(19960919)61:12<2119::AID-APP10>3.0.CO;2-2.

[7]   A. Gregorová, Z. Cibulková, B. Košíková, P. Šimon, Stabilization effect of lignin in polypropylene and recycled polypropylene, Polym. Degrad. Stab. 89 (2005) 553–558. doi:10.1016/j.polymdegradstab.2005.02.007.

[8]   M. Canetti, F. Bertini, A. De Chirico, G. Audisio, Thermal degradation behaviour of isotactic polypropylene blended with lignin, Polym. Degrad. Stab. 91 (2006) 494–498. doi:10.1016/j.polymdegradstab.2005.01.052.

[9]   D. Ye, S. Li, X. Lu, X. Zhang, O.J. Rojas, Antioxidant and Thermal Stabilization of Polypropylene by Addition of Butylated Lignin at Low Loadings, ACS Sustain. Chem. Eng. (2016) acssuschemeng.6b01241.

doi:10.1021/acssuschemeng.6b01241.

[10]   C. Xu, R. Arneil, D. Arancon, J. Labidi, R. Luque, Lignin depolymerisation

       strategies: towards valuable chemicals and fuels, Chem. Soc. Rev. Chem. Soc.

       Rev. 43 (2014) 7485–7500. doi:10.1039/c4cs00235k.

[11]   F.S. Chakar, A.J. Ragauskas, Review of current and future softwood kraft lignin

       process chemistry, Ind. Crops Prod. 20 (2004) 131–141.

       doi:10.1016/j.indcrop.2004.04.016.

[12]   W.O.S. Doherty, P. Mousavioun, C.M. Fellows, Value-adding to cellulosic

       ethanol : Lignin polymers, Ind. Crop. Prod. 33 (2011) 259–276.

       doi:10.1016/j.indcrop.2010.10.022.

[13]   P. Harmsen, W. Huijgen, L. López, R. Bakker, Literature Review of Physical and

       Chemical Pretreatment Processes for Lignocellulosic Biomass, Food Biobased

       Res. (2010) 1–49. http://www.ecn.nl/docs/library/report/2010/e10013.pdf.

[14]   S. Laurichesse, L. Avérous, Chemical modification of lignins: Towards biobased

       polymers, Prog. Polym. Sci. 39 (2014) 1266–1290.

       doi:10.1016/j.progpolymsci.2013.11.004.

[15]   A. Gregorová, B. Košíková, R. Moravčík, Stabilization effect of lignin in natural

       rubber, Polym. Degrad. Stab. 91 (2006) 229–233.

       doi:10.1016/j.polymdegradstab.2005.05.009.

[16]   S. Domenek, A. Louaifi, A. Guinault, S. Baumberger, Potential of Lignins as Antioxidant Additive in Active Biodegradable Packaging Materials, J. Polym. Environ. 21 (2013) 692–701. doi:10.1007/s10924-013-0570-6.

[17]   T. Dizhbite, G. Telysheva, V. Jurkjane, U. Viesturs, Characterization of the radical scavenging activity of lignins - Natural antioxidants, Bioresour. Technol. 95 (2004) 309–317. doi:10.1016/j.biortech.2004.02.024.

[18]   Pan X, Kadla J, Ehara K, et al (2006) Organosolv Ethanol Lignin from Hybrid Poplar as a Radical Scavenger : Relationship between Lignin Structure , Extraction Conditions , and Antioxidant Activity. J Agric Food Chem 54:5806–5813. doi: 10.1021/jf0605392

[19]   V. Ugartondo, M. Mitjans, M.P. Vinardell, Comparative antioxidant and cytotoxic effects of lignins from different sources, Bioresour. Technol. 99 (2008) 6683–6687. doi:10.1016/j.biortech.2007.11.038.

[20]   Frost & Sullivan, Strategic Analysis of the European and North American Plastics Additives Market, (2015). http://cds.frost.com (accessed May 12, 2017).

[21]   A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R. a Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T.J. Tschaplinski, G. a Tuskan, C.E. Wyman, Lignin valorization: improving lignin processing in the biorefinery., Science. 344 (2014) 1246843. doi:10.1126/science.1246843.

[22] L. Kouisni, No Title, J. Sci. Technol. For. Prod. Process. 2 (2012) 6.

[23] Z. Yuan, T.C. Browne, X. Zhang, Biomass fractionation process for bioproducts, (2011). https://www.google.com/patents/US20110143411.

[24] I. Vulic, G. Vitarelli, J.M. Zenner, Structure-property relationships: Phenolic antioxidants with high efficiency and low colour contribution, Polym. Degrad. Stab. 78 (2002) 27–34. doi:10.1016/S0141-3910(02)00115-5.

[25] J. Tocháček, Effect of secondary structure on physical behaviour and performance of hindered phenolic antioxidants in polypropylene, Polym. Degrad. Stab. 86 (2004) 385–389. doi:10.1016/j.polymdegradstab.2004.05.010.

[26] W. Camacho, S. Karlsson, Assessment of thermal and thermo-oxidative stability of multi-extruded recycled PP, HDPE and a blend thereof, Polym. Degrad. Stab. 78 (2002) 385–391. doi:10.1016/S0141-3910(02)00192-1.

[27] G. Litwinienko, T. Kasprzycka-Guttman, A DSC study on thermoxidation kinetics of mustard oil, Thermochim. Acta. 319 (1998) 185–191. doi:10.1016/S0040-6031(98)00410-9.

[28] G. Litwinienko, K. Jodko-Piórecka, Recent Developments in DSC Analysis to Evaluate Thermooxidation and Efficacy of Antioxidants in Vegetable Oils, in: Differ. Scanning Calorim., CRC Press, 2014: pp. 49–74. doi:doi:10.1201/b17739-5.

[29] L. Dehne, C. Vila, B. Saake, K.U. Schwarz, Esterification of Kraft lignin as a method to improve structural and mechanical properties of lignin-polyethylene blends, J. Appl. Polym. Sci. 134 (2017) 1–8. doi:10.1002/app.44582.

[30] R.R.N. Sailaja, Low density polyethylene and grafted lignin polyblends using epoxy-functionalized compatibilizer: Mechanical and thermal properties, Polym. Int. 54 (2005) 1589–1598. doi:10.1002/pi.1864.

[31] B. [Slovak A. of S. Kosikova Bratislava (Slovakia)], V. Demjanova, M. [Slovak T.U. Mikulasova Bratislava (Slovakia)], J.H. [Alcell T.R.T. Lora Inc., Valley Forge, PA (United States)], Biodegradable lignin/polyolefin composite films, in: United States, 1993. http://www.osti.gov/scitech/servlets/purl/140241.

[32] M. Mikulasova, B. Kosikova, P. Alexy, F. Kacik, E. Urgelova, Effect of blending lignin biopolymer on the biodegradability of polyolefin plastics, World J. Microbiol. Biotechnol. 17 (2001) 601–607. doi:10.1023/A:1012415023385.

Chapter 5

5   Conclusions and Recommendations

5.1   Conclusions

Lignin, a major component of biomass, is an attractive alternative to hindered phenol-based antioxidants for polymers due to its renewable nature and naturally occurring hindered phenolic structure. In this study, for the first time, lignin de-polymerization was explored as a promising approach to improve the reactivity of the lignin-based antioxidants for polymers (polyethylene, PE and polypropylene, PP).

In the first part of the research, a proprietary hydrolytic de-polymerization process was utilized to increase the antioxidant activity of two types of technical lignin: kraft lignin, KL (a by-product from the pulp and paper industry) and hydrolysis lignin, HL (a by-product from the pre-treatment processes in cellulosic ethanol plants). The addition of a lignin-based antioxidant: KL, de-polymerized KL (DKL), HL and de-polymerized HL (DHL) to PE or PP increased the oxidation induction time (OIT), activation energy for oxidative degradation, and thermal degradation temperature (except for HL). The antioxidant effects of the lignin-based antioxidants follow the order of: de-polymerized KL (DKL) > de-polymerized HL (DHL) > KL > HL, which is in the same order as their phenolic content and in the reverse order of molecular weights. Thus, it was concluded that lignin de-polymerization effectively decreases the molecular weight, improves its compatibility to the polymer matrix and increases its phenolic content, which account for the improved antioxidant activity of the de-polymerized lignins.

In the second part of the research, effects of addition amounts of DKL and DHL in PE on their thermo-oxidative stability were examined, compared with a PE blend with 0.5 wt% commercial antioxidant (Iraganox 1010). The OIT and activation energy for thermo-oxidative degradation of the PE blend increased with the increase of DKL or DHL content. The increase leveled off at 2.5 wt% DKL addition but augmented in an almost linear manner for DHL addition up to 5 wt%. The results also revealed that the addition

of 2.5 wt% DKL or 5 wt% DHL attained the same level of antioxidant activity as the addition of 0.5 wt% Irganox 1010. The lower phenolic concentration, complex molecular feature, and higher hydrophilicity of the de-polymerized lignins might account for their lower antioxidant activity than the commercial antioxidant at a given content. However, owing to the lower price of DKL or DHL compared with that of the commercial antioxidant or the neat PE, the addition of the larger amount of DKL and DHL did not increase the cost of the PE blends. Instead, the material cost of a PE blend that contains a larger amount of DKL (2.5 wt%) or DHL (5 wt%) is actually lower than that of a PE blend with a smaller amount of commercial antioxidant (0.5 wt%). Mechanical testing showed that DKL addition to PE did not alter the tensile properties of PE. Mechanical properties of all samples (PE, PE-2.5 DKL and PE-0.5irg) after 200h thermo-oxidative and UV exposure are similar likely due to short exposure time to heat and UV.

To conclude, de-polymerization proved to be an effective and cost-effective strategy to improve the reactivity and compatibility of technical lignins with polyolefin matrix. The benefits of adding de-polymerized lignin in polyolefins have two-fold benefits. Along with the benefit of depolymerized lignin (DL) being an cost-effective alternative to commercial antioxidants, it also has the environmental benefit as it is expected that the polyolefins-DL bio-blends are more biodegradable than neat polymer [16,31,32].

5.2   Summary of the major contributions of this research

1. In this research, for the first time, lignin de-polymerization was demonstrated as an effective method to improve the reactivity of the lignin-based antioxidants for polymers (polyethylene, PE and polypropylene, PP). The comparison between the de-polymerized lignin and the crude lignins showed that de-polymerization effectively improved the antioxidant activity of technical lignins and the compatibility of the lignin with polymer matrix owing to decreased molecular weight, increased phenolic content, and lower aliphatic hydroxyl content.

2. The research on varying contents of the de-polymerized lignins on PE proved that addition of 2.5 wt% of de-polymerized kraft lignin (DKL) and 5 wt% of de-polymerized hydrolysis lignin (DHL) could render the same level of thermo-oxidative stability rendered by 0.5 wt% of a commercial antioxidant. Even though needed in higher amount, de-polymerized lignin can be an inexpensive green alternative to commercial antioxidants.

5.3 Recommendations

Mechanical properties of the PE blend after longer time exposure to heat and UV should be further investigated in future work. The long term heat stability and long term UV stability of DKL and DHL in polyolefins can be studied in terms of longer heat and UV exposure, and different weathering conditions.

As final polymer blend can contain other additives to achieve the desired product characteristics, it should be worth investigating the synergistic effect of de-polymerized lignins and other additives.

Also, the effects of different de-polymerization conditions on the antioxidant activity can be studied in order to evaluate whether an optimum exists in terms of increasing phenolic content and decreasing aliphatic content.

A detailed cost analysis should be carried out to investigate the overall economic benefits of using de-polymerized lignin as a green alternative to commercial petroleum-based antioxidant for polymers.

Curriculum Vitae

Name: Afsana Sara Kabir

Post-secondary Western University
Education and   London, Ontario, Canada
Degrees: 2015-2017 M. E. Sc. in Chemical Engineering.

        Bangladesh University of Engineering and Technology
        Dhaka, Bangladesh
        2009-2014 B. Sc. in Chemical Engineering.

Honors and   Western Graduate Research Scholarship
Awards: Faculty of Engineering, Western University
        2015-2017

        PSAC 610 Scholarship for Outstanding Research Contributions
        Western University
        2017

        PSAC 610 Academic Achievement Scholarship
        Western University
        2016

        Technical Scholarship for Engineering Education in Bangladesh
        Bangladesh University of Engineering and Technology
        2009-2012

Related Work Teaching Assistant
Experience   The University of Western Ontario
        2016-2017

Publications and Presentations:

Kabir A, Mahmood N, Yuan Z, Kuboki T, Xu C. Modified lignin: a biobased antioxidant for polyolefins. 66th Canadian Chemical Engineering Conference; October 16-19; Quebec City 2016

Kabir A, Yuan Z, Kuboki T, Xu C. De-polymerization of crude lignins to improve the thermo-oxidative stability of polyolefins (Work in progress)

Kabir A, Yuan Z, Kuboki T, Xu C. Effects of de-polymerized lignin content on thermo-oxidative stability of polyethylene (Work in progress)

Hossen M, Rahman S, Kabir AS, Hassan F, Ahmed S. Systematic assessment of the availability and utilization potential of biomass in Bangladesh. Renewable and Sustainable Energy Reviews; 2017 Jan 31; 67:94-105 (published)

Rahman S, Hossen M, Kabir AS, Hassan F, Ahmed S. Categorical assessment and characterization of conventional and unconventional biomass resources in Bangladesh. Chemical Engineering Research Bulletin; 2015;17(1) (published)

Kabir AS, Mursalat M, Begum DA, Sharmin N. Insulation foam synthesis: An alternative to traditional roof casting insulation. International journal of emerging technology and advanced engineering. 2015; 5 (8) (published)