

Unmodified and Esterified Kraft Lignin-Filled Polyethylene Composites: Compatibilization by Free-Radical Grafting

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ABSTRACT: In this study, the effectiveness of free-radical grafting as a compatibilization method applied to composites containing Kraft lignin (KL) and esterified lignin was comparatively investigated. Maleated lignin (ML) was first obtained via esterification of KL with maleic anhydride. KL and ML were respectively incorporated into high density polyethylene (HDPE) up to 60% wt and dicumyl peroxide was used as a free-radical generator. The influence of lignin esterification and free-radical grafting on the morphological, mechanical, and thermal properties of lignin-based composites was studied. The incorporation of lignins into HDPE resulted in poor mechanical strength because of low compatibility. Morphological and mechanical evidences indicate improved compatibility between lignins and HDPE following free-radical grafting. The free-radical scavenging properties of KL allowed better compatibilization of KL-based composites compared with ML-based composites. In addition, thermal analysis results showed that free-radical grafting increases the thermal stability of ML-based composites. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41484.

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INTRODUCTION

With the development of biorefinery technologies in the pulp and paper industry, intensive efforts have been done to use refined lignocellulosic materials as high value-added products.¹ To this end, the use of biomass is an alternative to fossil resource for biochemical production despite technological barriers.² Nanocrystalline cellulose with wide range of applications has been recently produced at industrial scale.^{3,4} Similarly, industrial lignins are now available as byproducts from pulp processing, having relatively higher heating value than cellulose. Therefore, practically all of industrial lignins are burnt for thermal energy recovery, leaving only 1–2% for commercial uses in other niche applications such as adhesives, fuel pellets, surfactants, etc.^{5,6} There are several application openings for industrial lignins, especially for Kraft lignin (KL) because of the dominant position of Kraft pulping process: bulk and high-volume use as a feedstock to produce high value-added biocomposites.

Lignins can be blended with various materials such as proteins, starch and cellulose.^{7,8} As polyethylene is the largest volume plastic produced in the world, it is advantageous to partially replace polyethylene by technical grade KLs to use eco-friendly materials as alternatives to petroleum-based plastics. The cost of industrial scale KL production was estimated to be \$400–600/ton,⁹ whereas

the current price of high density polyethylene (HDPE) is around \$2500/ton (April 2014). Thereby, partial replacement of polyethylene by low-cost lignins is economically reasonable. It is expected that lignin-based composites could find applications in various fields, such as structural materials for automotive or construction purposes.

Unlike the simple chemical structure and high hydrophobicity of polyethylene, industrial lignins present nonuniform phenolic structure with a certain amount of hydroxyl groups. Also, lignin composition varies depending on both delignification procedure and lignocellulosic biomass origin. Due to poor affinity between lignins and polyethylene, the addition of lignins in polyethylene results in poor mechanical properties of the composites.¹⁰ To solve this problem, several compatibilization methods were suggested, but economic considerations restrict their broader use. For instance, catalytic grafting of polyethylene onto lignosulfonate lignin was found to effectively improve the compatibility of lignin-polyethylene composites, but a large quantity of waste organic solvents was generated from such modification.¹¹ The addition of polymeric compatibilizers, especially maleated polyethylene, was useful to obtain well compatibilized lignin-polyethylene composites. However, the low cost of lignin-based composites was offset by expensive compatibilizers addition.¹²

Table I. Sample Composition and Coding

Sample code	KL (wt %)	ML (wt %)	HDPE (wt %)	DCP (wt %)
HDPE	-	-	100	-
HDPE-3	-	-	100	0.72
2KL-PE	20	-	80	-
2KL-PE-3	20	-	80	0.72
4KL-PE	40	-	60	-
4KL-PE-1	40	-	60	0.24
4KL-PE-2	40	-	60	0.48
4KL-PE-3	40	-	60	0.72
6KL-PE	60	-	40	-
6KL-PE-3	60	-	40	0.72
2ML-PE	-	20	80	-
2ML-PE-3	-	20	80	0.72
4ML-PE	-	40	60	-
4ML-PE-1	-	40	60	0.24
4ML-PE-2	-	40	60	0.48
4ML-PE-3	-	40	60	0.72
6ML-PE	-	60	40	-
6ML-PE-3	-	60	40	0.72

It is well known that melt free-radical grafting is easy, inexpensive, and widely used to graft vinyl compounds onto polymers.^{13–16} Unlike for vinyl compounds, residual double bonds in lignins are not subject to free-radical attack, but the presence of potential grafting sites in lignins have been previously reported.⁷ Nevertheless, there is actually no information available in the published literature about radical-mediated grafting of lignin onto polyethylene. It is of interest to study the compatibilizing effect of free-radical grafting to produce lignin-polyethylene composites. Lignin modification by means of esterification was also performed to increase compatibility between lignins and polyolefins. Nevertheless, it was reported that no mechanical improvement was found if esterified lignin was added into a polyolefin matrix instead of unmodified lignin.¹⁷ However, double-bond functionality was introduced to lignins following esterification with maleic anhydride.¹⁸ Therefore, it is expected that the combination of free-radical treatment and esterification of lignins will have favorable effects on compatibility with HDPE.

In this investigation, KL was esterified with maleic anhydride and the obtained maleated Kraft lignin (ML) was incorporated into HDPE by melt processing. Free-radical grafting mediated by dicumyl peroxide (DCP) was then applied to formulations containing KL or ML. The composites were compared in terms of morphological, mechanical and thermal characterizations. Density was also studied in order to identify the best formulation.

EXPERIMENTAL

Materials

Softwood KL Indulin AT was kindly supplied by Westvaco Corporation. HDPE SCLAIR® 2908 was used as the polymer matrix

(NOVA Chemicals). This resin has a density of 0.961 g/cm³ and a melt flow index of 7 g/10 min (190°C, 2.16 kg). Thermal free-radical generator DCP was purchased from Sigma-Aldrich for grafting. Finally, 1-methylimidazol (Sigma Aldrich), dioxane (Fischer Scientific), maleic anhydride (Sigma Aldrich, South Korea), and ethyl ether (Fischer Scientific) were used as received. Deionized water was used when needed.

Esterification of Lignin

The procedure for lignin esterification with maleic anhydride was described in previous publications.^{19,20} To minimize reagents and solvents used in the reactions, quantitative esterification method of lignin was optimized. A typical procedure can be described as follows: KL was previously oven dried at 80°C overnight to remove moisture and volatiles. Then, 40 g of dried KL, 60 g of maleic anhydride and 200 mL of dioxane were placed into a 500 mL Erlenmeyer flask fitted with a condenser. The mixture was stirred and heated at 75°C. Then, 25 mL of dioxane containing 2 g of 1-methylimidazol was slowly added dropwise into the mixture during 90 min. It was observed that a part of esterified lignin agglomerated on the top of the solution progressively. After 90 min, the mixture was allowed to cool and 400 mL of ethyl ether were added into the mixture to precipitate the esterified lignin. After solvent removal using a pipet, the precipitated product was successively washed with water (3 × 400 mL), dried under hood at room temperature overnight, and again dried in a vacuum oven at 60°C overnight.

Characterization of Lignins

The Fourier transform infrared (FTIR) spectra of KL and ML were recorded on a Perkin Elmer spectrum 400 ATR-FT-IR spectrometer. The data were collected in the range between 4000 and 600 cm⁻¹ with a spectral resolution of 4 cm⁻¹.

Preparation of Composites

Lignin and modified lignin were vacuum-dried prior to composite processing. All composites were prepared by melt mixing at 160°C and 75 rpm in a Haake Büchler internal batch mixer. HDPE was first added into the mixing chamber and allowed to melt for 1 min. Afterwards, KL (or ML) and DCP were added simultaneously. After 5.5 min, a homogeneous composite was collected for molding. Table I lists the amounts of components in each sample with sample coding. From the formulations produced, rectangular plates (2.5 × 115 × 115 mm³) were formed under a force of 2–3 tons by compression molding at 165°C for 12 min in a laboratory Carver press.

Composites Characterization

Morphological analysis was done with a Scanning Electron Microscope (SEM, JEOL model JSM-840A). Samples were prepared by cryogenic fracture in liquid nitrogen. The exposed surface was then coated with a thin layer of Au/Pd with a Technics Hummer II, and subject to SEM analyses.

Tensile measurements were performed on an Instron Universal Testing Instrument model 5565, at a crosshead speed of 5 mm/min and room temperature. Five dumbbell shape specimens (Type V) were tested for each sample in accordance with ASTM D638. The flexural modulus (ASTM D790) was obtained using the same Instron at a rate of 5 mm/min via the three point

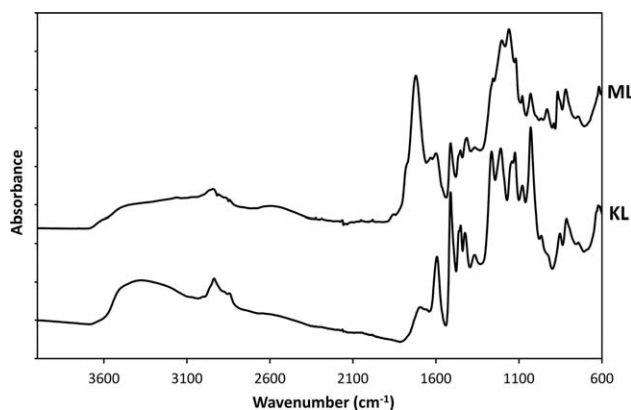


Figure 1. FTIR spectra of KL and ML.

bending fixture (support span = 60 mm). Five specimens of dimensions $75 \times 12.9 \times 2.5 \text{ mm}^3$ were examined for each condition. After flexural tests the specimens were V-notched with an automatic sample notcher ASN-120-N and then subject to Charpy impact testing (ASTM D256) with a Tinius Olsen model 104. Each sample was tested using 10 specimens. Hardness was measured by using a model 307L type D durometer according to ASTM D2240.

The molecular weight distribution of HDPE before and after free-radical treatment was measured by a gel permeation chromatography (GPC, Viscotek HT-GPC module 350) equipped with a refractive index detector and a viscometer. Measurement was carried out at 140°C with 1,2,4-trichlorobenzene as eluting solvent at an elution rate of 1 mL/min.

Thermogravimetric analysis (TGA) of vacuum-dried composite samples was performed in a Mettler Toledo TGA/SDTA 851 $^\circ$. Samples were heated from 25 to 700°C with a heating rate of $10^\circ\text{C}/\text{min}$ under an inert atmosphere with a constant nitrogen flow of 50 mL/min. For differential scanning calorimetry (DSC), a Mettler Toledo DSC 822 was used. The samples (around 10 mg) were heated at $10^\circ\text{C}/\text{min}$ up from 25 to 200°C under nitrogen. Crystallinity of HDPE was determined from the melting endotherm by the Polymer STARE software, based upon a value of 293 J/g for the 100% crystalline material heat of fusion.²¹

Quantachrome Ultrapyc 1200e gas pycnometer was used to measure density, with nitrogen as the measuring gas. The data reported are the average of three measurements.

RESULTS AND DISCUSSION

Efficiency of Esterification

The efficiency of esterification was evaluated through FTIR analysis and mass gain after esterification. The FTIR spectra of KL and ML are shown in Figure 1. Attribution of FTIR absorption bands for KL was reported elsewhere.²² The spectrum for KL contains O—H stretching band (3372 cm^{-1}), C—H stretching band (2936 cm^{-1}), and aromatic stretching band (1594 , 1512 , and 1425 cm^{-1}). Besides, the characteristic absorbance of guaiacyl units were observed at 1265 , 1124 , 1029 , 853 , and 813 cm^{-1} . The same features can be observed in the spectrum of ML. Additionally, the absorption intensity at 3372 and

1029 cm^{-1} , corresponding to O—H stretching and C—O stretching of primary alcohol respectively, were greatly reduced. Meanwhile, the increased peak intensity at 1721 cm^{-1} was attributed to ester groups and double bonds of maleic anhydride. Therefore, it was concluded that esterification between KL and maleic anhydride took place. The average mass gain of three experiments was measured to be $74 \pm 2\%$. This data indicated that esterification was total and complete according to the literature.²⁰

Morphology

SEM analysis provides morphological information about the compatibilization effect of melt free-radical grafting. The fractured surfaces of composites containing low and high KL contents (20 and 60% wt, respectively) are presented in Figure 2. As can be seen from Figure 2(a,c), large lignin particles were pulled out form the fractured surface, confirming weak adhesion between KL and polyethylene. Upon further increases in KL loading, filler-matrix delamination becomes even worse because of poor compatibility. However, smoother morphology is observed in Figure 2(b,d), which can be ascribed to the fact that free-radical treatment strengthened the interface adhesion between KL and HDPE. As a result, the fracture occurs inside both lignin particles and polyethylene instead of their interface. Also, our previous work pointed out the presence of lignin agglomeration in uncompatibilized composites.²³ It can be seen in Figure 2(b,d) that lignin particles size was significantly reduced by free-radical grafting, and large particles are no longer observed in the compatibilized composites, even for lignin loadings as high as 60% wt.

ML, having a porous structure, can be clearly identified in Figure 3. It can be seen that the pores shown in Figure 3(a) are much larger than those in other images, while Figure 3(d) presents the smallest pores. This phenomenon is explained by the fact that large cavities are weak points in ML particles and can easily collapse if a high amount of ML is incorporated or if free-radical grafting is applied. The combination of high lignin loading and free-radical grafting led to more important cavity collapse. It seems that ML porosity allows for mechanical anchoring of polyethylene, so that no filler-matrix delamination could be observed in Figure 3. Unlike KL, large ML particles in the composites can be seen after free-radical grafting, suggesting the rigid characteristics of ML.

Mechanical Properties

The results of mechanical characterizations are presented in Table II. Young's modulus of KL-based composites was increased from 502 to 606 MPa by lignin addition up to 40% wt. However, higher lignin loading (60% wt) decreased this value to 390 MPa. Lower Young's modulus can be ascribed to the fact that high KL content leads to discontinuity in the matrix phase, and the uncompatibilized interface between KL and polyethylene is not strong enough to allow sufficient stress transfer. The addition of 0.72% wt DCP led to a decrease of Young's modulus, but this decrease can be compensated by adding at least 40% wt KL. Moreover, 6KL-PE-3 shows a 76% higher Young's modulus than 6KL-PE.

Due to the porous structure of ML, uncompatibilized ML-HDPE composites generally exhibit lower Young's modulus than composites containing the same amount of KL, except for 6ML-

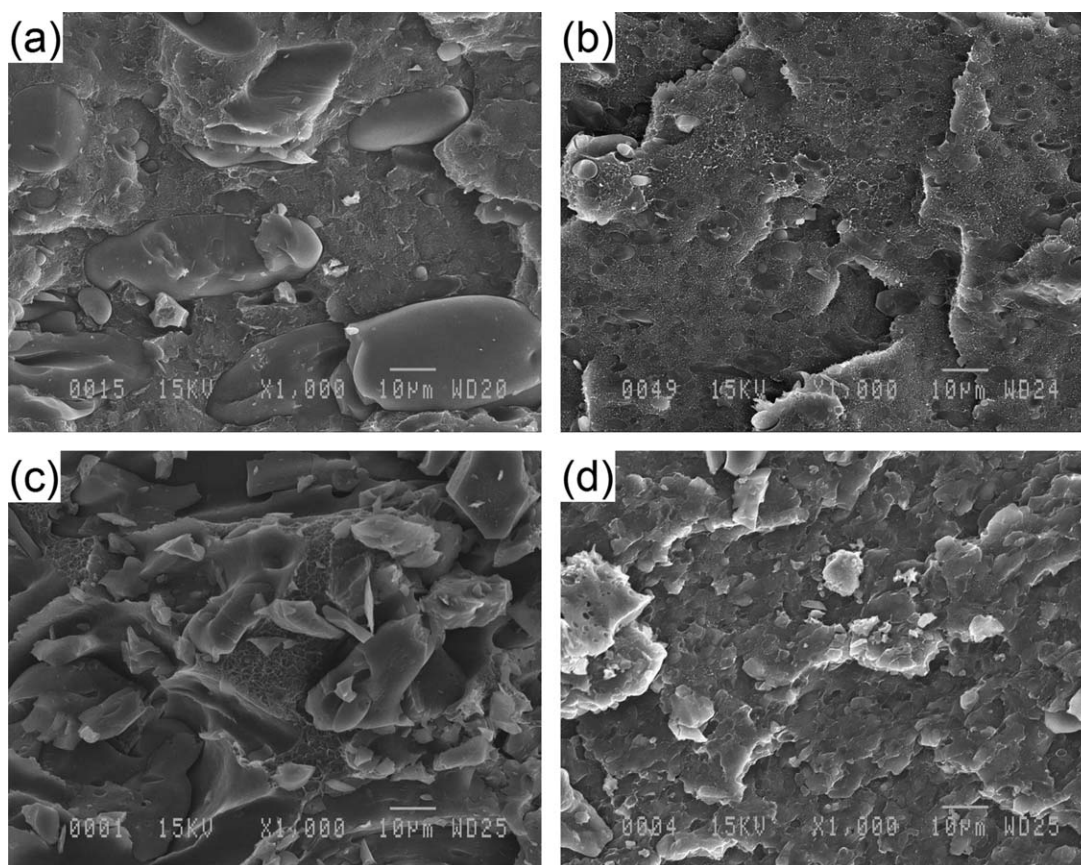


Figure 2. SEM micrographs of KL-based composites: (a) 2KL-PE, (b) 2KL-PE-3, (c) 6KL-PE, and (d) 6KL-PE-3. See Table I for composition details.

PE showing a 54% higher Young's modulus than 6KL-PE. Compatibilization by free-radical grafting displayed very limited effects on Young's modulus for composites containing high level of ML (40 and 60% wt) despite variation of DCP concentration. This phenomenon is the result of the balance between two opposite effects: polymer chain scission induced by free-radical grafting decreasing Young's modulus, and the reduction of ML porosity increasing this value.

The flexural modulus of KL-based composites was around 1628 MPa following KL addition up to 40% wt, and then decreased to 1230 MPa when the ratio of KL was 60% wt. The introduction of 20 or 40% wt ML into polyethylene decreased the flexural modulus by 12%. However, 6ML-PE showed a 26% higher flexural modulus than that of HDPE. Free-radical grafting had a positive effect on the flexural modulus of KL-based composites only if KL load was 60% wt. For example, the flexural modulus of 6KL-PE-3 increased by 96% compared to KL-PE. Similar to Young's modulus, 2ML-PE and 4ML-PE showed slightly lower flexural modulus than 2KL-PE and 4KL-PE respectively, whereas the flexural modulus of 6ML-PE was 66% higher than that of 6KL-PE. Free-radical grafting resulted in a decrease of flexural modulus of 2ML-PE-3 and 6ML-PE-3 by respectively 22% and 19%, but that of 4ML-PE-3 remained unchanged.

Because of incompatibility, the addition of lignins into HDPE led to lower tensile strength. For instance, the tensile strength of

HDPE was reduced from 28.6 to 4.2 MPa and 9.3 MPa upon adding of 60% wt KL and ML, respectively. As the free-radical treatment is supposed to produce polymer chain scission, the tensile strength of HDPE-3 was reduced from 28.6 to 25.1 MPa by adding 0.72% wt DCP. Nevertheless, free-radical treatment contributed to increase tensile strength of all the composites listed in Table II. This increase was significant for composites containing high amounts of KL or ML (40 and 60% wt). Especially for 6KL-PE-3, the tensile strength was increased by more than three times compared with 6KL-PE. This improvement can be explained by the fact that compatibilized interfaces allowed efficient stress transfer from the matrix to the particles. Therefore, the compatibilizing effect of free-radical grafting was confirmed.

The impact of DCP concentration on the tensile strength of 4KL-PE and 4ML-PE was also studied. It was found that higher DCP concentration produced higher tensile strength. Based on the results obtained, it seems that the highest value (0.72% wt) is the best for the range of conditions tested.

Elongation at break was strongly decreased by lignin addition. Adding only 20% wt reduced this value to <1%. It was found that the elongation at break of ML-HDPE composites was improved by free-radical grafting and this improvement was proportional to the amount of DCP added. Increased elongation at break by free-radical grafting could be compensated by the

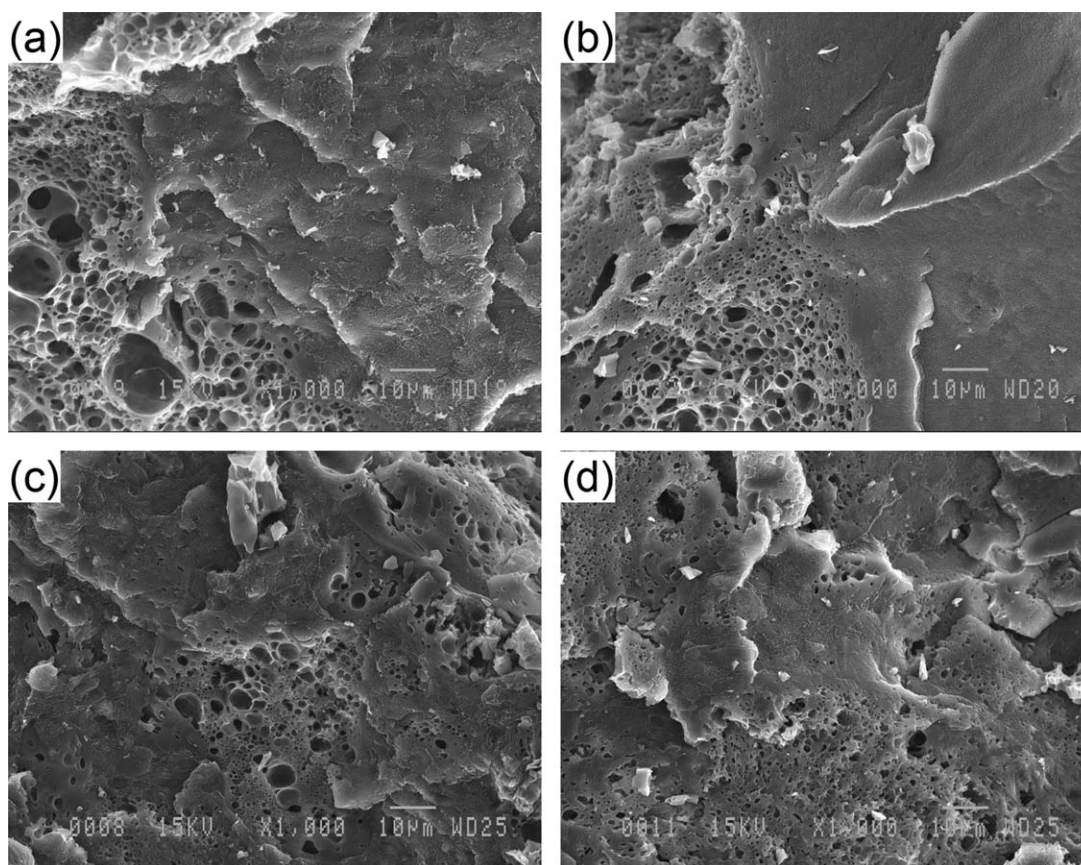


Figure 3. SEM micrographs of ML-based composites: (a) 2ML-PE, (b) 2ML-PE-3, (c) 6ML-PE, and (d) 6ML-PE-3. See Table I for composition details.

Table II. Mechanical Properties of the Composites

Sample	Young's modulus (MPa)	Flexural modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m ²)	Hardness (Shore D)
HDPE	502 (12)	1625 (159)	28.6 (0.8)	1167 (171)	4.5 (0.2)	69.9 (0.7)
HDPE-3	394 (9)	1165 (85)	25.1 (0.7)	783 (317)	32.1 (14.0)	69.3 (1.6)
2KL-PE	578 (27)	1628 (107)	23.1 (0.2)	10.6 (0.9)	1.5 (0.3)	72.3 (0.9)
2KL-PE-3	486 (25)	1409 (81)	25.5 (0.4)	22.2 (6.2)	1.7 (0.1)	72.4 (0.6)
4KL-PE	606 (41)	1770 (219)	14.0 (0.1)	4.0 (0.9)	2.0 (0.3)	73.1 (0.6)
4KL-PE-1	597 (36)	1979 (48)	20.9 (1.2)	4.9 (0.2)	1.9 (0.2)	76.0 (0.5)
4KL-PE-2	571 (11)	2091 (96)	21.1 (0.6)	5.3 (0.6)	2.0 (0.3)	74.9 (0.1)
4KL-PE-3	571 (23)	1804 (67)	23.1 (2.1)	9.5 (5.5)	1.9 (0.2)	74.7 (0.5)
6KL-PE	390 (46)	1230 (76)	4.2 (0.5)	4.8 (0.9)	1.0 (0.2)	73.1 (1.2)
6KL-PE-3	686 (55)	2405 (150)	14.0 (2.1)	2.3 (0.4)	0.8 (0.2)	78.8 (0.3)
2ML-PE	496 (10)	1407 (133)	15.8 (1.0)	6.0 (0.8)	2.4 (0.2)	71.3 (0.4)
2ML-PE-3	374 (8)	1097 (28)	16.2 (0.9)	24.1 (4.8)	6.0 (1.8)	70.5 (0.5)
4ML-PE	501 (27)	1447 (47)	11.6 (0.7)	3.6 (0.4)	1.7 (0.1)	72.2 (1.1)
4ML-PE-1	492 (8)	1609 (173)	14.2 (1.1)	5.0 (0.7)	2.5 (0.2)	72.7 (0.4)
4ML-PE-2	450 (22)	1372 (75)	13.9 (0.5)	5.9 (0.8)	3.1 (0.3)	72.4 (0.5)
4ML-PE-3	473 (7)	1390 (67)	16.7 (0.6)	7.9 (0.9)	3.2 (0.4)	69.9 (1.3)
6ML-PE	599 (47)	2045 (109)	9.3 (0.6)	1.8 (0.1)	0.7 (0.2)	74.0 (1.6)
6ML-PE-3	536 (34)	1650 (104)	12.2 (0.8)	2.9 (0.3)	1.8 (0.3)	72.5 (1.3)

Numbers in parentheses are standard deviations.

Table III. GPC Results of PE and PE-3

Sample	M_n (kg/mol)	M_w (kg/mol)	PI	$[\eta]$ (dL/g)	BF
HDPE	20.5	80.2	3.91	1.18	0.067
HDPE-3	25.4	158.3	6.23	1.35	0.347

presence of ML. For example, 0.72% wt of DCP can increase the elongation at break of 2ML-PE-3 by 3 times, while only increasing that of 4ML-PE-3 by 117%. This difference was due to the function that free radicals performed on composites compatibilization instead of HDPE modification. The elongation at break of KL-based composites was merely affected by DCP addition, the reason for which will be discussed later.

As can be seen in Table II, low compatibility between lignins and polyethylene resulted in a decrease of Charpy impact strength from 4.5 kJ/m² to as low as 0.7 kJ/m². There was no significant difference between the composites containing the same amount of KL and ML in terms of impact strength, except for 2ML-PE showing a 60% higher impact strength than 2KL-PE. Surprisingly, all of the KL-based composites displayed unaffected impact strength followed by free-radical grafting. This phenomenon is probably due to the free-radical scavenging characteristics of KL, a property of unmodified lignins related to their phenolic nature, which minimized polyethylene chain scission caused by free radical treatment.²⁴ Therefore, no improvement in elongation at break nor impact strength were observed for KL-based composites. It seems that the free-radical scavenging ability of KL was altered following esterification. As a result, the impact strength of ML-based composites increased with the amount of DCP added, but this increase was lowered by the presence of ML.

The hardness of polyethylene was found to be 69.9, and the highest hardness values were 73.1 and 74.0 recorded for uncompatibilized composites containing 60% wt of KL and ML,

respectively. DCP addition exerted limited effect on the hardness of HDPE-3. In general, the hardness of KL-based composites was increased following DCP addition, whereas that of ML-based composites was slightly decreased as if only the polyethylene matrix was altered by free radicals. This effect can be also ascribed to the free-radical scavenging effect of KL, owing to which crosslinking occurred on the surface and inside KL particles.

Although ML shows better interfacial adhesion to the polyethylene matrix than KL, esterification of KL brings no mechanical advantages to lignin-based composites. The main causes are the porous structure of ML and the loss of free-radical scavenging ability after esterification. Thereby, esterification of KL is not needed to obtain compatibilized composites. It is thus recommended to only apply free-radical grafting to KL-based composites for better compatibilization.

Polymer Properties of HDPE

The effect of DCP on the properties of HDPE was characterized via GPC and the results are presented in Table III. Free-radical treatment increased the branching frequency (BF) and the intrinsic viscosity of HDPE. At the same time, the molecular weight (M_n and M_w) of HDPE was increased. It was confirmed that free-radical treatment caused more polymer crosslinking than polymer chain scission to neat HDPE. High polydispersity index (PI) of HDPE-3 was primarily due to polymer chain scission of crosslinked polymer during melt processing. The obtained GPC results clarified the reduced mechanical strength of HDPE after free-radical treatment.

Thermal Properties

To investigate the thermal stability of the composites, the temperatures at 5 and 50% weight loss ($T_{5\%}$ and $T_{50\%}$, respectively) were recorded and presented in Table IV. Not only polymer chain scission, but also polymer crosslinking was induced by free-radical treatment. Therefore, 0.72% wt of DCP increased

Table IV. Thermal Properties of the Composites

Sample	TGA		DSC	
	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	Melting point (°C)	Crystallinity (%)
HDPE	444.5	475.0	138.6	73.2
HDPE-3	450.0	479.0	136.5	65.7
2KL-PE	358.5	479.7	136.1	73.9
2KL-PE-3	359.4	479.0	134.8	60.9
4KL-PE	319.4	481.6	135.7	68.6
4KL-PE-3	306.4	479.1	134.4	65.3
6KL-PE	302.6	485.6	135.1	67.4
6KL-PE-3	298.8	481.1	133.9	64.6
2ML-PE	335.7	479.6	137.4	59.4
2ML-PE-3	359.2	480.2	132.8	48.0
4ML-PE	279.3	479.1	139.0	61.6
4ML-PE-3	290.9	478.5	130.5	51.2
6ML-PE	238.8	472.8	134.8	69.0
6ML-PE-3	254.1	474.7	135.1	59.7

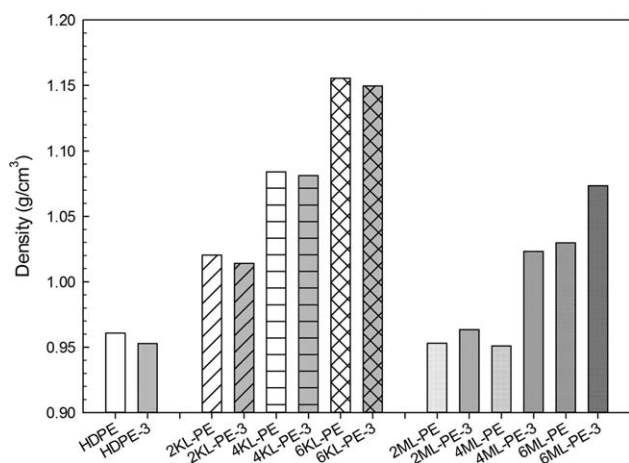


Figure 4. Density of the composites.

the $T_{5\%}$ and $T_{50\%}$ of HDPE-3 by 5.5 and 4.0°C, respectively. The thermal behavior of KL was studied in the literature,²⁵ and the results showed that KL has lower thermal degradation onset temperature than PE, but the aromatic chemical structure of KL gives high amounts of char at elevated temperature. As a result, the incorporation of 60% wt of KL into HDPE decreased $T_{5\%}$ by 142°C, and the $T_{50\%}$ by only 11°C. Likewise, the incorporation of 60% wt of ML decreased the $T_{5\%}$ of HDPE by 206°C, while the $T_{50\%}$ of all ML-based composites remained unaffected by ML addition. The low $T_{5\%}$ of ML-based composites can be explained by air entrapment in the cavities of the ML porous structure, and the high oxygen content of ester functionalities.

As KL played a role of free-radical scavenger, crosslinking of polyethylene was prevented by KL during free-radical grafting. Thereby, the $T_{5\%}$ of 6KL-PE-3 was decreased by 3.8°C compared with 6KL-PE, while the $T_{50\%}$ was decreased by 4.5°C. Unlike KL-HDPE composites, the addition of DCP into 6ML-PE increased $T_{5\%}$ by 15°C, while the $T_{50\%}$ of all ML-based composites was almost unaffected. As a conclusion, DCP is able to increase the thermal stability of ML-based composites.

DSC tests aimed at investigating the properties of the polyethylene matrix. As shown in Table IV, the melting point of HDPE was slightly decreased by KL addition (<3.5°C). The addition of 0.72% of DCP further decreased the melting point of polyethylene matrix in KL-based composites by about 1.3°C because slight polymer chain scission occurred. It was found that the crystallinity of polyethylene was related to the melting point of the composites. The incorporation of KL or DCP led to decreased crystallinity and decreased melting points.

Owing to the presence of large ML particles in ML-based composites, it was difficult to obtain precise DSC results with a small quantity of samples. Nonetheless, compatibilized ML-HDPE composites generally showed lower melting point and lower crystallinity than composites containing the same amount of KL, confirming the free-radical scavenging characteristics of KL inhibiting polyethylene modification by free-radicals.

Density

The density of KL was measured to be 1.207 ± 0.002 g/cm³, while that of ML was 1.044 ± 0.001 g/cm³. The effect of lignin

(KL or ML) content and DCP addition on composites density is presented in Figure 4. The density of KL-based composites increased proportionally with KL content. Free-radical treatment slightly decreased the density of HDPE. Likewise, the same effect observed for KL-HDPE composites was attributed to lower matrix density (HDPE vs. HDPE-3).

Surprisingly, the density of ML-based composites was nearly unaffected despite the presence of up to 40% wt of ML. A possible explanation would be that the increase of composites' density was offset by ML's higher porosity. Free-radical treatment or high lignin content (60% wt) resulted in increased composites density, thus confirming the morphological results presented in Figures 1 and 2.

CONCLUSION

The results of this study could contribute to the development of novel biocomposites based on KLs. Low cost and easy free-radical grafting was used for the first time in order to improve the compatibility of HDPE composites containing KL and ML. This compatibilization method was shown to be effective.

KL was esterified with maleic anhydride. FTIR spectroscopy and mass gain indicated that esterification was total and complete. Different concentrations (from 20 to 60% wt) of KL and ML were then introduced into HDPE via melt processing. Compatibilization by free-radical grafting was also applied to the composites using DCP as thermal free-radical generator. Morphological, mechanical, and thermal properties, as well as hardness and density of the composites were investigated.

SEM micrographs revealed the different dispersion state of lignins particles. The adhesion between KL and HDPE was clearly improved by free-radical grafting. Compared with KL, porous ML showed better adhesion to HDPE. Melt graft treatment of ML-HDPE composites led to ML particles cavity collapse. The presence of lignins generally decreased the mechanical properties of HDPE, but the introduction of KL showed less deterioration than ML. The addition of DCP alone into neat HDPE showed detrimental effects on all mechanical properties except for elongation at break and impact strength. However, the addition of DCP improved the mechanical properties of lignin-based composites with the optimum DCP concentration being 0.72% wt for the range of conditions tested. For example, the tensile strength of 6KL-PE-3 was increased by 233%, and that of 6ML-PE-3 was increased by 31% due to DCP addition. Free-radical grafting slightly decreased the thermal stability of KL-based composites, but greatly increased that of ML-based composites. Finally, the density of ML-based composites was increased after free-radical grafting because of cavity collapse.

Although the combination of free-radical grafting and lignin esterification showed no synergic effect, free-radical grafting alone was shown to be an efficient and economically affordable method to restore the mechanical strength of KL-based composites.

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