

Compatibilization of Kraft Lignin-Polyethylene Composites Using Unreactive Compatibilizers

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ABSTRACT: This article presents a novel approach to compatibilize Kraft lignin with polyethylene that involves the use of modified poly (styrene-co-ethylene-co-butylene-co-styrene) (SEBS) as unreactive compatibilizers. As SEBS shows no compatibilizing effect on Kraft lignin-polyethylene composites, SEBS was functionalized via nitration followed by amination to obtain nitrated (SEBS-NO₂) and aminated (SEBS-NH₂) SEBS. The compatibilizing effects of SEBS derivatives were studied by means of morphological and mechanical analyses. The results show that SEBS-NO₂ is less effective than SEBS-NH₂, the later displaying comparable compatibilizing efficiency to a commercial reactive compatibilizer based on maleated polyethylene. Overall, compatibilization was found to decrease lignin particle size. Addition of SEBS-NH₂ varying between 1% and 10% improved the tensile strength of composites by up to 96%, elongation at break by up to 64%, and impact strength by up to 48%. Finally, the crystallinity and density of the resulting composites were also studied. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41040.

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INTRODUCTION

Petroleum-based materials, especially polyolefins, have largely contributed to human being's modern life, but also contributed to oil reserves depletion and environmental issues. A common perspective of sustainable development is to partially replace polyolefins by biopolymers without sacrificing mechanical strength. Because of renewability, biodegradability, and high availability, lignocellulosic materials are used to produce eco-friendly biocomposites. The fast growing market of wood-plastic composites in the last decade revealed urgent demand for the biocomposites.¹ In the context of green economic development, it was not until recently that attention was given to promoting refined lignocellulosic materials, such as cellulose^{2,3} and lignins⁴ as feedstock for biocomposites.

As naturally occurring organic materials in all vascular plants, lignins are one of the most important biopolymers on Earth. Lignins are generally chemically extracted from lignocellulosic materials. Owing to the widespread use of Kraft process, Kraft lignin represents 95% of the world industrial lignins production.⁵ However, a large amount of Kraft lignin is incinerated for energy recovery without further value-added applications. Kraft lignin can be considered as a raw material to produce biofuels and chemicals,^{6,7} as well as additives for wood fuel pellets.⁸ Utilization of Kraft lignin in green material applications is also a

hopeful way to unleash Kraft lignin's potential.⁹ However, most of the polyolefins are nonpolar, hydrophobic, and devoid of functional groups. Based on the published literature, introduction of any type of lignin into polyolefins results in reduced mechanical strength because of lack of compatibility.^{10–12} To solve this issue, several methods have been proposed to overcome this drawback. Modifications of lignins such as hydrophobization,¹³ functionalization,¹⁴ as well as polymer grafting¹⁵ have been intensively studied to increase compatibility between lignins and polyolefins. Nevertheless, the addition of a compatibilizer is the easiest way to achieve the same objective.

Compatibilizers can be classified as reactive and unreactive. Reactive compatibilizers allow forming permanent linkage (covalent bonds) with composite components, whereas weak intermolecular interactions are established by unreactive compatibilizers. Polymeric reactive compatibilizers for lignin-polyolefin composites include polyethylene-*grafted*-maleic anhydride (MAPE),^{16–18} polypropylene-*grafted*-maleic anhydride (MAPP),^{18,19} and poly(ethylene-co-acrylic acid) (EAA).¹⁰ To the best of our knowledge, only poly(ethylene-co-vinyl acetate) (EVA) has been reported as an unreactive compatibilizer for lignin-polyolefin composites.^{16,20} Theoretically, EVA presents limited compatibilizing possibility because of the random arrangement of monomeric units. It is necessary to develop novel unreactive compatibilizers of high

efficiency that can advantageously replace the role of EVA in lignin–polyolefin composites.

Kraft lignin is hydrophilic because of hydroxyl (both alcoholic and phenolic) and ether groups.²¹ In addition, phenolic hydroxyl groups (which are liberated through cleavage of ether bonds during pulping process) and ether groups are electron donating groups, which increase the electron density of lignin's aromatic rings. An ideal unreactive compatibilizer is expected to interact with Kraft lignin via hydrogen bonding and π -stacking forces. As block copolymers were indicated as better compatibilizers than statistical copolymers,²² it is hopeful to obtain a block copolymer, the compatibilizing ability of which is stronger than EVA. Commercial triblock copolymers like poly(styrene-co-ethylene-co-butylene-co-styrene) (SEBS) contain two polystyrene end units, with poly(ethylene-butylene) middle blocks that are compatible with a polyolefin matrix. This designed structure allows SEBS to be an efficient compatibilizer for polyethylene-polystyrene blends.^{23,24} However, SEBS is unable to compatibilize lignin–polyolefin composites because of low affinity between essentially hydrophobic polystyrene blocks and Kraft lignins. In this study, Kraft lignin-high density polyethylene (HDPE) system was chosen because HDPE has the simplest chemical structure of all polyolefins and is commercially most important. Compatibilization through intermolecular interactions instead of covalent bonds is investigated. This is done via efficient unreactive compatibilizers based on SEBS. For this purpose, SEBS was chemically modified through nitration followed by reduction. SEBS derivatives were incorporated into HDPE composites by melt processing and the effect of modified SEBS on mechanical and morphological properties are analyzed. To complete characterization, density and crystallinity of the composites are also investigated.

EXPERIMENTAL

Materials

Softwood Kraft lignin Indulin AT was kindly supplied by Westvaco Corporation (Charleston, SC), while HDPE HD 6605.29, with a density of 0.948 g/cm³ and a melt flow index of 5 g/10 min (190°C, 2.16 kg) was purchased from ExxonMobil. SEBS Kraton® G1652, with 30 wt % styrene content was supplied by Kraton Performance Polymers. Statistic copolymer resin EVA Elvax®360 with 25 wt % vinyl acetate monomer content was obtained from DuPont. The commercial coupling agent used was MAPE Epolene® C-26, with an average molecular weight (M_w) of 65,000 g/mol and an acid number of 8 mg KOH/g, obtained from Westlake Chemical Corporation. Chloroform, concentrated nitric acid (HNO₃, 68–70%), concentrated sulfuric acid (H₂SO₄, 98%), sodium hydroxide (NaOH), anhydrous ethanol, tetrahydrofuran (THF), anhydrous tin (II) chloride (SnCl₂), concentrated hydrochloric acid (HCl, 36.5–38%), and deuterated chloroform were used as received without further purification. In all cases, deionized water was used.

SEBS Modification

SEBS nitration was studied by Huang et al.,²⁵ and a similar procedure was used. Forty g of SEBS was dissolved in 270 mL of chloroform. Afterwards, an acid mixture composed of 9.6 mL of concentrated HNO₃ and 9.6 mL concentrated H₂SO₄ was

added dropwise to the polymer solution with constant stirring over 20 minutes, the solution turning yellow instantaneously. The resulting solution was heated to 55°C with stirring for 40 minutes. Then, the nitration was quenched with 100 mL of cold water and the excess acid was neutralized with 100 mL of 25% NaOH solution. The modified polymer was precipitated into ethanol, thoroughly washed with water, filtered and dried overnight under hood. Nitrated SEBS (SEBS-NO₂), of bright yellow color, was later refined with 250 mL THF, then precipitated with deionized water, filtered, and subsequently dried under hood.

A typical procedure for the synthesis of aminated SEBS (SEBS-NH₂) is as follows: 25 g of SEBS-NO₂ and 280 mL of THF was placed into a 500 mL two-necked round-bottom flask fitted with a mechanical overhead stirrer and a reflux condenser. A solution containing 57.4 g of anhydrous SnCl₂ and 61 mL of concentrated hydrochloric acid was added dropwise into the flask under vigorous stirring. The polymer solution changed color from yellow to colorless immediately after the addition of reducing solution. The mixture was heated at 80°C for 2 hours, and a slightly yellow-colored micellar solution was obtained. After cooling, the reduced polymer was precipitated into 600 mL of water. The excess solvent was removed without drying the product. The wet product was then refined in 100 mL THF and precipitated again into water. After solvent removal, 240 mL of THF was used to disperse the reduced polymer, and the acidity of the polymer was neutralized with 60 mL of 20% NaOH solution; the color turned from pale yellow to pale blue. The resulting SEBS-NH₂ was precipitated into ethanol, washed successively with water and ethanol, filtered and dried at ambient temperature under vacuum overnight. The product was stored under nitrogen in dark bottles to prevent oxidation.

Characterization of Unmodified and Modified SEBS

Fourier transform infrared (FTIR) spectra of SEBS and derivatives were recorded on a Perkin Elmer spectrum 400 ATR-FT-IR spectrometer. A total of 64 scans were collected in the range between 4000 and 600 cm⁻¹ with a spectral resolution of 4 cm⁻¹. Also, ¹H NMR spectra were obtained at 400 MHz on a Varian Inova AS400 NMR spectrometer. Samples for ¹H NMR spectroscopy were prepared by dissolving about 40 mg of product in 1.2 mL of deuterated chloroform containing tetramethylsilane as an internal reference.

Composites Preparation

Lignin was dried at 80°C overnight to remove volatiles prior to melt processing. The composites were prepared in a Haake Büchler internal batch mixer at 90 rpm, 160°C. HDPE was first added into the mixing chamber and allowed to melt for 1 minute. Afterwards, Kraft lignin and compatibilizers were added simultaneously. After 5.5 minutes, a homogeneous composite was collected for molding. Table I lists the amounts of components in each sample. From the compounds produced, plates having dimension of 2.5 × 115 × 115 mm³ were formed by compression molding at 165°C for 12 minutes in a laboratory Carver press. After cooling to ambient temperature, the overflowing films, about 400 μ m thick, were collected for morphological

Table I. Sample Composition and Coding

| Sample code | Kraft lignin (wt %) | HDPE (wt %) | Compatibilizers (wt %) | | | | |
|--------------------------|---------------------|-------------|------------------------|------|------|----------------------|----------------------|
| | | | EVA | MAPE | SEBS | SEBS-NO ₂ | SEBS-NH ₂ |
| PE | 0 | 100 | - | - | - | - | - |
| LigPE | 40 | 60 | - | - | - | - | - |
| LigPE-2.5EVA | 40 | 57.5 | 2.5 | - | - | - | - |
| LigPE-2.5MAPE | 40 | 57.5 | - | 2.5 | - | - | - |
| LigPE-2.5SEBS | 40 | 57.5 | - | - | 2.5 | - | - |
| LigPE-2.5NO ₂ | 40 | 57.5 | - | - | - | 2.5 | - |
| LigPE-1NH ₂ | 40 | 59 | - | - | - | - | 1 |
| LigPE-2.5NH ₂ | 40 | 57.5 | - | - | - | - | 2.5 |
| LigPE-5NH ₂ | 40 | 55 | - | - | - | - | 5 |
| LigPE-7.5NH ₂ | 40 | 52.5 | - | - | - | - | 7.5 |
| LigPE-10NH ₂ | 40 | 50 | - | - | - | - | 10 |

measurements. The plates were collected and specimens for mechanical measurements were cut to desired shapes with cutting dies.

Morphological Testing

Thin films produced during compression molding were characterized using an optical microscope Leica DM LS2 at 400× magnification. Digital images were directly taken with a digital camera. The particle sizes were measured by the software *Nano-measurer* based on the original optical images. At least 150 distinct particles were analyzed for each sample.

Scanning Electron Microscope (SEM) was used to characterize the composites. Micrographs were taken at a magnification of 5000× by a JEOL model JSM-840A. The molded samples were placed first in liquid nitrogen for 30 seconds before fracture. The exposed surface was coated with a thin layer of Au/Pd with a Technics Hummer II and then subjected to electron microscopic analyses.

Mechanical Testing

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 bending fixture (support span = 60 mm). Five specimens of dimensions 75×12.9×2.5 mm³ were examined for each condition. After flexural tests the specimens were V-notched with an automatic sample notcher ASN-120-N and then subjected to Charpy impact testing (ASTM D256) with a Tinius Olsen model 104. Each sample was tested using 12 specimens.

Differential Scanning Calorimetry (DSC)

Thermal analysis of vacuum-dried composite samples were carried out on a Mettler Toledo differential scanning calorimetry (DSC) 822 at a scan rate of 10°C/min over a temperature range from 25°C to 200°C. The measurements were made using around 12 mg of sample under a nitrogen flow of 50 mL/min.

Crystallinity of the polyethylene matrix in the composites was determined from the melting endotherm by Polymer STAR^e software, based upon a value of 293 J/g for the 100% crystalline material heat of fusion.²⁶

Density

Composite densities were determined using a Quantachrome Ultrapyc 1200e gas pycnometer, with nitrogen as the measuring gas. The data reported are the average of three measurements.

RESULTS AND DISCUSSION

Nitration and Amination Reactions

The goal of SEBS modification is to obtain hydrophilic polystyrene units with enhanced electron density. It is well known that styrene units of SEBS are subject to electrophilic aromatic substitution, so that nitro groups can be easily grafted onto the aromatic rings of SEBS through nitration. However, prolonged reaction time combined with high temperature results in SEBS cross-linking. Therefore, the nitration procedure described above was optimized to achieve a high degree of substitution while preventing polymer cross-linking.

Aromatic amine is a strong electron donating function with high hydrophilicity. It is thus convenient to convert the nitro function of SEBS to amine for increased compatibilizing efficiency. The reduction of SEBS-NO₂ by SnCl₂ was reported by Kausar et al.²⁷ In their work, NaOH was added into the polymer solution near the end of reaction without tin salts removal. As a result, the obtained product was contaminated by tin salts. In this study, improvement has been made in the purification of SEBS-NH₂. The tin salt-contaminated solution was purged prior to neutralization of the modified polymer. However, it was observed that repetitive filtration during purging easily led to SEBS-NH₂ agglomeration. For this reason, a small quantity of solvent was left after every purge.

FTIR Analyses

Infrared spectroscopy proved to be useful in the structure elucidation of modified SEBS functional groups. Figure 1 shows FTIR spectra of unmodified and modified SEBS. Compared

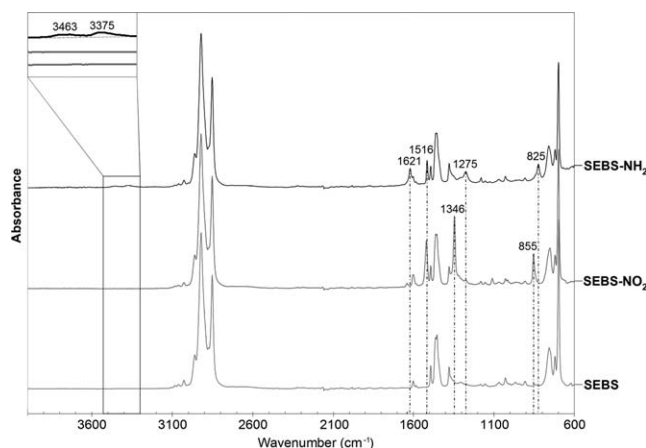


Figure 1. FTIR spectra of SEBS, SEBS-NO₂, and SEBS-NH₂.

with SEBS, SEBS-NO₂ exhibited two N=O stretching vibrations at 1520 cm⁻¹ (asymmetrical) and 1346 cm⁻¹ (symmetrical). The C-N stretching vibration is also observed at 855 cm⁻¹. A new peak at 1641 cm⁻¹ is mainly attributed to an overtone absorption of aromatic C=C vibrations. For SEBS-NH₂, spectral features of the nitro function can no longer be observed, thus suggesting an almost complete reduction of SEBS-NO₂. Two weak peaks at 3463 and 3375 cm⁻¹ are, respectively, attributed to asymmetrical and symmetrical N-H stretching of aromatic amines. The N-H bending vibration observed at 1516 cm⁻¹ and N-H wagging vibration at 825 cm⁻¹ are present. The signal at 1275 cm⁻¹ is attributed to C-N stretching vibration, which shifted from 855 cm⁻¹ after reduction. Moreover, the absorption of aromatic C=C vibration shifted from 1602 to 1621 cm⁻¹.

From FTIR spectra, it is confirmed that nitration of SEBS was complete and nitro functions were totally converted to amine functions; the desired products were thereby obtained.

¹H NMR Analyses

The ¹H NMR spectra of unmodified and modified SEBS are given in Figure 2. The signal of respective protons in aromatic region were denoted from a to g, and the integrated peak areas

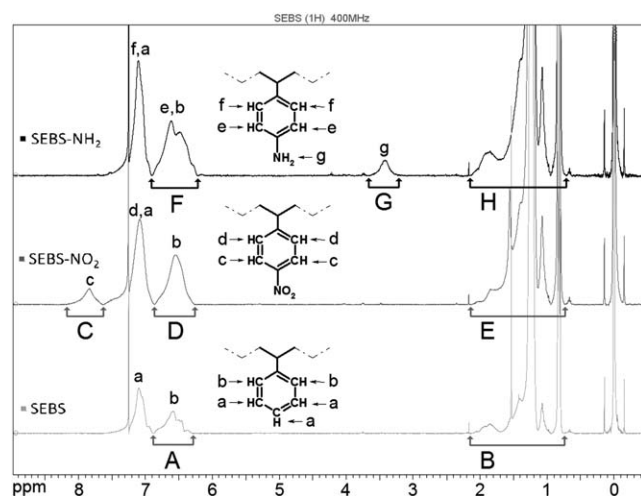


Figure 2. ¹H NMR spectra of SEBS, SEBS-NO₂, and SEBS-NH₂ and assignment of aromatic ring resonances.

were denoted from A to H. Two broad peaks at 7.10 and 6.59 ppm for SEBS are assigned to the protons in meta-para and ortho positions, respectively. Three aromatic resonances for SEBS-NO₂ indicated the incomplete para-substitution of aromatic rings. The signal of amine protons appears at 3.43 ppm and provides additional spectroscopic evidence of aminated SEBS.

¹H NMR spectroscopy is commonly used to quantify functional groups containing protons. The degree of nitration (DN) of aromatic rings can be estimated according to one of the following equations, using the required information from ¹H NMR spectra as presented in Figure 2:

$$DN = \frac{C}{C+D} \times 100\% \quad (1)$$

or

$$DN = \left(\frac{D \times B}{E \times A} - 1 \right) \times 100\% \quad (2)$$

The DN value obtained is 19.3% from eq. (1) and 20.7% from eq. (2). Therefore, about 20% of SEBS styrene units were nitrated. The degree of amination (DA) of aromatic rings is estimated to be 14.3% as deduced through eq. (3). The difference between DA and DN values could be explained by proton loss because of air oxidation of amine groups during drying.

$$DA = \frac{G}{F} \times 100\% \quad (3)$$

Morphology

It was found in our previous work that the state of lignin dispersion in HDPE was tightly related to compatibilization.²⁸ It is clear from Figure 3 that translucent brown lignin particles can be distinguished inside transparent polyethylene films. From image analysis, lignin particle sizes are listed in Table II. There was no obvious difference between LigPE, LigPE-2.5EVA, LigPE-2.5SEBS, and LigPE-2.5NO₂ in which Kraft lignin particles have average size of approximately 17 μm with high standard deviation. Therefore, the addition of 2.5 wt % EVA, SEBS, or SEBS-NO₂ presented no or negligible improvement on composite homogeneity. Surprisingly, the image of LigPE-2.5MAPE showed highly homogenous morphology with blurred interface (interphase) between lignin and HDPE. This phenomenon can be explained by the fact that lignin particles were fragmented to smaller dimensions during melt processing and MAPE was capable of preventing lignin particles' coalescence/agglomeration owing to its reactive property. Although using unreactive compatibilizers did not produce composites with such blurred interfaces, composites homogeneity can be significantly improved by SEBS-NH₂. Addition of 1 wt % of SEBS-NH₂ inhibited the formation of large lignin aggregates as the average lignin particle size recorded in LigPE-1NH₂ was only 10.1 μm. The addition of higher concentrations of SEBS-NH₂ led to higher homogeneity with smaller lignin particles, the average size being 4.3 μm for the addition of 5 wt % SEBS-NH₂. Beyond this concentration threshold, no significant morphological differences were observed by optical microscopy.

Figure 4 shows SEM micrographs of selected samples. It can be seen for LigPE, LigPE-2.5EVA, LigPE-2.5SEBS, and LigPE-1NH₂

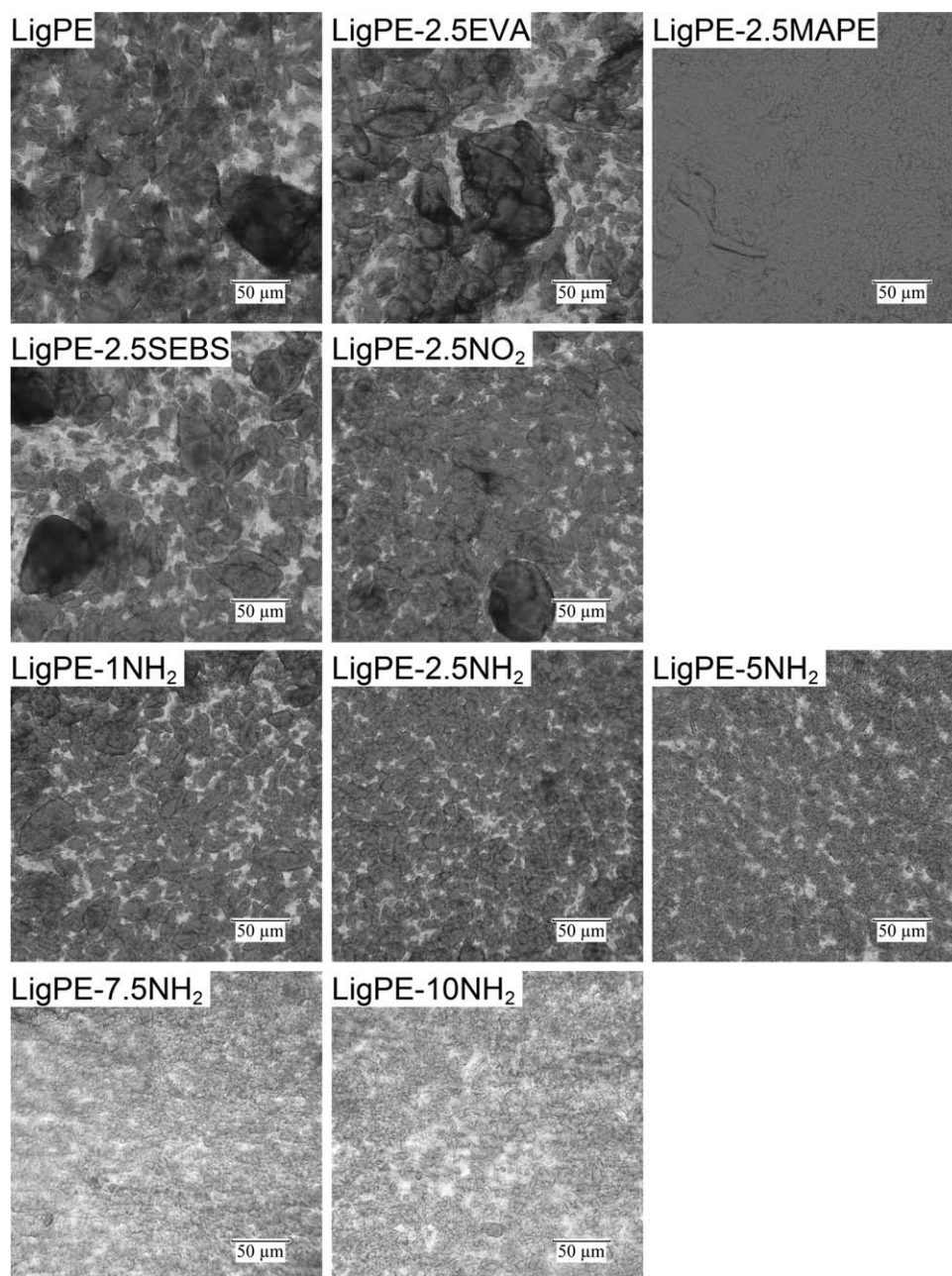


Figure 3. Optical microscopy images of Kraft lignin-HDPE composites (intensity differences are only because of camera angles). Magnification: 400×

that lignin particles tended to pull-out from the fractured surface, suggesting poor adhesion with HDPE. LigPE-NO₂ appeared to display better interface with less filler–matrix detachments, while no pull-out can be observed for LigPE-2.5NH₂. Thus strongly compatibilized interfaces were found in LigPE-2.5MAPE, LigPE-5NH₂, LigPE-7.5NH₂, and LigPE-10NH₂, where the fracture occurred simultaneously inside Kraft lignin particles and HDPE matrix rather than at interfaces, thus confirming high interfacial strength.

SEBS appeared to be miscible with HDPE through van der Waals attractions and polymer chains entanglement, but showed low

affinity towards lignin owing to its high hydrophobicity and low aromatic electron density. As a result, addition of SEBS had negligible influences on mechanical and morphological properties of Kraft lignin-HDPE composites. SEBS-NO₂ has lower aromatic electron density because of strong electron withdrawing capacity of nitro groups, which inhibits the adhesion of SEBS-NO₂ to Kraft lignin. On the other hand, nitro groups contain hydrogen-bonding acceptor sites and SEBS-NO₂ exhibited a compromised affinity to Kraft lignin and acted as a weak unreactive compatibilizer. Contrary to SEBS-NO₂, SEBS-NH₂ displayed higher compatibilizing efficiency for Kraft lignin-HDPE composites. Because

Table II. Average Kraft Lignin Particle Sizes, Crystallinity of the HDPE Matrix, and Density of the Samples

| Sample code | Mean particle diameter (μm) | Crystallinity (%) | Density (g/cm^3) |
|--------------------------|--|-------------------|------------------------------------|
| PE | – | 56.4 | 0.944 |
| LigPE | 17.8 (12.4) | 52.8 | 1.067 |
| LigPE-2.5EVA | 16.9 (13.7) | 53.6 | 1.070 |
| LigPE-2.5MAPE | – ^a | 60.5 | 1.057 |
| LigPE-2.5SEBS | 17.8 (15.7) | 55.5 | 1.070 |
| LigPE-2.5NO ₂ | 16.5 (13.8) | 49.9 | 1.072 |
| LigPE-1NH ₂ | 10.1 (7.9) | 54.4 | 1.069 |
| LigPE-2.5NH ₂ | 6.0 (2.7) | 55.3 | 1.070 |
| LigPE-5NH ₂ | 4.3 (1.8) | 55.5 | 1.068 |
| LigPE-7.5NH ₂ | 4.1 (1.5) | 54.6 | 1.068 |
| LigPE-10NH ₂ | 4.4 (2.1) | 54.3 | 1.070 |

Numbers in parentheses represent the standard deviations.

^aIt was not possible to determine particle size by optical microscopy.

the aromatic electron density of SEBS-NH₂ is intensively increased by amine groups, the π -stacking forces between Kraft lignin and SEBS-NH₂ were equally enhanced. Moreover, amine function has both hydrogen-bonding acceptor and donor sites that strengthen intermolecular interactions between Kraft lignin and SEBS-NH₂.

Mechanical Properties

Mechanical analyses are generally a good way to evaluate the effect of compatibilizers in composite systems. Here, tensile and flexural moduli are reported in Figure 5. However, no clear relationship was found between modulus and compatibilization. Addition of 40 wt % Kraft lignin into HDPE increased tensile modulus and flexural modulus by 29% and 24%, respectively. It appeared that these two moduli depended upon the weight fraction of compatibilizers rather than the type of compatibilizers. There was no significant difference in tensile and flexural moduli among samples containing 2.5 wt % of compatibilizers, but a higher concentration of SEBS-NH₂ resulted in lower tensile and flexural moduli. In addition, LigPE-1NH₂ showed 13%

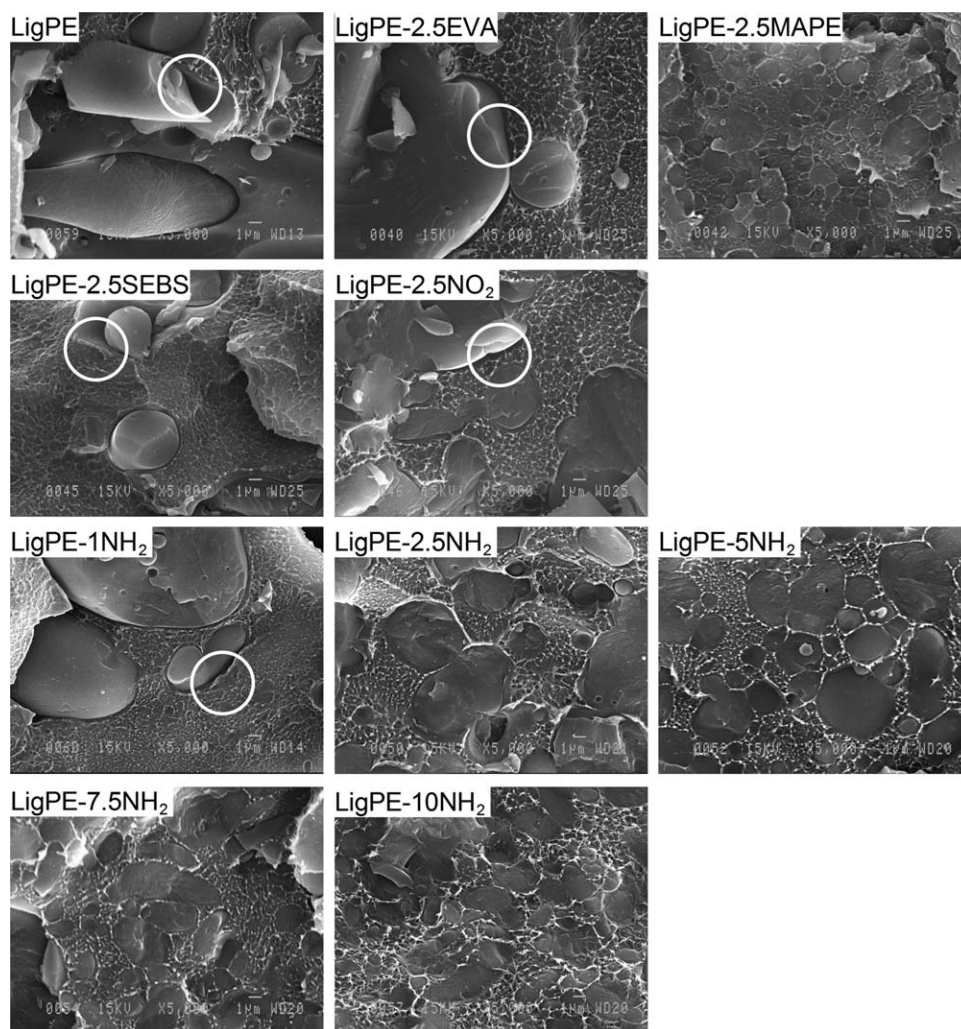


Figure 4. SEM images of Kraft lignin-HDPE composites, where filler–matrix detachments have been located and marked with white circle. Magnification: 5000 \times

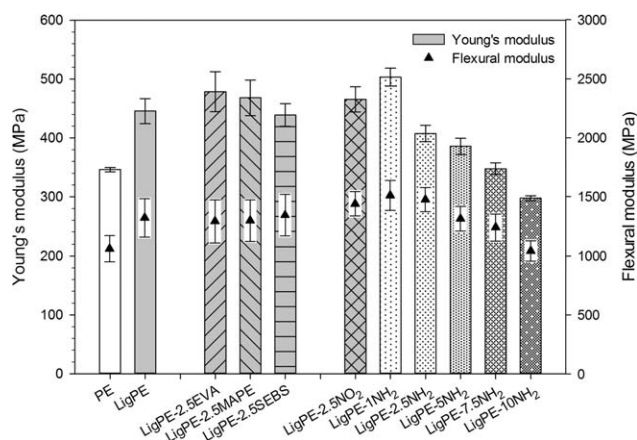


Figure 5. Effect of compatibilizers on tensile and flexural moduli of the samples.

higher tensile modulus than LigPE, which was ascribed to lignin cross-linking by SEBS-NH₂ at low content.

As indicated in Figure 6, addition of 40 wt % Kraft lignin alone reduced HDPE's tensile strength by half, and this is why effective compatibilization is necessary to improve, or at least restore tensile strength of neat HDPE. LigPE-2.5EVA and LigPE-2.5SEBS did not improve tensile strength, while addition of 2.5 wt % SEBS-NO₂ was able to restore tensile strength from 11.0 to 13.6 MPa. But the most effective compatibilizers were MAPE and SEBS-NH₂, for which tensile strength was similar to neat HDPE. Tensile strength enhancement can be explained by strong interactions of compatibilizers with both HDPE and Kraft lignin. This suggests high affinity between amino-functionalized SEBS and Kraft lignin through unreactive intermolecular interactions.

It was shown that addition of 2.5 wt % of SEBS-NH₂ was sufficient to obtain good tensile strength, but samples with higher concentration displayed no more improvement, and even reduced tensile strength. The negative effects of using excess compatibilizers have been reported elsewhere.^{29,30} It is known that excess compatibilizer molecules are located in the bulk

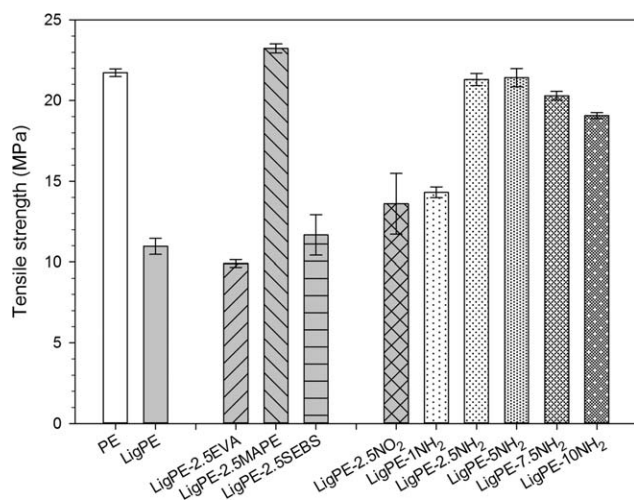


Figure 6. Effect of compatibilizers on tensile strength of the samples.

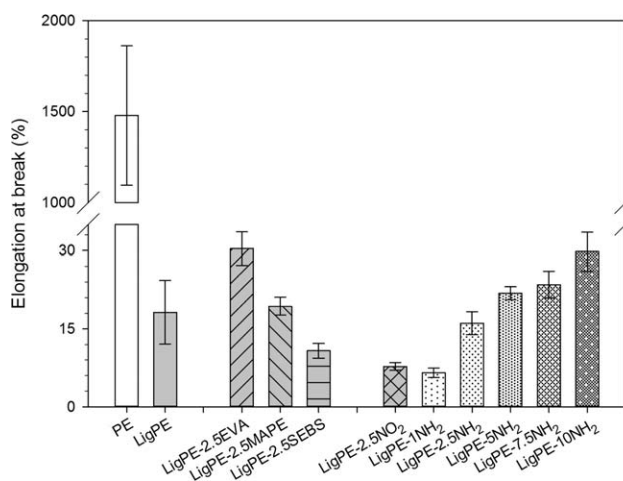


Figure 7. Effect of compatibilizers on elongation at break of the samples.

matrix and decrease structural integrity acting as plasticizers instead of being engaged in compatibilization.

Compared with neat PE, LigPE presented merely 1% elongation at break (Figure 7). Addition of 2.5 wt % EVA allowed increasing the elongation at break by 67%. This result confirms the work of Luo et al.¹⁶ The presence of 2.5 wt % SEBS or SEBS-NO₂ in Kraft lignin-HDPE composites led to lower elongation at break values, which may be ascribed to reduced polyethylene matrix integrity. The low elongation at break value of LigPE-1NH₂ is probably because of cross-linking and lowered elasticity of lignin itself. The addition of 2.5 wt % MAPE or SEBS-NH₂ did not affect the elongation value of composites. The elongation at break of composites was obviously increased with SEBS-NH₂ loading, LigPE-10NH₂ exhibiting high-elongation at break comparable to that of LigPE-2.5EVA composite.

Charpy impact test results are illustrated in Figure 8. As expected, addition of 40 wt % Kraft lignin reduced impact strength of HDPE from 10.3 to 2.8 kJ/m². All the compatibilizers tested (EVA, MAPE, SEBS, SEBS-NO₂, and SEBS-NH₂) at low concentrations ($\leq 2.5\%$) provided no significant impact on strength enhancement. Nevertheless, SEBS-NH₂ at higher contents, especially at 10%, was able to restore impact strength from 2.8 to 4.1 kJ/m².

According to the obtained results from mechanical tests, it was possible to replace 40 wt % of fossil resource-based polyethylene by biorenewable Kraft lignin in the production of HDPE-based biocomposites. The mechanical properties of the studied biocomposites were acceptable because of the use of a novel unreactive compatibilizer SEBS-NH₂.

DSC and Density Analyses

DSC was performed to understand the thermal properties of composites containing various compatibilizers and the results are detailed in Table II. The degree of crystallinity in LigPE-2.5MAPE is slightly higher than that of all other samples. This may be ascribed to the nucleating effect of Kraft lignin in presence of MAPE. For all the other samples, crystallinity seems independent of compatibilizer type and loading for SEBS-NH₂, thus suggesting that the compatibilizers did not modify the

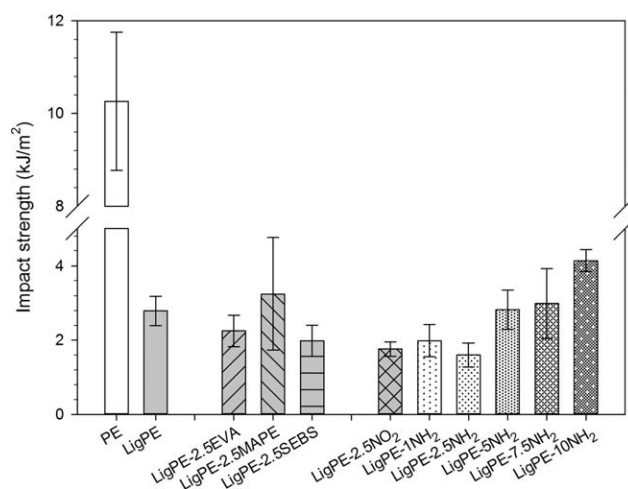


Figure 8. Effect of compatibilizers on Charpy impact strength of the samples.

properties of the matrix; the improvements in mechanical strength being only a result of enhanced interface.

Indulin AT has a density of 1.198 g/cm³ and as expected, incorporation of 40 wt % Kraft lignin into HDPE resulted in increased density from 0.944 to 1.067 g/cm³. Because all the compatibilizers used are polymeric materials having densities similar to HDPE, and the crystallinities measured in all samples were similar, the densities of the composites were barely affected by the type/content of compatibilizer used.

CONCLUSIONS

Compatibilization of Kraft lignin-polyethylene composites has been achieved using unreactive compatibilizers based on commercial block copolymer SEBS. SEBS was subjected to nitration and amination reactions, and SEBS derivatives were identified by means of FTIR spectroscopy and ¹H NMR analysis. Various compatibilizers including SEBS derivatives were incorporated into Kraft lignin-HDPE composites via melt processing.

The mechanical results indicated that SEBS-NH₂ is a more efficient unreactive compatibilizer than EVA. The compatibilizing efficiency of SEBS-NH₂ is comparable to a reactive compatibilizer MAPE. The addition of 2.5 wt % of SEBS-NH₂ was enough to double the tensile strength of the composite compared to the Kraft lignin alone-HDPE composites. Higher SEBS-NH₂ contents led to decreased tensile and flexural moduli of composites, but increased elongation at break values and Charpy impact strength. Using the same amount of SEBS-NO₂ was found to be less advantageous than SEBS-NH₂ to increase composites' mechanical properties, while SEBS addition alone showed no mechanical improvement.

Morphological analysis showed that homogeneous Kraft lignin-HDPE composites with compatibilized interface have been obtained by using efficient compatibilizers such as MAPE and SEBS-NH₂. Enhanced mechanical and morphological properties were principally because of compatibilized interface, because modification of the HDPE matrix crystallinity was not observed

for most samples according to DSC results. Also, the compatibilizers used exhibited no influence on final composite density.

The results obtained in this work help to clarify the compatibilizing mechanisms between Kraft lignin and HDPE for composites produced with unreactive compatibilizers. It was found that an efficient unreactive compatibilizer for the system studied must be partially miscible with polyethylene and capable of interacting with Kraft lignin by means of hydrogen bonding and π -stacking forces, so as to decrease interfacial energy.

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