

# Mechanical Properties of Polypropylene Blended with Esterified and Alkylated Lignin

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**ABSTRACT:** Lignin does not show miscibility with commercial polyolefins. Therefore, industrial waste lignin was modified in two different ways and subsequently blended with commercial polypropylene (PP) up to 25 wt %. A Brabender electronic plasticorder was used for melt mixing at 190°C. The influence of different modifications on the mechanical properties and processing stability was studied for both polymer blends. The blends of PP and lignin modified (esterified) with maleic anhydride showed less deterioration in the mechanical properties compared

to blends of PP and alkylated lignin with dichloroethane. Intermolecular interactions between the PP matrix and modified lignin were concluded on the basis of indicative values derived from various relevant theoretical models to the experimental data. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1701–1712, 2012

**Key words:** mechanical properties; miscibility; modification; polymer blends

## INTRODUCTION

Thermoplastics, such as polypropylene (PP) and polyethylene, are used in high volumes for short-term applications, such as packing, medical, automobile, agricultural, and related areas, where its applications are enhanced appreciably. At present, most of the fillers used in thermoplastics are inorganic materials, such as glass beads, calcium carbonate, talc, kaolin, and various silicates. However, a major problem of such materials is the nonuniformity and poor dispersion of these materials in low-polarity polymer matrixes.<sup>1</sup> However; currently, researchers are trying to replace these inorganic fillers with newer types of organic fillers. Lignin, being largely available and modifiable, has become a promising alternative for this purpose as biobased composites have gained prominence over the past 2 decades because of both environmental concerns and waste disposal problems.<sup>2</sup> Lignin is a complex organic phenolic polymer skeleton available as industrial waste material from pulp and paper industry in large quantity.

Lignin has been used for many new products, such as resins<sup>3,4</sup> and adhesives for polymer blending,<sup>5,6</sup> and for the preparation of low-molecular-weight fuel additives.<sup>7,8</sup> Because of its phenolic nature, it is expected that it can increase the antioxidation, thermal, and light stability of polymeric materials. It is interesting to use it in polymers because of its low density, low abrasive, and low cost.<sup>9</sup>

The use of Kraft lignin as a copolymer or polymer additive has also received considerable attention.<sup>10</sup> A recent review of industrial applications of lignin in polymers was published by Lora and Glasser.<sup>11</sup> The most straightforward application has been the use of lignin as a filler material in thermoplastic<sup>12–16</sup> and thermosetting<sup>17,18</sup> polymers and rubbers<sup>19</sup> with limited positive to negative effects on the mechanical properties with lignin addition. Most workers have blended it with various thermoplastics in considerably higher proportions.<sup>2,13,20</sup> The antioxidant properties of lignin have been used to stabilize polymer matrix composites against photooxidation and thermooxidation.<sup>2,21</sup> The effect of lignin composition on the thermal behavior of different composites based on crystallizable polymers was also investigated.<sup>22–26</sup> The nucleating effect of lignin in the PP matrix was reported by Canetti et al.<sup>23</sup> and in poly(3-hydroxybutyrate) by Weihua et al.<sup>26</sup>

Buvnova et al.<sup>27</sup> observed increased thermal stability in several lignin-blended thermoplastics. The thermal and photochemical stability of polyolefins was found to be increased with the addition of

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lignin, but the mechanical properties showed some deterioration with the lignin content.<sup>12</sup> This was attributed to the incompatibility and lower solubility of polar lignin molecule in nonpolar polymers.

The mechanical properties of lignin/PP blends up 30% w/w were studied extensively by Kharade and Kale,<sup>12</sup> and they found that the tensile strength was reduced, whereas the impact properties remained unaffected, and the melt viscosity increased with the lignin content. Similar results were reported by Alexy et al.<sup>13</sup> Pucciariello et al.<sup>28</sup> reported that the elongation was drastically reduced, whereas the modulus values were improved.

A major limitation of these lignocellulosic materials is their hydrophilicity; hence, the modification of these materials will enhance their barrier and mechanical properties. It can easily be seen that the chemical modification of lignin can be used to improve the polymer–lignin compatibility and to introduce reactive sites. The available hydroxyl groups on the lignin molecule are reactive and plentiful in number. Such groups can act as local centers of high polarity that are capable of hydrogen bonding.<sup>29</sup> The modification of these reactive nuclei results in an effective alteration of the lignin solubility behavior.<sup>29,30</sup> Increasing the length of the aliphatic chain can be expected to reduce the polarity of the Kraft lignin and improve its solubility in nonpolar solvents.<sup>31</sup> Acetylation, propionation, butyration, and so on of the Kraft lignin hydroxyl groups result in an increase in the aliphatic carbon chain. The introduction of double-bond functionality to Kraft lignin allows the modified lignin to copolymerize with the monomers in the resin. This may be beneficial for the mechanical properties of the polymer.<sup>32</sup> A similar improvement in the performance characteristics was observed by Sailaja<sup>33</sup> by modification via grafting with a hydrophobic polymer.

In this work, industrial waste lignin was modified by maleic anhydride (MA) and dichloroethane with the aim of increasing its solubility and compatibility toward PP. Modified lignins were blended in different proportions with commercial-grade PP. The effects of different modifications of lignin on the mechanical properties and processing stability were studied. The application of the experimental data in the same established theoretical models was used to study the adhesion and intermolecular interaction between the modified lignin and PP.

## EXPERIMENTAL

### Materials

The materials used to prepare the binary blends were commercial-grade PP, supplied by Bajaj Polymer (Nagpur, India) with a melt flow index (MFI) of 4.26 g/10 min at 230°C and a 2.16-kg load. Kraft lig-

nin was isolated from the black liquor provided by Simplex Paper Mills (Gondia, Maharashtra state, India). Maleic anhydride, dichloroethane, and all other reagents were procured from Merck, Mumbai, India.

### Methods

#### Isolation and purification of lignin

The black liquor was filtered, and the filtrate was acidified with dilute hydrochloric acid. It was then allowed to settle down for 30 min. Again, it was filtered and washed successively with distilled water to remove acid. The precipitated lignin was dried in an oven overnight at 90°C. Oven-dried crude lignin was then dissolved in 1,4-dioxane and filtered to remove 1,4-dioxane insoluble impurities. 1,4-Dioxane was removed by distillation, but before that, pure lignin was precipitated by the addition of a definite portion of distilled water to collect some precipitable fraction of lignin. This purified lignin was used for further chemical modification.

#### Modification of lignin

*Modification by Maleic anhydride (MALig).* MA (40 g) was placed in a 250-mL, round-bottom flask fitted in modified microwave oven and irradiated until it produced a molten mass. Purified lignin (20 g) was added to the molten MA in several small portions in a separately setup 2RML-Rotamantle (Remi, Mumbai, India) set at 100°C. Then, the reaction mixture was remounted in Microwave oven (Kenstar model, 2.45 GHz) India, (for 20 min) with intermittently controlled irradiation. The reaction mixture was then poured into an excess of cold water and filtered to recover an insoluble residue (MALig). It was further washed successively with distilled water to remove unreacted MA and dried in oven at 80°C for 24 h. The reaction was monitored, and completion was determined with a weight percentage gain formula (on an oven-dried basis).<sup>34</sup>

*Modification by dichloroethane (CELig).* Purified lignin (20 g) was mixed with an excess of dichloroethane and 10 g of anhydrous aluminum chloride in a 250-mL, round-bottom flask. The resultant mixture was refluxed for 20 min with 30-s pulsed exposures in a modified microwave oven. The resultant reaction product was filtered, washed with an excess of distilled water, and then dried in air oven at 80°C for 24 h.

#### Blend preparation

The polymer blends PPMALig and PPCELig were prepared by the melt mixing of PP and modified lignin in different proportions (i.e., 5, 10, 15, 20, and 25 wt %) at 190°C for 10 min at 60 rpm in a Brabender electronic Plasticorder Haake AEV 153 mixer, Duisburg, Germany. Pure PP processed under similar

**TABLE I**  
**Values of the Parameters Found for the PPMALig and PPCELig Blends for Different Models Applied to the Theoretical Data**

	Model	Symbol	Blend		No adhesion
			PPMALig	PPACELig	
Tensile strength	Turcsanyi	$B$	1.9	0.5	0.246 <sup>a</sup>
Young's modulus	Halpin-Tsai	$R_m$	1.45	1.8	
	Sato-Furukawa	$\xi$	0.008	0.011	1.0 <sup>b</sup>
Elongation at break	Nielsen	$K$	0.5	0.85	1.21 <sup>c</sup>

<sup>a</sup> A higher value indicates better adhesion.

<sup>b</sup> 0, perfect adhesion; 1, no adhesion.

<sup>c</sup> A lower value indicates better adhesion.

conditions was investigated as a reference material. During the process, dry nitrogen was continuously purged into the mixing chamber to ensure minimum thermooxidative degradation. The obtained extrudates were cut into pieces less than 10 mm in diameter by a granulator. Dumbbell-shaped specimens were then prepared by injection molding at 190°C according to ISO 527-2 specifications (type 1BA),<sup>35,36</sup> which was used for the analysis of the mechanical properties of the blends and pure PP. Rectangular-shaped specimens were used to determine the impact strength of the blends. Five specimens were tested for each blend formulation to obtain a reliable average of the tensile properties and their corresponding standard deviation.

### Material characterization

The Fourier transform infrared (FTIR) spectra of pure lignin and modified lignin were recorded on Shimadzu 100 FTIR Spectrophotometer, Japan, spectrophotometer with KBr pellets in the scan range from 4000 to 400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

The tensile properties, including the relative tensile strength (RTS), relative elongation at break (REB), and relative Young's modulus (RYM), were obtained by testing of the dumbbell-shaped specimens on a Universal testing machine (Instron UK232) Gracely, PA, with load of 1 N at a strain rate of 50 mm/min. The relative impact strength (RIS) of the unnotched specimen was obtained on an Izod impact tester (CEAST-6545, serial 11036) Akron, Ohio, USA, at room temperature. The dimensions of the Izod specimens were  $63 \times 12.5 \times 3.1 \text{ mm}^3$ ; at least five specimens were tested for each sample. The relative mechanical properties, that is, RTS, REB, RYM, and RIS, were determined according to eq. (1). The impact and tensile tests were performed according to ASTM D 256A and ASTM D 1708 methods, respectively:

$$\text{Relative mechanical properties} = \frac{\text{Mechanical properties of the blends}}{\text{Mechanical properties of the pure PP}} \quad (1)$$

The morphological analysis of the PPMALig and PPCELig blends was done with scanning electron microscopy (SEM; JEOL JSM-6380A) Tokyo, Japan. The samples were coated with palladium.

The rheological properties and processing stability of the prepared blends were measured on an MFI tester (Dynisco D4059, Holiborn, Germany) according to ASTM D 1238 at 230°C and with 2.16 kg of weight.

## RESULTS AND DISCUSSION

### FTIR spectroscopy

Figure 1 shows the FTIR spectra of purified lignin, MALig, and CELig. With regard to the spectra of lignin, the absorbance for 3400  $\text{cm}^{-1}$  was due to stretching of hydroxyl groups. The absorbance at 2923  $\text{cm}^{-1}$  arose from C-H stretching, and a small group peaks at 1511, 1462, 1421, and 1327  $\text{cm}^{-1}$  corresponded to aromatic skeletal vibrations, and the  $\beta$ -0-4 ether bond was observed at 1117  $\text{cm}^{-1}$ . The methoxyl group band was observed at 2939, 2881, 1460, and 1425  $\text{cm}^{-1}$ , the C=C vibrations of the aromatic ring were observed at 1514  $\text{cm}^{-1}$ , and the band at 1600  $\text{cm}^{-1}$  was characteristic of the quinoid structure and carbonyl groups at 1664 and 1720  $\text{cm}^{-1}$ .

MALig showed a peak for aromatic C=O stretching at 1771  $\text{cm}^{-1}$  and a peak at 1726  $\text{cm}^{-1}$  for aliphatic C=O, which was due to the resultant ester. We also observed peaks for phenolic -OH at 3400  $\text{cm}^{-1}$ , C-O of primary alcohol at 1038  $\text{cm}^{-1}$ , C-O of secondary alcohol at 1097  $\text{cm}^{-1}$ , guaiacyl C-H at 1040  $\text{cm}^{-1}$ , ether C-O at 1100  $\text{cm}^{-1}$ , C-O stretching of secondary alcohol and aliphatic ether at 981  $\text{cm}^{-1}$ , and C-O stretching of primary alcohol and aromatic C-H in-plane deformation at 908  $\text{cm}^{-1}$ . An increase in the relative peak intensity at 1726  $\text{cm}^{-1}$  was attributed to esterification. Other peaks were already described in detail in our earlier work.<sup>37</sup> These data show that considerable esterification took place. Considerable increases in the intensities of all peaks related to methyl C-H stretching were due to alkylation by dichloroethane, which resulted in CELig.

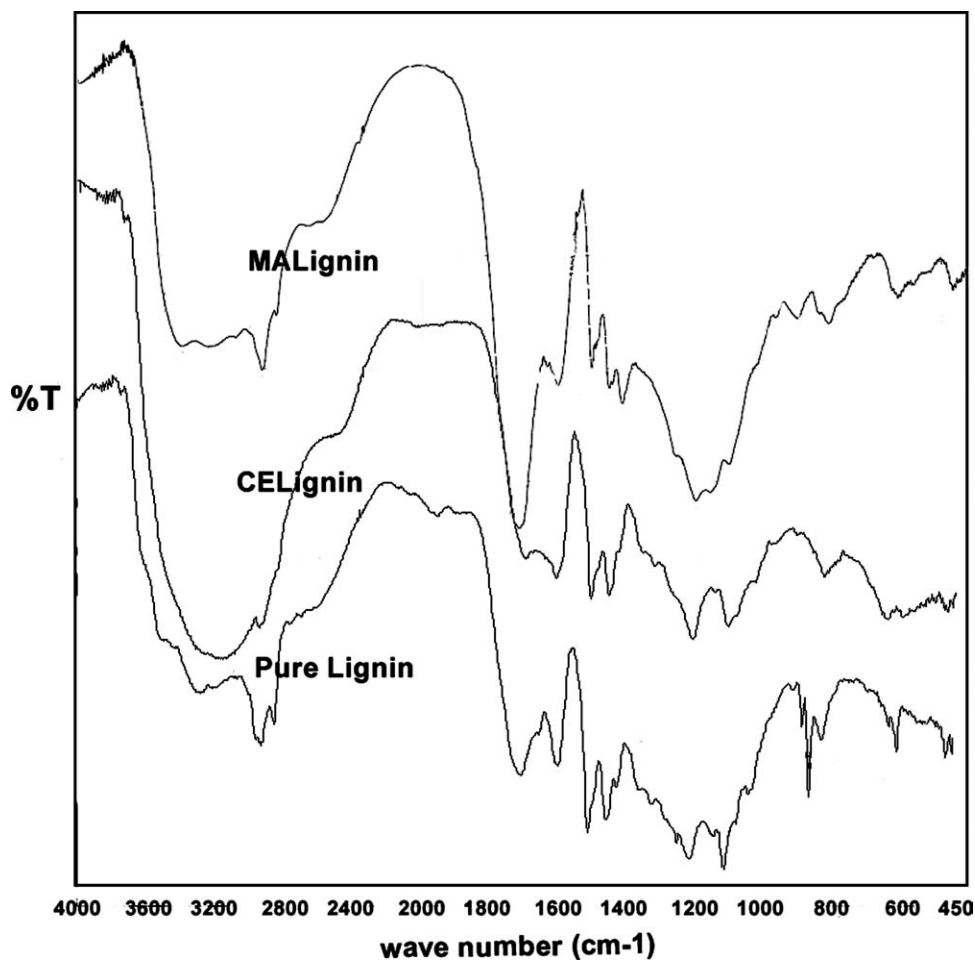


Figure 1 FTIR spectra of pure lignin, MALig, and CELig.

## RIS

Figure 2 represents the plot of RIS (Impact strength of the blends/Impact strength of pure PP) of PPMALig and PPCELig blends against the weight fraction of modified lignin (MALig and CELig) in the blends. The impact strength of all of the blends decreased with increasing weight fraction of modified lignin in the blends. The samples thickness was the same for both types of blends; therefore, the energy required to fracture a sample was decreased with increasing modified lignin content in both types of blends. These findings seem to be consistent with those of Sailaja and Deepti.<sup>2</sup> A decrease in RIS showed less compatibility between the modified lignin added in the PP matrix, but the extent of the decrease in the RIS value was found to be greater in the PPCELig blends than in the PPMALig blends. At the highest weight fraction of modified lignin (0.25) in the blend, the RIS decreased by about 36% in the case of PPMALig and about 60% in the case of the PPCELig blends. Comparatively higher RIS values for the PPMALig blends indicated little higher compatibility between the PP matrix and MALig compared to the CELig and PP matrix.

## RTS

The tensile properties were first determined from primary stress–strain curves of the blends (figure not shown). The maximum tensile strength of both types of blends decreased with increasing volume fraction ( $\phi$ ) of modified lignin in the blends. The

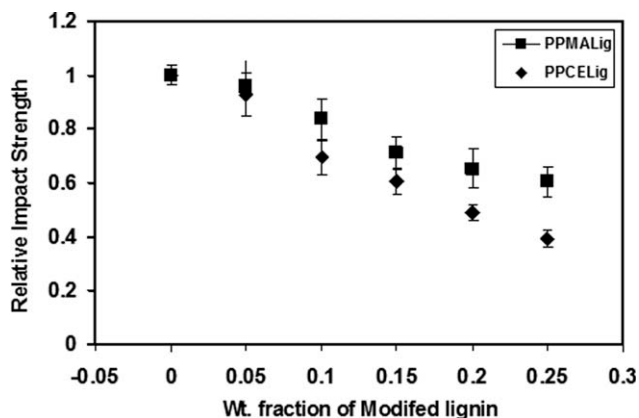
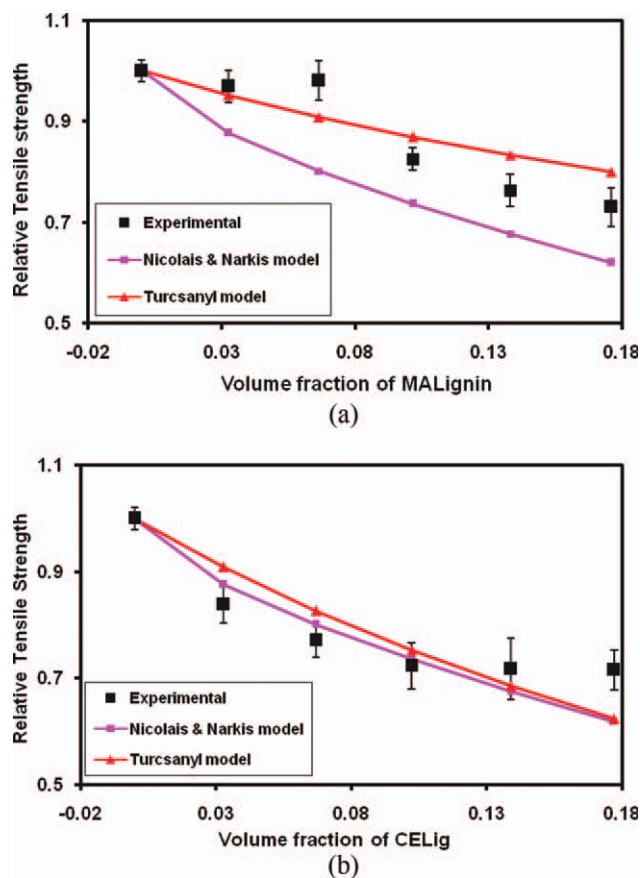


Figure 2 Effect of the weight fraction of MALig and CELig on RIS of the blends.





**Figure 3** (a) Effect of  $\phi$  of MALignin on RTS of the PPMA-Lig blends and (b) effect of  $\phi$  of CELig on RTS of the PPCELig blends. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

plots of RTS, that is, the ratio of the tensile strength of the blends to that of pure PP,  $\sigma_b/\sigma_{PP}$  (where  $\sigma_b$  and  $\sigma_{PP}$  are the tensile strengths of the blend and neat PP, respectively) versus  $\phi$ , are presented in Figure 3(A,B). The  $\phi$  values of the both MALignin and CELignin used in the blends were obtained from the value of the weight percentage of MALignin and CELignin in the blends and its density values. The tensile strength showed a continuous decrease with increasing  $\phi$ ; this indicated that the modified lignin weakened the blend. A decrease in the effective cross-sectional area of the matrix in the presence of MALignin and CELignin, which created a stress-concentration point, may have led to such weakening.

In the case of the PPMALignin blends, the decrease in the RTS value was very negligible up to 10 wt % MALignin loading in the blends. However, after that, a continuous decrease in the RTS value was observed. A comparatively greater decrease in the RTS value was observed in the PPCELignin blends compared to the PPMALignin blends. This observation further supported a difference in extent of intermolecular interaction and a predictably consequent easier dispersion of MALignin in the PP matrix compared to that of

CELignin in the PP matrix. This was predictable because of the higher miscibility and compatibility of MALignin in the polymer matrix. The suitably increased aliphatic content in MALignin may have been another reason for the greater compatibility of MALignin in the PP matrix. However, this effect was more up to 10 wt % MALignin. A higher proportion showed a continuous decrease in the RTS values. On the basis of a lesser fall in the values of RTS up to 10 wt % and a greater decrease in RTS at higher proportions of modified lignin, we concluded that after the modified lignin attained saturation in the molten PP matrix, its further content may have acted as a filler of lesser contribution to the strength in the corresponding resultant blends. The strength of a particulate polymer blend relies on the parameter of particle loading, interface adhesion, and particle size; this was reviewed in detail by Fu et al.<sup>38</sup> Poor adhesion between CELignin and the PP matrix gave rise to a transfer of stress between the matrix and CELignin and to a yielding of the PPCELignin blends for values lower than those corresponding PPMALignin blends.

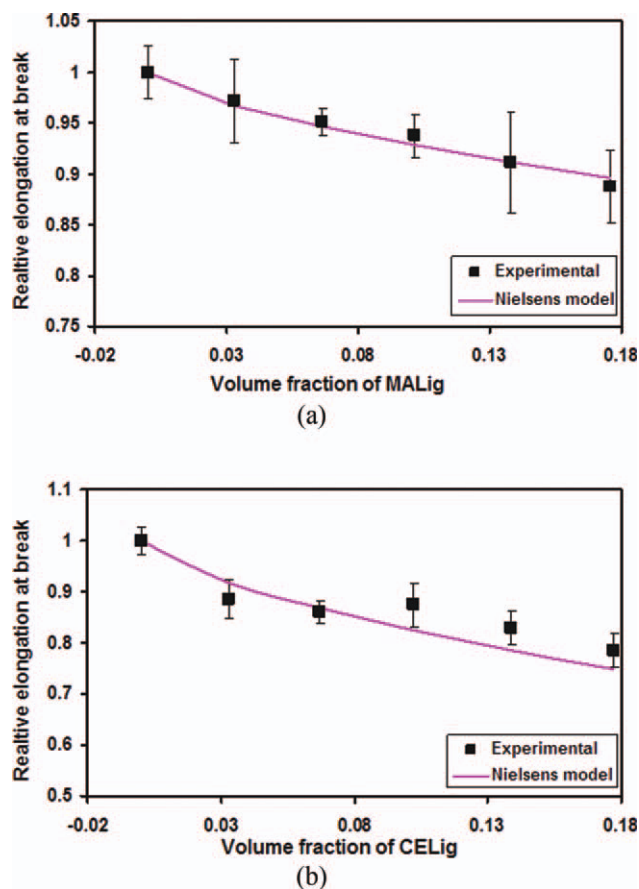
For more careful exploration of the degree of interfacial adhesion between the two phases, the results were analyzed with models featuring an adhesion parameter. The characteristics of all theories are the relationship between  $\phi$  and the projected area fraction of particulate inclusions. The Nicolais and Narkis model [eq. (2)] gives a geometrical model for the tensile strength of a composite with uniformly distributed filler particles of equal radius.<sup>39–46</sup> The tensile strength in these no-adhesion type two-phase structures is proportional to the area function or  $\phi$  of the discontinuous phase:

$$\text{RTS} = \frac{\sigma_b}{\sigma_{PP}} = 1 - 1.21\phi^{2/3} \quad (2)$$

where  $\phi$  is the volume fraction of the modified lignin, which was calculated according to eq. (3):

$$\phi_i = \frac{(w_i/\rho_i)}{\sum (w_i/\rho_i)} \quad (3)$$

where  $w_i$  and  $\rho_i$  are the weight fraction and density of component  $i$ , respectively. The densities for the neat PP, MALignin, and CELignin were 0.913, 1.424, and 1.414 g/cm<sup>3</sup>, respectively. The theoretical data obtained from eq. (2) are plotted in Figure 3(A,B). This model is based on assumption that the tensile strength decreases because of the reduction in the effective cross sectional area caused by spherical filler particles. No adhesion between the matrix and the filler particles was assumed because the applied stress was not transferred to rigid filler particles. As shown in Figure 3(A), in the case of the PPMALignin



**Figure 4** (a) Effect of  $\phi$  of MALig on REB of the PPMA-Lig blends and (b) effect of  $\phi$  of CELig on REB of the PPCELig blends. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

blends, the theoretical values did not match the experimental results, as a good fitting was not observed. That lack of fitting could be attributed to the existence of some weak attraction forces between the polymer and the MALig surface, and therefore, the adhesion degree was not zero, as assumed by that model. However, in the case of the PPCELig blends, the theoretical values were slightly closer to the experimental values; this indicated negligible or very weak interactions between CELig and the PP matrix [Fig. 3(B)].

For very strong particle matrix interfacial bonding, the empirical model, given by Turcsanyi<sup>2,47,48</sup> [eq. (4)], was applied; the model describes the compositional dependence of tensile strength. The Turcsanyi model includes an exponential factor that accounts for the effect of adhesion-modified lignin–polymers in tensile strength:

$$\text{RTS} = \frac{\sigma_b}{\sigma_{\text{PP}}} = \frac{1 - \phi}{1 + 2.5\phi} \exp(B\phi) \quad (4)$$

where the term  $(1 - \phi)/(1 + 2.5\phi)$  corresponds to a reduction in the area occupied by the matrix due to

the presence of modified lignin in the blends and  $B$  is the empirical constant related to the interfacial properties, that is, the interface size and interface strength, whose value was calculated with trial and error to match the theoretical values with the experimental results. In the validity domain, the polymer/filler pair is characterized essentially by the value of the parameter  $B$ , which is obviously connected with the interfacial properties of a given system and also depends on the yield stress of the matrix. The value of  $B$  is 0.246 is for no matrix–filler interaction when particles do not carry any load and whose value increases with improved adhesion.<sup>48</sup> The  $B$  values [from eq. (4)] for the PPMALig and PPCELig blends were calculated to match the experimental data and were found to be 1.9 and 0.5, respectively, as given in Table I. The obtained  $B$  value in case of the PPMALig blends showed that there was good interaction between MALig and the PP matrix, whereas the analogous  $B$  value in the case of the PPCELig blends was somewhat lower compared to the former. This again showed much weaker adhesion between CELig and PP. The application of both models to the PPMALig and PPCELig blends were in conformity and in agreement. Although the tensile results were not all independent, they did not reflect different degrees of deformation. The surprising result was that they all indicated some adhesion between the modified lignin (MALig and CELig) and the polymer matrix.

## REB

Plots of REB (with values obtained from the stress–strain curve for both types of blends, PPMALig and PPCELig) versus  $\phi$  of modified lignin are shown in Figure 4(A,B). All of the blends showed comparatively lower elongations at break than the pure PP. In both types of blends, the maximum reduction in REB was found at a 5 wt % loading of modified lignin. However, after that, the rate of reduction in REB was very small, with an increasing proportion of lignin derivative (modified lignin weight percentage) in the blends, ranging up to 25 wt %. The decrease in REB values at 5 wt % modified lignin loading was also due to the higher stiffness of lignin particles compared to that of PP. The modified Nielsen's model eq. (5) is generally used to predict the theoretical value of REB for the adhesion in the case of spherical particles with good adhesion to the matrix.<sup>40,47,49</sup>

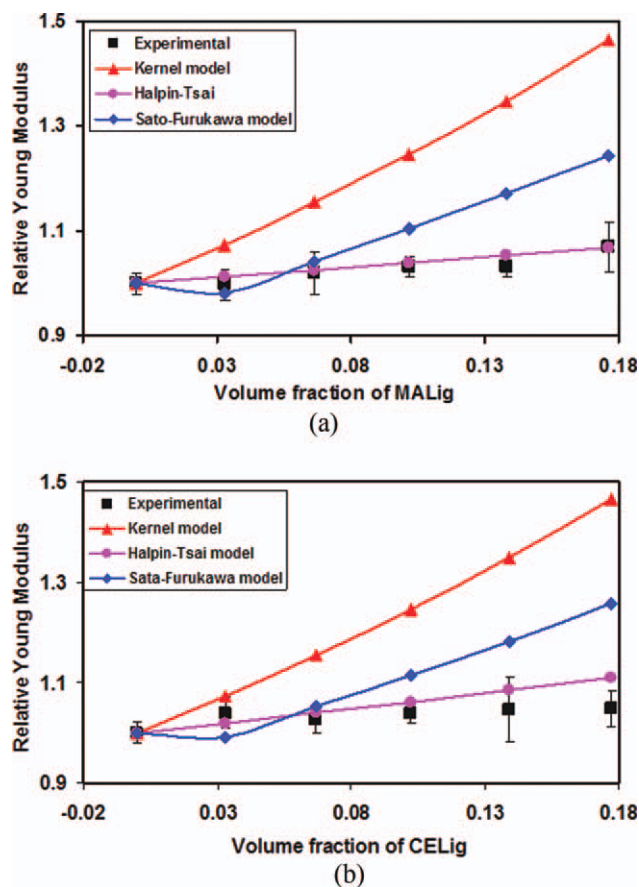
$$\text{REB} = \frac{\varepsilon_b}{\varepsilon_{\text{PP}}} = \left(1 - k\phi^{2/3}\right) \quad (5)$$

where  $\varepsilon_b$  is the elongation at break value for the blends,  $\varepsilon_{\text{PP}}$  is the elongation at break value for pure PP, and  $k$  is the adjustable parameter, which

depends on the filler geometry. It was obtained on a trial-and-error basis to match the theoretical values with the experimental results. The value of the phase interaction parameter, also known as the *weightage factor* ( $k$ ), describes the blend structure. With no adhesion in the presence of a spherical dispersed phase,  $k = 1.21$ ,  $k = 1$  stands for no strain concentration, and when the dispersed phase does not weaken the structure,  $k = 0$ . The value of  $k < 1.21$  indicates interphase adhesion; the lesser the value is, the better the adhesion is. The experimental data generated for both types of blends for REB were fitted to Nielsen's equation [eq. (5)]. Figure 4(A,B) shows the fitting curves to the experimental data for the PPMALig and PPCELig blends, respectively. The  $k$  values were found to be 0.5 and 0.85 for the PPMALig and PPCELig blends, respectively. The value of  $k$  was less than unity; this indicated a good degree of interfacial interactions with an extent of discontinuity in the structure.

## RYM

Figure 5(A,B) shows the plots of RYM ( $M_b/M_{PP}$ , where  $M_b$  and  $M_{PP}$  are the Young's modulus of the blends and pure PP, respectively) of the PPMALig and PPCELig blends against  $\phi$  of the modified lignin. The RYM value increased with increasing  $\phi$  of modified lignin in both cases. At lower  $\phi$  (0.05), the observed modulus climbed more rapidly, and for higher  $\phi$  (up to 0.25), the modulus increased only slightly. To explain the steep increase at low modified lignin fraction, one could argue that the first small amount of modified lignin concentrated in the amorphous fraction and had an exaggerated effect on the overall modulus. The increase in RYM values may have been due to the higher modulus of lignin particles as compared to that of PP. At the highest  $\phi$ , the modulus increased to about 7 and 5% for the PPMALig and PPCELig blends, respectively. This showed that both of the modified lignins made it a little stiffer. A similar trend was also observed by Rusu and Tudorachi,<sup>50</sup> Saileja and coworkers,<sup>49,51</sup> and Luo et al.,<sup>52</sup> but increases in the RYM value reported by them were 100–170% with the addition of 25 wt % unmodified lignin, and their values decreased between 50 and 75% with the addition of different compatibilizers. However, in this case, an increase in the RYM value was much lower compared to those reported earlier. This may have been due to the increased compatibility of the modified lignin in the PP matrix. Because of the greater compatibility, the stiffening effect of modified lignin on the PP matrix was less compared to that of the unmodified lignin reported earlier. RYM clearly showed the possibility of some intermolecular interaction between the modified lignin and the PP matrix.



**Figure 5** (a) Effect of  $\phi$  of MALig on RYM of the PPMALig blends and (b) effect of  $\phi$  of CELig on RYM of the PPCELig blends. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

To model the experimental results obtained for the tensile modulus of the blends, Kerner's model [eq. (6)] was used for composites that contained spherical particles in the matrix, in which the filler particles were more rigid than the matrix:<sup>47</sup>

$$\text{RYM} = \frac{M_b}{M_{PP}} = 1 + \left( \frac{\phi}{1 - \phi} \right) \left( \frac{15(1 - \nu)}{8 - 10\nu} \right) \quad (6)$$

where  $\nu$  is the Poisson ratio of PP taken to be 0.35. As shown in Figure 5(A,B), the theoretical values were somewhat higher than the observed corresponding values for both the PPMALig and PPCELig blends. These results agreed well with the previous analysis.

For further analysis of the experimental results, the Halpin-Tsai model [eq. (7)] was applied.<sup>40,47</sup> This equation allowed us to determine the modified lignin tensile modulus by fitting the obtained experimental data:

$$\text{RYM} = \frac{M_b}{M_{PP}} = \frac{1 + G\eta_m\phi}{1 - \eta_m\phi} \quad (7)$$



**TABLE II**  
**Comparison of the Tensile Properties of the Modified Lignin-PP Blends with the Unmodified Lignin-PP Blends**

Lignin (wt %)	RTS	REB	
0	1.00	1.00	Kharade and Kale <sup>12</sup> (PP/unmodified lignin blends)
5	0.80	0.409	
10	0.79	0.318	
15	0.72	0.27	
20	0.69	0.27	
25	0.47	0.22	
0	1.00 (0.021)	1.00 (0.026)	This work (PPMALig blends)
5	0.969 (0.032)	0.911 (0.041)	
10	0.98 (0.039)	0.974 (0.013)	
15	0.825 (0.022)	0.957 (0.021)	
20	0.763 (0.032)	0.931 (0.05)	
25	0.73 (0.038)	0.887 (0.036)	
0	1.00 (0.021)	1.00 (0.026)	This work (PPCELig blends)
5	0.838 (0.034)	0.876 (0.038)	
10	0.77 (0.031)	0.886 (0.022)	
15	0.722 (0.044)	0.876 (0.042)	
20	0.717 (0.058)	0.83 (0.033)	
25	0.715 (0.038)	0.786 (0.034)	

Standard deviations are given in parentheses.

where

$$\eta_m = \frac{R_m - 1}{R_m + G} \quad (8)$$

where  $\eta_m$  is the constant which can be calculated by using eq. 8.,  $G$  is also a constant which is calculated by using equation  $G = (7-5u)/(8-10u)$ ,  $R_m$  is the ratio of the filler modulus to the matrix modulus, and its value was found to be 1.45 and 1.8 for PPMALig and PPCELig blends, respectively. Thus, good fitting to the experimental data was obtained for a value of the tensile modulus for both modified lignins (2.726 GPa for MALig and 3.384 GPa for CELig). The fitting curves to the experimental data are shown in Figure 5(A,B). For further analysis of the experimental results, the Sato-Furukawa model<sup>53,54</sup> was used per eq. (9). Sato-Furukawa gives the theoretical modulus for the case where the adhesion is so poor that the polymer matrix pulls away from the filler surface to give cavities around the filler particles:

$$\begin{aligned} \text{RYM} &= \frac{M_b}{M_{PP}} \\ &= \left[ \left( 1 + \frac{\phi^{2/3}}{2 - 2\phi^{1/3}} \right) (1 - \psi\xi) - \frac{\phi^{2/3}\psi\xi}{(1 - \phi^{1/3})\phi} \right] \end{aligned} \quad (9)$$

where

$$\psi = \left( \frac{1 + \phi^{1/3} - \phi^{2/3}}{1 - \phi^{1/3} + \phi^{2/3}} \right) \quad (10)$$

where  $\psi$  is a constant which can be calculated by using eq. 10. where  $\xi$  is an adjustable parameter whose value was calculated on a trial-and-error basis to match the theoretical results with the experimental data. The value of  $\xi$  itself shows the extent of adhesion between the components of blends; it is 0 for perfect adhesion and 1 for no adhesion. The calculated value of  $\xi$  was found to be 0.008 for the PPMALig blends, which showed little stronger adhesion between MALig and the PP matrix. The corresponding  $\xi$  value for the PPCELig blends was 0.011. This suggested a still comparatively weaker type of interaction between CELig and the PP matrix.

To study the effect of the modifications of lignin on the mechanical properties of the blends, we compared the tensile results of the PPMALig and PPCELig blends with that of the PP/unmodified lignin blends reported by Kharade and Kale,<sup>12</sup> as shown in Table II.

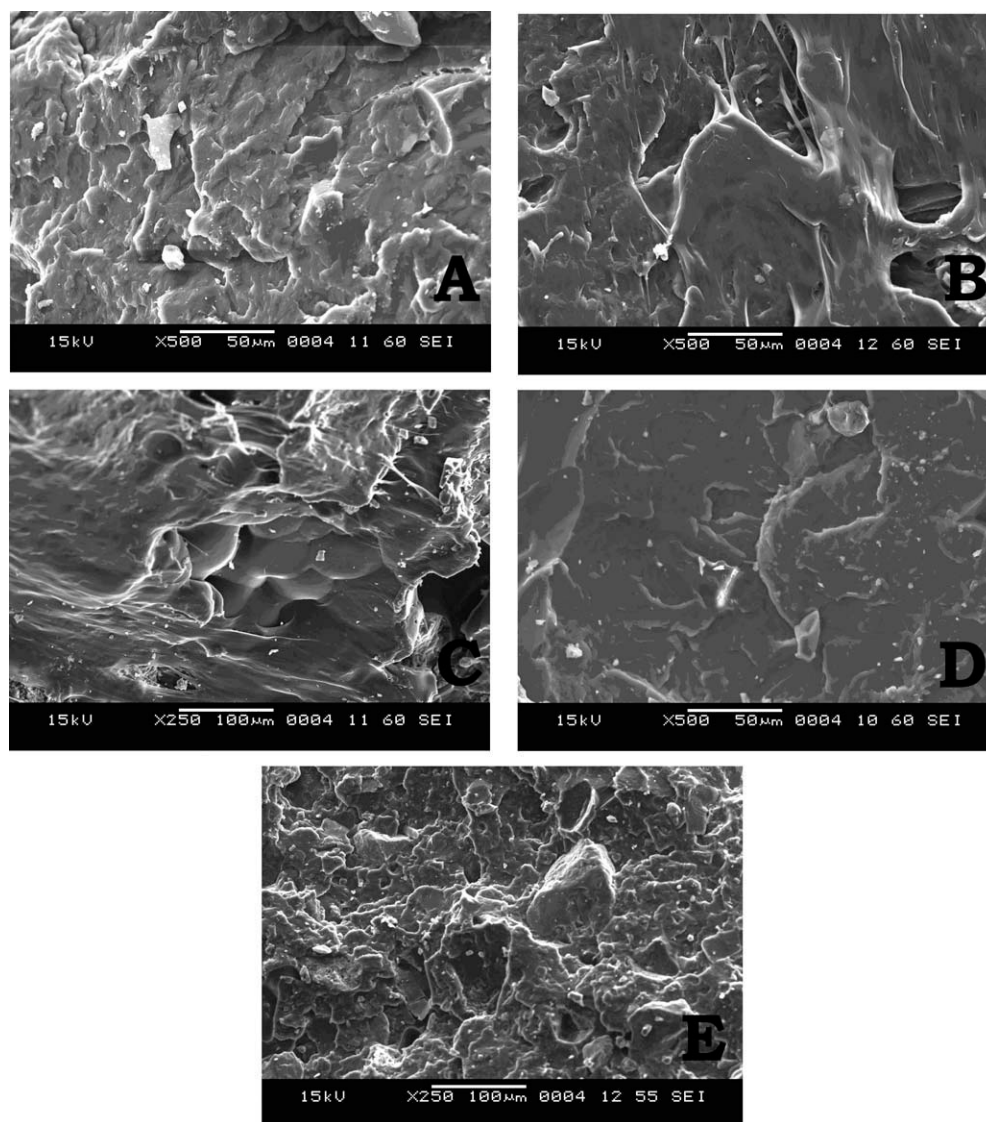
Table II shows that the PPMALig blends had comparatively higher RTS values than the PP/unmodified lignin blends, whereas the PPCELig blends showed comparable RTS values with those of the PP/unmodified lignin blends. The REB values for both the PPMALig and PPCELig blends were much higher than those of the PP/unmodified lignin blends. The REB values presented in Table II show that both types of modifications of lignin provided a slight advantage over unmodified lignin with respect to their stiffness in respective blends.

### Surface morphology of the PP/modified lignin blends

To further investigate the interactions between the modified lignin and PP matrix, we performed morphological investigations by SEM analysis of the fractural surfaces of the PPMALig and PPCELig blends. This is shown in Figures 6(A-E) and 7(A-E), respectively.

It is well known that the dispersion of the filler in the polymer matrix and the interfacial interactions between the filler and matrix are key factors in the enhancement of the mechanical properties of the polymer composites.<sup>38</sup> In the case of the PPMALig blends, the MALig particles were well dispersed and also homogeneously distributed within the PP matrix. This is shown in Figure 6(A-E). In this case, better interfacial interaction between MALig and the PP matrix was achieved. Further, no holes and agglomerations took place, even up to 25 wt % loading. All this positive impact was attributed to increased compatibility of MALig in the PP matrix, whereas in the case of the CELig blends, the lignin particles were uniformly distributed up to 15 wt % loading. Upon further increases in the CELig loading, agglomeration started; this can clearly be seen in Figure 7(A-E), and small holes also appeared





**Figure 6** SEM micrographs of PPMALig blends: (A) PPMALig-5, (B) PPMALig-10, (C) PPMALig-15, (D) PPMALig-20, and (E) PPMALig-25.

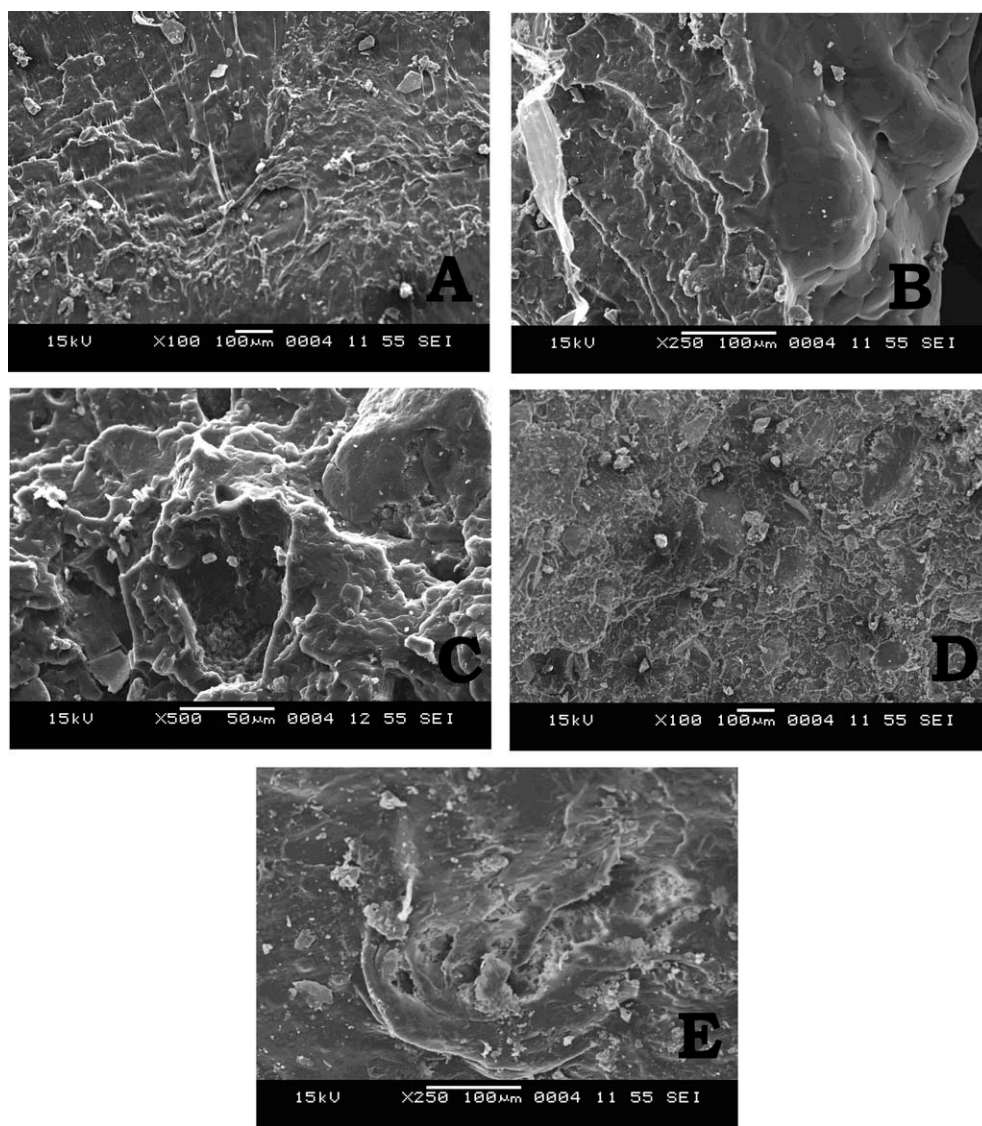
because of the saturation of the CELig. This may have been due to less compatibility of CELig with the PP matrix compared to that of MALig.

#### Processing stability of the blends

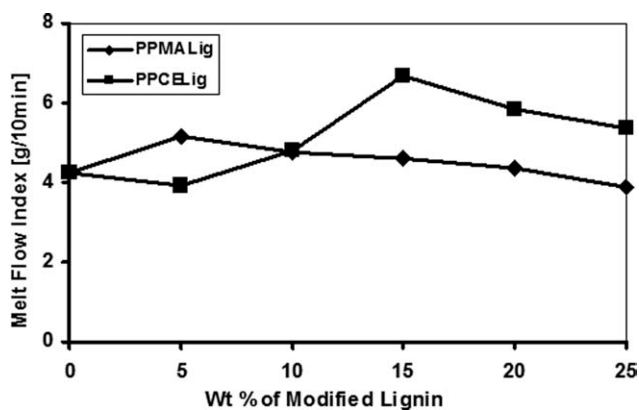
The MFI values of pure PP and all of the blends were determined to have a qualitative indication of the effect of type and weight percentage of the modified lignin on the viscosity. Figure 8 shows the MFI as a function of the weight percentage loading of MALig and CELig in the blends. In the case of the PPMALig blends, the MFI increased instantly for 5 wt % MALig loading in the blend; after that, a continuous decrease in the MFI value was observed with increasing weight percentage of MALig in the blends, and as a consequence, there was an increase in the viscosity. In the case of the PPCELig blends,

the MFI values increased up to 15 wt % loading. After that, it decreased continuously with increasing CELig loading in the blends. During processing, the molecular weights of the polymer and their distribution could be modified in particular. The molecules underwent mechanical stress, which could have resulted in the rupture of micromolecules themselves with the consequence of a decrease in the molecular weight. In this study, both types of blends showed different behavior toward MFI, as discussed previously. Pucciariello et al.<sup>55</sup> reported a continuous decrease in MFI with increasing straw lignin percentage in polyolefin. Alexy et al.<sup>13</sup> found a continuous increase in the MFI value of blends with increasing wood lignin percentage in polyolefins.

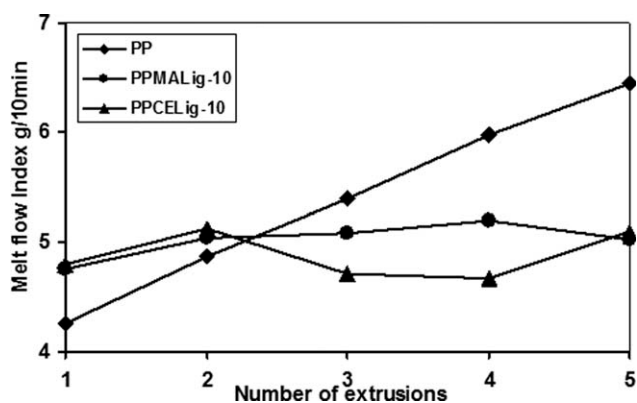
The influence of lignin addition on the processing stability of PP was studied at 10 wt % modified lignin. The processing stability was determined as MFI



**Figure 7** SEM micrographs of the PPCELig blends: (A) PPCELig-5, (B) PPCELig-10, (C) PPCELig-15, (D) PPCELig-20, and (E) PPCELig-25.



**Figure 8** Effects of the weight percentages of MALig and CELig on the MFIs of blends.



**Figure 9** Dependence of MFI on the number of extrusions for PP, PPMA Lig, and PPCELig blends.

dependence on the number of successive extrusions. Each sample was extruded five times (as shown in Fig. 9) for both the PPMALig and PPCELig blends. The MFI value for pure PP was found to increase rapidly with increasing processing cycles, whereas in both types of blends, the MFI remained nearly constant with increasing numbers of cycles. This showed that modified lignin also played the role of an effective processing stabilizer in PP.

### CONCLUSIONS

In the context of the use of biopolymers in commercial polymers such as PP, we partly succeeded in a quicker modification of lignin with the proper use of microwaves. FTIR spectroscopy indicated that chemical changes occurred in lignin to result in MALig and CELig. When compared with their blends with PP, MALig was more miscible than CELig, and the overall greater compatibility, solubility, and intermolecular interactions of the former better contributed to the mechanical properties than the latter; this was also confirmed by the application of various well-established theoretical models to the experimental data. Both types of modifications proved advantageous in connection to the consequent blends' mechanical properties (e.g., tensile strength, elongation at break, Young's modulus, impact strength) compared to blends arising out of unmodified lignin. Compositions of blends ranging up to 10 wt % of modified lignin were found to be better than those with higher proportions. In the case of the PPMALig blends, the deterioration in the mechanical properties was negligible up to 10 wt % MALig loading. On further increasing weight percentage loading, a slight deterioration in the mechanical properties was observed. In the PPCELig blends, a continuous deterioration in the mechanical properties was observed up to 25 wt %. In both types of blends, MFI remained the same with increasing numbers of extrusions; this indicated the ability of the suitably modified lignin to act as an effective processing stabilizer in PP, with the potential to compete with conventional inorganic stabilizers, many of which are more expensive, toxic, and abrasive.

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