

# Preliminary Studies on the Use of Modified ALCELL Lignin as a Coupling Agent in the Biofiber Composites

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**ABSTRACT:** ALCELL lignin has been employed as a coupling agent in empty fruit bunch fiber (EFBF)–polypropylene (PP) composites. The lignin has been chemically modified with toluene diisocyanate (TDI) to various weight loadings. The evidence of the reaction between TDI and lignin has been observed by using Fourier transform infrared (FTIR) analysis. The effect of lignin as a coupling agent on mechanical properties has been studied. The results show that the TDI-modified lignin is able to impart greater compatibility between EFBF and PP. This is reflected in the greater mechanical properties shown by the composites with TDI-modified lignin than in those with the unmodified lignin. Scanning electron microscopy (SEM) studies showed that TDI modification of lignin resulted in a better blending and compatibility between lignin and PP matrix. The glass-transition temperature of the lignin increases as the WPG is increased. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1333–1340, 2001

**Key words:** toluene diisocyanate; ALCELL lignin; coupling agent; polypropylene; lignocellulosics; empty fruit bunch fiber

## INTRODUCTION

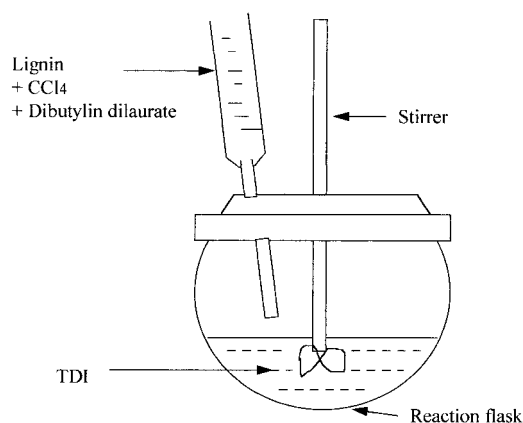
Compatibility between lignocellulosic material and polymer plays a crucial role in determining the properties of a composite. The compatibility and interfacial bond strength between lignocellulosic material and polymer matrix are expected to be poor in composites of lignocellulosics–thermoplastics, which results from the hydrophilic and hydrophobic nature of lignocellulosics (contributed by hydroxyl groups in cellulose, lignin, and hemicellulose) and thermoplastics, respectively. Various chemical reagents have been employed to enhance the compatibility between the constituent materials. These include Epolene, E-43 (maleic anhydride modified-polypropylene),<sup>1</sup> poly[methylene (polyphenyl isocyanate)] (PMPPIC),<sup>2</sup> -methacryloxy-propyltrimethoxysilane (A-174),<sup>3</sup> vinyltri (2-methoxy

ethoxy) silane (A-172),<sup>4</sup>  $\gamma$ -aminopropyltriethoxysilane,<sup>5</sup> poly(propylene-acrylic acid),<sup>6</sup> and poly(propylene-ethylene acrylic acid).<sup>6</sup>

In this study, lignin is used as a coupling agent between empty fruit bunch fibers (EFBF) of oil palm and polypropylene (PP) matrix. Because lignin contains polar hydroxyl groups and nonpolar hydrocarbon and benzene rings, it is believed that it can play a role in improving the compatibility between both components. The compatibility is expected to be further enhanced by chemically modifying the lignin with appropriate chemical reagent. Attempts to utilize lignin in various polymer systems have been documented.<sup>7–9</sup> Toluene diisocyanate (TDI) was employed in this study to provide better bridging between lignin and PP matrix. It is thought that compatibility between EFBF and PP could be achieved through three types of interaction: (1) interaction of nonpolar hydrocarbon chain and benzene ring of lignin with PP (dispersion forces); (2) interaction of benzene rings of TDI (chemically attached to lignin)

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**Figure 1** Experimental setup for TDI–lignin reaction.

with PP; and (3) interaction of hydroxyl groups of lignin with EFBF. Incorporation of lignin in the composite has the added advantage of acting as antioxidant stabilizer in the composite.<sup>10</sup> The extent of reaction has been monitored by measuring the weight increase after reaction and FTIR analysis.

## EXPERIMENTAL

### Materials

EFBF in fiber form was obtained from Sabutek (M) Sdn. Bhd. (Teluk Intan, Perak, Malaysia). PP was purchased from Polypropylene Malaysia Sdn. Bhd. (Malaysia) with melt-flow index of 12.0 g/10 min and density of 0.903 g/cm<sup>3</sup>. ALCELL lignin was obtained from Repap Technologies. Toluene diisocyanate (tolylene-2,4-diisocyanate; TDI) was purchased from Chembumi (M) Sdn. Bhd. (Penang, Malaysia).

### Methods

#### Reaction of TDI and Lignin

Lignin was dispersed in CCl<sub>4</sub>, in which dibutyl tin dilaurate was added as a catalyst. The dispersion was filled in a dropping funnel. TDI was placed in a round-bottom flask of capacity 500 mL. The lignin dispersion was added dropwise into TDI with constant stirring until the addition of lignin solution was complete (Fig. 1). The TDI-modified lignin so produced was washed with acetone several times before refluxing with fresh acetone for 3 h, to remove unreacted chemical reagents. Because CCl<sub>4</sub> is soluble in acetone it was also expected to be removed completely along with the unreacted isocya-

nates. The lignin was then oven-dried at 80°C before incorporating in the formulations for the preparation of the biofiber–polypropylene composite.

Small samples of both the unmodified and the TDI-modified lignin were dispersed in dry potassium bromide (KBr). Each mixture was ground to a fine powder in a mortar and then pressed to form moisture-free KBr pellets. All the spectra were obtained by the KBr technique, using a Perkin–Elmer 1600 Infrared Spectrometer (Perkin–Elmer, Foster City, CA).

### Filler Preparation

EFBF filler was obtained in the form of long strands of fibers, which were then ground into small particles. An Endecott's sieve was used to separate the particles into different sizes. The filler size used in this study was of mesh 60–35 (i.e., 270–500 μ).

### Filler Treatment

Three levels of lignin were employed: 1, 5, and 10% (based on the weight of the EFBF filler). Lignin powder (either unmodified or TDI-modified) was dissolved in ethanol (15% solution) before being mixed with the filler. The mixture was dried in an oven at 80°C for 3 h to allow for complete evaporation of the ethanol.

### Compounding and Processing

The compounding of EFBF filler and PP was carried out using a Haake Rheocord System, consisting of a Haake Rheodrive 5000 (drive unit) and Haake Rheomix 600 with roller blade (mixer). The mixing was carried out at 180°C for 20 min with a rotor speed of 25 rpm. The weight ratio of EFBF to PP is 40 : 60. The compound was then transferred to a mold with dimensions of 160 × 160 × 3 mm. The compound was preheated for 10 min at 160°C followed by hot-pressing at the same temperature for another 10 min. Cooling was carried out for 5 min under pressure.

### Testing

The sheet produced was cut into two types of test samples, that is, flexural and tensile tests. Flexural testing was conducted according to ASTM D790 (i.e., a three-point bending system), using Universal Testing Machine Model STM-10. The samples (dimensions of 15 × 1.5 × 0.3 cm) were tested at a cross-head speed of 2.0 mm/min. Flexural toughness was calculated from the area un-

**Table I TDI/Lignin Ratio (w/w) Versus Chemical Loading of TDI in the Lignin**

TDI/Lignin	Chemical Loading <sup>a</sup> (%)
1/2	2
2/3	13
1/1	18

<sup>a</sup> Based on the oven-dried weight before reaction.

der the stress–strain curve. The calculations for flexural modulus and flexural strength are given below.

$$\text{Flexural modulus} = \frac{L^3 \Delta W}{4bd^3 S}$$

$$\text{Flexural strength} = \frac{3WL}{2bd^2}$$

where

$L$  = the span between the centers of supports (m)

$W$  = ultimate failure load (N)

$\Delta W$  = the increment in load (N)

$b$  = the mean width of the sample (m)

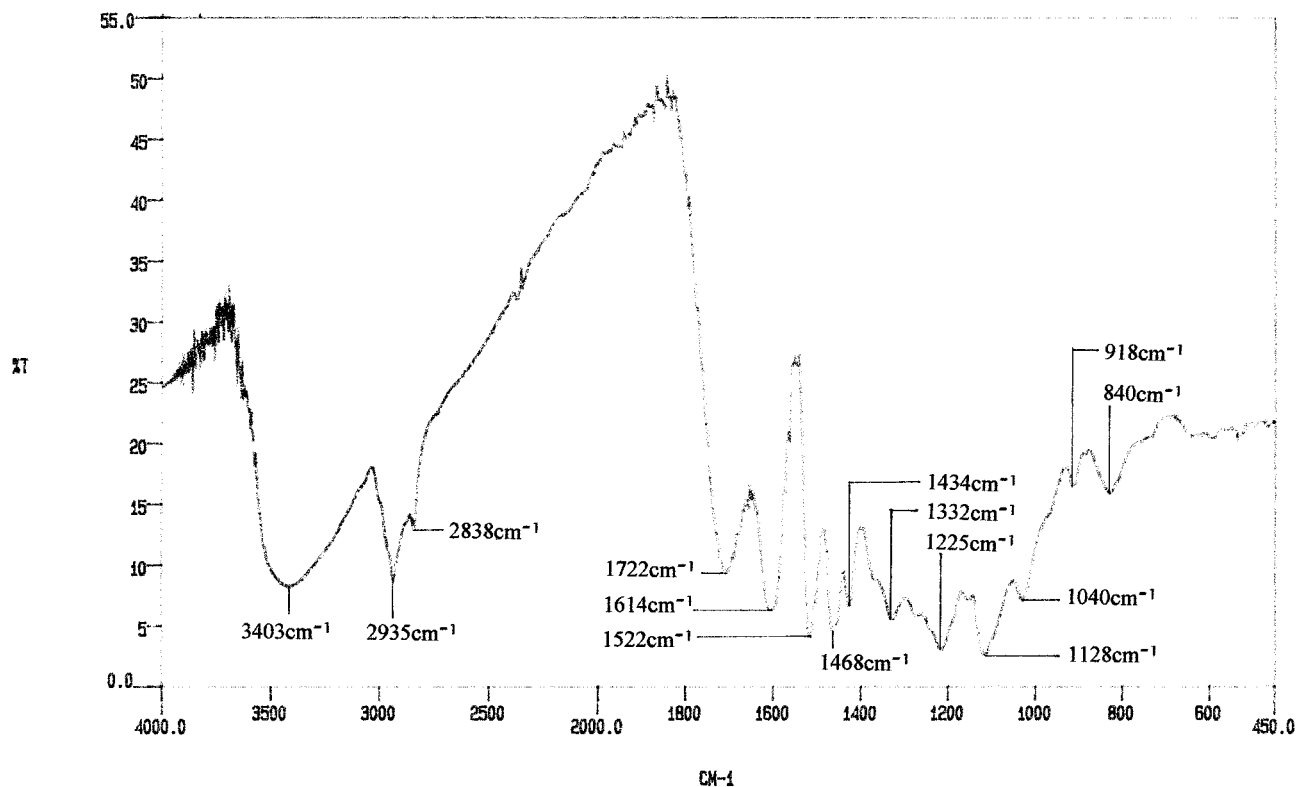
$d$  = the mean thickness of the sample (m)

$S$  = the increment in deflection (m)

Tensile tests were conducted according to ASTM D618. The sheet produced was cut into test samples with the dimensions of  $15 \times 1.9 \times 0.3$  cm (length  $\times$  width  $\times$  thickness). The test was carried out using a Universal Testing Machine at a cross-head speed of 5 mm/min. Tensile toughness was determined by measuring the area under the stress–strain curve.

### Morphological Study

The surfaces of the PP, PP/unmodified lignin, and PP/TDI-modified lignin samples were investigated with a Leica Cambridge S-360 scanning electron microscope (Leica, Milton Keynes, Buckinghamshire, UK). The mixing of lignin with PP was carried out using the same procedure as mentioned earlier. The objective is to get some information regarding the compatibility of unmodified and TDI-modified lignin with PP matrix. The specimens were mounted on an aluminum stub and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination.



**Figure 2** FTIR spectrum of unmodified lignin.

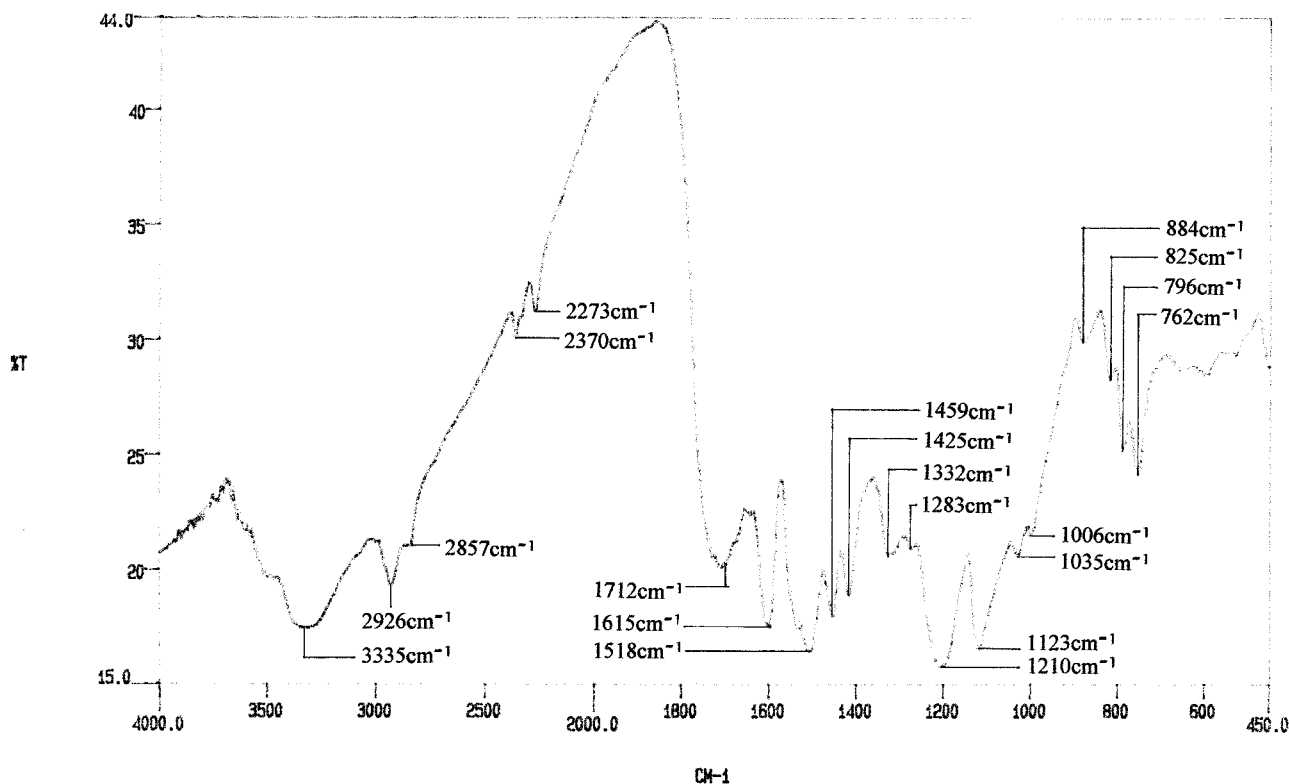


Figure 3 FTIR spectrum of 2% TDI-modified lignin.

## RESULTS AND DISCUSSION

### Chemical Modification of Lignin with TDI

Table I shows that the chemical loading of TDI in the lignin increases with the increase in TDI/lignin ratio in the reaction medium. Evidence that a chemical reaction between lignin and TDI has taken place is seen in Figures 2, 3, and 4 (unmodified lignin, 2% TDI-modified lignin, and 18% TDI-modified lignin, respectively). TDI-modified lignin was thoroughly washed in acetone and dried prior to the FTIR analysis. Thus, any unreacted reagent and urethane residues formed during the reaction would be removed by this procedure. The spectra for TDI-modified lignin both at 2 and 18% loading show a small peak at about  $1542\text{ cm}^{-1}$ , which is the result of the N—H deformation frequencies of secondary amines.<sup>11</sup> However, there are two strong peaks at about 762 and  $796\text{ cm}^{-1}$ , which result from N—H deformation of bonded secondary amines.<sup>8</sup> Although it is not conclusive, peaks at 825, 884, and  $1006\text{ cm}^{-1}$  may show evidence of the substituted benzene ring of lignin.<sup>12</sup> Peaks at about  $2273\text{--}2370\text{ cm}^{-1}$  show evidence of unreacted  $\text{—N=C=O}$  groups of TDI. The strong absorption at about 3335 and 2926

$\text{cm}^{-1}$  in all of the FTIR spectra is the result of hydroxyl absorption. Because the substitution of TDI is not high enough to eliminate all hydroxyl groups, these bands are always present.

### Effect of TDI-Modified Lignin as Coupling Agent on the Flexural and Tensile Properties of EFBF-PP Composites

Figure 5 shows the effect of the degree of TDI loading in the TDI-modified lignin on the tensile strength of the EFBF-PP composites. The results demonstrate that all composites with TDI-modified lignin display higher tensile strength than those with unmodified lignin. It is clearly seen that the strength increases with the increase in the level of modification. It is also obvious that composites with the modified lignin show a trend of increasing strength as the percentage of lignin is increased. However, composites with the unmodified lignin display a considerable reduction in strength as the percentage of lignin is increased. The tensile moduli of the composites, as shown in Figure 6, display the same trend as the tensile strength results.

The toughness of the composites is enhanced with the addition of TDI-modified lignin as op-

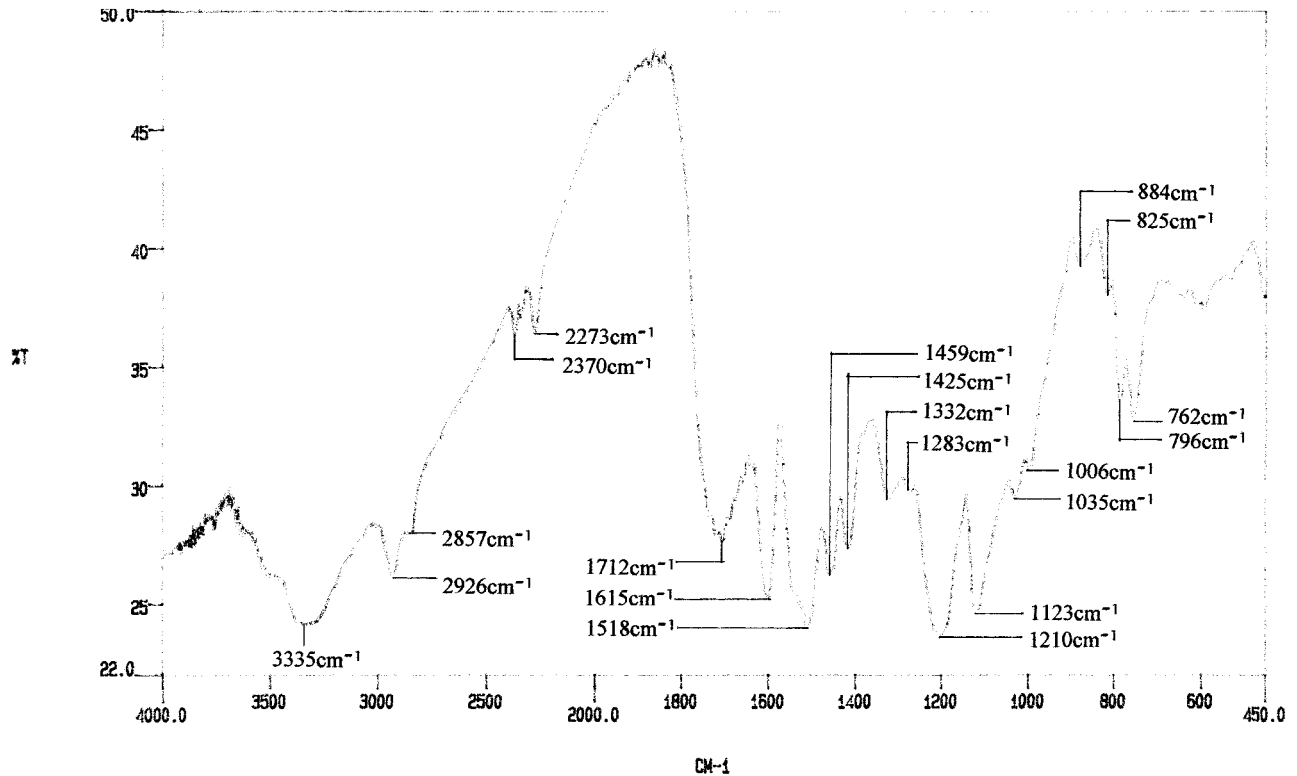


Figure 4 FTIR spectrum of 18% TDI-modified lignin.

posed to that of the composites with unmodified lignin (Fig. 7). The results show that the toughness increases as the degree of modification is increased. Thus, it can be inferred that more energy is needed to break the composite with the modified lignin than to break composites with the unmodified lignin. This indicates that modified lignin is able to impart greater compatibility between EFBF and PP, which requires more energy to break them apart.

Figure 8 shows the results of elongation at break (EB). It seems that the addition of lignin

has no significant effect on the EB of the composites with modified lignin. However, the EB of the composites with unmodified lignin is significantly higher than the rest of the composites at 10% lignin loading. This phenomenon is consistent with the tensile modulus results, of which the composites with unmodified lignin display significantly lower values than those of composites with modified lignin.

Figure 9 depicts the effect of TDI modification of lignin on the flexural strength of EFBF-PP composites. The effect of TDI modification of lig-

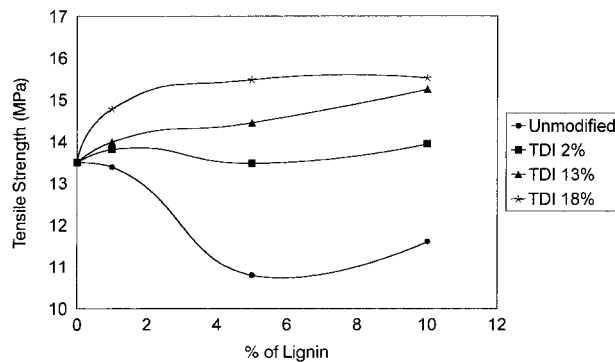


Figure 5 Effect of TDI loading in the TDI-modified lignin on tensile strength.

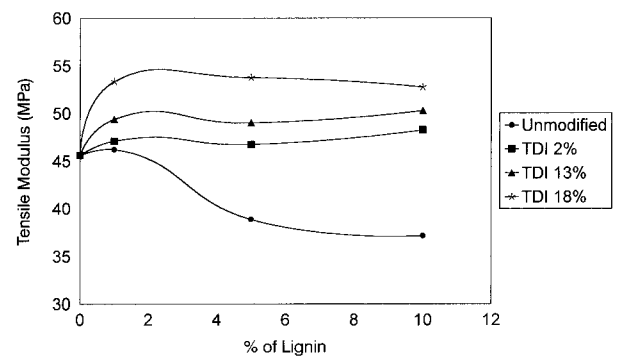


Figure 6 Effect of TDI loading in the TDI-modified lignin on tensile modulus.

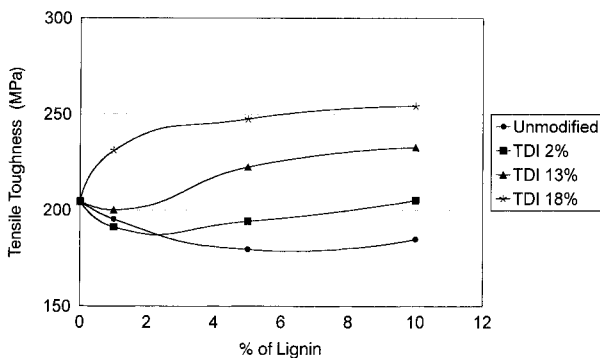


Figure 7 Effect of TDI loading in the TDI-modified lignin on tensile toughness.

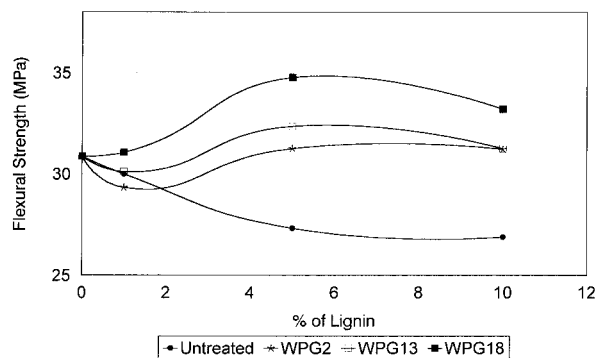


Figure 9 Effect of TDI loading in the TDI-modified lignin on flexural strength.

nin on flexural strength shows the same trend as that of tensile strength results. All composites with TDI-modified lignin display higher flexural strength than that of composites with unmodified lignin. It is clearly seen that the strength increases with an increase in the level of modification. The strength is significantly increased with the addition of 1 and 5% of modified lignin, especially for lignin with TDI loading of 18%. However, further incorporation of the lignin (10%) does not result in any changes for all levels of TDI loading. The strength of the unmodified composites is gradually reduced as the amount of lignin added is increased. The flexural moduli of the composites, as shown in Figure 10, display the same trend as that of flexural strength results. The toughness of the composites is also enhanced with the addition of TDI-modified lignin compared to that of composites with unmodified lignin (Fig. 11). As shown earlier by the tensile tests, the flexural toughness also increases as the degree of modification is increased.

From the SEM micrographs (Figs. 12–14), it can be seen that the TDI-modified lignin blends

well with the PP matrix. The homogeneity observed in the matrix shows that the PP bulk itself should have been suitably modified, at the time of mixing, by interaction with the TDI-modified lignin. This is an ideal condition created in the matrix material, characterized by good compatibility with the surface of the modified organic fiber. This phenomenon is expected to promote good adhesion between the fibers and the resin matrix. Because the mixing is carried out at high temperature (i.e., 180°C), it is believed that the deposited modified lignin would undergo softening at the time of exposure to high temperature during mixing. Under these conditions, modified lignin, which remains with the fiber at the time of mixing with PP after undergoing softening, can not only form a good coating on the fibers and establish tenacious covalent bonds with them, but also be diffused into the PP resin matrix in the immediate vicinity of the fibers, tending to form an interphase compatible with the organic fibers. Thus, the films of TDI-modified lignin can function as a coupling agent between the fibers and the modified PP matrix. This type of promotion of interfa-

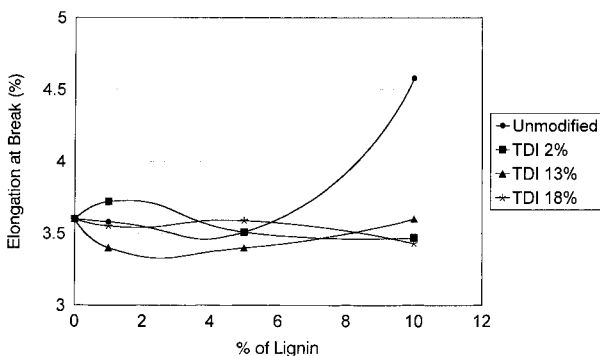


Figure 8 Effect of TDI loading in the TDI-modified lignin on the elongation at break.

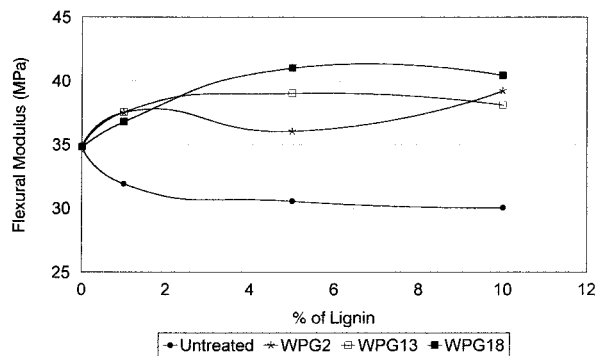
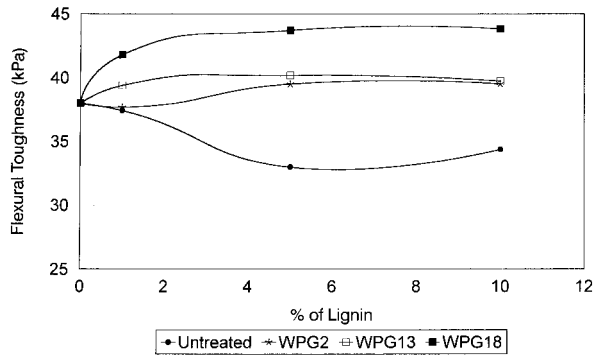


Figure 10 Effect of TDI loading in the TDI-modified lignin on flexural modulus.



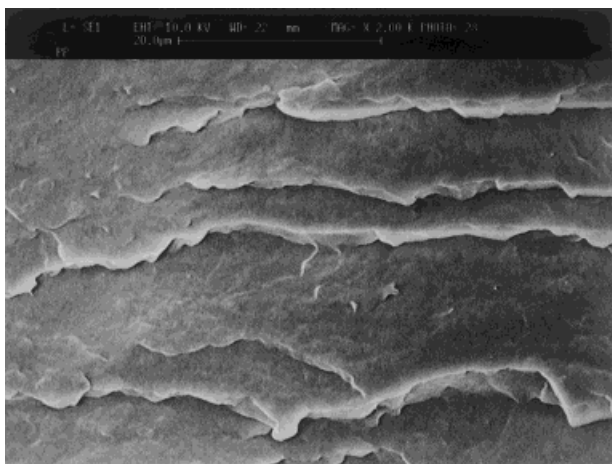


**Figure 11** Effect of TDI loading in the TDI-modified lignin on flexural toughness.

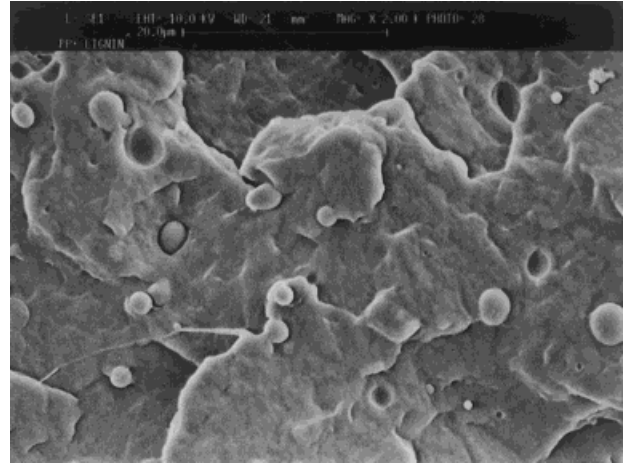
cial adhesion is similar to the action of silane coupling agents in epoxy–glass fiber systems, in which the coupling agent is added to the resin matrix.<sup>13</sup>

In Figure 14, it is obvious that the lignin forms a continuous and compatible interface between the organic fibers and the PP matrix. In contrast, in the unmodified samples (Fig. 13), the degree of compatibility at the interfacial region between the lignin and the matrix leaves much to be desired. The lignin is loosely embedded in the matrix and, in some cases, the lignin particles are extracted out of the matrix. The enhanced mechanical properties of the composites made from the fibers treated with TDI compared to those made from fibers treated with unmodified lignin are attributable to the following two important factors, as established in the present studies:

1. The presence of an effective coupling agent between the organic fibers and the resin matrix.



**Figure 12** SEM micrograph for PP (magnification  $\times 2000$ ).

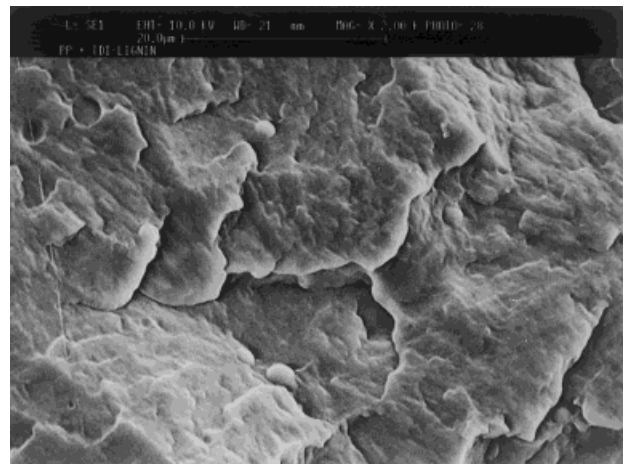


**Figure 13** SEM micrograph for PP/unmodified lignin ( $\times 2000$ ).

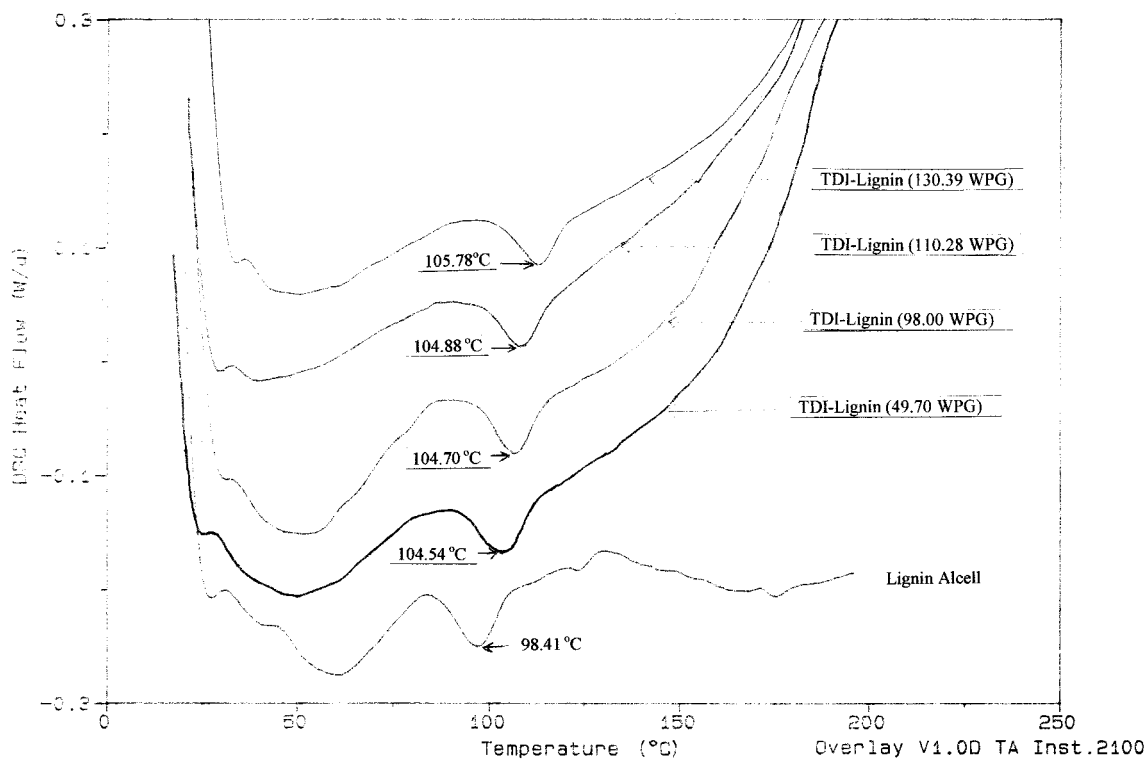
2. The increased value of  $T_g$  observed in our differential scanning calorimetry studies. The latter studies showed that the  $T_g$  of unmodified lignin is at 98.41°C and increases as the WPG is increased (Fig. 15).

## CONCLUSIONS

1. From the results of TDI loading and the evidence from FTIR spectra, TDI is shown to chemically react with lignin. The degree of modification can be regulated by the TDI/lignin ratio.
2. Modification of lignin with TDI is able to impart greater compatibility between EFBF and PP. This is reflected in the improve-



**Figure 14** SEM micrograph for PP/TDI-modified lignin ( $\times 2000$ ).



**Figure 15** DSC analysis of unmodified and TDI-modified lignin.

- ments shown in both the tensile and the flexural properties.
- SEM studies show that TDI modification of lignin resulted in the enhanced compatibility of the EFBF fibers with the PP matrix.
  - The  $T_g$  of the lignin increased as the WPG is increased.

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## REFERENCES

- Myers, G. E.; Chahyadi, I. S.; Coberly, C. A.; Ermer, D. S. *Int J Polym Mater* 1991, 15, 21.
- Kokta, B. V.; Raj, R. G.; Daneault, C. *Polym Plast Technol Eng* 1989, 28, 247.
- Rozman, H. D.; Kon, B. K.; Abusamah, A.; Kumar, R. N.; Mohd Ishak, Z. A. *J Appl Polym Sci* 1998, 69, 1993.
- Raj, R. G.; Kokta, B. V.; Groleau, G.; Daneault, C. *Polym Plast Technol Eng* 1990, 29, 339.
- Maldas, D.; Kokta, B. V.; Raj, R. G.; Daneault, C. *Polymer* 1988, 29, 1255.
- Mohd Ishak, Z. A.; Aminullah, A.; Ismail, H.; Rozman, H. D. *J Appl Polym Sci* 1998, 68, 2189.
- Saraf, V. P.; Glasser, W. G. *J Appl Polym Sci* 1984, 29, 1831.
- Saraf, V. P.; Glasser, W. G.; Wilkes, G. L.; McGrath, J. E. *J Appl Polym Sci* 1985, 30, 2207.
- Reimann, A.; Morck, R.; Yoshida, H.; Hatakeyama, H. *J Appl Polym Sci* 1990, 41, 39.
- Kosikova, B.; Kacurakova, M.; Demianova, V. *Chem Pap* 1993, 47, 132.
- Sarkanen, K. V.; Chang, H. M.; Ericsson, B. *Tappi J* 1967, 50, 572.
- Rowell, R. M. *Forest Products Abstr* 1983, 6, 363.
- Plueddemann, E. P. *J Appl Polym Sci Appl Polym Symp* 1970, 14, 95.