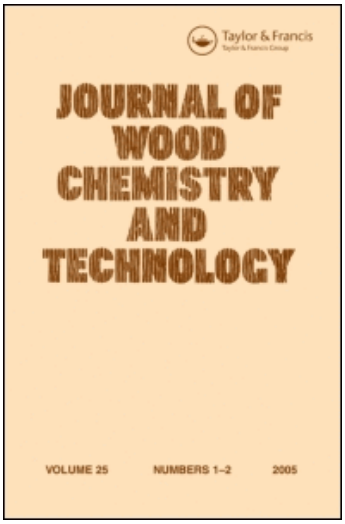

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The Effect of Glycol Type, Glycol Mixture, and Isocyanate/Glycol Ratio on Flexural Properties of Oil Palm Empty Fruit Bunch-Polyurethane Composites

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ABSTRACT

Oil palm empty fruit bunch (EFB)-polyurethane (PU) composites were produced. The effects of the isocyanate (NCO)/glycol (OH) ratio, glycol type, and mixtures (polyethylene glycol PEG 400 (M_w 400) and polypropylene glycol PPG 400 (M_w 400)) on the flexural properties were investigated. The NCO/OH ratio had a significant effect on the flexural properties of the EFB-PU composites. Composites made with PEG 200 exhibited higher flexural properties than with PEG 400 and PPG 400. The flexural properties were also found to be influenced by the PPG 400/PEG 400 ratio.

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INTRODUCTION

Utilization of biomass resources has been the subject of many studies. In Malaysia, oil palm empty fruit bunch (EFB) is a biomass by-product from the palm oil industry. The production of EFB is estimated to be about 2.8–3.0 million tons per year.[1] Studies have been carried out on utilizing EFB to make particle board,[2] medium density fiberboard,[3] pulp,[4] and composites.[5–9] In general, utilization of biomass in plastic-lignocellulosic composites has several advantages, such as low density, greater deformability, less abrasiveness to equipment, biodegradability, and low cost. However, in producing a good polymer-lignocellulosic composite, the main obstacle is the compatibility between the lignocellulosic fiber and polymer matrix. The properties of the lignocellulosic composites are dominated by the interfacial interaction between the lignocellulosic filler and polymer matrix. Generally, there are two types of interaction at the interfacial region, i.e., primary and secondary bonds or covalent and hydrogen bonds, respectively. While, covalent bonding at the interfacial region exists in thermoplastic-wood composites with the incorporation of coupling agent, it is more prevalent in thermoset-lignocellulosic composites. This is because lignocellulosic hydroxyl (OH) groups can serve as reaction sites with various functional groups in the thermoset system. According to Hatakeyama et al.,[10] natural polymers having more than two OH groups per molecule could be used as a polyol for polyurethane preparation, if the hydroxyl groups react with isocyanate.

Polyurethane (PU) is one of the most useful three-dimensional polymers due to its unique features. It can be produced in the form of sheets, foams, adhesives, etc. Recently, many attempts have been made to utilize lignocelluloses as raw materials for PU synthesis. Desai et al.[11] prepared PU from starch and studied the swelling and mechanical properties. The starch-PU showed better mechanical properties than trimethylol propane-PU with a higher degree of crosslinking. These properties were found to be dependent on the NCO/OH ratio. Kurimoto et al.[12,13] reported that the NCO/OH ratio contributed to the formation of a three dimensional network in the PU preparation. The effect of soft segment content and its molecular weight had been studied by Reimaan et al.[14] and Saraf et al.[15] The results showed that the degree of crosslinking and tensile properties depended mainly on the ratio of soft/hard segment ratio, and was unaffected by variations in the sequence length of the soft segment at a given soft segment content.[14]

In this study we used EFB for a dual purpose in the production of PU composites, i.e., as a filler and as a reactive component. Reactive

component means that EFB would serve as polyol in the PU forming isocyanate-OH reaction.

EXPERIMENTAL

Material

The EFB was obtained in fiber form from Sabutek Sdn. Bhd. Teluk Intan, Perak, Malaysia. Diphenylmethane diisocyanate (MDI) was supplied by Aldrich Chemical Company, Inc. PEG 200, PEG 400, and PPG 400 were obtained from Fluka Chemika.

Preparation of EFB-PU Composites

The method for preparing EFB-PU composites was described in detail previously.[16] The OH group contribution from glycol (PEG 200, PEG 400, or PPG 400) in the EFB-PU system was 40%, with the remaining contributed by EFB. In the study of glycol mixtures, the ratio of PPG 400/PEG 400 was varied; 100/0, 75/25, 50/50, 25/75, and 0/100 based on the OH percentage. In the study of the NCO/OH ratio study, the ratio varied from 0.8 to 1.3 (mol).

Mechanical Testing

The EFB-PU composites produced were cut into flexural test (three point bending) samples of $8 \times 1.2 \times 0.8$ cm (length × width × thickness). The tests were performed according to ASTM D790 using Universal Testing Machine Model STM-10 with a cross-head speed of 2 mm/min. Flexural toughness was calculated from the area under the stress–strain curve.

Fourier Transform Infrared (FTIR)

The EFB-PU composites were ground into powder form, dried, and dispersed in dry potassium bromide. The mixture was then pressed into pellets. The samples were run using a Nicolet Avatar 380 FTIR.

Scanning Electron Microscopy (SEM) Study

The mode of fracture of test samples was investigated with a Leica Cambridge S-360 scanning electron microscope. The specimens were mounted on an aluminium stub and sputter coated with a thin layer of gold to avoid electrostatic charging during examination.

RESULTS AND DISCUSSION

Effect of NCO/OH Ratio

Table 1 shows the effect of the NCO/OH ratio on the EFB-PU flexural properties. It can be seen that the flexural strength increased as the NCO/OH ratio was increased from 0.8 to 1.1. However, no further improvement was observed when the NCO/OH ratio was increased from 1.1 to 1.3. According to Desai et al.,[11] when the NCO/OH ratio is 1.2, the PU formed is isocyanate (NCO) group terminated. The free NCO groups could react further with the urethane linkages, thus increasing the chemical crosslinking and leading to a change in morphology. This result is in line with those of Saraf and Glasser[17] where, by using kraft lignin and a NCO/OH ratio of more than 1.0, a straight-line relationship in tensile strength independent of the NCO/OH ratio was observed. The flexural modulus results show that the stiffness of EFB-PU composites increased when the NCO/OH ratio was first increased, but no further benefit was observed for ratios from 1.1–1.3. This might be due to (i) an increase in the amount of aromatic ring as the MDI content is increased, or, (ii) the formation of allophanate lingkages as the result of the reaction between excess NCO and urethane groups. From the flexural toughness results, it can be seen that an increase occurred as the NCO/OH ratio was increased from 0.8 to 0.9, but no further change was observed as the NCO/OH ratio was increased further.

Figure 1 shows the infrared spectra for EFB-PU composites produced from various NCO/OH ratios (0.8, 1.1, and 1.3). Composites with 0.8 and 1.1 NCO/OH ratios show no absorption within 2260–2280 cm^{-1}, while the composite made with a 1.3 NCO/OH ratio

Table 1. The flexural properties of EFB-PU composites produced from various NCO/OH ratios.

NCO/OH	Flexural strength (MPa)	Flexural modulus (GPa)	Flexural toughness (MPa)
1.3	65.2 (±5.3)	2.4 (±0.6)	5.4 (±0.2)
1.2	66.6 (±6.2)	2.7 (±0.3)	5.5 (±0.4)
1.1	68.0 (±4.6)	2.9 (±0.5)	5.8 (±0.4)
1.0	50.0 (±6.5)	2.2 (±0.2)	5.6 (±0.5)
0.9	46.1 (±6.0)	1.7 (±0.1)	5.4 (±0.2)
0.8	30.9 (±5.6)	1.4 (±0.2)	3.6 (±0.3)

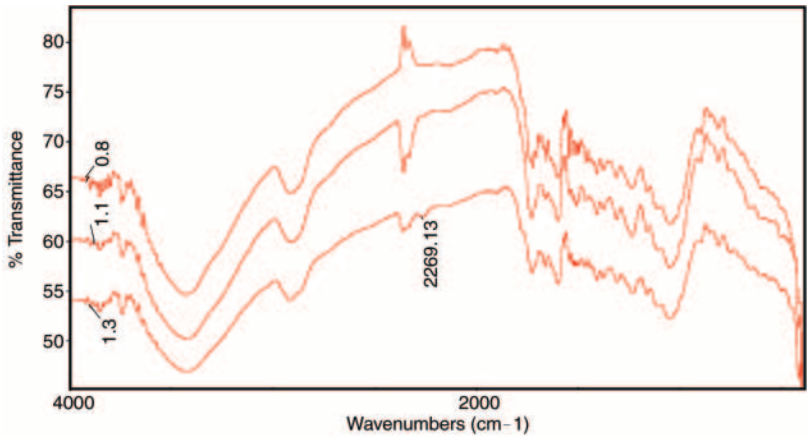

Figure 1. Infrared spectra for EFB-PU composites produced from various NCO/OH ratios.

does. This absorption might be due to the excess NCO groups in EFB-PU system. This result is in agreement with the study carried out by Desai et al.,[11] where at high NCO/OH ratio the PU formed was terminated by isocyanates.

From the scanning electron micrographs (Figs. 2 and 3), it can be seen that the EFB-PU composites which were produced from low NCO/OH ratio (0.8) exhibited more fiber pullout than the samples with the higher NCO/OH ratio (1.3). At higher magnification (Fig. 4), it can be seen that for sample with the NCO/OH ratio of 0.8, even though fiber pull-out occurrences could still be detected, there are still evidences of good interaction between fiber and matrix (Fig. 5). This indicates that some interaction has occurred between OH groups from EFB and NCO, even when the ratio of NCO/OH is low. Figure 6 shows the sample with the higher NCO/OH (1.3), where the interaction between fiber and matrix becomes more obvious.

According to Cheradame et al.,[18] when the NCO/OH ratio is lower than unity, the PU is mostly produced through condensation of isocyanate and polyol, and results in low modulus and rupture strength of the PU. When NCO/OH ratio is close to 1, the enhancement of the mechanical properties is prevalent, as the result of the participation of lignin in the polycondensation reaction. Thus it can be concluded that at low NCO/OH ratios, the reaction might be dominated by the reaction of NCO with OH from glycols, as the latter are more accessible than OH

Figure 2. SEM micrograph of sample with NCO/OH = 0.8 (magnification 20X).

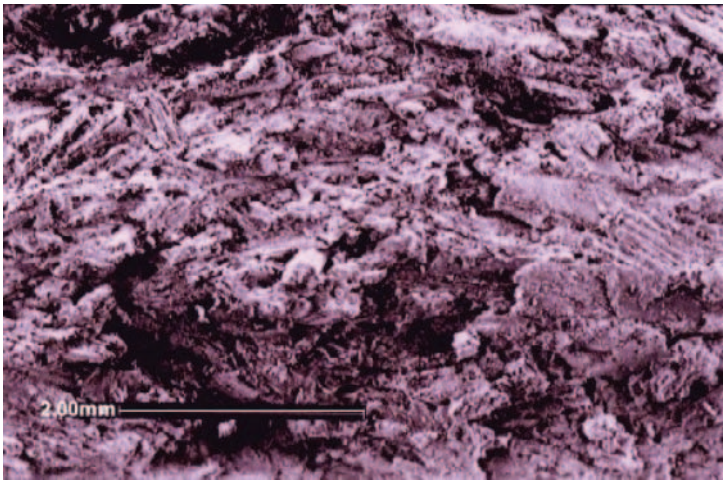

Figure 3. SEM micrograph of sample with NCO/OH = 1.3 (magnification 20X).

from EFB. EFB is a solid material, and thus, the accessibility of EFB's OH groups to the NCO might play a vital part in the reaction at low NCO/OH ratios. However, as the NCO/OH ratio is increased, the involvement of OH groups from EFB may become more prevalent. This may be the explanation for improvements of mechanical properties

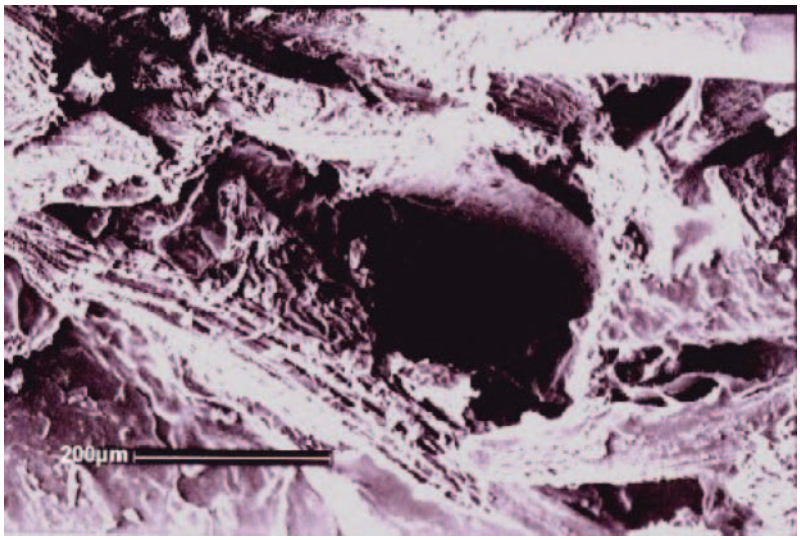

Figure 4. SEM micrograph of sample with NCO/OH = 0.8 (magnification 150X).

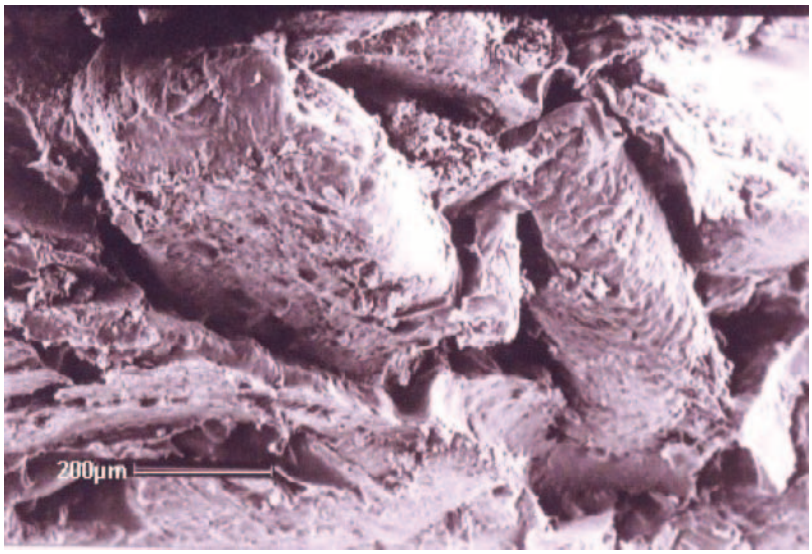

Figure 5. SEM micrograph of sample with NCO/OH = 0.8 (magnification 100X).

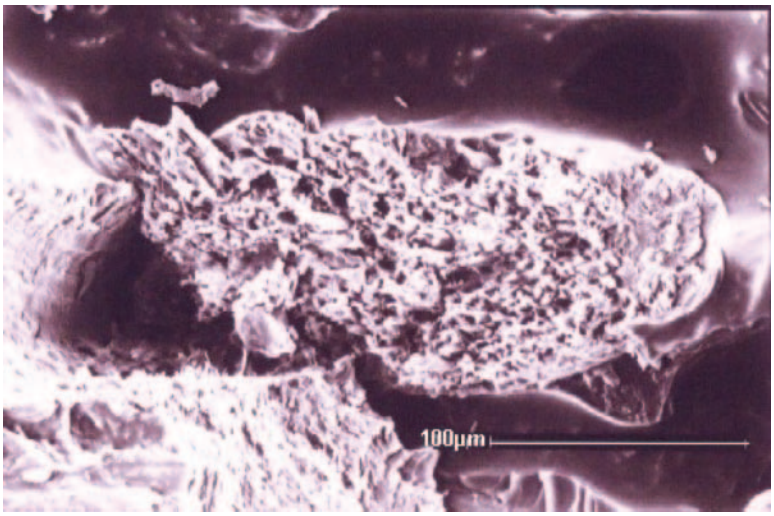

Figure 6. SEM micrograph of sample with NCO/OH = 1.3 (magnification 400X).

for the PU prepared with an NCO/OH ratio of 1. However, as the NCO/OH ratio is further increased, no further improvement is observed. At this stage, any allophanate linkages produced[17] might not be sufficient enough to impart any significant differences on the mechanical properties. In addition, excess isocyanates might be left unreacted as shown by FTIR spectroscopic analysis.

Effect of Glycol Type

Table 2 presents the mechanical properties of EFB-PU composites produced from various glycols. PEG 200, which has shorter chain length, displays a higher modulus than those one with a longer chain length (PEG 400). It is obvious that composites with PPG 400 demonstrate higher flexural strength and modulus as compared to PEG 400. This phenomenon might be attributed by the methyl groups along the glycol chains, and the shorter chain length with PPG 400 than PEG 400. However, no significant differences in the toughness of the composites was observed.

Table 2. The flexural properties of EFB-PU composites produced from various glycols.

Glycol type	Flexural strength (MPa)	Flexural modulus (GPa)	Flexural toughness (MPa)
PEG 200	68.0 (±4.6)	2.9 (±0.5)	5.8 (±0.4)
PEG 400	28.1 (±4.1)	0.8 (±0.1)	5.7 (±1.2)
PPG 400	41.0 (±5.2)	1.5 (±0.2)	4.2 (±0.8)

Table 3. The flexural properties of EFB-PU composites produced from various glycol mixtures.

%PPG 400/ %PEG 400	Flexural strength (MPa)	Flexural modulus (GPa)	Flexural toughness (MPa)
100/0	41.0 (±5.2)	1.5 (±0.2)	4.2 (±0.8)
75/25	42.1 (±2.6)	1.6 (±0.1)	4.8 (±1.1)
50/50	46.0 (±3.6)	1.5 (±0.1)	7.3 (±0.9)
25/75	35.2 (±4.6)	1.0 (±0.1)	7.2 (±1.3)
0/100	28.1 (±4.1)	0.8 (±0.1)	5.7 (±1.2)

Effect of Glycol Mixture

Table 3 shows the mechanical properties of the EFB-PU composites produced from glycol mixtures consisting of different ratios of PPG 400 and PEG 400. The stiffness of the EFB-PU composites increased as the proportion of PPG 400 was increased. It was expected, as discussed in the previous section, that composites made with PPG 400 would produce stiffer material than those made with PEG 400.

From the SEM study (Fig. 7), there is no evidence of discontinuous phase in the PU matrix produced from the mixture. This shows that the two glycols are miscible. It is clearly seen that good interaction has occurred between the matrix and EFB.

CONCLUSIONS

This study demonstrated that the NCO/OH ratio plays a significant role in the flexural properties of EFB-PU composites. Composites made with PEG 200 displayed higher flexural properties than both PEG 400 and PPG 400. This might be attributed to the pendant

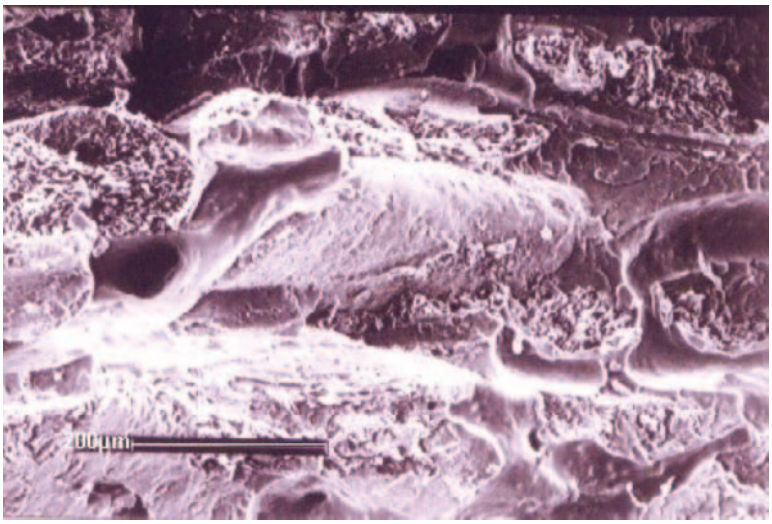

Figure 7. SEM micrograph of sample with PPG400 (50%) (magnification 150X).

methyl group along the chain and a lower chain length than PEG 400. The flexural properties appeared to be influenced by the PPG 400/PEG 400 ratio.

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