

Polyurethane Composites Based on Oil Palm Empty Fruit Bunches: Effect of Isocyanate/Hydroxyl Ratio and Chemical Modification of Empty Fruit Bunches with Toluene Diisocyanate and Hexamethylene Diisocyanate on Mechanical Properties

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ABSTRACT: This study focuses on the effect of isocyanate (NCO)/hydroxyl (OH) group ratios and chemical modification of oil palm empty fruit bunches (EFBs) with toluene diisocyanate (TDI) and hexamethylene diisocyanate (HMDI) on the mechanical properties of EFB–polyurethane (PU) composites. The tensile, flexural, and impact properties are affected by the NCO/OH ratios. The tensile strengths, flexural strengths, and toughness increase as the NCO/OH increases; however, the modulus decreases. The reduction in the modulus is attributable to the increased flexibility of the PU linkages. Chemical modification of the EFBs increases the tensile strength, flexural strength, and toughness; however, the modulus is lowered as the per-

centage of treated EFB is increased. Impact strength results show that the strength increases as the NCO/OH ratio is increased. At NCO/OH ratios of 1.0 and 1.1, the composites with HMDI-treated fibers exhibit higher impact strength than those with TDI-treated and untreated fibers, respectively. This may be due to the longer and more flexible chain length of HMDI as compared to TDI, which enables the composites to absorb more energy before failure. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2290–2297, 2007

Key words: composites; empty fruit bunches; polyurethane

INTRODUCTION

Recently, utilization of biomass resources has been the subject of various studies. Oil palm empty fruit bunches (EFBs), one of the biomass materials, are a by-product of the palm oil industry in Malaysia. The production of EFBs is estimated to be around 2.8–3.0 million tonnes/year.¹ Many studies have been carried out on the utilization of EFBs, such as for particleboard,² medium density fiberboard,³ pulp,⁴ and composites.^{5–9} In general, utilization of biomass in lignocellulosic composites has been attributed to having several advantages such as low density, greater deformability, less abrasiveness to equipment, biodegradability, and low cost. However, in producing a good lignocellulosic composite, the main obstacle to be resolved is the compatibility between the fiber and the matrix. The properties of lignocellulosic composites are dominated by the interfacial inter-

action between the lignocellulosic filler and the polymer matrix. Generally, there are two types of interaction at the interfacial region: primary and secondary bonding. Primary and secondary bondings include covalent and hydrogen bonds, respectively. Although covalent bonds at the interfacial region exist in thermoplastic–wood composites with the incorporation of a coupling agent, they are more prevalent in the thermoset–lignocellulosic composites because lignocellulosic hydroxyl (OH) groups could 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 polyols for polyurethane (PU) preparation if the groups could be reacted with isocyanate. PU is one of the most useful three-dimensional polymers because of its unique features. It can be produced in the form of sheets, foams, adhesives, and so forth. Many recent 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 of the PU. The results showed that the starch–PU had better mechanical properties than trimethylol propane–PU and the degree of crosslinking was higher for starch–PU. In contrast,

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these properties were also found to depend on the isocyanate (NCO)/OH ratio. Kurimoto et al.^{12,13} revealed in their study that a suitable NCO/OH ratio contributed to the formation of three-dimensional networks in the PU. The effect of the soft segment content and its molecular weight was studied by Reimann et al.¹⁴ and Saraf et al.¹⁵ The results showed that the degree of crosslinking and tensile properties depended mainly on the soft/hard segment ratio and were unaffected by variations in the sequence length of the soft segment at a given soft segment content.¹⁴ Rozman et al.'s study showed that EFB in powder form could be used as a reactive component, that is, as the cosupplier of OH groups in addition to poly(ethylene glycol) (PEG) in the production of PU through an isocyanate–OH reaction.¹⁶

This study aims at using EFB in mat form as a dual purpose material (i.e., as a reinforcing agent and reactive component) in the production of EFB–PEG–diphenyl methane diisocyanate (MDI) PU composites. In addition, the effect of the NCO/OH ratio and chemical modification of EFBs with hexamethylene diisocyanate (HMDI) and toluene diisocyanate (TDI) on the mechanical properties are also investigated.

EXPERIMENTAL

Materials

The oil palm EFB fiber strands were supplied by Sabutek Sdn. Bhd. (Teluk Intan, Perak, Malaysia). PEG with a molecular weight of 200 (PEG 200) was obtained from Fluka Chemika; MDI, TDI, and HMDI were purchased from Chembumi Sdn. Bhd. (Penang, Malaysia). The chemical composition of the EFB is provided in Table I. The average fiber length is 104 mm, and the average diameter is 557 μm .

Preparation of EFB mat–PU composite

EFB fibers obtained from the supplier were first cleaned with water followed by drying in an oven at 105°C. The amount of dried fibers that was used depended on the desired percentage of EFB fibers in the composite. The amount of EFB fibers was 30, 35, 40, and 45% (based on the overall weight of the composite). The fibers were suspended in water using a deckle box so that the fibers would be distributed evenly across the box. A mat was formed on plastic mesh as the water was drained out at the bottom of the box. The dimensions of the square mat were approximately 15.5 \times 15.5 cm^2 . The mat was then dried in an oven at 105°C for approximately 24 h before being cold pressed in a Carver laboratory press to obtain a more condensed mat with approximately 0.8-cm thickness.

TABLE I
Chemical Composition of EFB

Chemical Composition of EFB	Average (%)	SD
Extractives	2.30	0.19
Lignin	17.75	0.75
Holocellulose	82.20	0.83
Hydroxyl	3.37	0.24
Ash (900°C)	2.14	0.02

MDI was mixed with PEG 200 at 22°C for 10 min to form a prepolymer. The ratios of NCO to the overall amount of OH (EFB and PEG 200) in the system were 0.8, 1.0, and 1.1. The mixtures were then spread evenly on the fiber mat before being placed in a stainless steel mold with dimensions of 15.5 \times 15.5 \times 0.8 cm^3 . Each mat was then pressed in a Carver laboratory press at 125°C and 800 kgf/cm^2 for 5 h. The composites thus produced were then postcured for another 8 h at 105°C. The target density of the composite board was 1.0 g/cm^3 . Each composite was then conditioned at 23°C and 50% relative humidity before testing.

Reaction of TDI and HMDI with EFB fibers

The dried EFB fibers were dispersed in hexane, in which dibutyl tin dilaurate was added as a catalyst. TDI or HMDI was slowly added into the solution in 1-mL quantities. The mixture was then stirred for 2 min. Stirring was stopped when all the TDI or HMDI had been added into the solution. The reaction times for the TDI reaction were 1, 2, and 3 h. The reaction times for the HMDI reaction were 1, 2, 3, 8, 16, and 24 h. All treated EFBs were then washed several times with acetone before reflux with fresh acetone for 3 h to remove chemical reagent residues. The reacted EFBs were then oven dried at 105°C before being used in making the PU boards.

Testing

The composite board that was produced was cut into flexural, tensile, and impact tests samples. Flexural tests were conducted according to ASTM D 790 using an Instron model 1114 machine. The three-point bending test was carried out at a 0.2 cm/min crosshead speed on 8.0 \times 1.2 \times 0.8 cm^3 samples. Tensile tests were conducted in accordance with ASTM D 3039, using the same machine and crosshead speed on 12.0 \times 1.2 \times 0.8 cm^3 samples. A Charpy impact test according to ASTM D 256 was conducted on 7.0 \times 1.2 \times 0.8 cm^3 samples. The impact tests were conducted using a Ray–Ran Pendulum Impact System. In each case, a minimum of 10 samples were tested.

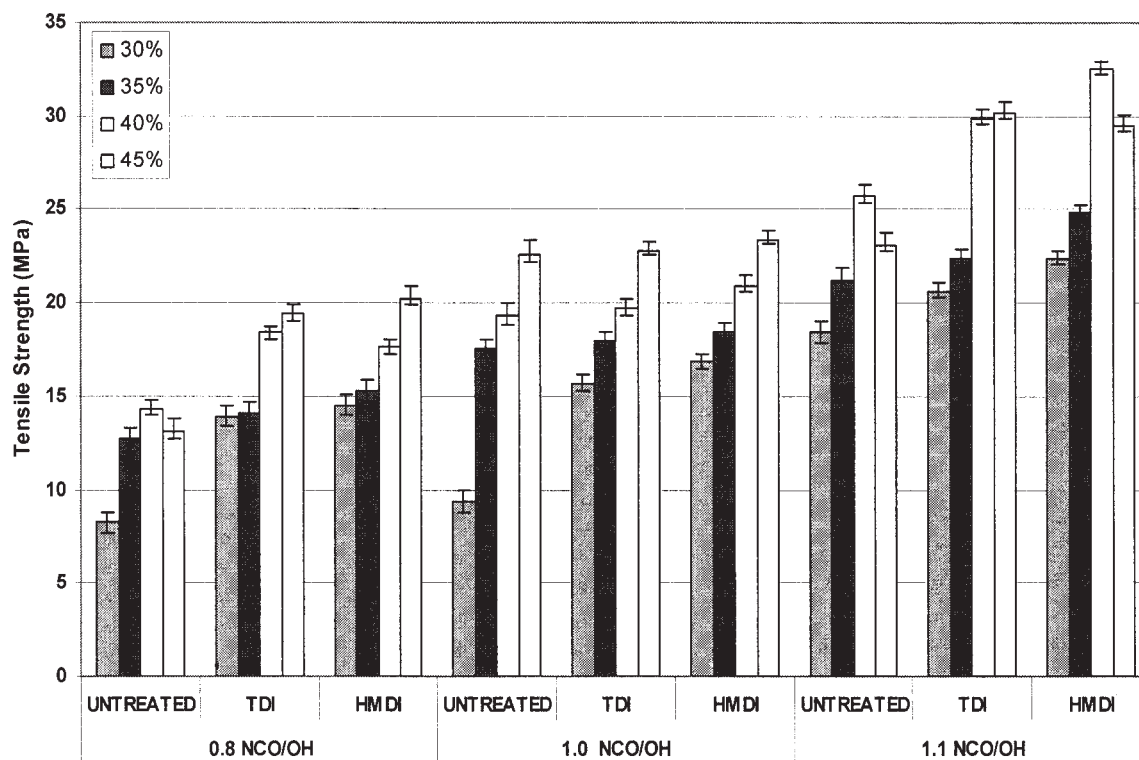


Figure 1 The effect of the NCO/OH ratio and TDI and HMDI modifications on the tensile strength of EFB-PU composites.

RESULTS AND DISCUSSION

Figure 1 shows the tensile strength results for PU composites with untreated and treated EFBs at various NCO/OH ratios. For all types of composites, the tensile strength increases as the NCO/OH ratio is increased. These results are in agreement with the study conducted by Rozman et al.,¹⁷ which showed a similar trend in the case of ground EFB-PU composites. The results indicate that as the NCO/OH ratio is increased, more NCO groups will be available to react with PEG as well as the OH groups from the EFBs. This will result in the formation of a three-dimensional PU network consisting of PEG-TDI-EFB in addition to the expected PEG-TDI bonds as the dispersed phase.

It can also be seen that for all types of composites at various NCO/OH ratios, the tensile strength increases with the increase in fiber loading. This shows that the incorporation of more EFBs has enabled the system to contain a higher stress distribution. Thus, it indicates that the EFBs contribute in forming a cohesive network with the isocyanates. This is believed to be true because lignocellulosic materials having more than two OH groups per molecule can act as polyols in the preparation of PU.¹⁰ A lignocellulosic-PU system can be produced through urethane bonds that consist of a three-dimensional network of saccharide, lignin, and

isocyanate. The results are consistent with the studies carried out by Yoshida et al.,¹⁸ Reimann et al.,¹⁹ Tan,²⁰ Saraf et al.,¹⁵ and Hatakeyama et al.²¹ Yoshida et al.¹⁸ attributed the increase in the tensile strength to the increase in the reaction between the lignin and the isocyanates in forming a three-dimensional network of crosslinkings.

The results also show that the composites with either TDI- or HMDI-treated EFBs display higher strength than the untreated ones. This indicates that the introduction of isocyanates from TDI or HMDI have enhanced the interaction between EFBs and the PU matrix, possibly through the reaction of the EFB-attached NCO with the OH from polyglycols. This indicates that, in addition to the linkages formed through OH from EFBs and the PU matrix, additional bonding will be formed in the isocyanate-treated composites. No significant differences are observed between TDI- and HMDI-treated samples.

By looking at the tensile modulus results (Fig. 2), it is obvious that the modulus decreases as the NCO/OH ratio is increased. This indicates that the presence of more NCO groups has resulted in the formation of more flexible linkages in the system. This may arise from the formation of longer urethane chains linking the EFBs and the matrix. In addition, the PU chains that are formed are believed to be able to absorb stress generated during the tensile test. This is clearly evident in the results for

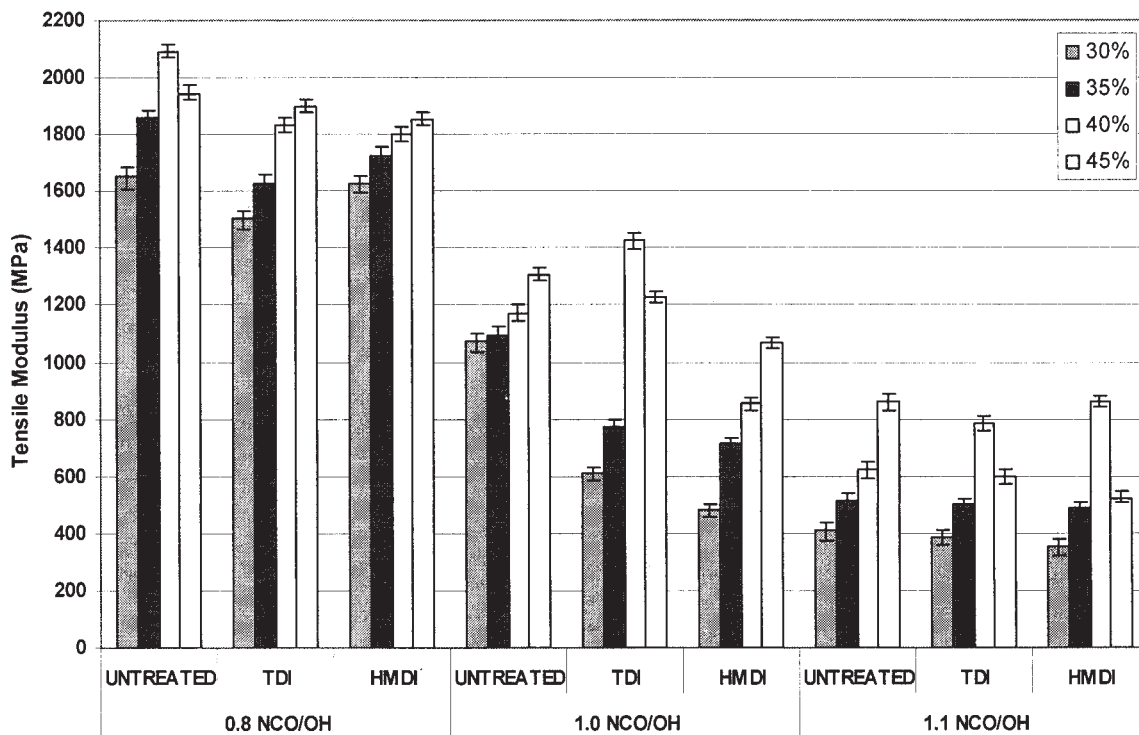


Figure 2 The effect of the NCO/OH ratio and TDI and HMDI modifications on the tensile modulus of EFB-PU composites.

the tensile toughness, which are shown in Figure 3. In addition to the enhancement of the toughness as the NCO/OH is increased, the toughness also

increases as the percentage of EFB is increased. Thus, this also indicates that the EFBs contribute in forming a cohesive network with the isocyanates

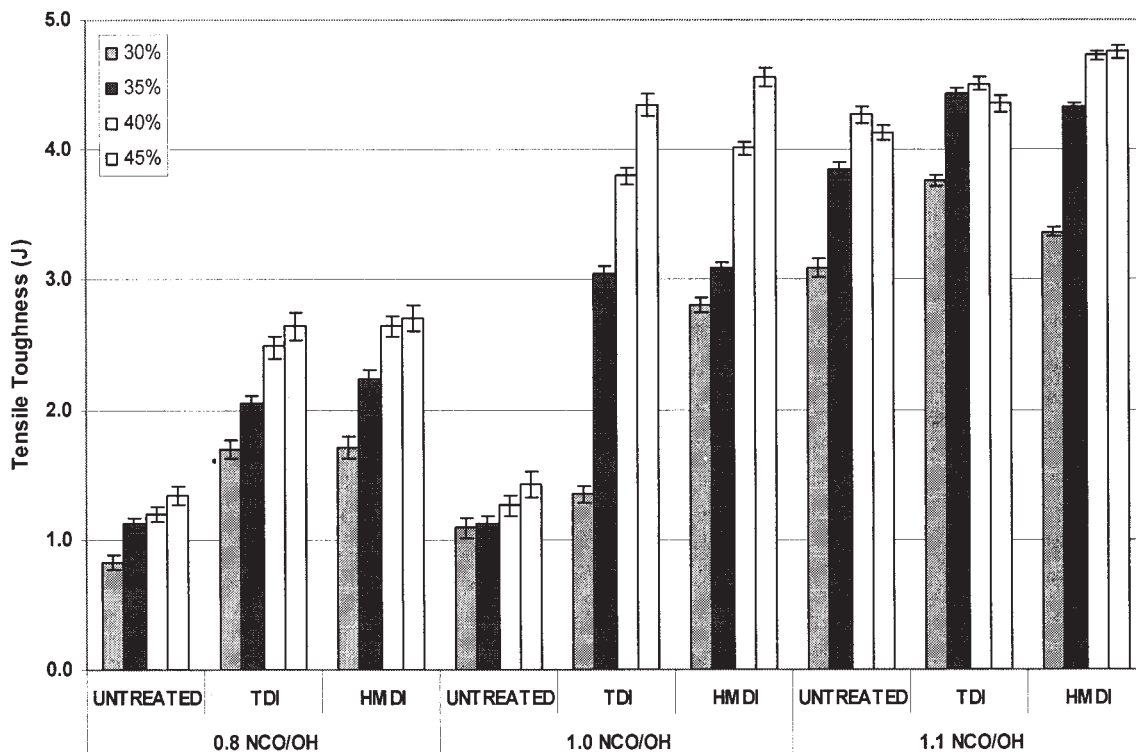


Figure 3 The effect of the NCO/OH ratio and TDI and HMDI modifications on the tensile toughness of EFB-PU composites.

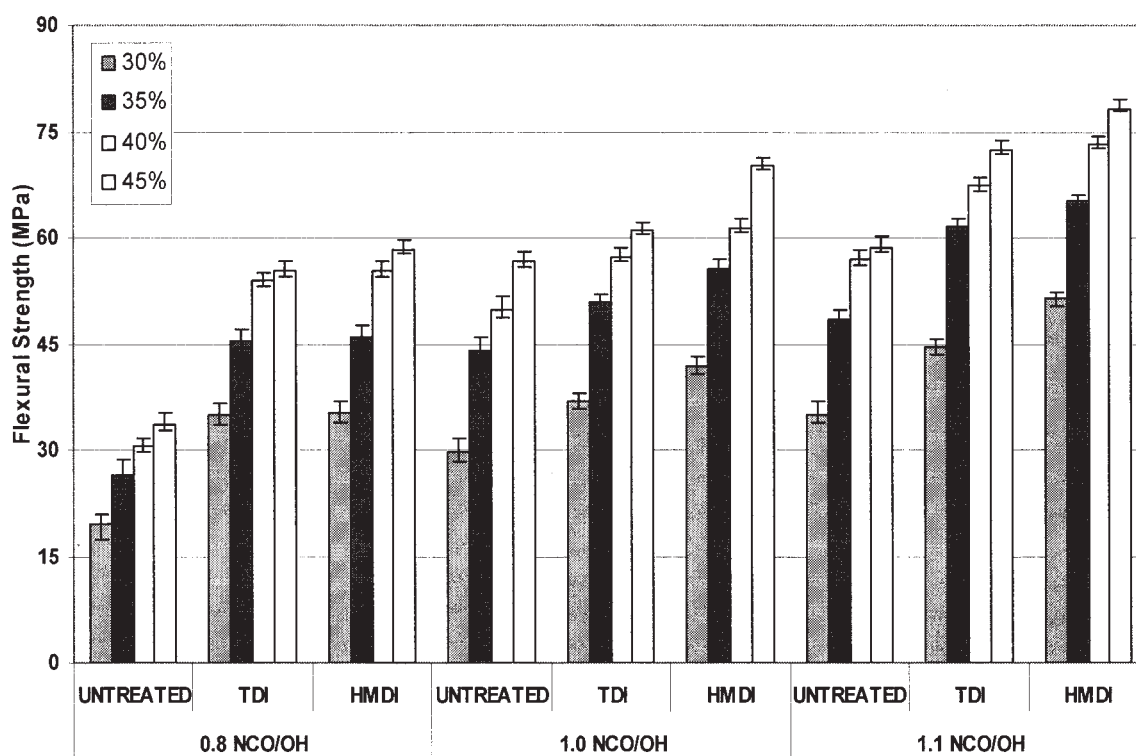


Figure 4 The effect of the NCO/OH ratio and TDI and HMDI modifications on the flexural strength of EFB-PU composites.

that can absorb and distribute the stress evenly. The involvements of EFBs in forming cohesive networks are further enhanced by chemical modification with TDI and HMDI. This provides additional active sites for further reactions with polyglycols in forming urethane linkages, in addition to the readily available OH groups from the EFBs. This phenomenon is clearly evident when comparing the composites with untreated and TDI- and HMDI-treated EFBs, which show that the treated samples possess higher toughness than the untreated ones. However, there is no significant difference detected between the TDI- and HMDI-treated composites. From the results it is also obvious that the modulus increases as the percentage of EFB in the composite increases. This is expected because, as a lignocellulosic material, EFBs possess inherent stiffness that contributes to the overall stiffness of the composites.

Figure 4 shows that, for all types of composites, the flexural strength increases as the NCO/OH ratio is increased. These results are similar to the tensile strength results presented earlier. Thus, the results indicate that, as the NCO/OH ratio is increased, more NCO groups will be available to react with PEG as well as the OH groups from the EFBs. This will result in the formation of a three-dimensional PU network consisting of PEG-NCO-EFB in addition to the expected PEG-NCO bonds. In general, it is obvious that, for all types of composites at various NCO/OH ratios, the flexural strength increases with

the increase of fiber loading. This shows that the incorporation of more EFBs has produced composites with higher ability to absorb stress.

The results also show that the composites with either TDI- or HMDI-treated EFBs display higher flexural strength than those of the untreated ones. This demonstrates that the introduction of isocyanates, either from TDI or HMDI, enhanced the interaction between EFBs and the PU matrix. It is possible through the reaction of the EFB-attached isocyanates with the OH from polyglycols, indicating that, in addition to the linkages formed between OH from EFBs, additional bonds were formed in the isocyanate-treated composites. No significant differences were detected between TDI- and HMDI-treated samples.

Flexural modulus results (Fig. 5) show that the modulus increases as the percentage of EFBs is increased for all composites. However, the stiffness decreases with the increase in the NCO/OH ratio. These results are similar to the tensile results. It is interesting to note that the decrease in the stiffness is accompanied by the increase in the flexural toughness (Fig. 6). Thus, as in the case of the tensile properties, this indicates that the EFBs contribute in forming a cohesive network with the isocyanates, which could absorb and distribute the stress evenly. The involvement of EFBs in forming cohesive networks is further enhanced by chemical modification with TDI and HMDI. It provides additional active sites

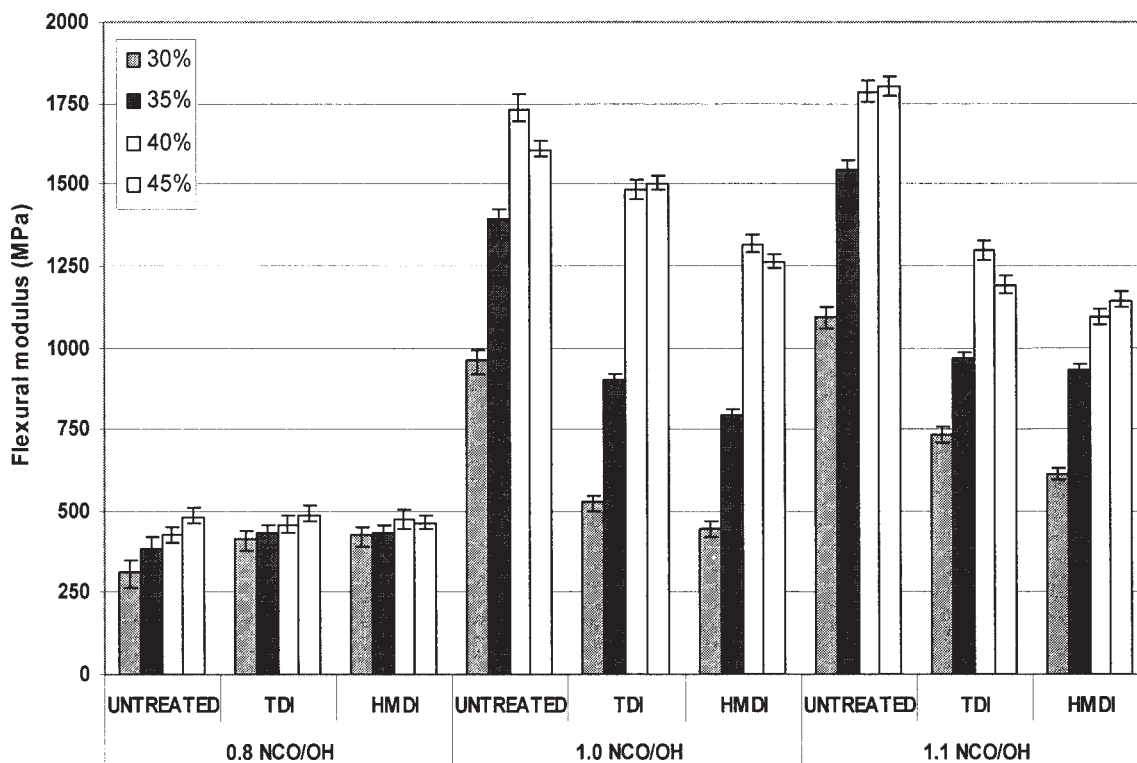


Figure 5 The effect of the NCO/OH ratio and TDI and HMDI modifications on the flexural modulus of EFB-PU composites.

for further reactions with polyglycols in forming urethane linkages, in addition to the readily available OH groups from EFBs. This phenomenon is clearly

evident when comparing the composites with untreated and TDI- and HMDI-treated EFBs, which demonstrates that the treated samples possess higher

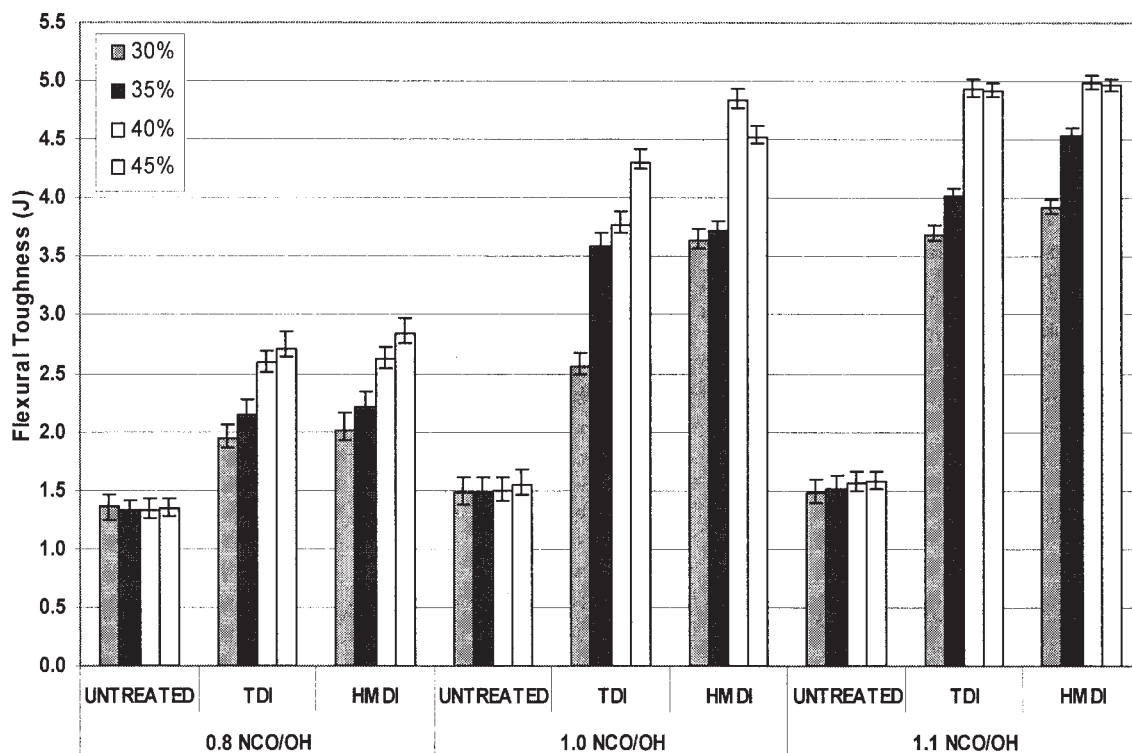


Figure 6 The effect of the NCO/OH ratio and TDI and HMDI modifications on the flexural toughness of EFB-PU composites.

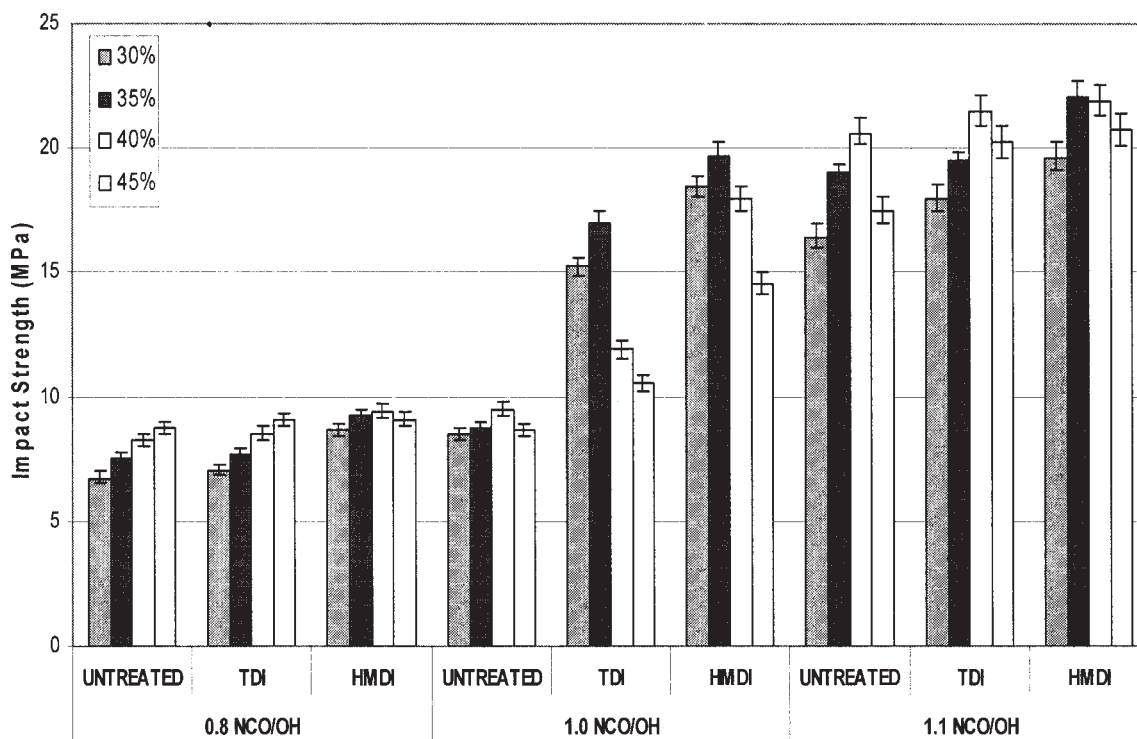


Figure 7 The effect of the NCO/OH ratio and TDI and HMDI modifications on the impact strength of EFB-PU composites.

toughness than the untreated ones. However, there is no significant difference detected between the TDI- and HMDI-treated composites.

Impact strength results (Fig. 7) show that the strength increases as the NCO/OH ratio is increased. It can be seen that at NCO/OH ratios of 1.0 and 1.1, the composites with HMDI-treated EFBs display higher impact strength than those with the TDI-treated and untreated EFBs. This indicates that the longer and more flexible chain length of HMDI, as compared to TDI, enabled the composites to absorb more energy before failure. It is believed that, at an NCO/OH ratio of 1.0, the amount of fibers to achieve a threshold value is 35%, which is true for TDI- and HMDI-treated fibers. At a ratio of 1.1, the amount of fibers to achieve a threshold value is 40%. Thus, with a higher NCO/OH ratio, more fibers can be incorporated to achieve a threshold value. However, at an NCO/OH ratio 0.8, no significant difference was detected.

CONCLUSIONS

EFBs were utilized as one of the reactive components in the formation of PU composites, which was shown by the increased flexural and tensile properties as the percentage of EFB was increased. The tensile, flexural, and impact properties were affected by the NCO/OH ratio. The tensile and flexural strength and toughness increased as the NCO/OH increased.

The modulus was lowered accordingly, which was attributed to increased flexibility of the PU linkages. Chemical modification of the EFBs resulted in increased tensile and flexural strength and toughness, with a lowering of the modulus as the percentage of treated EFB increased. This was attributed to cohesive networks being formed that could absorb and distribute the stress evenly. The impact strength results showed that the strength increased as the NCO/OH ratio increased. At NCO/OH ratios of 1.0 and 1.1, the composites with HMDI-treated fibers exhibited higher impact strength than those with TDI-treated and untreated fibers. This might be due to the longer and more flexible chain length of HMDI compared to TDI, which enabled the composites to absorb more energy before failure.

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