Swelling Properties of Chemically Modified Oil Palm Empty Fruit Bunch Based Polyurethane Composites

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ABSTRACT: In this study, the diffusion of various types of solvent in oil palm empty fruit bunch/polyurethane composites, produced from chemically modified empty fruit bunches, was investigated. The solubility parameters and polymer–solvent interaction parameters of the produced composites were determined. The void contents of the composites were also determined before swelling tests to eliminate the free solvent present in the system. From the results obtained, we found that the diffusion of the solvents was dependent on the compatible group available and the voids present in the system. The solubility parameters of the empty fruit bunch/polyurethane composites with different degrees of chemical modification were 11.6 and 11.7 $(cal/cm^{-3})^{1/2}$. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 995–1004, 2008

Key words: composites; diffusion; polyurethanes; swelling

INTRODUCTION

Natural-fiber- or lignocellulosic-material-based plastic composites are among the most rapidly growing markets of this decade. According to Rossi,[1] in 2002, the demand for these products in North America and Western Europe amounted to about 1.3 billion pounds, valued at roughly 900 million U.S. dollars, which represented an almost 20% growth from the year 2001. In North America, building products made from lignocellulosic materials, especially decking, account for two-thirds of the market because of its cost effectiveness compared to natural wood. In western countries, automotive products, such as interior door panels, exterior skirting, and underbody panels, were produced from long natural fibers, such as flax, hemp, jute, or kenaf, reinforcing a variety of thermosets and thermoplastics. These applications of lignocellulosic materials are principally replacing glass fibers in reinforced plastics. This is due to the several advantages offered by natural fibers as reinforcement materials; natural fibers are lower priced, lighter, more easily recycled, and easier to handle during production compared to glass fibers.

However, in the production of a good lignocellulose-based composite, the mechanism and efficiency of stress transfer between the components often determine the performance of the composite, and this transition region is called the *interface.* With possible chemical reactions between the components at the interface, the performance of the composites will be improved. One example of these composites is lignocellulosic-fiber-based polyurethanes (PUs). Lignocellulosic fibers are classified as hydroxyl (OH)-rich materials that may react with isocyanate groups to form an interfacial region, which is a urethane linkage.[2] According to Zetterlund et al.,[3] natural polymers consists of two or more OH groups per molecule, and they can be used as polyols in the preparation of PU. Among them, saw dust from the wood industry, risk husk from rice mills, coir from the coconut industry, and empty fruit bunches (EFBs), fronds, and trunks from the palm oil industry are examples of the lignocellulosic materials available.

Many attempts have been carried out to use lignocellulosic materials as hard segments in PU synthesis.[3–9] According to Hatakeyama et al.,[4] lignin can reduce the mobility of the main chain in PU systems due to its highly branched polymeric structure, which has a rigid phenyl propane structure as a repeating unit. This explanation is in agreement with that of Hirose et al.,[5] who stated that plant components could function as hard segments in PU production. With the incorporation of plant components in the PU system, the glass-transition temperature and mechanical properties of PU can be improved.

In this study, we aimed to investigate the effect of the use of chemically modified EFB in the preparation of EFB–PU composites on their sorption properties in various types of solvent. Mathew et al.[10] reported that the sorption properties of polymers are

controlled by their structure, crosslink density, type of crosslink, temperature, and so on. In this regard, the solubility parameters and polymer–solvent interaction parameters (χ's) for EFB–PU composites prepared from various types of chemically modified EFB were studied. Glycidyl methacrylate (GMA), epichlorohydrin (ECH), and propylene oxide (PO) were the reagents used to modify EFB. A one-shot process was used to produce composites with a NCO/OH ratio of 1.1 and a EFB/polyol ratio of 60/40 (w/w).

EXPERIMENTAL

Materials

The EFB in fiber form was obtained from Sabutek Sendirian Berhad Teluk Intan (Perak, Malaysia). Diphenylmethane diisocyanate (MDI) was supplied by Aldrich Chemical Co., Inc. (Milwaukee, WI) PEG 200, GMA, and ECH were obtained from Fluka Chemika (Buchs, Switzerland), whereas PO and hydroquinone were supplied by BDH Chemical, Ltd., (Poole, UK) and Merck–Schuchardt (Darmstadt, Germany), respectively. Solvents with different solubility parameters and of analytical grade, such as toluene [8.9 (cal/cm^3)$^{1/2}$], acetone [9.9 (cal/cm^3)$^{1/2}$], N,N'-dimethylformamide [DMF; 12.1 (cal/cm^3)$^{1/2}$], and ethanol [12.7 (cal/cm^3)$^{1/2}$],[11] were used.

EFB chemical modification[12]

EFB modification with GMA

Predried EFB was added to a round-bottom flask consisting of GMA in a solvent mixture of DMF and pyridine at a ratio of 1:1. If pyridine alone is used, an uncontrollable exothermic reaction is triggered, which would degrade the EFB, as reported in a previous study.[12] The reaction temperature and reaction time were fixed at 90°C and 3 h, respectively. In addition, hydroquinone (5% based on GMA) was used to prevent the homopolymerization of GMA. The amount of GMA was varied in this chemical modification to obtain different weight percentage gains (WPGs), which could be obtained as follows:

TABLE I
T_d and M_d Values and Void Contents of the EFB–PU Composites with EFB–GMA

Sample	WPG (%)	T_d (g/cm^3)	M_d (g/cm^3)	Void (%)
COMR	0	1.25	1.12	10.4 ($\pm$0.30)
COMGMA01	9.76	1.01	0.96	5.0 ($\pm$0.53)
COMGMA02	15.46	1.02	0.97	4.9 ($\pm$0.41)
COMGMA03	21.41	1.03	0.98	4.9 ($\pm$0.58)
COMGMA04	27.84	1.07	1.02	4.7 ($\pm$0.39)

TABLE II
T_d and M_d Values and Void Contents of the EFB–PU Composites with EFB–ECH

Sample	WPG (%)	T_d (g/cm^3)	M_d (g/cm^3)	Void (%)
COMR	0	1.25	1.12	10.4 ($\pm$0.30)
COMECH01	7.21	1.20	1.08	10.0 ($\pm$0.26)
COMECH02	13.96	1.19	1.09	8.4 ($\pm$0.35)
COMECH03	22.49	1.18	1.09	8.5 ($\pm$0.32)
COMECH04	32.57	1.18	1.09	8.5 ($\pm$0.33)

$$\text{WPG (\%)} = [(W_m - W_d)/W_d] \times 100$$

where W_m is the weight of the oven-dried EFB after modification (g) and W_d is the weight of the oven-dried EFB before modification (g).

EFB modification with ECH

The preparation of EFB modified with ECH was similar to that mentioned in the previous section.

EFB modification with PO

The predried EFB was added to a reaction flask consisting of PO and pyridine as a swelling agent. The reaction time and reaction temperature were fixed at 24 h and 60°C, respectively. The amount of PO used was varied to obtain EFB-modified PO with different WPGs.

EFB–PU composite preparation

The EFB (unmodified and modified) was dried in an oven at 105°C for approximately 20 h before use. PEG200 was dried with a type 3 Å molecular sieve; for 24 h. In the preparation of the EFB–PU composite, the EFB was mixed with MDI at room temperature followed by the addition of PEG 200. A stream of nitrogen was applied during the mixing process. Mixing was carried out in a water bath at a temperature of 30°C with a mechanical stirrer at 500 rpm for 5 min. Each of the precured EFB–PU was then pressed at 125°C for 5 h at a pressure of 500 kg/cm^2. The sample was cooled to room temperature before

TABLE III
T_d and M_d Values and Void Contents of the EFB–PU Composites with EFB–PO

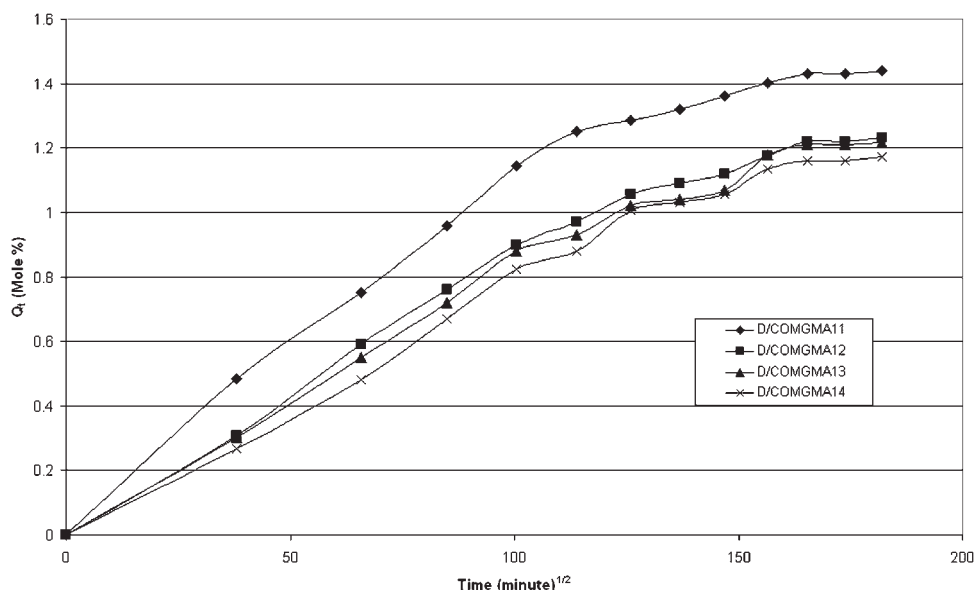| Sample	WPG (%)	T_d (g/cm^3)	M_d (g/cm^3)	Void (%)
COMR	0	1.25	1.12	10.4 ($\pm$0.30)
COMPO01	6.08	1.20	1.03	14.2 ($\pm$0.58)
COMPO02	10.53	1.18	1.02	13.6 ($\pm$0.72)
COMPO03	15.36	1.17	1.02	12.8 ($\pm$0.64)

Figure 1 Molar percentage DMF uptake of the EFB–PU composites prepared from EFB–GMA with different WPGs.

it was removed from the mold. Subsequently, the sample was postcured in an oven at 125°C for 24 h before testing.

Void content determination

The void content of each EFB–PU composite was determined according to ASTM D 2734–70 with six replicates. First, the theoretical density (T_d; g/cm^3) of each sample was calculated and compared with the measured density. The missing fraction of each sample was considered the void content. T_d of the EFB–PU composites and the void content were calculated by the following equation:

$$T_d = 100/[(\%MDI/\rho_{MDI}) + (\%PEG200/\rho_{PEG200}) + (\%EFB/\rho_{EFB})]$$

where %MDI is the weight percentage of MDI, ρ_{MDI} is the density of MDI (1.18 g/cm^3), %PEG200 is the weight percentage of PEG200, ρ_{PEG200} is the density of PEG200 (1.12 g/cm^3), %EFB is the weight percentage of EFB (unmodified and modified), and ρ_{EFB} is

the density of EFB (unmodified and modified, g/cm^3).

Density determination

A Pyrex Gay–Lussac bottle (a density bottle or specific gravity bottle) with capacity of 25 mL was used to determine the density of EFB (unmodified and modified). In this case, toluene was used as the medium to measure the density of the EFB because it was a nonswelling agent for most of the lignocellulosic materials. The equations shown next were used to calculate the density of EFB. The density of the composites was determined by the measurement of its dimensions and weight:

$$SG_T = (W_3 - W_1)/(W_2 - W_1)$$

$$SG_{EFB} = \{(W_4 - W_1)/[(W_3 - W_1) - (W_5 - W_4)]\} \times SG_T$$

where SG_T is the specific gravity of toluene, W_1 is the weight of the empty density bottle (g), W_2 is the

TABLE IV
n and k Values for the Composites Prepared from EFB–GMA in DMF and Toluene

Sample	DMF		Toluene	
	n	k ($\times 10^{-3}$)	n	k ($\times 10^{-3}$)
COMR	0.55	6.30	0.56	3.94
COMGMA01	0.57	4.87	0.55	6.54
COMGMA02	0.52	6.17	0.60	4.14
COMGMA03	0.54	5.02	0.53	6.96
COMGMA04	0.56	3.70	0.58	4.99

TABLE V
n and k Values for the Composites Prepared from EFB–GMA in Acetone and Ethanol

Sample	Acetone		Ethanol	
	n	k ($\times 10^{-3}$)	n	k ($\times 10^{-3}$)
COMR	0.52	3.94	0.65	0.94
COMGMA01	0.52	5.73	0.53	3.35
COMGMA02	0.50	6.22	0.54	3.10
COMGMA03	0.50	6.46	0.51	3.60
COMGMA04	0.52	4.53	0.56	2.29

TABLE VI
n and k Values for the Composites Prepared from EFB–ECH in DMF and Toluene

Sample	DMF		Toluene	
	n	k ($\times 10^{-3}$)	n	k ($\times 10^{-3}$)
COMR	0.55	6.30	0.56	3.94
COMECH01	0.53	6.91	0.64	2.00
COMECH02	0.57	4.44	0.58	2.73
COMECH03	0.56	4.66	0.61	2.12
COMECH04	0.51	5.94	0.61	1.16

weight of the density bottle filled with distilled water (g), W_3 is the weight of the density bottle filled with toluene (g), SG_{EFB} is the specific gravity of EFB, W_4 is the weight of the density bottle filled with EFB (one third full; g), and W_5 is the weight of the density bottle filled with EFB and toluene (g).

The void content was determined as follows:

$$\text{Void content (\%)} = [(T_d - M_d)/T_d] \times 100$$

where T_d is the theoretical density (g/cm^3) and M_d is the determined density (g/cm^3).

Swelling test

Predried EFB–PU composite samples with dimensions of $3 \times 0.8 \times 0.5$ cm^3 (length $\times$ width $\times$ thickness) were immersed in different types of solvent. The changes in weight and thickness were monitored periodically until they became constant. The surface of each sample had to be dried with absorbent paper before they were weighed and quickly reimmersed in the respective solvent. This process could not be more than 30 s long to avoid solvent evaporation.

Generally, the solvent molecules could exist in two states in the composites, which were unbound molecules in the void and bound molecules with the appropriate constituents in the composites. Hence, the void content of each type of composite should have been determined to obtain the actual absorption with the assumption that those solvent molecules present in the voids were unbound. The unbound solvent molecules in the void were cor-

TABLE VIII
n and k Values for the Composites Prepared from EFB–PO in DMF and Toluene

Sample	DMF		Toluene	
	n	k ($\times 10^{-3}$)	n	k ($\times 10^{-3}$)
COMR	0.55	6.30	0.56	3.94
COMPO01	0.52	8.50	0.55	6.32
COMPO02	0.55	6.08	0.52	8.49
COMPO03	0.54	6.37	0.62	3.74

rected for all of the sorption studies carried out on the basis of the predetermined void contents, and the equation is shown next:

$$M_s(g) = \rho_s \times [V - (\% \text{ void} \times V)]$$

where M_s is the mass of solvent absorbed at equilibrium swelling (g), ρ_s is the density of the solvent, and V is the volume of the solvent absorbed, which we could obtain by dividing the increment weight of the immersed sample by the solvent density.

To determine the mode of the sorption (Fickian or non-Fickian) and the mechanism of the sorption, the data obtained were fitted to the following equation:[13,14]

$$\text{Log}(Q_t/Q_\infty) = \text{Log } k + n \text{ Log } t$$

where Q_t is the molar percentage of solvent absorbed at time t, Q_∞ is the molar percentage of solvent absorbed at equilibrium (corrected), n is the slope of the graph $\text{Log}(Q_t/Q_\infty)$ against $\text{Log } t$ and k is a constant.

The values of n and k were determined by linear regression analysis.[15–17] According to Harogappad and Aminabhavi,[13] the k value gives an idea about the extent of the polymer–solvent interaction, and the n value decides the mode of the sorption mechanism. The diffusion coefficient or diffusivity (D) of a solvent in a composite could be determined by the following equation:[16–18]

$$D = \pi/16(h\theta/Q_\infty)^2$$

where h is the initial thickness of the samples and θ is the slope of the graph of Q_t against $t^{1/2}$ before 50% sorption.

TABLE VII
n and k Values for the Composites Prepared from EFB–ECH in Acetone and Ethanol

Sample	Acetone		Ethanol	
	n	k ($\times 10^{-3}$)	n	k ($\times 10^{-3}$)
COMR	0.52	3.94	0.65	0.94
COMECH01	0.50	4.89	0.59	1.44
COMECH02	0.50	5.45	0.63	0.93
COMECH03	0.50	5.09	0.66	0.55
COMECH04	0.52	3.39	0.59	0.84

TABLE IX
n and k Values for the Composites Prepared from EFB–PO in Acetone and Ethanol

Sample	Acetone		Ethanol	
	n	k ($\times 10^{-3}$)	n	k ($\times 10^{-3}$)
COMR	0.52	3.94	0.65	0.94
COMPO01	0.66	3.40	0.58	4.16
COMPO02	0.64	3.74	0.57	3.77
COMPO03	0.54	7.26	0.57	4.20

TABLE X
D, S, and P Values of the Composites with EFB–GMA with Different WPGs in DMF and Toluene

	DMF			Toluene		
Sample	$D \times 10^{-5}$ (cm^2/s)	S	$P \times 10^{-5}$ (cm^2/s)	$D \times 10^{-5}$ (cm^2/s)	S	$P \times 10^{-5}$ (cm^2/s)
COMR	18.1 (±1.7)	0.71 (±0.07)	12.9 (±1.3)	4.39 (±0.87)	0.10 (±0.01)	0.43 (±0.09)
COMGMA01	19.4 (±1.6)	1.02 (±0.08)	19.9 (±1.0)	53.40 (±0.74)	0.10 (±0.01)	5.58 (±0.21)
COMGMA02	16.0 (±0.2)	0.87 (±0.07)	13.9 (±0.3)	38.60 (±0.53)	0.09 (±0.01)	3.43 (±0.44)
COMGMA03	15.3 (±1.5)	0.87 (±0.07)	13.3 (±1.4)	46.40 (±2.43)	0.10 (±0.01)	4.51 (±0.56)
COMGMA04	12.6 (±0.6)	0.83 (±0.04)	10.6 (±0.5)	38.60 (±1.56)	0.11 (±0.01)	4.31 (±0.32)

The sorption coefficient (S) is related to the maximum sorption of the solvent, which can be obtained from the ratio of the weight of the solvent absorbed at the equilibrium state to the initial weight of the polymer.[15] S of the EFB–PU composites was calculated with the following equation:[16,17]

$$S = M_s/M_p$$

where M_s is the mass of solvent absorbed at equilibrium swelling (g) and M_p is the mass of the composite at the initial state (g).

The permeability of the EFB–PU composites could be expressed by permeability coefficient (P), which was calculated by the following equation:[16,17]

$$P = DS$$

The swelling coefficient (α) was obtained by the next equation. The solubility parameter of each series of EFB–PU composites was obtained when the maximum swelling was achieved:[15,19]

$$\alpha = (M_s/M_p) \times (1/\rho_s)$$

where M_s is the mass of the solvent in the swollen sample at equilibrium (g), M_p is the mass of the composite at the initial state (g), and ρ_s is the density of the respective solvent (g/cm^3).

χ of each type of composite was determined by the equation shown next:[15,19]

$$\chi = \beta + V_s[(\delta_p - \delta_s)^2/RT]$$

where β is the lattice constant (0.34), V_s is the molar volume of the solvent (cm^3/mol), δ_p is the solubility parameter of the composite [(cal/cm^3)$^{1/2}$], δ_s is the solubility parameter of the solvent [(cal/cm^3)$^{1/2}$], R is the gas constant (1.983 cal mol^{-1} K^{-1}), and T is the temperature (K).

RESULTS AND DISCUSSION

Void content

Tables I–III depict the density of the EFB–PU composites prepared from EFB–GMA, EFB–ECH, and EFB–PO, respectively, with different WPGs. In general, the densities of the EFB–PU composites prepared from modified EFB were lower than those prepared from the unmodified EFB. Hill and Khalil[20] explained that this phenomenon was attributed to the incorporation of lignocellulosic materials with lower densities in the preparation of composites. According to the study carried out by Mohd Ishak et al.,[21] the increase in the density of the composites prepared could be attributed to the use of a higher density material as a reinforcing agent. Thus, it is quite reasonable to suggest that the use of modified EFB, which is relatively lower in density (from previous results[12]) than unmodified EFB, may result in the reduction in density in the produced EFB–PU composites.

When the T_d and M_d values of each EFB–PU composites tabulated in Tables I–III are compared, the M_d values are marginally lower than the T_d values. According to Zhang et al.,[22] the decrease in density could be attributed to the presence of void in the composites, which may be located in the interface between the fiber and matrix. In addition, the void may be located in the matrix and the fiber lumen.[20]

TABLE XI
D, S, and P Values of the Composites with EFB–GMA with Different WPGs in Acetone and Ethanol

	Acetone			Ethanol		
Sample	$D \times 10^{-5}$ (cm^2/s)	S	$P \times 10^{-5}$ (cm^2/s)	$D \times 10^{-5}$ (cm^2/s)	S	$P \times 10^{-5}$ (cm^2/s)
COMR	1.07 (±0.13)	0.22 (±0.01)	0.24 (±0.04)	2.03 (±0.23)	0.20 (±0.02)	0.41 (±0.06)
COMGMA01	22.00 (±0.25)	0.26 (±0.01)	5.83 (±0.07)	6.00 (±0.12)	0.25 (±0.01)	1.51 (±0.09)
COMGMA02	17.80 (±0.48)	0.26 (±0.01)	4.60 (±0.16)	6.48 (±0.08)	0.25 (±0.01)	1.60 (±0.08)
COMGMA03	26.00 (±3.96)	0.23 (±0.01)	6.02 (±1.01)	4.95 (±0.09)	0.24 (±0.01)	1.17 (±0.02)
COMGMA04	13.50 (±0.84)	0.24 (±0.01)	3.27 (±0.35)	5.20 (±0.04)	0.30 (±0.01)	1.57 (±0.08)

TABLE XII
D, S, and P Values of the Composites with EFB–ECH with Different WPGs in DMF and Toluene

Sample	DMF			Toluene		
	$D \times 10^{-5}$ (cm^2/s)	S	$P \times 10^{-5}$ (cm^2/s)	$D \times 10^{-5}$ (cm^2/s)	S	$P \times 10^{-5}$ (cm^2/s)
COMR	18.1 ($\pm$1.7)	0.71 ($\pm$0.07)	12.9 ($\pm$1.3)	4.39 ($\pm$0.87)	0.10 ($\pm$0.01)	0.43 ($\pm$0.09)
COMECH01	17.4 ($\pm$1.8)	0.68 ($\pm$0.05)	11.8 ($\pm$0.5)	9.22 ($\pm$0.79)	0.10 ($\pm$0.01)	0.92 ($\pm$1.42)
COMECH02	13.0 ($\pm$1.2)	0.65 ($\pm$0.05)	8.4 ($\pm$0.7)	5.58 ($\pm$0.16)	0.10 ($\pm$0.01)	0.53 ($\pm$0.04)
COMECH03	10.4 ($\pm$1.4)	0.65 ($\pm$0.06)	6.7 ($\pm$0.9)	6.93 ($\pm$0.63)	0.10 ($\pm$0.01)	0.71 ($\pm$0.05)
COMECH04	8.66 ($\pm$0.2)	0.66 ($\pm$0.06)	5.7 ($\pm$0.2)	3.33 ($\pm$0.16)	0.09 ($\pm$0.01)	0.30 ($\pm$0.02)

Oksman et al.[23] investigated the morphology of sisal–epoxy composites. They found that there was no epoxy resin in the natural fiber lumen. This would have resulted in a reduction in density of the composites produced and, consequently, would have increased the void content. Hence, the difference between the densities of each EFB–PU composite produced was probably caused by the void presence in the interface region, matrix, and unfilled fiber lumen.

In the preparation of lignocellulose-based composites, void can be formed because of the incompatibility between the filler and matrix or within the matrix itself. Elvy et al.[24] found that the incorporation of a coupling agent could increase the adhesion of a polymer to the lignocellulose filler. This resulted in the reduction of void formation. However, Nair et al.[25] reported that benzoylation and alkaline treatment tended to produce small voids on the fiber surface that could promote mechanical interlocking between the lignocellulosic filler and the matrix. In the context of the EFB–PU composites, void could be formed when the environmental relative humidity interacted with isocyanate, which would have given rise to carbon dioxide that subsequently led to void formation. The void could be located in the matrix and at the interface between the EFB and the matrix. On the other hand, the void content of the EFB–PU composites could be contributed by the lumen in the EFB. According to Kellogg,[26] the dry cell wall consists of not more than 5% of the void volume. The existence of void can act as a stress concentration point where the crack propagation of the EFB–PU

composites begins. Hence, the information of void content in the composites is important for the understanding of the sample properties.

In addition to the density, Tables I–III also show the void contents of the EFB–PU composites produced from different types of chemically modified EFB. For the EFB–PU composites prepared from EFB–GMA (Table I), the void content was significantly lower than that of the unmodified ones, and no significant difference was observed among the composites from EFB–GMA with various WPGs. As mentioned in the previous discussion, the void content was found to decrease with increasing compatibility between the matrix and lignocellulosic filler.[24] Hence, this reduction in void content was probably due to a better compatibility between EFB–GMA and the PU matrix than that between EFB and the PU matrix.

For EFB–PU composites prepared from EFB–ECH, the void content is slightly lower than EFB–PU composites prepared from unmodified EFB. The same explanation for composites prepared from EFB–GMA probably holds for this observation. However, the void content was relatively higher compared to that of the composites prepared from EFB–GMA. This was attributed to the relatively lower compatibility between EFB–ECH and the PU matrix compared to that of the composites with EFB–GMA. When the molecular lengths of the molecules GMA and ECH are compared, GMA has a longer chain that could have facilitated the interaction between EFB–GMA and the PU matrix compared to the interaction between EFB–ECH and the

TABLE XIII
D, S, and P Values of the Composites with EFB–ECH with Different WPGs in Acetone and Ethanol

Sample	Acetone			Ethanol		
	$D \times 10^{-5}$ (cm^2/s)	S	$P \times 10^{-5}$ (cm^2/s)	$D \times 10^{-5}$ (cm^2/s)	S	$P \times 10^{-5}$ (cm^2/s)
COMR	1.07 ($\pm$0.13)	0.22 ($\pm$0.01)	0.24 ($\pm$0.04)	2.03 ($\pm$0.23)	0.20 ($\pm$0.02)	0.41 ($\pm$0.06)
COMECH01	1.11 ($\pm$0.09)	0.22 ($\pm$0.01)	0.24 ($\pm$0.02)	1.33 ($\pm$0.14)	0.20 ($\pm$0.01)	0.27 ($\pm$0.02)
COMECH02	2.34 ($\pm$0.42)	0.13 ($\pm$0.01)	0.31 ($\pm$0.06)	1.03 ($\pm$0.09)	0.18 ($\pm$0.01)	0.19 ($\pm$0.02)
COMECH03	1.72 ($\pm$0.12)	0.13 ($\pm$0.01)	0.22 ($\pm$0.04)	0.79 ($\pm$0.05)	0.19 ($\pm$0.01)	0.15 ($\pm$0.01)
COMECH04	1.83 ($\pm$0.14)	0.09 ($\pm$0.01)	0.17 ($\pm$0.02)	0.89 ($\pm$0.03)	0.18 ($\pm$0.01)	0.16 ($\pm$0.01)

TABLE XIV
D, S, and P Values of the Composites with EFB–PO with Different WPGs in DMF and Toluene

	DMF			Toluene		
Sample	$D \times 10^{-5}$ (cm^2/s)	S	$P \times 10^{-5}$ (cm^2/s)	$D \times 10^{-5}$ (cm^2/s)	S	$P \times 10^{-5}$ (cm^2/s)
COMR	18.1 (±1.7)	0.71 (±0.07)	12.9 (±1.3)	4.39 (±0.87)	0.10 (±0.01)	0.43 (±0.09)
COMPO01	28.8 (±2.7)	1.68 (±0.10)	48.4 (±8.0)	34.70 (±4.81)	0.17 (±0.01)	5.84 (±0.60)
COMPO02	26.5 (±1.7)	1.68 (±0.10)	44.6 (±3.8)	32.80 (±1.86)	0.19 (±0.01)	6.23 (±0.36)
COMPO03	26.6 (±2.7)	1.67 (±0.11)	44.4 (±6.1)	34.10 (±2.11)	0.19 (±0.01)	5.53 (±0.68)

TABLE XV
D, S, and P Values of the Composites with EFB–PO with Different WPGs in Acetone and Ethanol

	Acetone			Ethanol		
Sample	$D \times 10^{-5}$ (cm^2/s)	S	$P \times 10^{-5}$ (cm^2/s)	$D \times 10^{-5}$ (cm^2/s)	S	$P \times 10^{-5}$ (cm^2/s)
COMR	1.07 (±0.13)	0.22 (±0.01)	0.24 (±0.04)	2.03 (±0.23)	0.20 (±0.02)	0.41 (±0.06)
COMPO01	32.40 (±1.21)	0.27 (±0.02)	8.06 (±0.28)	24.50 (±2.05)	0.20 (±0.02)	4.99 (±0.59)
COMPO02	37.30 (±1.28)	0.27 (±0.02)	10.20 (±0.59)	14.30 (±0.97)	0.28 (±0.01)	3.96 (±0.35)
COMPO03	29.40 (±2.21)	0.26 (±0.03)	7.46 (±0.92)	16.80 (±1.25)	0.24 (±0.03)	4.05 (±0.47)

PU matrix. Thus, the compatibility between EFB–GMA and the PU matrix was better compared to those of the others.

Table III reveals that the void content of the EFB–PU composites prepared from EFB–PO was higher than that of the control (COMR) and also higher than that of any of the other composites studied. This was taken proof that EFB–PO gave a relatively higher sorption capability of moisture during the composite preparation compared to other chemically modified EFBs. Thus, in the subsequent reaction, water molecules may have interacted with isocya-

nate and gave rise to carbon dioxide, which left behind voids in the system.

Swelling tests

Figure 1 depicts one example of the molar percentage of solvent uptake by 100 g of composite plotted against the square root of time (min); the values n and k were determined by linear regression analysis. Tables IV–IX show the n and k values of all types of composite produced. Unnikrishnan and Thomas[14] reported that when the value of n lies close to 0.5,
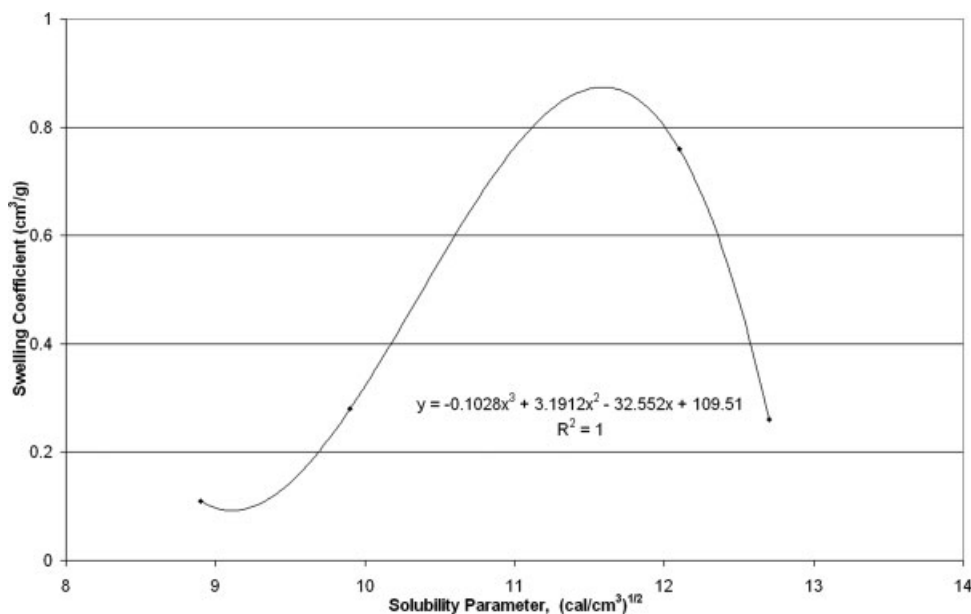

Figure 2 Swelling coefficients versus solubility parameters of the solvents for the EFB–PU composites prepared from untreated EFB.

TABLE XVI
Solubility Parameters of the EFB–PU Composites
Prepared from EFB–GMA

Composite	WPG (%)	Solubility parameter of the EFB–PU composites $(cal/cm^3)^{1/2}$
COMR	0	11.6
COMGMA01	9.76	11.6
COMGMA02	15.46	11.6
COMGMA03	21.41	11.6
COMGMA04	27.84	11.6

the sorption mechanism can be classified as Fickian. Meanwhile, when $n = 1$, the mechanism is non-Fickian. This is in contrast to a statement made by Desai et al.[15] The observed value of n varied from 0.58 to 0.69, and it was classified as non-Fickian. Aithal and Aminabhavi[18] categorized the diffusion process to be anomalous when n varies from 0.51 to 0.68. However, according to a study carried out by Sreekala et al.[16] in lignocellulosic-based composites, the diffusion mechanism is classified as Fickian when the value of n is very close to 0.5 (0.42–0.62). From the results obtained in the EFB–PU composites, we observed that the n value was between 0.50–0.66. Hence the diffusion mechanism observed for all of the EFB–PU composites prepared in all types of solvent were Fickian. In other words, the sorption kinetics of the EFB–PU composites depended on the concentration of the solvent and time. However, no consistent trend was observed for the k value, which characterized the interaction between the solvent and composites.

According to Sreekala and Thomas,[17] D characterizes the ability of the solvent molecules to diffuse into the composites, whereas S measures the extent of the sorption, and P is the net effect of the diffusion and sorption. The D, S, and P values of all of the types of composite studied are presented in Tables X–XV, respectively. In the DMF sorption study, D was significantly reduced for composites with EFB–GMA and EFB–ECH, whereas the use of EFB–PO as a reinforcement in EFB–PU composite preparation increased D. According to Pothan and Thomas,[27] the main factors that need to be consid-

ered in the diffusion process are (1) polarity of the molecular structure and (2) degree of crosslinking. Nevertheless, void content is another factor that cannot be neglected. Composites from EFB–PO demonstrated a higher void content, which resulted in a higher diffusion of DMF molecules into the composites. For composites from EFB–GMA and EFB–ECH, although they possessed a tighter network, the DMF molecule could diffuse through the void in the system. Hence, this resulted in a low ability of the solvent to diffuse into the composites. The reduction of D was attributed to the formation of a three-dimensional network. Hence, the degree of crosslinking of the EFB–PU composites prepared from EFB–PO was relatively lower than the composites prepared from EFB–ECH and EFB–GMA.

For S, it seemed that a looser network structure was obtained in the composites with EFB–PO due to its higher sorption. This increased the DMF sorption, where a looser network facilitated the diffusion of the solvent into the system. Meanwhile, the composites with EFB–ECH showed a tighter network structure compared to the composites prepared from unmodified EFB. This resulted in the restriction of chain mobility and, subsequently, reduced the DMF sorption. However, the composites with EFB–GMA showed an increasing trend in absorption. These results indicate that the increase in the degree of polarity of the composites was due to the hydrophilic nature of GMA. The S values in acetone, toluene, and ethanol were relatively lower compared to those observed in DMF. From the results, D increased in acetone, toluene, and ethanol when EFB–GMA and EFB–PO were used in the preparation of the EFB–PU composites. This was attributed to compatible groups, such as methyl groups from GMA and PO. In addition, the attached GMA introduced new C=O groups in the EFB. Hence, this facilitated the penetration of the solvent into the composites due to the increasing compatibility.[28] No significant difference was observed in the composites with EFB–ECH in this case. P of all types of EFB–PU composites followed the trend observed in D, as discussed earlier. Higher void contents facilitated permeability; hence, a higher P was obtained.

TABLE XVII
Solubility Parameters of the EFB–PU Composites
Prepared from EFB–ECH

Composite	WPG (%)	Solubility parameter of the EFB–PU composites $(cal/cm^3)^{1/2}$
COMR	0	11.6
COMECH01	7.21	11.6
COMECH02	13.96	11.7
COMECH03	22.49	11.7
COMECH04	32.57	11.7

TABLE XVIII
Solubility Parameters of the EFB–PU Composites
Prepared from EFB–PO

Composite	WPG (%)	Solubility parameter of the EFB–PU composites $(cal/cm^3)^{1/2}$
COMR	0	11.6
COMPO01	6.08	11.6
COMPO02	10.53	11.6
COMPO03	15.36	11.6

TABLE XIX
χ Values for the EFB–PU Composites Prepared from EFB–GMA in Various Types of Solvent

Composite	Ethanol	Toluene	DMF	Acetone
COMR	0.46	1.64	0.37	0.70
COMGMA01	0.46	1.64	0.37	0.70
COMGMA02	0.46	1.64	0.37	0.70
COMGMA03	0.46	1.64	0.37	0.70
COMGMA04	0.46	1.64	0.37	0.70

TABLE XXI
χ Values for the EFB–PU Composites Prepared from EFB–PO in Various Types of Solvent

Composite	Ethanol	Toluene	DMF	Acetone
COMR	0.46	1.64	0.37	0.70
COMPO01	0.46	1.64	0.37	0.70
COMPO02	0.46	1.64	0.37	0.70
COMPO03	0.46	1.64	0.37	0.70

The solubility parameters of all types of EFB–PU composite were determined by the plotting of the swelling coefficients of the samples against the solubility parameters of the solvents, as depicted in Figure 2 as an example. The solubility parameters of all of the composites produced were in the range 11.0–12.0. The actual solubility parameters of the composites were obtained from the maximum value of the equation shown in the figure. The solubility parameter results obtained are demonstrated in Tables XVI–XVIII. From the results obtained, the solubility parameter of the EFB–PU composites prepared from EFB–GMA and EFB–PO was 11.6. For composites prepared from low WPGs of EFB–ECH, the solubility parameter was 11.6 and increased to 11.7 when higher WPGs EFB–ECH was used (Table XVII). This increase was attributed to the high number of crosslinks and the distribution of chain branches or substitutive groups along the polymer backbone, which resulted in the restriction of chain mobility and the need for higher energy to overcome this limitation.[29]

Tables XIX–XXI depict the χ values of all of the types of composites produced. To obtain a completely miscible system, according to Flory–Huggins theory, the value of χ must be less than 0.5.[19,29,30] Thus, the results obtained indicate that toluene and acetone were not suitable solvents in this case. On the other hand, the relative swelling of the lignocellulosic material in various types of solvent must be considered. According to Stamm,[31] the relative swellings of lignocellulosic material in toluene, acetone, and ethanol are 0.016, 0.63 and 0.83, respectively. This showed that the swelling of the EFB in toluene, acetone, and ethanol was relatively lower than in DMF (1.23). In other words, DMF demonstrated the highest swelling coefficient compared to the others.

Thus, DMF and EFB–PU composites were miscible, with χ values of 0.36 and 0.37, respectively. These values were in line with the study carried out by Yoshida et al.,[32] where χ was determined for a series of PU–kraft lignin produced, and the values were in the range 0.38–0.39.

CONCLUSIONS

The network structure of the EFB–PU composite played an important role in the determination of the diffusion of solvents in the composite. Composites with higher void contents, such as the EFB–PO based composite, demonstrated higher capabilities for absorbing solvent. This was attributed to the presence of void, which could facilitate the penetration of solvent into the system. Meanwhile, the compatibility between the new attached group and solvent could have been a determining factor in this study. However, with a higher number of crosslink points, the sorption of the composites could be controlled. When we compared S values in the results obtained, we noticed that the sorption of the composite systems decreased in the following order: DMF > Acetone > Ethanol > Toluene. This was attributed to the compatibility of DMF with the PU matrix and EFB, which was better as compared those of to the others. With the consideration of all of the factors, the χ values obtained from solvent sorption results indicated that DMF and the EFB–PU composites were miscible.

References

1. Rossi, L. $900 Million Market for Natural and Wood Fiber Plastic Composites in North America and Europe According to New Principia Partners Study, 2002. http://www.global-hemp.com.news/2002/november/900_million_market.shtml (accessed July 2004).
2. Rial, T. G.; Wolcott, M. P. J Mater Sci Lett 1998, 17, 317.
3. Zetterlund, P.; Hirose, S.; Hatakeyama, T.; Hatakeyama, H.; Albertsson, A. C. Polym Int 1997, 42, 1.
4. Hatakeyama, H.; Hirose, S.; Hatakeyama, T.; Nakamura, K.; Kobashigawa, K.; Morohoshi, N. J Macromol Sci Pure Appl Chem 1995, 32, 743.
5. Hirose, S.; Kobashigawa, K.; Izuta, Y.; Hatakeyama, H. Polym Int 1998, 47, 247.
6. Kurimoto, Y.; Takeda, M.; Koizumi, A.; Yamauchi, S.; Doi, S.; Tamura, Y. Bioresour Technol 2000, 74, 151.

TABLE XX
χ Values for the EFB–PU Composites Prepared from EFB–ECH in Various Types of Solvent

Composite	Ethanol	Toluene	DMF	Acetone
COMR	0.46	1.64	0.37	0.70
COMECH01	0.46	1.64	0.37	0.70
COMECH02	0.44	1.74	0.36	0.74
COMECH03	0.44	1.74	0.36	0.74
COMECH04	0.44	1.74	0.36	0.74

7. Pavier, C.; Gandini, A. Eur Polym J 2000, 36, 1653.
8. Bledzki, A. K.; Zhang, W.; Chate, A. Compos Sci Technol 2001, 61, 2405.
9. Rozman, H. D.; Tay, G. S.; Abubakar, A. J Wood Chem Technol 2003, 23, 249.
10. Mathew, A. P.; Packirisamy, S.; Kumaran, M. G.; Thomas, S. Polymer 1995, 36, 4935.
11. Grundert, F.; Wolf, B. A. In Polymer Handbook; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1989; p VII/173.
12. Tay, G. S.; Rozman, H. D. J Appl Polym Sci 2007, 106, 1697.
13. Harogoppad, S. B.; Aminabhavi, T. M. Polymer 1990, 31, 2346.
14. Unnikrishnan, G.; Thomas, S. Polymer 1994, 35, 5504.
15. Desai, S.; Thakore, I. M.; Devi, S. Polym Int 1998, 47, 172.
16. Sreekala, M. S.; Kumaran, M. G.; Thomas, S. Compos A 2002, 33, 763.
17. Sreekala, M. S.; Thomas, S. Compos Sci Technol 2003, 63, 861.
18. Aithal, U. S.; Aminabhavi, T. M. J Appl Polym Sci 1991, 42, 2837.
19. Rosen, S. L. Fundamental Principles of Polymeric Materials, 2nd ed.; Wiley: New York, 1993.
20. Hill, C. A. S.; Abdul Khalil, H. P. S. J Appl Polym Sci 2000, 78, 1685.
21. Mohd Ishak, Z. A.; Yow, B. N.; Ng, B. L.; Khalil, H. P. S. A.; Rozman, H. D. J Appl Polym Sci 2001, 81, 742.
22. Zhang, F.; Endo, T.; Qiu, W.; Yang, L.; Hirotsu, T. J Appl Polym Sci 2002, 84, 1971.
23. Oksman, K.; Wallstrom, L.; Berglund, L. A.; Filho, R. D. T. J Appl Polym Sci 2002, 84, 2358.
24. Elvy, S. B.; Dennis, G. R.; Ng, L. T. J Mater Process Technol 1995, 48, 365.
25. Nair, K. C. M.; Diwan, S. M.; Thomas, S. J Appl Polym Sci 1996, 60, 1483.
26. Kellogg, R. M. In Concise Encyclopedia of Wood and Wood-Based Materials; Schniewind, A. P.; Cahn, R. W.; Bever, M. B., Eds.; Pergamon: Oxford, 1989.
27. Pothan, L. A.; Thomas, S. J Appl Polym Sci 2004, 91, 3856.
28. Strong, A. B. Plastics: Materials and Processing; Prentice Hall: Bew Jessey, OH, 2000.
29. Grulke, E. A. In Polymer Handbook; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1989; p VII/519.
30. Painter, P. C.; Coleman, M. M. Fundamentals of Polymer Science: An Introductory Text; Technomic: Basel, Switzerland, 1997.
31. Stamm, A. J. Wood and Cellulose Science; Ronald Press: New York, 1964.
32. Yoshida, H.; Morck, R.; Kringstad, K. P.; Hatakeyama, H. J Appl Polym Sci 1987, 34, 1187.