

Mechanical Properties of Polyurethane Composites From Oil Palm Resources

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ABSTRACT

Approximately 22% of waste from the oil palm industry consists of empty fruit bunch (EFB). This type of biomass along with a vast quantity of agricultural residues can be utilized in natural fibre-based composites. Previous studies on palm kernel oil have successfully turned it into a polyurethane polyol in producing natural oil-based polyurethane foam. The incorporation of different EFB fibre sizes at levels of 5.5% of 45-56 μm , 4.5% of 100-160 μm and 2.5% of 200-315 μm in the foam has shown tremendous improvement in the mechanical properties of the composites compared to the control foam. The compressive strength increased by 11.1%, 11.6% and 29.1% for the 45-56 μm , 100-160 μm and 200-315 μm fibre size, respectively. The 45-56 μm fibre size at 5.5% fibre loading showed the maximum compression strength and modulus. There is more tearing of cellular structure during expansion of the foams when larger size of fibres and larger amount of fibres are used. These lead to poor composite's strength. Micrographs of the cellular structure of the EFB-filled polyurethane foam showed that the presence of the fibrous EFB of size 200-315 μm torn the cellular structure, whereas the powder form of EFB filled the struts of the cellular network and enhanced the strength of the cell's wall.

Key Words:

empty fruit bunch fibres;
palm kernel;
oil-based polyurethane foam;
mechanical properties.

INTRODUCTION

Agrowaste and agroforest materials, for example sawdust, wood fibres, sisal and bagasse are slowly penetrating the market of reinforced plastics and filled polymers presently dominated by glass fibre and other mineral reinforcements. The use of natural

fibres is interesting because of their renewable nature, low cost, low density, and amenability to chemical modification.

Nevertheless, conventional wisdom holds that although wood fibres have been used as fillers in plastics

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for a long time, they do not act as reinforcing fillers. This means that while certain properties (e.g., stiffness) increase with filler content, and others (e.g., cost) decrease, the ultimate strength of a composite of wood fibres in a matrix decreases with increasing filler content [1].

The composite properties depend on those of the individual components and on their interfacial compatibility. Several research works have been carried out to identify the parameters that govern mechanical behaviour of particulate composites. Generally, it has been found that the reinforcement effect increases with decreasing particle size and with increasing adhesion to the matrix [2]. Rozman et al. (2001) and Mohd et al. (1998) have used oil palm empty fruit bunch fibre (EFB) as filler in their plastic composites. Rozman et al. (2001) have blended EFB and glass fibre in the polypropylene (PP) matrix to form a hybrid composite with improving strength by the usage of coupling agents. Coupling agents used were Epolene (E-43-a maleic anhydride-modified PP) and 3-(trimethoxy silyl)-propylmethacrylate (TPM). The flexural strength and modulus increased as the loading of coupling agents is increased. Both readings are as high as 22 MPa and 3.2 GPa, respectively at 5% of E-43 and 17 MPa and 2.8 GPa, respectively when TPM is used. The presence of the coupling agents improved the compatibility between both the glass fibre and EFB, and the PP matrix, resulting in the increased stiffness [3].

Mohd et al. (1998) have reported that the role of EFB as reinforcing agent is not fully realized when they prepared blend of EFB with high-density polyethylene (HDPE) to form a composite even with the treatment of EFB with coupling agents such as 3-aminopropyltrimethoxysilane (3-APM) and 3-aminopropyltriethoxysilane (3-APE). Poor strength is displayed by the composites in the aspect of tensile strength, elongation-at-break and impact strength due to strong tendency of the EFB to exist in the form of bundles. This nature of EFB has a strong influence on the efficiency of stress transfer and mode of failure of the composites, resulted in a relatively poor stress transfer from the matrix to the filler [4]. Ridzuan et al. (2002) have successfully produced medium-density fibreboard (MDF) from EFB fibre. Higher dosage of urea formaldehyde resin used as binder improved the physical and mechanical properties of the MDF [5].

Lignocellulosic materials such as empty fruit bunch fibres from the oil palm industry are either burnt or stored under conditions, which do not meet the standards customary in Western Europe. Forest Research Institute of Malaysia (FRIM) and Malaysian Palm Oil Board (MPOB) have carried out years of fundamental research in finding potential of using oil palm residues as raw materials for various products. About 18.68 million tons of FEB have been generated besides 270.72 million tons from other biomass by the oil palm sector during the period of 2001-2005 in Peninsular Malaysia alone [6]. As such, efficient processing mechanism is indeed essential to create demand of the oil palm fibres in manufacturing value-added products.

Incorporation of lignocellulosic materials in polyurethane (PU) rigid foam could provide a powerful approach for the enhancement of its mechanical properties and the introduction of biodegradability to the foam products. Glasser et al. have prepared PU from hydroxyalkylated lignin [7]. Hirose et al. have found that molasses could be used to produce PU foams and sheets [8]. Hatakeyama et al. attempted several types of lignin, wood meal and wood tar residue for making PU in the form of sheet, foam and composites [9].

This paper explores the theoretical understanding of composites, which comes primarily from mechanical engineering, and what that can tell us about wood fillers in polyurethane. This view of wood-polymer composites can help us in two ways. It gives us a basis from which to make comparisons of composite performance. It also serves as a background understanding on the relationship of size and loading percentage of filler in the matrix with the mechanical properties of the composites. This paper focuses on two objectives, that is to study the potential of empty fruit bunch fibre as filler in polyurethane and to identify the effect of the EFB fibre size and loading on the mechanical properties of the low-density polyurethane rigid foam.

EXPERIMENTAL

Materials

Refined, bleached and deodorized palm kernel oil (RBD PKO) was supplied by Lee Oilmill, Klang, Malaysia and was used without further purification. The palm kernel oil-based polyester as the starting raw

material was prepared and characterized as reported by Badri et al. [10-11]. The crude isocyanate (4,4-diphenylmethane diisocyanate) was obtained from Cosmopolyurethane, Port Klang, Malaysia.

Polyurethane additives such as silicone surfactant (Tegostab B8408) and amine catalyst (dimethylhexane-diamine) were obtained from local chemical suppliers. The EFB strands of 3 cm long were obtained from Sabuteks Sdn Bhd, Perak, Malaysia and were refined using Refiner Mechanical Pulping Machine model Sprout Waldron Refiner 150A. The fibres were screened to sizes of 45-56, 100-160 and 200-315 μm , and dried in a vacuum oven at 105°C for 20 h. The moisture content is then being determined.

Sample Preparation

The palm kernel oil-based polyester and the polyurethane additives were blended with water as the blowing agent using a Cole-Parmer overhead mixer with speed of 2000 rpm for 300 s. The surfactant and the catalyst were used at fixed amounts. The EFB fibres/powder were added based on weight percentage of the overall weight of polyol resin (w/w %). The mixture was then stirred for another 60 s for homogeneity of resin mixture.

The polyurethane foams were prepared by adding the crude isocyanate to the resin mixture as listed in formulations tabulated in Table 1. The first stage of foaming involved the observation of the reactions and its flowability. The reaction stages are classified as the cream time, CT (starting of reaction), fibre time, FT (phase change from liquid phase of resin and isocyanate to solid phase, the polyurethane) and tack-free time, TFT (completion of reaction). The free-rise density was also determined by dividing the mass of the

free-rise foam with its volume. The flowability of the composite systems was monitored using method described by Colvin [12] and measured as flow index in unit of cm g^{-1} . For the second stage, the same mixture was prepared and was poured into a 1-L closed mould and allowed to rise at room conditions. After 30 min, the polyurethane block was taken out and conditioned at ambient temperature for 16 h. The block was cut into specific dimensions based on British Standard BS4370: Part 1: 1988 for further evaluations.

Characterizations

Measurement of the Apparent Density

Foams samples were cut using a bench-saw into cubes of 100 mm \times 100 mm \times 100 mm in dimensions. Foam core density was calculated following BS4370: Part 1: 1988 (method 2) using the equation of mass, kg divided by volume m^{-3} . The apparent moulded density was determined by the same method but without trimming off the outer part (skin) of the foam. Only foam with core density of 37-38 kg.m^{-3} will be taken as testing samples.

Dimensional Stability

The percentage of change in the linear dimension of the foams was determined by exposing the specimens under two different conditions. The specimens were tested at $-15\pm 2^\circ\text{C}$ for 24 h and at $+70\pm 2^\circ\text{C}$ with 90% relative humidity for 24 h (BS 4370: Part 1: 1988-Method 5B).

Compression

The compressive strength test was carried out on a Universal Testing Machine Model Testometric Micro 350 following BS 4370:Part 1: 1988 (Method 3) at $23\pm$

Table 1. Resin formulations for unfilled and EFB fibres-filled PU foams for 45-56, 100-160 and 200-315 μm particle sizes.

Ingredients	0 (%)	1.5 (%)	2.5 (%)	3.5 (%)	4.5 (%)	5.5 (%)	6.5 (%)
PKO-based polyol	100	100	100	100	100	100	100
B8408	2	2	2	2	2	2	2
Amine	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Water	4.5	5.0	5.3	5.6	5.9	6.2	6.4
EFB	-	1.61	2.70	3.79	4.88	5.98	7.08
Total pbw	106.95	109.06	110.45	111.79	114.23	115.63	115.93

Note: Although an increasing amount of water might affect the OH/NCO ratio, this study fixed the blending ratio of the resin to the crude MDI at 100:100 for better comparison.

2°C at a cross-head speed of 50 mm min⁻¹. Square bars (50 mm side) were cut from the moulded foam at rising direction of the foam. The compression stress at 10% deflections, compression stress at 5% strain and compression modulus were noted which followed the standard of BS 4370:Part1:1988.

The replicates for all the characterizations will follow requirements of the British Standard as specified in BS4370: Part 1:1988.

RESULTS AND DISCUSSION

The specimens were prepared with a core-density ranging from 37 to 38 kg.m⁻³. Thus, an excess amount of water was added as the weight percentage of EFB particulate increased as shown in Table 1. This is in relation to the hygroscopic property of EFB where the added water is absorbed by the EFB. The additional water required resulted in dilution of the whole resin system, led to dilution of catalyst in the system. This resulted in a slower chemical reaction when more fibres are added into the resin. Smaller EFB size created a much faster reaction due to its higher surface ratio. Since EFB consisted of 65% holocellulose, the hydroxyl site on the molecular structure becomes the active site for the reaction (13-14). Higher surface ratio resulted in larger active surface for the reaction to take place. The results are shown in Tables 2-4. The flow of the whole polyurethane system (Figures 1-3) was restricted by the EFB loading percentage and size. Higher EFB loading and larger EFB size deteriorated the cellular structure of the foam creating layers of ruptured cell wall. As the EFB loading increased, the viscosity of the

Table 2. Reaction time of 45-56 µm EFB in the polyurethane composite.

EFB loading (%)	0	1.5	2.5	3.5	4.5	5.5	6.5
Cream time (s)	23	24	24	24	20	24	23
Fibre time (s)	71	92	92	75	85	91	90
Tack-free-time (s)	105	146	146	117	141	144	145

Table 3. Reaction time of 100-160 µm EFB in the polyurethane composite.

EFB loading (%)	0	1.5	2.5	3.5	4.5	5.5	6.5
Cream time (s)	23	25	23	24	24	25	25
Fibre time (s)	71	74	72	74	81	84	83
Tack-free-time (s)	105	120	107	126	136	147	188

Table 4. Reaction time of 200-315 µm EFB in the polyurethane composite.

EFB loading (%)	0	1.5	2.5	3.5	4.5	5.5	6.5
Cream time (s)	23	24	22	22	24	28	30
Fibre time (s)	71	71	67	67	73	82	98
Tack-free-time (s)	105	117	116	145	128	141	173

systems increased. This resulted in difficult flow of the system and an increase in the foam density was observed. This phenomenon is observed less in composite with smaller EFB. This is clearly shown in Figures 1-3.

The dimensional stability test was carried out to observe any severe expansion and shrinkage problems on the foam (percentage of change in linear dimension should be lesser than 1 and 3% for testing conditions of -15°C and 70°C for 24 h, respectively following the

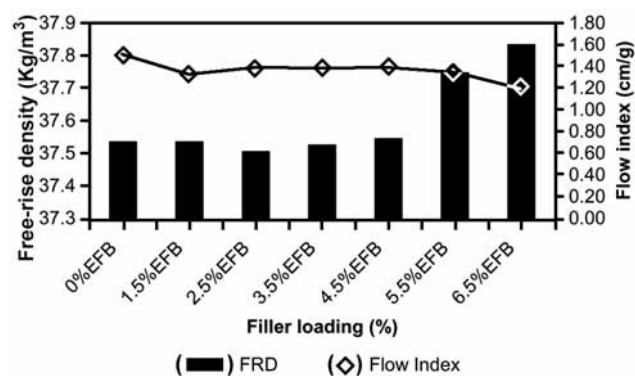


Figure 1. Free-rise density (FRD) and flow index of 45-56 µm EFB in the polyurethane composite.

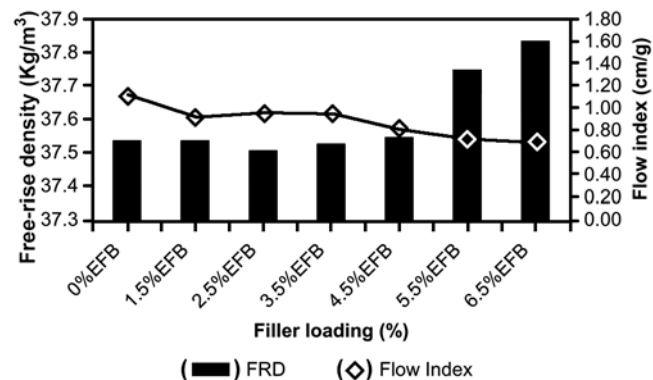


Figure 2. Free-rise density (FRD) and flow index of 100-160 µm EFB in the polyurethane composite.

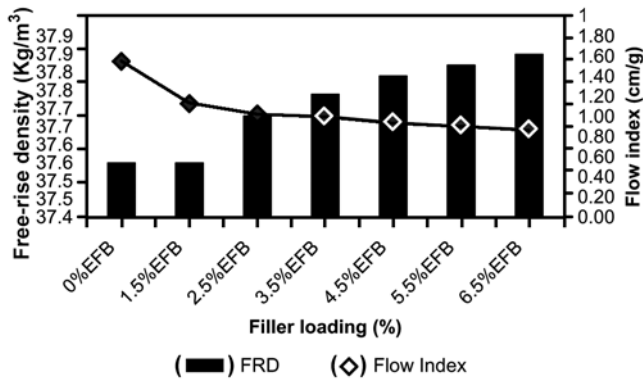


Figure 3. Free-rise density (FRD) and flow index of 200-315 μm EFB in the polyurethane composite.

British Standard). This is to ensure the stability upon heat or cold temperature. Since this property depends on the cell shape and size, the thickness of the foam is the major part that is of concern, as it represents the foam rise direction. The larger the size of the fibre, the

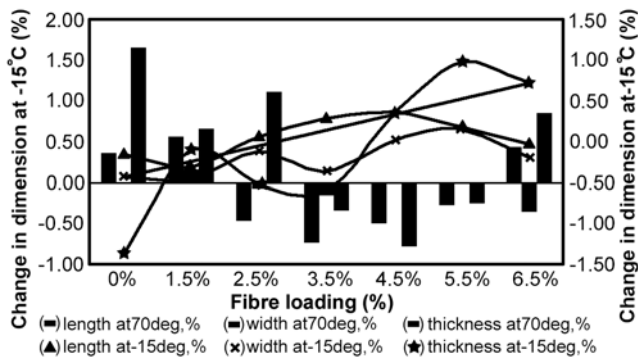


Figure 4. Percentage change in the linear dimension of the 45-56 μm EFB in the polyurethane composite at -15 and 70°C for 24 h.

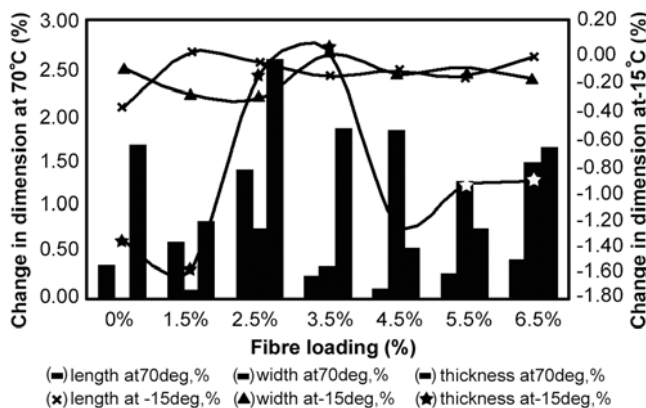


Figure 5. Percentage change in the linear dimension of the 100-160 μm EFB in the polyurethane composite at -15 and 70°C for 24 h.

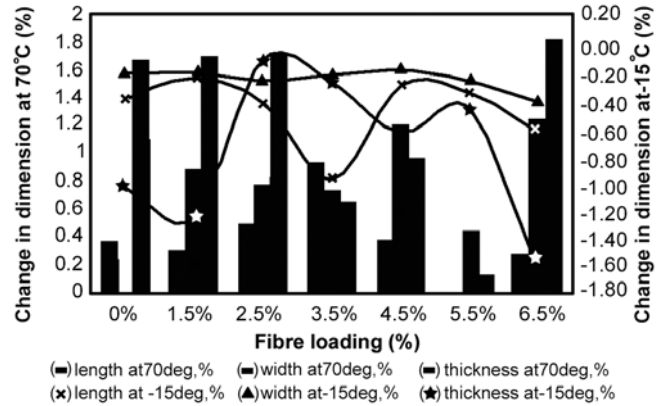


Figure 6. Percentage change in the linear dimension of the 100-160 μm EFB in the polyurethane composite at -15 and 70°C for 24 h.

higher the percentage of linear change in the foam dimensions as a function of thickness is. EFB Particulate with 45-56 μm size showed a within-range result for both testing temperatures as shown in Figure 4. The 200-315 μm EFB particulate (Figure 5) exhibited a deteriorating dimensional stability. This is due to tearing of the cell wall during expansion of the foam and resulted in a faster diffusion rate of carbon dioxide produced during the polymerization, outward to be replaced by the air inward. The same explanation is applied to 100-160 μm EFB composite which is represented by Figure 6.

Maximum stress at 10% deflection (industrial standard of more than 180 kPa) for 45-56, 100-160 and 200-315 μm were observed at 5.5, 4.5 and 2.5% of fibre loading, respectively (Figure 7). The trend decreased thereafter. No obvious fluctuation on the 45-56 μm particulate curve was observed. The compressive strength increased by 11.1%, 11.6% and 29.1% for

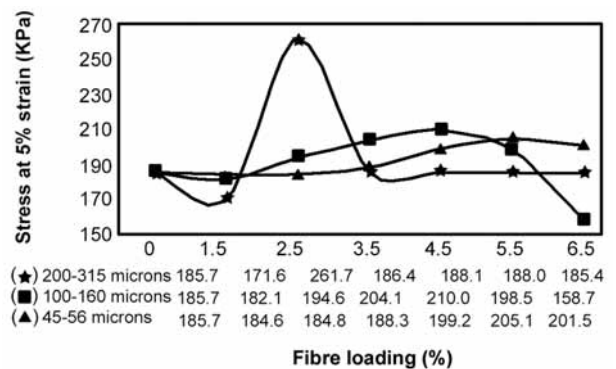


Figure 7. Compressive stress at 10% deflection as a function of fiber contents for various sizes of EFB particulate.

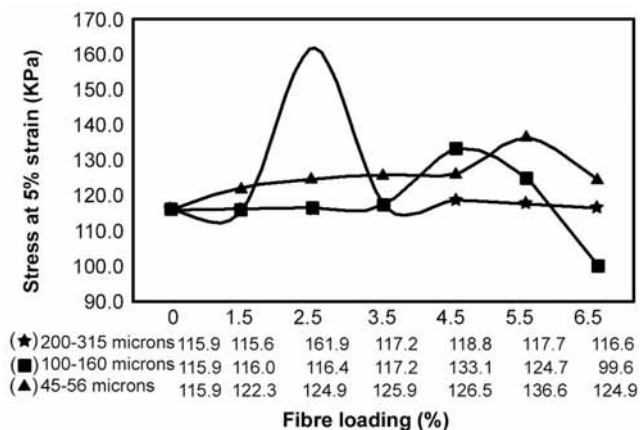


Figure 8. Compressive stress at 5% strain as a function of fibre contents for various sizes of EFB particulate.

the 45-56 μm , 100-160 μm and 200-315 μm fibre size, respectively. The same trend was observed at 5% strain as shown in Figure 8. Better dispersion of particulate matter in powder form was observed in the polymer

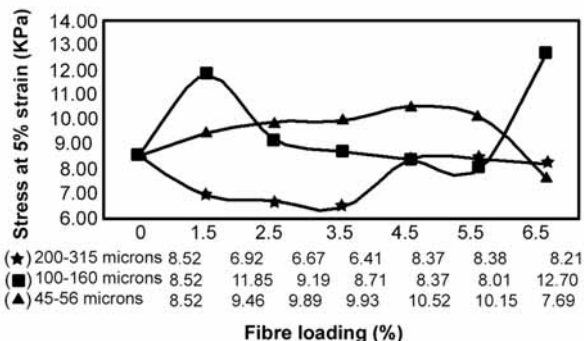
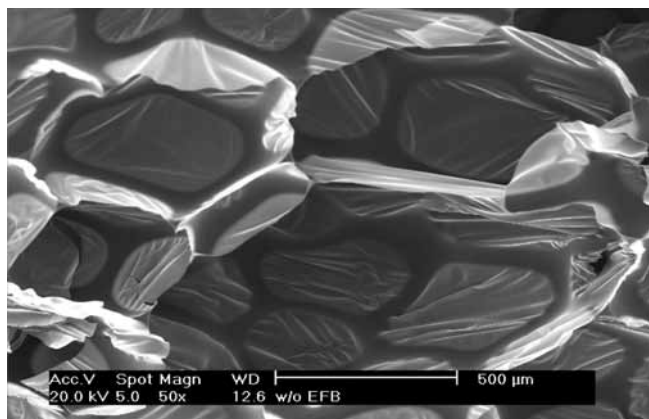
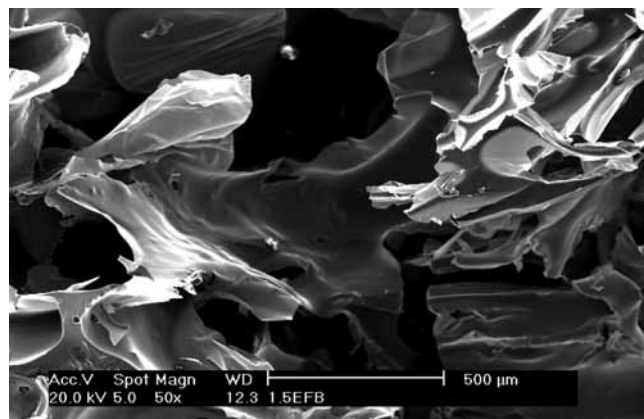


Figure 9. Compression modulus as a function of fibre contents for various sizes of EFB particulate

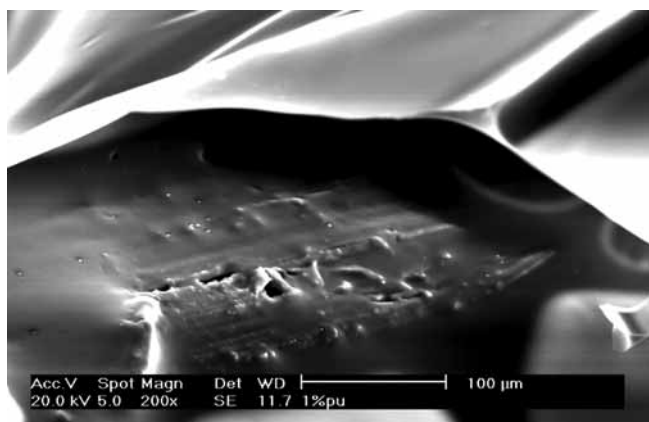
matrix. The particulate tends to form a morphological domain in the matrix so that the regions of discontinuities, which are possible with a fibrous matrix, are absent. Fibre with a high degree of lignin (which contains polar hydroxyl groups) on its surface may have the tendency to agglomerate through the formation of the hydrogen bonding. The agglomeration may then



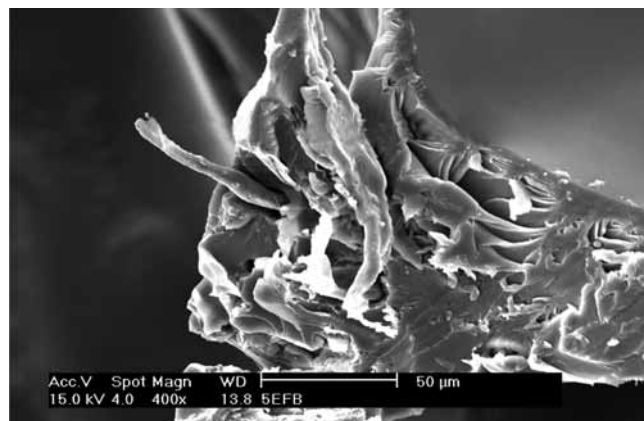
(a)



(c)



(b)



(d)

Figure 10. SEM Micrographs of the: (a) unfilled PU, (b) EFB-filled PU with EFB in powder form, (c) EFB-filled PU with EFB in fibrous form, and (d) fibre bundle pull-out in the PU composite.

produce discontinuity in the matrix, which subsequently creates stress concentration point in the composite samples. The subject can be exemplified further with the qualitative evidence obtained from the scanning electron microscopy (SEM) study as shown in Figure 9.

The modulus of the unfilled and filled foams produced are shown in Figure 10. The modulus for 45-56, 100-160 and 200-315 μm of particulate obtained was at maximum of 5.5, 4.5 and 2.5% fibre loading, respectively. Generally, it appears that sample with smaller particle size produces higher compression modulus, similar to the trend observed in the compression stress in Figure 7. This is parallel to previous works with EFB in thermoset matrix where the smaller the particle size the higher the strength, where factors other than fibre length such as mode of failure, plasticization and better tendency for consolidation in moulding play significant role [7-9]. It is believed that the deciding factor in the present case appears to be the availability of EFB hydroxyl, OH groups which created an active participation with the isocyanate in the formation of urethane bonding, leads to an integrated thermoset matrix. Lower aspect ratio in the 100-160 and 200-315 μm EFB -PU composites prepared less exposed OH sites, resulting in the creation of more stress points and poor compression stress and modulus. The limiting factor is the accessible OH groups.

From SEM studies (Figure 10), one would arrive with the conclusion that the interphase morphology with reduced quantity of PU would normally be associated with reduced strength values as the OH content of the EFB increases (since lesser polyol is used to keep the OH constant). However, this is valid only when smaller EFB particle (Figure 10b) is used rather than larger size such as the 200-315 μm EFB (Figure 10c). This clearly shows that an effective interaction has occurred between OH groups of smaller EFB particle and isocyanate to produce sufficient covalent bonds to give rise to higher mechanical strength at much higher fibre loading. It can be seen that the 45-56 μm EFB at 5.5% loading is nicely embedded in the matrix (Figure 10b). It is clear that the interfacial region between these two components is continuous. This is an indication that some interaction has occurred between OH from EFB and the isocyanate.

Those samples with EFB size of either 100-160 μm and 200-325 μm (Figure 10d) appear to have some

occurrence of fibre pull-out. Less matrix is deposited per unit area for samples with bigger size EFB (smaller surface area) as opposed to smaller EFB (larger surface area). This would leave explain why fibre pull-out are quite obvious in these samples.

CONCLUSION

PU Foam with refined 45-56 μm EFB particulate showed a superior compressive stress. This again may be attributed to the higher surface area of the EFB in powder form, which may produce better hindrance to stress-impact propagation. This may again indicate the influence of the higher surface area of the powdered EFB, as it leads to more contact surface with the matrix.

These data support the importance of compatibilizing the filler with the matrix. At higher filler levels, all polyurethane systems seem to exhibit decreasing strength. This may be due to decreased wetting of the fibre by the matrix as the ratio of filler surface area to matrix volume has reached the highest values possible (saturating point). Higher filler loading will decrease the degree of encapsulation of matrix around the filler. In fact, at higher filler loading, the filler has the tendency to tear the wall of the cellular structure. These walls, which tend to support the whole system becoming weakened and upon higher loading, the PU system would lose its strength. This is clearly shown in the decrease in modulus which indicate the poor rigidity of the PU foam.

The overall increase in the compression stress and modulus for the refined EFB-filled composites shows the ability of the filler either in fibre or powder form to impart greater stiffness to the composites. However, lignocelulosic materials present high moisture absorption and low microbial resistance, which are disadvantages that need to be considered and corrected.

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SYMBOLS & ABBREVIATIONS

EFB	Empty fruit bunch
RBD	Refined, bleached, deodorized
PU	Polyurethane
PKO	Palm kernel oil
CT	Cream time
FT	Fibre time
TFT	Tack free time
BS4370	British Standard 4370
pbw	Part by weight
MDI	2,4-Diphenylmethane diisocyanate
NCO	Nitrogen-carbon-oxygen
OH	Hydroxyl

REFERENCES

1. Saheb D.N., Jog J.P., Natural fibre polymer composites: A review. *Adv. Polym. Technol.*, **18**, 351-363 (1999).
2. Wu J., Yu D. Chan C., Kim J., Mai Y., Effect of fibre pre-treatment condition on the interfacial strength and mechanical properties of wood fibre/PP composites. *J. Appl. Polym. Sci.*, **76**, 1000-1010 (2000).
3. Rozman, H.D., Tay G.S., Kumar R.N., Abusamah A., Ismail H., Mohd Ishak Z.A., Polypropylene-oil palm empty fruit bunch-glass fibre hybrid composites: A preliminary study on the flexural and tensile properties. *Eur. Polym. J.*, **37**, 1283-1291(2001).
4. Mohd Ishak Z.A., Aminullah A., Ismail H., Rozman H.D., Effect of silane-based coupling agents and acrylic acid based compatibilizers on mechanical properties of oil palm empty fruit bunch filled high-density polyethylene composites. *J. Appl. Polym. Sci.* **68**, 2189-2203 (1998).
5. Ridzuan R., Shaler S., Mohd Ariff J., Properties of medium-density fibreboard from oil palm empty fruit bunch fibre., *J. Oil Palm Res.* **14**, 34-40 (2002).
6. Haron N., Ibrahim W.A., Mohd Idris M.A., Availability of oil palm residues in peninsular Malaysia. In: *Proc. of the 4th Nat. Sem. on Util. Oil Palm Tree: Oil Palm Residues-Progress Towards Commerce.*, 207-214 (1997).
7. Glasser W.G., Saraf V.P., Hydroxyalkylated lignin from plants as potential reinforcement in polyester matrix. *J. Appl. Polym. Sci.*, **29**, 1831-1839(1984).
8. Hirose S., Kobashigawa K., Hatakeyama H., Sen-I-Gakkaishi., Properties of polyurethane composites from pineapple molasses., *J. Appl. Polym. Sci.* **50**, 538-547 (1993).
9. Hatakeyama H., Hirose S., Nakamura K., Hatakeyama T.Ed. Kennedy J.F., Phillips, G.O. , Williams, P.A., *Cellulose: Chemical, Biochemical and Material Aspects*. UK Ellis Harwood (1993).
10. Badri K.H., Ahmad S.H., Zakaria S., Preparation and characterization of polyurethane polyol from RBD palm kernel oil., *Proc. Malay. Sci. Technol. Cong.*'99, 61-68 (1999).
11. Badri K.H., Ahmad S.H., Zakaria S., Development of a zero-ODP polyurethane foam from RBD palm kernel oil polyol, *J. Mater. Sci. Lett.*, **19**, 1355-1356 (2000).
12. Colvin B.G., Low cost polyols from natural oils. *UTech Asia '95*, **36**, 1-10 (1995).
13. Sanadi A.R., Young R.A., Clemons C., Rowell R.M., Recycled newspaper fibres as reinforcing fillers in thermoplastics: Part I. Analysis of tensile and impact properties in polypropylene, *J. Reinf. Plast. Comp.*, **13**, 54-67 (1994).
14. Benli S., Yilmazer Ü., Pekel F., Özkaz, S., Effect of fillers on thermal and mechanical properties of polyurethane elastomer., *J. App. Polym. Sci.*, **68**, 1057-1065 (1998).
15. Wu J.S., Friedrich K., Grosso M., Impact behavior of short fibre/liquid crystal polymer composites, *Composites* **20**, 223-233 (1989).
16. Marcovich N.E., Reboredo M.M., Aranguren M.I., Dependence of the mechanical properties of the wood-flour-polymer composites on the moisture content., *J. Appl. Polym. Sci.*, **70**, 2121-2131 (1998).