

The Effect of Glycidyl Methacrylate Treatment of Empty Fruit Bunch (EFB) on the Properties of Ultra-Violet Radiation Cured EFB-Unsaturated Polyester Composite

H. D. Rozman, A. R. Rozyanty, G. S. Tay, R. N. Kumar

Bio-Resource, Paper and Coatings Technology Division, School of Industrial Technology, Universiti Sains Malaysia, 11800 Pulau Pinang, Malaysia

Received 28 May 2008; accepted 24 November 2008

DOI 10.1002/app.29791

Published online 26 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, biofiber composites cured by ultra-violet, were produced using pulp made from empty fruit bunch (EFB) as the reinforcing agent and unsaturated polyester as the matrix. The conversion of EFB fibers into pulp was carried out using organosolv pulping process. The EFB pulp was then chemically treated with glycidyl methacrylate (GMA) to different percentage of weight percent gain and the composites were made with different percentages of pulp loading. Results showed that the Kappa number of EFB decreased as the NaOH concentration in organosolv pulping increased. Composites which

were made from GMA-treated EFB showed better mechanical properties (tensile, flexural, and impact strength) than those of the unmodified. Fourier transform infrared spectroscopy showed peaks that proved the occurrence of grafting between GMA and OH from EFB pulp. Scanning electron microscope analysis showed the evidence of the enhancement of the compatibility between EFB and matrix. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2677–2682, 2010

Key words: composites; ultraviolet radiation; oil palm empty fruit bunch

INTRODUCTION

The utilization of natural fiber reinforcement in synthetic polymer composites has gained importance over the years.¹ Natural fiber is renewable and can be used in fiber reinforced composites to replace glass and other nonrenewable fibers. These fibers are cheaper and less abrasive to tools. The oil palm industry in Malaysia generates large quantities of biomass. Recent investigations show that various products can be produced from the by-products of the palm oil industry, such as oil palm component-plastic composite,² oil palm component-rubber composite,³ sheet molding compound,⁴ and pulp-paper.⁵ Besides low cost, natural fibers in composites have lower specific gravity, higher specific tensile strength, biodegradable, and are less energy intensive to process.⁶ Ultra-violet (UV) curable systems are used in surface coatings and have several distinct advantages such as solvent free, environmentally friendly, and energy saving.⁷ The entire curing process occurs at room temperature and hence does not require expensive high temperature equipment for the curing.⁸ In view of the above advantages and

the success of the photofabrication of polymer matrix composites, attempts have been made to produce polymer matrix composites reinforced with NaOH-treated empty fruit bunch (EFB) fibers and employing UV radiation to cure the polymer matrix.

The thermoset fiber reinforced polymer matrix composites are currently produced from unsaturated polyester resins by thermally induced initiators. Examples are polyester prepregs, sheet molding compounds, bulk molding compounds, etc.⁹ The production of these composites involves high temperatures and requires expensive molds and hydraulic presses. Room temperature curing of such systems takes a long time. UV radiation are widely used throughout the world and also in Malaysia in surface coatings especially in wood industry and followed by printing, electronic, and adhesive industry.¹⁰ In recent times photocuring process has been adopted for making composites that may prove superior to the thermal curing systems. This process employs UV radiation to cure the composites. In view of the advantages of UV curing system and the success of the photofabrication of polymer matrix composites by the use of UV radiation,¹¹ attempts have been made to apply the radiation curing technology for the production of biofiber-composites. In this study, the effect of surface treatment of EFB with glycidyl methacrylate (GMA) was studied.

Correspondence to: G. S. Tay (taygs@usm.my).

EXPERIMENTAL

Materials

Unsaturated polyesters P9728 was purchased from Euro Chemo Pharma Sdn. Bhd., Malaysia. EFB was obtained from Sabutek Sdn. Bhd (M), Teluk Intan, Perak, Malaysia. Photoinitiator IRGACURE 1800 was supplied by Ciba Specialty (Singapore) Pte. Ltd.

Preparation of composites

EFB was pulped using pulper IBSTEK ZAT 92 under the following conditions; fiber : liquor ratio (1 : 8, weight based) at 165°C for 2 h. The composition of the liquor was as follows: 30% ethanol, 0.1% anthraquinone with either 20 or 30% of NaOH concentration. Fibers were formed into mat (20 × 20 cm²) in a deckle box by the procedure reported earlier¹¹ and dried in an oven at 105°C for 24 h. After that, mats were pressed using hot press Gotech Testing Machine Inc model GT-7014-100 (2 min, 500 kg/cm², 100°C) and the thickness of the mats were controlled to ~ 1 mm. Three percent (3%) of photoinitiator IRGACURE 1800 was mixed with unsaturated polyester and poured onto EFB mat. The mat was impregnated with resin and the air bubbles if any were removed by means of a hand roller. The mat was then sandwiched between two glass panels. After impregnation, mats were passed through 1ST UV machine (model M20-1-Tr-SLC) for twenty passes at conveyor speed of 10 m/min. The machine consists of a medium pressure mercury arc lamp with the UV radiation wavenumber of 180–450 nm.

Chemical treatment of EFB pulp

The EFB pulp was reacted at 90°C with GMA which was diluted in *N,N*-dimethylformamide (2 : 3, *v/v* ratio) for two selected period of reaction times (90 and 150 min). To minimize the risk of free radical reaction at the unsaturated ends of GMA during the reaction, hydroquinone (5% weight of GMA) was added. After reaction, the treated pulp was separated from the liquid reagents by filtration, rinsed with acetone and refluxed with excess acetone for about 3 h to remove solvent, unreacted reagent, and any nonbonded polymer formed during the reaction. Chemical loadings of the reagents were calculated as follows:

$$\text{Weight percent gain (WPG)(\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 is the oven-dried (105°C) weight before reaction and W_1 is the oven-dried (105°C) weight after reaction.

Small samples were withdrawn from these products, milled to fine flour and examined in transmission as KBr discs using Fourier transform infrared (FTIR) spectroscopy. All recorded spectra comprised 200 scans using Nicolet Avatar 360, operating at 4 cm⁻¹ resolution.

Testing

The composites produced were cut into three types of test sample: i.e., flexural, tensile, and impact tests. Tensile tests were carried out on samples with dimension of 10 × 1.5 × 0.2 cm³, using Universal Testing Machine model STM-10 at a crosshead speed of 1 mm/min, according to ASTM D-3039. Flexural tests were conducted according to ASTM D-790, i.e., a three-point bending method using Universal Testing machine model STM-10. The samples, with dimension of 8 × 1.2 × 0.2 cm³ were tested at a crosshead speed of 1.0 mm/min. The Izod impact tests were carried out on unnotched samples with dimension of 6.5 × 1.2 × 0.2 cm³, using an Impact Pendulum Tester (Zwick) model 5101 according to ASTM D252. A minimum of eight samples were tested in each case. Kappa number test was used to determine the delignification degree according to TAPPI 236 cm-85. The percentage of curing of unsaturated polyester resin with and without GMA was determined by the Gel Content test according to ASTM D2765.

Scanning electron microscope study

The fracture surfaces of tensile test samples were studied with a Scanning electron microscope (SEM) (Model Leica Cambridge S-360). The samples were mounted on an aluminum stub using double-sided tape and then gold-coated with a Polaron SEM coating unit to prevent electrical charging during examination.

RESULTS AND DISCUSSIONS

Table I shows that as the percentage of NaOH increases from 20 to 30% in the solution, the Kappa number decreases and the gel content (degree of cure) increases. As the Kappa number reflects the quantity of lignin present in a sample, the results show that as the amount of lignin decreases, the crosslinked-fraction of the matrix (gel content) increases. This indicates that as the quantity of lignin decreases, the extent of UV radiation being absorbed by the former is also decreased. This would leave more light energy to cure the monomer system to produce crosslinked polymer matrix. During the curing of composites by UV radiation, lignin competes with photoinitiator for the photon. Thus, if less

TABLE I
The Effect of NaOH Content on the Kappa Number, Brightness and Gel Content

Sample	Untreated pulp	GMA-treated pulp	GMA-treated EFB pulp-unsaturated polyester composite	
	Kappa no.	WPG (%)	Brightness (%)	Gel content (%)
20% NaOH	12	0	41	98.0
		5	34	98.2
		8	30	98.8
		12	27	99.1
30% NaOH	8	0	45	98.5
		5	36	98.7
		8	33	99.5
		12	28	99.6

lignin is present in the composite, more photoinitiator would be able to absorb the radiation and disintegrate to produce free radicals. Hence, more crosslinks would be produced through the unsaturation sites along the polyester molecular chain.

The results also show that the gel content increases in tandem with brightness. As a sample becomes brighter, UV light would be able to penetrate into greater depth of the sample and results in greater degree of curing and thus increase the gel content. It should be noted that as the weight percent gain (WPG) is increased, the gel content increases. This proves that GMA which is chemically attached to EFB promotes the radical copolymerization with the unsaturated sites on the unsaturated polyester resin. The results also indicate that the effect of the reaction of attached GMA to EFB with unsaturated polyester resin with regards to gel content outweighs the reduction in brightness.

Figures 1 and 2 show that all composites display an increasing trend of tensile strength and modulus as the WPG increases. This indicates that through modification of EFB surface with GMA, the distribu-

tion of stress transfer from the matrix to the fiber is somewhat improved. This may be attributed to the increased compatibility at the interfacial region between EFB and the polyester matrix. The increased compatibility may affect the mobility of the resin polymer, thus, resulting in the increased modulus. This phenomenon is further supported by the elongation at break results (Fig. 3), which is reciprocal to those of tensile modulus. This phenomenon is supported by the SEM study which will be discussed later. Overall, composites with 10% EFB display higher tensile strength and modulus than those with 15% EFB. This is expected because the more lignocellulosic component is incorporated into a polymer matrix, the greater will be the disruption of the homogeneity of the matrix.² This influences the efficient stress transfer from the matrix to the fiber. Thus, in general, those with 15% EFB exhibit lower mechanical properties. The same behavior is shown for flexural and impact properties.

As shown by previous studies,^{3,12,13} the compatibility between the matrix and filler or reinforcing agent is crucial in obtaining optimum mechanical

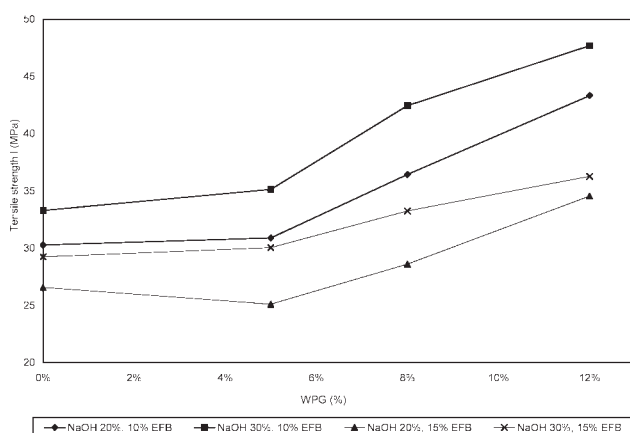


Figure 1 The effect of WPG of GMA on the tensile strength of EFB-unsaturated polyester composite.

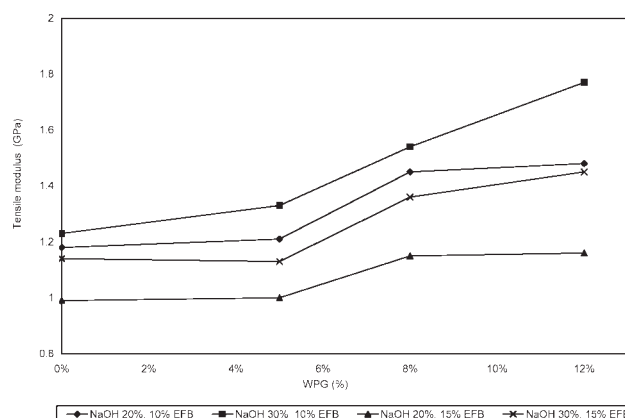


Figure 2 The effect of WPG of GMA on the tensile modulus of EFB-unsaturated polyester composite.

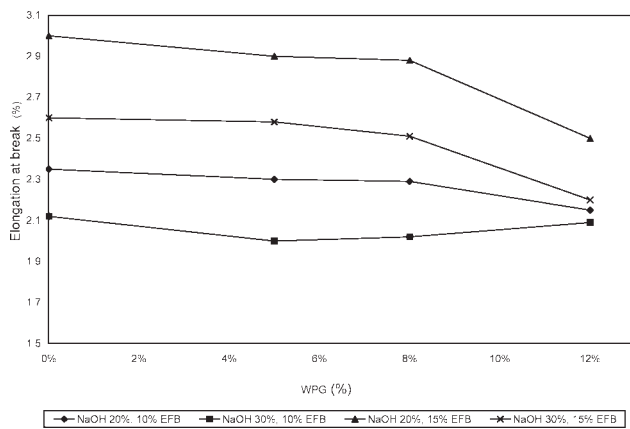


Figure 3 The effect of WPG of GMA on the elongation at break of EFB-unsaturated polyester composite.

properties. It is even more important in the case of plant fibers where they are hydrophilic when compared with the hydrophobic matrix.

The modification of EFB with GMA through the reaction of OH of the former with the epoxy groups of the latter, introduces thermally and photochemically labile terminal C=C groups [eq. (1)]. With the presence of radical initiator in the unsaturated polyester system, the C=C groups are expected to form covalent bonding with the matrix system [eq. (2)]. Thus, a system of covalent bonding is expected, linking EFB via GMA with the unsaturated polyester matrix. This, in turn enhances the compatibility at the interfacial region of the two components.

The improvement in the compatibility may be due to the sequence of reactions which are shown below:

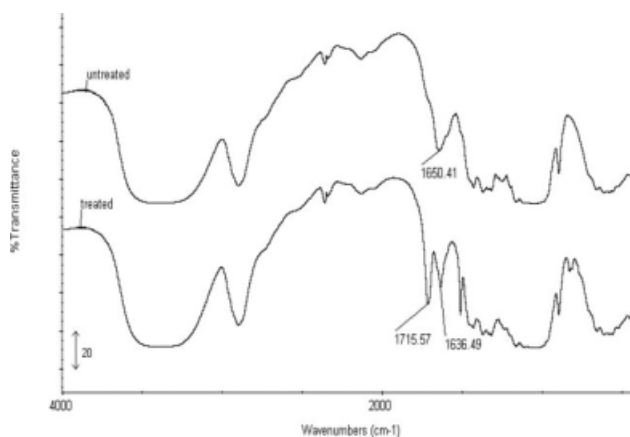
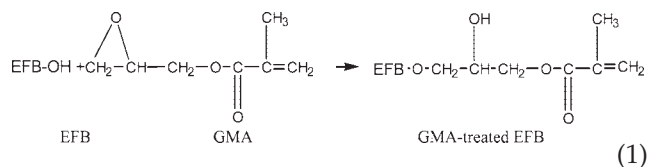


Figure 4 FTIR spectra of untreated EFB fiber and GMA-treated EFB fiber.

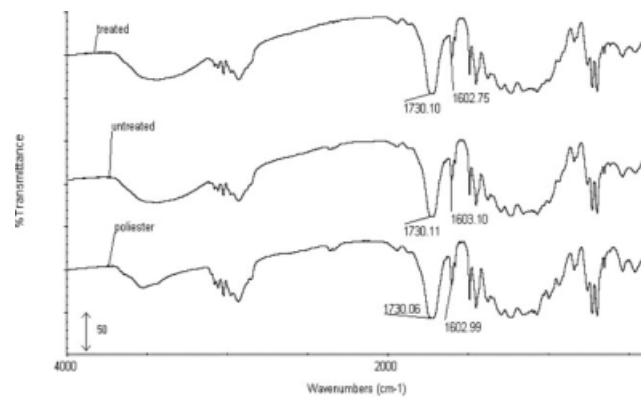
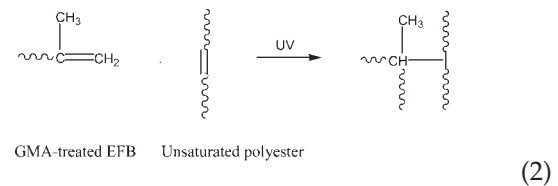


Figure 5 FTIR spectra of untreated EFB-unsaturated polyester composite, GMA-treated EFB-unsaturated polyester composite, and neat unsaturated polyester.



These explanations are supported by FTIR analysis results. A new peak appears at about 1715 cm^{-1} . This shows the introduction of C=O groups from GMA onto EFB surface. The presence of C=C absorption peak at 1636 cm^{-1} is clearly evident in the GMA-treated EFB as shown in Figure 4. However, the peak disappears on incorporation of GMA-treated EFB into the unsaturated polyester system (Fig. 5). Thus, it shows that the C=C groups from GMA-treated EFB react with the C=C of polyester resin during curing. The evidence from SEM study which will be later discussed supports this statement.

Figures 6 and 7 show that all composites display an increasing trend of flexural strength and modulus as the WPG increases. The trend is similar to those

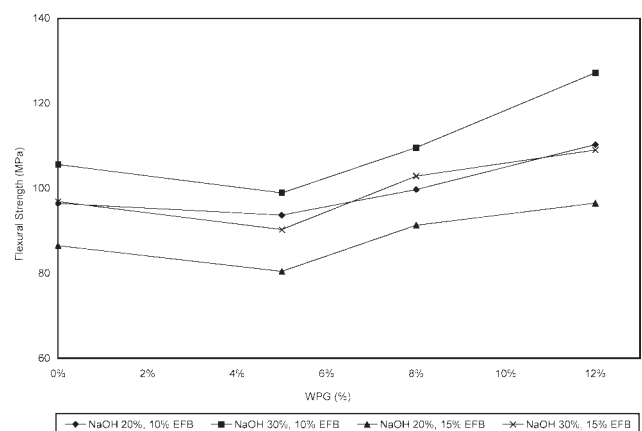


Figure 6 The effect of WPG of GMA on the flexural strength of EFB-unsaturated polyester composite.

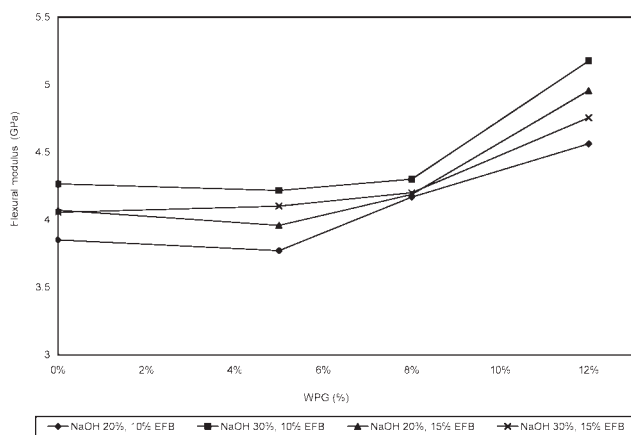


Figure 7 The effect of WPG of GMA on the flexural modulus of EFB-unsaturated polyester composite.

of tensile properties. This again indicates that through modification of EFB surface with GMA, the distribution of stress transfer from the matrix to the fiber is improved. This may be due to the increased compatibility at the interfacial region between EFB and the polyester matrix. The increased compatibility may affect the mobility of the resin polymer perpendicular to the testing direction, thus, resulting in the increased modulus.

Figure 8 shows the effect of pulping on the impact strength of the composites. The results show that those being subjected to 30% NaOH are superior in impact strength than those being exposed to 20% NaOH. As the impact strength test measures the energy needed to bring a sample into failure, this indicates that those with fibers being exposed to 30% NaOH possess better interfacial bonding. This ensures efficient stress transfer from the matrix to the fibers. This is believed to be due to the higher degree of delignification which increases the bright-

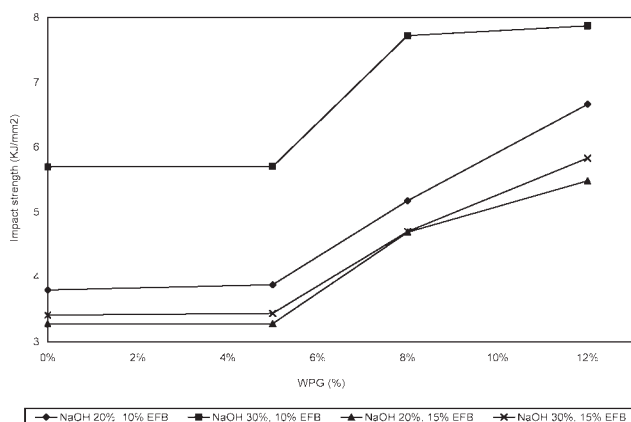


Figure 8 The effect of WPG of GMA on the impact strength of EFB-unsaturated polyester composite.

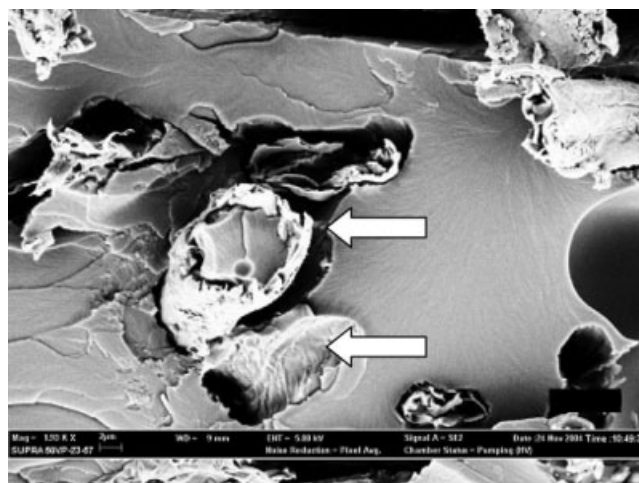


Figure 9 SEM micrograph of untreated EFB fiber embedded in unsaturated polyester matrix (30% NaOH pulping process, magnification: 1.93K ×).

ness for EFB exposed to 30% NaOH. This, in turn allows better penetration of UV radiation to the middle section of the composite for the crosslinking to occur.

Figure 9 shows the SEM micrograph of untreated EFB composite. It is obvious that the untreated fiber is loosely embedded in the polymer matrix. There is also evidence of fiber pull-out during failure. However, for the GMA-treated EFB composite (Fig. 10), the fibers are tightly embedded in the matrix with evidence of fiber breakage during failure. This indicates good wetting between the fiber and matrix. Without good wetting, a strong interfacial adhesion cannot be achieved.^{14,15} According to Cautinho et al.,¹⁶ interfacial adhesion is crucial in getting optimum strength properties of composites.

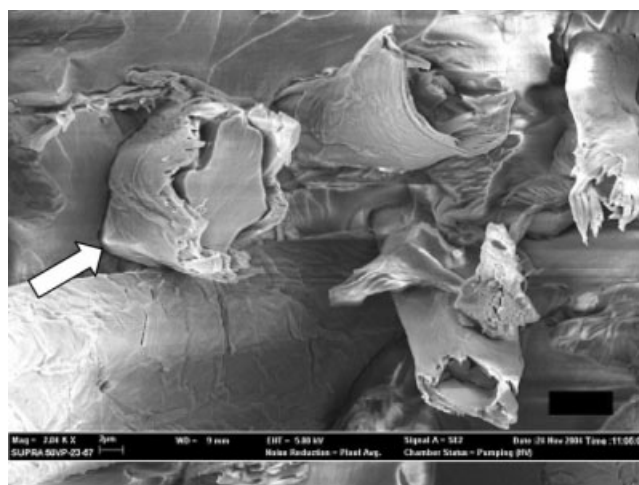


Figure 10 SEM micrograph of GMA-treated EFB fiber embedded in unsaturated polyester matrix (30% NaOH pulping process, 12 WPG, magnification: 2.00K ×).

CONCLUSIONS

Overall, chemical treatment of EFB with GMA had produced composites with significant improvements in mechanical properties. This was attributed to the improvement in the compatibility in the interfacial region. The enhancement of the compatibility was possible through the copolymerization of C=C groups from GMA and C=C groups from unsaturated polyester resin. Analysis of FTIR and SEM showed chemical and physical evidences, respectively, for the reaction of chemically attached-GMA with unsaturation sites on the unsaturated polyester.

References

1. Gassan, J.; Bledzki, K. A. *Composites* 1997, 28A, 1001.
2. Rozman, D. H.; Tay, S. G.; Abubakar, A.; Kumar, N. R. *Eur Polym J* 2001, 37, 1759.
3. Ismail, H.; Jaffri, M. R.; Rozman, D. H. *Polym Int* 2000, 49, 618.
4. Kumar, N. R.; Wei, M. L.; Rozman, D. H.; Abubakar, A. *Int J Polym Mater* 1997, 37, 43.
5. Rushdan, I. *Oil Palm Bull* 2002, 44, 19.
6. Mohamad, H. L.; Nada, A. M. *J Appl Polym Sci* 2001, 80, 2018.
7. Paul, P. *Surface Coating: Science and Technology*, 2nd ed.; Wiley: New York, 1996.
8. Crivello, V. J.; Narayan, R.; Sternstein, S. S. *J Appl Polym Sci* 1997, 64, 2073.
9. Raju, S. D.; Alfred, L. C. *Processing of Composites*; Hanser Publishers: Munich, 1999.
10. Zaman, K.; Mahmood, M. H.; Ravijst, J. P. In *Proceedings of RadTech Asia '97*; Yokohama, Japan, November 4-7, 1997; pp 800-804.
11. Rozman, D. H.; Faiza, M. A.; Kumar, N. R. *Polym Plast Technol Eng* 2008, 47, 358.
12. Rozman, D. H.; Kon, K. B.; Abusamah, A.; Kumar, R. N.; Mohd. Ishak, Z. A. *J Appl Polym Sci* 1998, 69, 1993.
13. Gassan, J.; Bledzki, A. K. *Composites* 1997, 28A, 1001.
14. Felix, J. M.; Gatenholm, P. *J Appl Polym Sci* 1991, 42, 609.
15. Chen, X.; Guo, Q.; Mi, Y. *J Appl Polym Sci* 1998, 69, 1891.
16. Cautinho, F. M. B.; Costa, T. H. S.; Carvalho, D. L. *J Appl Polym Sci* 1997, 65, 1227.