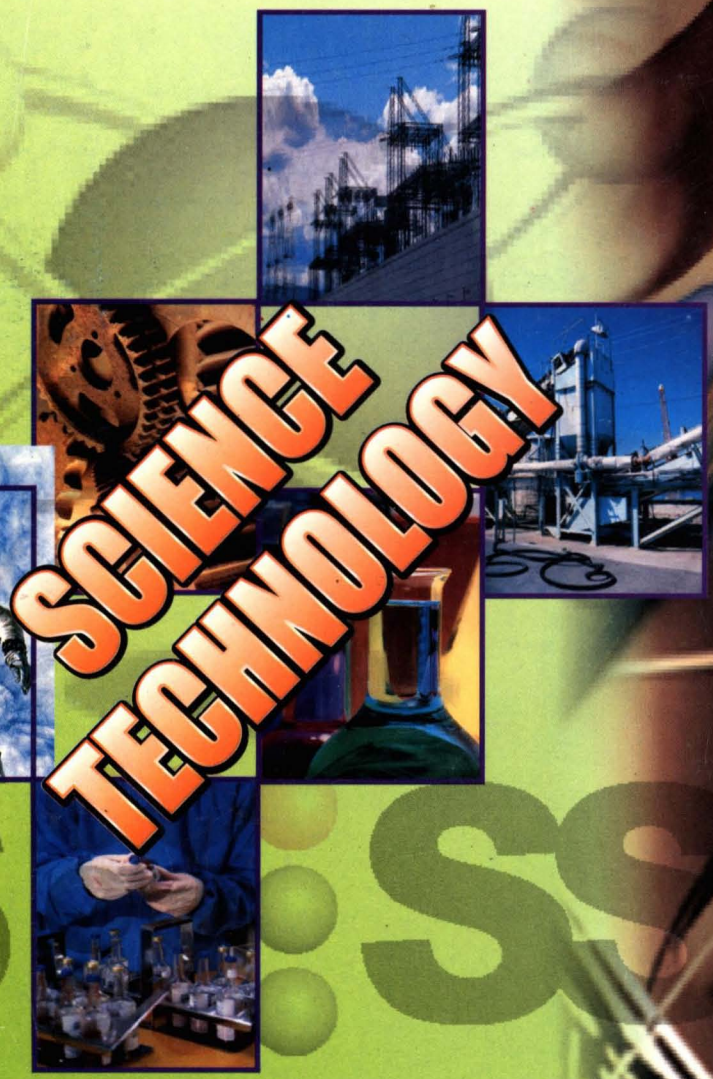
UNIVERSITI TEKNOLOGI MARA

ISO 9001:2000 No Sijil :0500132

Globalising Knowledge and Information



NATIONAL SEMINAR ON SCIENCE TECHNOLOGY & SOCIAL SCIENCES 2006

30-31 May 2006

Swiss Garden Resort & Spa

Kuantan, Pahang

The Effect of Maleic Anhydride-Grafted Polypropylene (MAPP) on Properties of Paper Sludge and Kaolin Filled Polypropylene (PP)/Ethylene Propylene Diene Terpolymer (EPDM) Hybrid Composites

Salmah
H. Ismail
A. Abu Bakar

ABSTRACT

Polypropylene (PP)/ethylene propylene diene terpolymer (EPDM) hybrid composites were made using kaolin and paper sludge (PS) fillers as reinforcing agents in the PP/EPDM matrix and maleic anhydride-grafted polypropylene (MAPP) was used a compatibilizer. Result indicates that the increasing loading of kaolin in kaolin/paper sludge wt (%) has increased the tensile strength and elongations at break but decrease the Young's modulus and water absorption of PP/EPDM/Kaolin/PS hybrid composites. The presence of MAPP has improved the mechanical properties (such as tensile strength and elongation at break) but reduced the water absorption of PP/EPDM/Kaolin/ PS hybrid composites. This observation was due to improvement in the wetting of filler surface and better filler matrix interaction of hybrid composites as evidenced from scanning electron microscopy studies.

Keywords: *paper sludge, polypropylene, ethylene propylene diene terpolymer, maleic anhydride, composites.*

Introduction

Lignocellulosic-filled plastic composites, have received a lot of attention particularly on the types of fibre, filler characterization, types of coupling agent and so forth. The utilization of lignocellulosic material as reinforcing component in polymer composites has become more attractive particularly for price driven/high volume applications (Xanthos 1983. Klason et.al. 1985, Dalvag 1985, Raj et.al. 1989a, Raj et.al. 1989b, Yam et.al. 1990, Myers 1991, Felix 1991 and Joseph 1996). However, the use of high-density inorganic filler, such as, kaolin or mica, in a thermoplastic composite also offers a wide variety of property improvement, particularly in the ultimate strength of the material. Never-the less, their incorporation may not be favourable in terms of cost effectiveness on a volumetric basis. Thus, the growth of lignocellulosic-plastic composites has been attributed to the density factor of the lignocellulosic filler in addition to other advantages such as, greater deformability, less abrasiveness to expensive moulds and mixing equipment, and of course lower cost. Hence, it would be possible to utilize both inherent characteristics of lignocellulosic and inorganic to produce composites, which has a more favourable balance of properties. Therefore, hybrid composites of lignocellulosic and inorganic material as reinforcement in a common thermoplastic matrix would provide versatility on the properties of the composite materials. Research works on lignocellulose fibre hybrid composites showed that their properties could effectively be utilized in hybrid composites (Thwe & Liao 2003; Kalaprasad et.al. 1996; Rozman et al. 2001a, 1999, 2001b; Ismail et al. 2003a, 2003b).

Generally, to improve the compatibility between the filler and matrix, coupling agents such as silane, titanate and maleic anhydride grafted polypropylene (MAPP) have been used (Qiao et al. 2004]).

In this study polypropylene (PP)/ethylene propylene diene terpolymer (EPDM) blend was chosen as a polymer matrix, kaolin and paper sludge were used as fillers, MAPP was used as a compatibilizer to improve the interfacial adhesion between the filler and PP/EPDM matrix. The effect of compatibilizer on mechanical properties, water absorption and morphology of the PP/EPDM/kaolin/paper sludge hybrid composites were examined.

Experimental

Materials

Polypropylene homopolymer used in this study was of injection molding grade, from Titan PP polymers (M) Sdn Bhd, Johor, Malaysia (code 6331) with MFI value of 14.0 g/10 min at 230 ^{0}C. Ethylene propylene diene monomer, grade Mitsui EPT 3072 E was obtained from Luxchem Trading Sdn Bhd., Selangor, Malaysia. MAPP was obtained from Aldrich Chemical Company. Paper sludge (PS) a waste product from paper mills process was obtained from Nibong Tebal Paper Mill Sdn Bhd, Penang, Malaysia. Paper sludge was dried in vacuum oven at 80 ^{0}C for 24 hour to make it free from moisture and then grinded to become powder. An Endecotts sieve was used to obtain an average filler sizes of 63 μm (density, 2.2 g/cm^3). Kaolin was obtained from Ipoh Ceramic Sdn Bhd., Ipoh, Malaysia, with average size of 9.7μm (density, 2.2 g/cm^3). The formulation of PP/EPDM/PS composites used in this study is shown

in Table 1. Tables 2 and 3 show the results of semi-quantitative analysis of paper sludge and kaolin used in this study.

Table 1: Formulation of PP/EPDM/Kaolin/PS hybrid composites with the presence of MAPP

Materials	**Composite 1**	**Composite 2**
Polypropylene (PP) (wt %)	50	50
Ethylene propylene diene terpolymer (EPDM) (wt %)	50	50
Kaolin/Paper sludge (PS) (wt /wt)	0/60, 15/45, 30/30, 45/15, 60/0	0/60, 15/45, 30/30, 45/15, 60/0
MAPP (wt %)	-	3

Table 2: Semi quantitative analysis of paper sludge using X- Ray Flourescene Spectrometer Rigaku RIX 3000

Component	Wt (%)
Na_2O	0.057
MgO	3.0
Al_2O_3	7.1
SiO_2	10.0
P_2O_5	0.065
SO_3	0.14
Cl_2O	0.19
K_2O	0.035
CaO	20.0
TiO_2	0.11
MnO	0.018
Fe_2O_3	0.19
ZnO	0.017
SrO	0.011
LOI (Organic)	59.0

Table 3 Semi quantitative analysis of kaolin using X- Ray Flourescene Spectrometer Rigaku RIX 3000

Components	Wt (%)
MgO	0.33
Al_2O_3	30
SiO_2	63
P_2O_5	0.065
SO_3	0.030
K_2O	1.5
CaO	0.042
TiO_2	0.025
Fe_2O	0.84
NiO	0.012
Br_2O	0.59
Rb_2O	0.044
ZrO_2	0.018
LOI	3.5

Mixing Procedure

Composites were prepared in a Haake Reomix PolyDrive. Mixing was done at 180 ^{0}C and 50 rpm. EPDM was first charged to start the melt mixing. After 3 min, filler and MAPP were added followed by PP at the fifth minutes. Mixing was continued for another 5 min. At the end of 10 min, the composites were taken out and sheeted through a laboratory mill at 2.0 mm nip setting. Sample of composites were compression molded in an electrically heated hydraulic press. Hot-press procedures involved preheating at 180 ^{0}C for 6 min followed by compressing for 4 min at the same temperature and subsequent cooling under pressure for 4 min.

Measurement of Tensile Properties

Tensile tests were carried out according to ASTM D- 412 on an Instron 3366. 1 mm thick dumb bell specimens were cut from the moulded sheets with a Wallace die cutter. A cross head speed of 50 mm/min was used and the test was performed at 25 ± 3 ^{0}C.

Water Absorption Test

The composite samples were immersed in distilled water at room temperature. The water absorption was determined by weighing the samples at regular intervals. A Mettler balance type AJ150 was used, with a precision of ± 1 mg. The percentage of water absorption, M_t was calculated by

$$M_t = \frac{W_N - W_d}{W_d} x100\% \qquad (1)$$

Where W_d and W_N are original dry weight and weight after exposure, respectively.

Morphology Study

Studies on the morphology of the tensile fracture surface of the composites were carried out using a scanning electron microscope (SEM), model Leica Cambridge S-360. The fracture ends of specimens were mounted on aluminium stubs and sputter coated with a thin layer of gold to avoid electrostatic charging during examination

Results and Discussion

Figure 1 shows the effect of partial replacement of paper sludge by kaolin on tensile strength of untreated and treated filled PP/EPDM hybrid composites. It can be seen that the tensile strength of PP/EPDM hybrid composites increases slightly with increasing loading of kaolin. Kaolin has better adhesion with PP/EPDM matrix compared to paper sludge due to its smaller particle size and better dispersion in PP/EPDM matrix. At a similar kaolin/paper sludge loading, the hybrid composites treated with MAPP have higher tensile strength than untreated hybrid composites. The enhancement in the tensile strength of treated hybrid composites with the addition MAPP may be attributed to the efficient stress transfer between the filler and the matrix as a result of improved adhesion between treated filler and matrix. Generally, MAPP is used as a compatibilizer because it can efficiently improve the fibre matrix bonding due to the formation of covalent linkages and hydrogen bond between maleic anhydride and the hydroxyl group of the fibre (Qiao, X et. al. 2004).

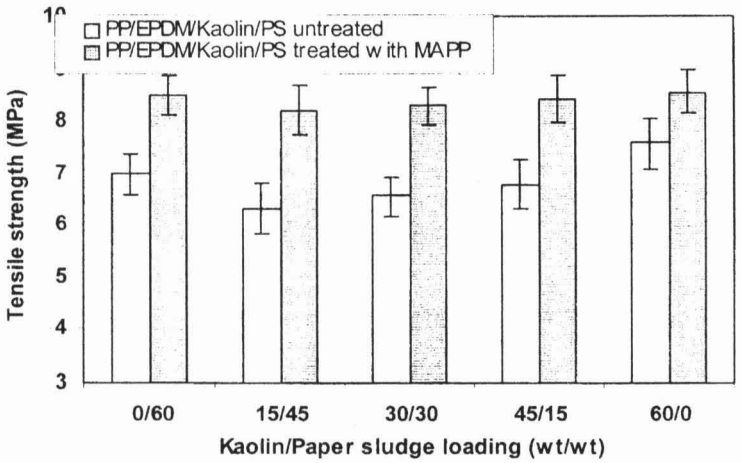


Fig. 1: The Effect of Filler Loading on Tensile Strength of Untreated and Treated PP/EPDM/Kaolin/PS hybrid Composites with MAPP.

The effect of partial replacement of paper sludge by kaolin on elongation at break of untreated and treated hybrid composites is shown in Figure 2. It can be seen the elongation at break of the hybrid composites increases with increasing loading of kaolin. At similar kaolin/paper sludge loading the elongation at break of hybrid composites treated with MAPP is lower than untreated hybrid composites. Again this is due to the better adhesion between kaolin/paper sludge with PP/EPDM matrix with the presence of MAPP.

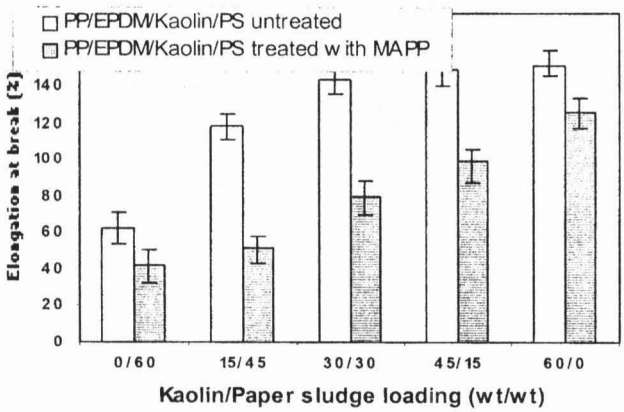


Fig. 2. The Effect of Filler Loading on Elongation at Break of Untreated and Treated PP/EPDM/Kaolin/PS Hybrid Composites with MAPP

Figure 3 shows the effect of partial replacement of paper sludge by kaolin on Young' modulus of untreated and treated hybrid composites. It shows clearly that the Young's modulus of the hybrid composites decrease with increasing kaolin loading. This result indicates that paper sludge has advantage over kaolin in improving the stiffness of PP/EPDM hybrid composites. However, at a similar kaolin/paper sludge loading, the Young's modulus of treated hybrid composites with MAPP is higher than untreated hybrid composites.

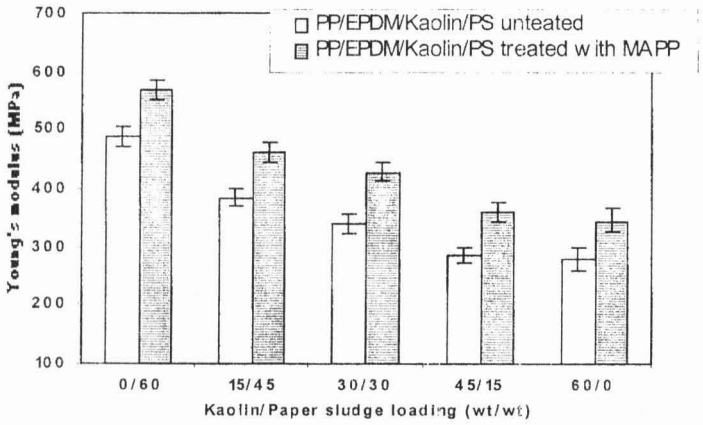


Fig. 3: The Effect of Filler Loading on Young's Modulus of Untreated and Treated PP/EPDM/Kaolin/PS Hybrid Composites with MAPP

Figure 4 shows the water absorption of PP/EPDM/Kaolin/PS hybrid composites versus swelling time. It can be seen that the water absorption of hybrid composite increase with increasing swelling time. Figure 4 also shows that increased loading of kaolin has decreased the water absorption of hybrid composites. In our previous work [18], we have reported that PP/EPDM/PS composites exhibit higher water absorption than PP/EPDM/Kaolin composites. The tendency of organic materials to form hydrogen bond with water molecules is higher than inorganic materials.

Figure 5 shows the variation of equilibrium swelling at 55 days immersion in water for untreated and treated hybrid composites. It can be seen that the increasing kaolin loading decreased the equilibrium water absorption of PP/EPDM/Kaolin/PS hybrid composites. However, at a similar filler loading, treated hybrid composites with MAPP show lower equilibrium water absorption than untreated hybrid composites. The reduction in water absorption with the presence of MAPP is attributed to the improved of interfacial adhesion that reduces the water accumulation in the interfacial voids and prevents water molecules from entering the PP/EPDM/Kaolin/PS hybrid composites.

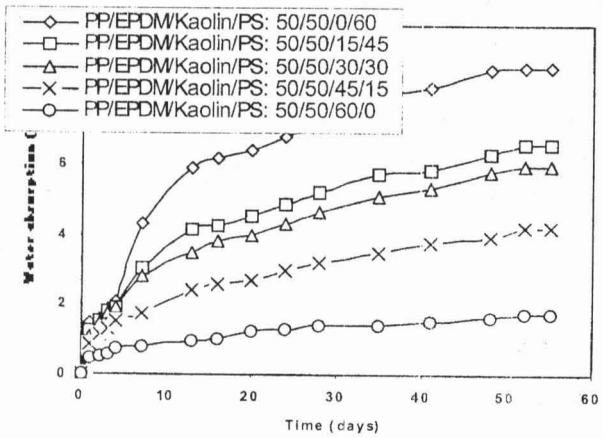


Fig. 4: Percentage of Water Absorption versus Time of PP/EPDM/Kaolin/PS Hybrid Composites with Different Filler Loading.

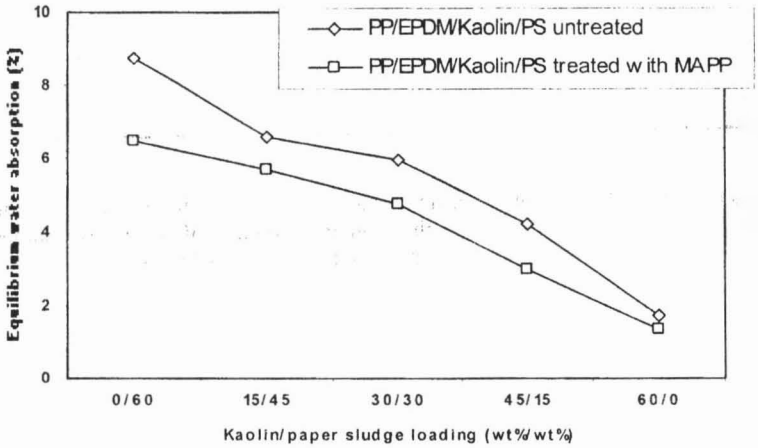


Fig. 5: Percentage Equilibrium Swelling versus Filler Loading of Untreated and Treated PP/EPDM/Kaolin/PS Hybrid Composites with MAPP.

Figure 6 shows the tensile fracture surface of untreated 30/30 (wt/wt) kaolin/paper sludge of PP/EPDM/Kaolin/PS hybrid composites at magnification of 200X. It can be seen the presence of unwetted paper sludge on the surface. This indicates the absence of good interfacial adhesion between filler and the matrix. Figure 7 shows the tensile facture surface of 30/30 (wt/wt) of kaolin/paper sludge treated hybrid composite. It can be seen that most of the fillers coated with PP/EPDM matrix due to the presence of MAPP, a good filler-matrix interaction occurred between the anhydride group of MAPP and hydroxyl group at the surface filler. Consequently, a positive effect on properties of composites was obtained.

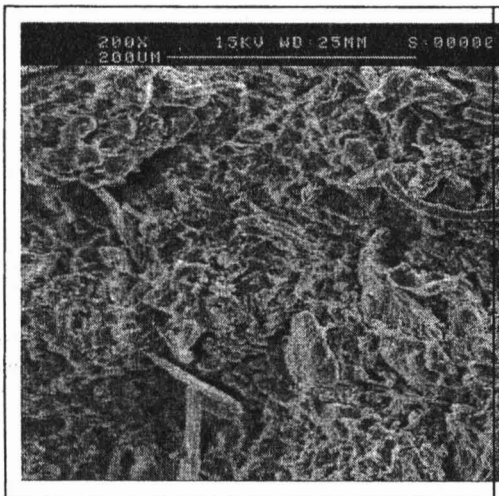


Fig. 6: Scanning Electron Micrograph of Tensile Fracture Surface of PP/EPDM/Kaolin/PS Hybrid Composites (30/30) kaolin/paper sludge (wt/wt)) at Magnification 200X

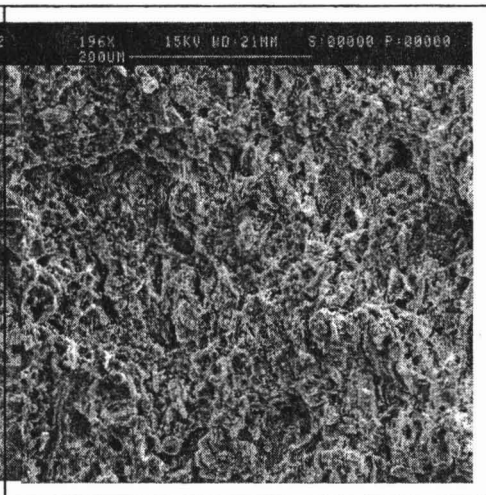


Fig. 7: Scanning Electron Micrograph of Tensile Fracture Surface of PP/EPDM/Kaolin/PS Hybrid Composites with MAPP(30/30) kaolin/paper sludge (wt/wt)) at Magnification 200X

Conclusion

The presence of MAPP increased the tensile strength and Young's modulus but decreased the elongation at break and water absorption of PP/EPDM/Kaolin/PS hybrid composites. Scanning electron microscope studies indicate that the interfacial adhesion between kaolin/paper sludge and PP/EPDM matrix was improved with the presence of MAPP.

References

Dalvag, H.,Klason, C. & Stromvall, H. E. (1985). The Efficiency of Cellulosic Fillers in Common Thermoplastic. Part II. Fi ling with Processing Aids and Coupling Agent. *Intern. J. Polym. Mater.*,11: pp. 9-38.

Felix, J. M. & Gatenholm, C. (1991).The Nature of Adhesion in Composite of Modified Cellulose Fibers and Polypropylene. *J. Appl. Polym. Sci.*, 42:pp. 609-620.

Ismail, H., Hong, H.B., Ping, C. Y. & Abdul Khalil, H.P.S. (2003a). Polypropylene/Silica/Rice Husk Ash Hybrid Composites: A study on the Mechanical, Water Absorption and Morphological Properties. *J. Thermoplast. Comp. Mater.*, 16(2):pp. 121-137.

Ismail, H., Salmah. & Nasir, M. (2003b). The Effect Dynamic Vulcanization on Mechanical Properties and Water Absorption of Silica and Rubberwood Filled Polypropylene/Natural Rubber Hybrid Composites. *Intern. J. Polym. Mater.*, 53(3):pp. 229-238.

Joseph, K., Thomas, S. & Pavithran, C. (1996). Effect of Chemical Treatment on the Tensile Properties of Short Fibre-reinforced Polyethylene Composites. *Polymer*,37: pp. 5139-5149.

Kalaprasad G., Thomas, S., Pavitran, V., Neelakantan, N. R & Balakrishnan, S. (1996). Hybrid Effect in the Mechanical Properties of Short Sisal/Glass Hybrid Fiber Reinforced Low Density Polyethylene Composites. *J. Reinf. Plast. Comp.*, 15: pp. 48-73.

Klason, C., Kubat, J. & Stromvall, H. E. (1984). The Efficiency of Eellulosic Fillers in Common Thermoplastics Part I. Filling without Processing Aids on Coupling Agents. *Intern. J. Polym. Mater.*, 10: pp. 159-187.

Myers, G. E., Chahyadi, I. I., Coberly, C. A. & Ermer, D. S. (1991). Wood Flour/Polypropylene Composite: Influence of Malaeted Polypropylene and Process and Composition Variables on Mechanical Properties. *Intern. J. Polym. Mater.*, 15: pp. 21-44.

Qiao, X., Zhang, Y., Zhang, Y. (2004). Maleic Anhydride Grafted Polypropylene as a Coupling Agent for Polypropylene Composites Filled with Ink-eliminated Waste Paper Sludge Flour. *J. Appl. Polym. Sci.*, 9: pp. 2320-2325.

Raj, R. G., Kokta, B. V, Dembele, F. & Sanschargrain, B. (1989a). Compounding of Cellulosic Fibers with Polypropylene: Effect of Fiber Treatment on Dispersion in the Polymer Matrix. *J. Appl. Polym. Sci.*, 38: pp. 1987-1996.

Raj, R. G., Kokta, B. V., Groleau, G. & Daneault, C. (1989b). Use of Wood Fiber as a Filler in Polyethylene Studies on Mechanical Properties. *Plast. Rubber Process Appl.*, 11: pp. 215-221.

Rozman, H. D., Tay, G. S., Kumar, R. N., Abusamah, A., Ismail, H. & Mohd. Ishak, Z. A. (2001a). Polypropylene Oil Palm Empty Fruit Bunch-glass Fibre Hybrid Composites: A Preliminary Study on the Flexural and Tensile Properties. *European. Polym. Journal*, 37: pp. 1283-1291.

Rozman, H. D., Tay, G. S., Kumar, R. N., Abusamah, A., Ismail, H. & Mohd. Ishak, Z. A. (1999). Polypropylene Hybrid Composites: A Preliminary Study on the use of Glass and Coconut Fiber as Reinforcement in Polypropylene Composites. *Polym. Plast. Technol. Eng.*, 38:pp. 997-1011.

Rozman, H.D., Tay, G. S., Kumar, R.N., Abusamah, A., Ismail, H. & Mohd. Ishak, Z. A. (2001b). The Effect of Oil Extraction of the Oil Palm Empty Fruit Bunch on the Mechanical Properties of Polypropylene-oil Palm Empty Fruit Bunch-glass Fibre Hybrid Composites. *Polym. Plast. Technol. Eng.*, 40(2): pp. 103-115.

Salmah., Ismail, H. & Azhar A. A. (2005). A Comparative Study on the Effects of Paper Sludge and Kaolin on Properties of Polypropylene/Ethylene Propylene Diene Terpolymer Composites. *Iranian Polym. J.*, 14(8): pp. 705-713.

Thwe, M. N. & Liao, K. Durability of Bamboo-glass Fiber Reinforced Polymer Matrix-hybrid Composites. *Comp. Sci. Technol.*, 63: pp. 365-370.

Xanthos, M. (1983). Processing Conditions and Coupling Agents Effect in Polypropylene/Wood Flour. *Plast. Rubber Process Appl.*, 3: pp. 223-228.

Yam, L., Gogoi, B. K., Lai. C. C. & Selke, S. E. (1990). Composite from Compounding Wood Fibers with Recycled High Density Polyethylene. *Polym. Eng. Sci.*, 3:pp. 693-699.

SALMAH, School of Material Engineering, Northern Malaysia University College of Engineering (KUKUM), 02600, Jejawi, Perlis, Malaysia. irsalmah@kukum.edu.my

H. ISMAIL & A. ABU BAKAR, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia.