EFFECT OF MAPP AS COUPLING AGENT ON THE MECHANICAL PROPERTIES OF PALM FIBER EMPTY FRUIT BUNCH AND CELLULOSE POLYPROPYLENE BIOCOMPOSITES

M. Khalid ^{1*}, S. Ali¹, L.C Abdullah¹, C.T Ratnam² and S.Y. Thomas Choong¹ ¹ Dept. of Chemical and Environmental Engineering, Universiti Putra Malaysia, 43400 Selangor, Malaysia. ² Malaysian Institute for Nuclear Technology Research (MINT), Bangi 43000 Kajang Malaysia ^{*}Email: <u>khalids@engineer.com</u>

ABSTRACT

In this paper maleic anhydride grafted polypropylene, MAPP (GR-205) was used as a coupling agent for the PP-cellulose (derived from oil palm empty fruit bunch fiber) and PP-oil palm empty fruit bunch fiber (EFBF) biocomposites. Different sets of biocomposites were prepared by blending PP-cellulose and PP-EFBF at a fixed ratio of 70/30 (wt/wt %) using brabender mixer at 180 °C. The MAPP was added at varying concentrations (2, 3, 5, and 7 wt %) during the blending. The biocomposite were subsequently molded with hot press under pressure for the test specimen preparation. The effect of MAPP concentration on the mechanical properties such as tensile, flexural and impact strengths of both the biocomposites were studied. It was found that 30 wt % filler (cellulose and EFBF) loading with 2 wt % MAPP concentration give the best results for the EFBF biocomposites. Nearly 58 % increase in tensile strength of PP-EFBF was observed in respect of control (without MAPP) biocomposite. The MAPP enhanced the EFBF matrix adhesion, resulting in an improvement in EFBF biocomposite performance. On the other hand there were no significant changes observed in the PP-cellulose biocomposites properties on addition of MAPP.

Keywords: cellulose, EFBF, polypropylene, MAPP, mechanical properties.

INTRODUCTION

The use of cheap agro-based renewable natural lignocellulosic fibers such as jute, sisal, coir, EFB etc. in preparing composites with various thermoplastic and thermosetting resins has gained much momentum in the recent years [1-6]. Extensive research has been carried out on the agro fiber plastic composites which have been reported by a number of workers [7, 8]. This is due to their low cost, easy availability, nonabrasive nature, low density and moreover their high specific properties and biodegradability characteristics. A broad range of agrobased fibers is being utilized as the main structural components or as filler agents in these composite materials. Malaysia is the leading producers of palm oil. Abundance of oil palm cellulosic material that can be readily obtained from the by products, provides a new area of interest for research development. Extensive research has been carried out on empty fruit bunch fiber (EFBF) and other type of wood flour in the thermoplastic [9,10]. It is known that incorporation of fillers as reinforcing materials significantly changes various properties of thermoplastics [11, 12]. In this study, effect of MAPP on a relative new type of palm fiber derivative (cellulose) was investigated. The MAPP treated EFB fiber was used for comparative studies. The fiber/ matrix interface has an important role in the micromechanical behavior of composites. Therefore, the bonding nature between the fiber and matrix depends on the atomic arrangement, chemical properties of the fiber and chemical constitution of polymeric matrix. Despite the advantages mentioned above the use of agro fibers in the preparation of thermoplastic composites has not been versatile because of the poor final properties of the composite. This is possibly due to limited thermal stability during processing, poor dispersion characteristics of the fiber in the thermoplastic melt and limited compatibility of the fibers with the matrix [13,14]. However by the implementation of suitable chemical methods for the surface modification of the fibers, the properties can be improved substantially. Extensive research has been carried out with different kinds of coupling agents for surface modification of agro fibers in order to increase the adhesive action with the thermoplastic matrix. Schneider et al. [15] used maleated polypropylene wax as coupling agent to improve the properties of composites prepared from jute and kenaf reinforced PP. Karmaker et al. [16] used MAPP (G-3002) as coupling agent to improve the tensile and flexural strengths of the composites prepared from jute and PP. The present study reveals the effect of treatment of the coupling agent, MAPP (G-205) on the properties of PP-cellulose and PP-EFBF biocomposites.

MATERIALS AND METHODS

Materials

Homopolymer polypropylene (PP) grade 600G (Melt index 11 g/10min, density 900 kg/cm³) was supplied by Petronas Polymers Marketing & Trading Division Malaysia and MAPP-GR205 was obtained from Dow Chemicals Co. Ltd., Singapore. Empty fruit bunch fiber (EFBF) was obtained from Malaysian Palm Oil Board (MPOB). Reagent grade sodium hydroxide (NaOH), acetic acid (CH₃COOH), acetone ((CH₃)₂CO) and technical grade sodium chlorite (NaClO₂) were obtained from Fisher Chemicals Sdn. Bhd., Malaysia for cellulose preparation. The cellulose was extracted from EFBF at lab scale by chlorination method (ASTM D1104).

Preparation of Composite

The EFBF were first washed thoroughly with 2% detergent water to remove the adhered oil and contaminants, and dried in an air oven at 100°C for 24 hours. The dried fibers were designated as untreated fibers and a part of this untreated fiber was taken for cellulose preparation. Prior to mixing, cellulose and EFB fibers were dried for 12 hr in a hot air oven at 105°C in order to remove the moisture content. The dried fillers (EFBF and cellulose) were cut using cutter (Retsch Muhle, Germany) and was passed through 25 μ sieve to obtain uniform size of the filler. The compounding of polypropylene, MAPP, cellulose and EFBF was carried out by using Brabender Plasticorder (PL2000-6, Germany) twin-screw compounder at 180°C for 20 min at a roller speed of 50 rpm. The compositions of biocomposites are given in Table 1. The blended samples were cut using the cutter and placed between a two-piece copper molding set. The mold was pressed with hot press at 190°C for 5 minutes of preheating and 3 minutes of complete pressing followed by cooling for 3 minutes under pressure equipped with chiller facilities. The pressure for heating and cooling was maintained to 150 kg/cm². Molded sheets of 1, 2 and 3 mm thickness were prepared for tensile, flexural and impact testing respectively.

Composite	PP (wt %)	MAPP (wt %)	Cellulose (wt %)	EFBF (wt %)
0	70	0	30	30
2	70	2	30	30
3	70	3	30	30
5	70	5	30	30
7	70	7	30	30

Table 1: Composition of PP/cellulose and PP/EFB composite

Mechanical Testing

Three important mechanical properties namely tensile, flexural or bending and impact were tested. All test specimen dimensions were according to the respective ASTM standards. All tests were performed at room temperature.

Tensile Test

All tensile testing specimens were cut into dog-bone shape. The tensile tests were conducted according to ASTM 1882L using INSTRON (Model 4301) Universal Testing Machine with load cell of 1 kN, using a crosshead speed of 50 mm/min. Tests were performed until tensile failure occurred. Seven specimens were tested and at least five replicate specimens were presented as an average of tested specimens.

Flexural Modulus

A flexure load involves the ability of the material to bend. Flexural loads combine tensile, compression and shear loads. The upper surface of the laminate is put into compression, the central portion experiences shear, and the lower face undergoes tension. The flexural samples were cut into rectangular specimens and the flexural

modulus was determined using an INSTRON (Model 4301) Universal Testing Machine in accordance with ASTM D790-97 standard. 3-point bend method was implied for the test. The support span was 43 mm and the cross-head speed during the tension was 1.3 mm/min with load cell of 1kN, and each test was performed until failure occurred. Seven specimens were tested and at least five replicate specimens were presented as an average of tested specimens.

Impact Test

Impact resistance of a composite material is one of the most important properties for a design engineer to consider. Materials often absorb applied forces very quickly. Depending on the application, these could be falling objects, blows, collisions, drops, etc. A material is also more likely to fail when it is subjected to an impact blow in comparison to the same force being applied more slowly. The impact properties of the polymeric materials are directly related to the overall toughness of the material. The impact strength test was developed to overcome the deficiencies of flexural impact tests. The impact tests were conducted according to ASTM D235 standard. The Izod method was carried out using notched samples by Impact Pendulum Tester (Model Ceast CE UM-636), using a 4 Joule hammer. Seven specimens were tested and at least five replicate specimens were presented as an average of tested specimens.

RESULTS AND DISCUSSIONS

Tensile Properties

Filler plays an important role in determining the mechanical properties of cellulose filled-thermoplastic composites. The most crucial factor that affects the mechanical properties of the fiber-reinforced materials is the fiber-matrix interfacial adhesion. The quality of interfacial bonding is determined by several factors, such as the nature of fiber and polymer components, the fiber aspect ratio, the processing procedure and the treatment of the polymer of the fiber [17,18]. The most important factor for good fiber reinforcement in the composite is the strength of adhesion between the matrix polymer and the fiber. Due to the presence of hydroxyl and other polar groups in the fiber, the moisture absorption is high which leads to weak interfacial adhesion between the fibers and the hydrophobic matrix, which makes debonding. Therefore in order to enhance the mechanical properties of the composites, the hydrophilic nature of the fibers has to be minimized by suitable chemical modifications. This would not only decrease the moisture absorption of the fibers but also would significantly increase the wettability of the fibers with the matrix polymer and the interfacial bond strength. Figure 1 shows MAPP-treated PP-cellulose and PP-EFBF biocomposites. Coupling agents were used to provide compatibility between filler and immiscible polymers matrix through reduction of the interfacial tension [19]. It is observed that 2 wt % MAPP gave the best results for both the biocomposites. There was a tremendous increase in the tensile strength of PP-EFBF biocomposite (nearly 58 % compared to control sample). This shows that MAPP has greatly improved the resin pickup and wettability of EFBF during composite preparation. On the other hand PPcellulose biocomposite did not show any significant increase in the tensile strength compared to the control sample. This result shows a good compatibility of cellulose sites with the resin, and any further enhancement with the addition of MAPP was not observed. However, with a further increase in the concentration of MAPP from 2 to 7 % a decrease was observed in the tensile properties of both the bio-composites. The reasons might be that MAPP has a lower molecular weight compared to the matrix PP which seems to be responsible for plasticizing effect [20].



Figure 1: Effects of coupling agent (MAPP) on tensile strength of PP-biocomposites at 30 wt % filler loading

Flexural Modulus

However, incorporation of MAPP (Figure 2) did not show any significant improvement in the flexural modulus of both cellulose and EFBF biocomposites. In contrast the flexural modulus decreased with increase in MAPP content. The decrease in the modulus of the biocomposite may possibly due to the plasticizing effect of low molecular weight MAPP which caused a reduction of the composite stiffness [20].



Figure 2: Effects of coupling agent (MAPP) on flexural modulus of PP-biocomposites at 30 wt % filler loading

Impact Strength

Figure 3 shows the effect of MAPP on the impact strength of PP-cellulose and PP-EFBF biocomposite. Colom *et al.* [21] reported that the impact strength of the polyolefin cellulosic fiber composites was found to be increased after treating the fiber surface with maleated-ethylene. However, this could only beneficial at low fiber content. At high fiber content (about 30–40 wt %), the impact properties of the treated composite could be lower than those of the untreated. This is agreed to the results shown in Figure 3, which shows a decrease on the impact strength of the composites with the presence of the MAPP coupling agent above 2 wt %. However, PP-cellulose biocomposite shows more promising results without any MAPP addition as its mechanical strength are still higher then PP-EFBF biocomposite.



Figure 3: Effects of coupling agent (MAPP) on impact strength of PP-biocomposites at 30 wt % filler loading

CONCLUSIONS

The results of the present study showed that a useful PP-EFBF biocomposite with good tensile and impact strength could be successfully developed using MAPP as a coupling agent. However, PP-cellulose biocomposite did not show significant changes in the mechanical properties indicating that the MAPP works well with the lignocellulosic fibers. With the increase in the concentration of MAPP in the PP matrix above 2 wt % there is a substantial decrease in mechanical strength. Further testing should be done at still lower concentration of MAPP. In conclusion it can be postulated that, MAPP modified EFB fiber and PP matrix can be molded into a value added and cost effective biocomposite material.

ACKNOWLEDGMENTS

The author would like to thank the staff of Malaysian Institute for Nuclear Technology Research (MINT) and Universiti Putra Malaysia for their support to carry out this research.

REFERENCES

- Mishra, S., Mishra, M., Tripathy, S.S., Nayak, S.K. and Mohanty, A.K. (2001) Graft Copolymerization of Acrylonitrile on Chemically Modified Sisal Fibers. Macromolecular Materials and Engineering, 286(2):107-113.
- [2] Coutinho, F.M.B., Costa, T.H.S. and Carvalho, D.L. (1997) Polypropylene-wood Fiber Composites: Effect of Treatment and Mixing Conditions on Mechanical Properties. Journal of Applied Polymer Science 65(6): 1227-1235.
- [3] John, M. Felix. and Paul, Gatenholm (1991) The Nature of Adhesion in Composites of Modified Cellulose Fibers and Polypropylene. Journal of Applied Polymer Science **42**(3): 609-620.
- [4] Rout, J., Mishra, M., Tripathy, S.S., Nayak, S.K. and Mohanty, A.K. (2001) The Influence of Fiber Surface Modification on the Mechanical Properties of Coir-polyester Composites. Polymer Composites 22(4): 468–476.
- [5] Mishra, S., Mishra, M., Tripathy, S.S., Nayak, S.K. and Mohanty, A.K. (2001) Potentiality of Pineapple Leaf Fibre as Reinforcement in PALF-Polyester Composite: Surface Modification and Mechanical Performance. Journal of Reinforced Plastics and Composites 20(4): 321–334.
- [6] Sanadi, A.R., Caulfield, D.F., Jacobson, R.E. and Rowel, R.M. (1995) Renewable Agricultural Fibers as Reinforcing Fillers in Plastics: Mechanical Properties of Kenaf Fiber-polyproylene Composites. Industrial and Engineering Chemistry Research 34(5): 1889–1896.
- [7] Zaini, M. J., Ismail, Z. Fuad, M. Y. A. and Mustafah, J. (1995) The effect of filler content and the size on the mechanical properties of polypropylene/oil palm wood flour composite. Polymer International 40(1): 51-56.
- [8] Maldas, D. and Kokta, B.V. (1993) Interfacial Adhesion of Lignocellulosic Materials in Polymer Composites: An Overview. Composite Interfaces 1(1): 87-108.

- [9] Rozman, H. D., Tay, G. S. Abubakar, A. and Kumar, R. N. (2001) Tensile properties of oil palm empty fruit bunch-polyurethane composites. European Polymer Journal 37(9): 1759-1765.
- [10] Mohanty, A. K., Misra, M. and Drazl, L. T. (2005) Natural fibers, biopolymers and biocomposites (chapter 12), CRC press, New York.
- [11] Coutinho, F.M.B., Costa, T.H.S. (1999) Performance of polypropylene-wood fiber composites. Journal of Polymer Testing 18 (8): 581-587.
- [12] Jiken, L., Malhammar, G. and Selden, R. (1991) The effect of mineral fillers on impact and tensile properties of polypropylene. Journal of Polymer Testing **10**(55):329-344.
- [13] Bledzki, A.K., Reihmane, S. and Gassan, J. (1998) Thermoplastics Reinforced with Wood Fillers: A Literature Review. Polymer- Plastic Technology Engineering 37(4): 451-468.
- [14] Rowell, R.M., Sanadi, A.R., Caulfield, D.F. and Jacobson, E. (1997) Utilization of Natural Fibers in Plastic Composites: Problems and Opportunities. In: Leão, A.L.; Carvalho, F.X. & Frollini, E. eds. Lignocellulosic-Plastic Composites, São Paulo, USP & UNESP, p. 23-51
- [15] Schneider, James P., Madison and Karmaker, Ajit C. (1995) Composites from Jute and Kenaf Reinforced Polypropylene, ANTEC 2086.
- [16] Karmakar, A.C. and Youngquist, J.A. (1996) Injection Molding of Polypropylene Reinforced with Short
- [17] Jute Fibers. Journal of Applied Polymer Science **62**: 1147-1151.
- [18] Kim, J. K., Lu, S. and Mai, Y. W. (1994) Interfacial debonding and fiber pull-out stresses. Part IV: influence of interface layer on stress transfer. Journal of Material Science **29**:554-561.
- [19] Pochiraju, K. V., Tandon, G. P. and Pagano, N. J. (2001) Analysis of single fiber pushout considering interfacial friction and adhesion. Journal of Mechanics and Physics of solids **49**(10):2307-2338.
- [20] Pritchard, G. (1998) Quick reference guide. In Plastics additives: An A-Z reference, ed. G. Pritchard, pp 12. Chapman and Hall: New York.
- [21] Mohanty, S., Verma, S.K. Nayak, S.K. and Tripathy, S.S. (2004) Influence of fiber treatment on the performance of sisal–polypropylene composites. Journal of Applied Polymer Science **94**(3):1336–1345.
- [22] Colom, X., Carrasco, F.P. and Canavate, P. (2003) Effects of different treatment on the interface of HDPE/lignocellulosic fiber composites. Composites Science and Technology 63(2): 161-169.