

EFFECT OF TRIMETHYLOLPROPANE TRIACRYLATE (TMPTA) ON THE MECHANICAL PROPERTIES OF PALM FIBER EMPTY FRUIT BUNCH AND CELLULOSE FIBER BIOCOMPOSITE

M. KHALID ^{1*}, A. SALMIATON ¹, C. T. RATNAM ², C. A. LUQMAN ³

¹ Department of Chemical & Environmental Engineering Faculty of Engineering
Universiti Putra Malaysia (UPM) Serdang 43400 Selangor D. E. Malaysia.

² Malaysian Nuclear Agency, Bangi 43000 Kajang Malaysia

³ Institute of Tropical Agriculture (INTROP), Universiti Putra Malaysia (UPM)
Serdang 43400 Selangor D. E. Malaysia.

*Corresponding author: khalidchem@gmail.com

Abstract

The effect of trimethylolpropane triacrylate (TMPTA) as a coupling agent, on the mechanical and morphological properties of the PP-cellulose (derived from oil palm empty fruit bunch fiber) and PP-oil palm empty fruit bunch fiber (EFBF) biocomposites has been studied. The ratio of PP:cellulose and PP:EFBF is fixed to 70:30 (wt/wt%) while the concentration of the coupling agent is varied from 2.0 to 7.0 wt%. Results reveal that at 2.0 wt% of TMPTA concentration, tensile strength, flexural modulus, impact strength and Rockwell hardness of PP-cellulose biocomposite are significantly improved. The enhancement of mechanical properties in the presence of TMPTA is believed to be attributed to crosslinking of multifunctional monomer with the hydroxyl groups of cellulose resulting in better adhesion and superior PP-cellulose biocomposite properties. However, there are no significant changes observed in the PP-EFBF biocomposite properties upon the addition of TMPTA.

Keywords: Cellulose, EFBF, Polypropylene, TMPTA, Mechanical Properties.

1. Introduction

In the past decade an enormous interest in the development of new composite materials with natural fibers has been shown by important industries such as the automotive, construction and packaging industry. Composite materials are created by combining two or more components to achieve desired properties which could not be obtained with the separate components.

Agro-based composites using thermoplastics as a continuous phase can result in better water resistance and dimensional stability compared to composites with low polymer content. Agro and wood-based composites with a continuous thermoplastic phase also give the opportunity to process the composite using conventional thermoplastic processing equipment [1]. These composites can be used to replace impregnated wood in many outdoor applications but can also be used as replacement for neat plastics. There are environmental and economical reasons for replacing part of the plastics with wood but the wood could also work as reinforcement of the plastics.

The elastic modulus of wood fibers is approximately 40 times higher than that of polyethylene and the strength about 20 times higher [2]. Compared to inorganic fibers, natural fibers present some advantages such as lower density and lower price, they are less abrasive to the processing equipment, harmless, biodegradable, renewable, and their mechanical properties can be comparable to those of inorganic fibers [3, 4]. All these properties have made natural fibers very attractive for industries like the automotive industry, that search a product with mechanical properties comparable with glass fibre reinforced thermoplastics, but lighter and harmless to workers.

Many studies have been developed based on composites containing lignocellulosic fibers from the forest and paper industry such as cellulose, wood fibre and wood dust. Others studies have been based on agricultural fibers such as kenaf, sisal, hemp, coir, rice husk, etc. [5-7]. In spite of all the advantages mentioned above, there are also some drawbacks in using wood fillers as reinforcement in thermoplastics. The main drawbacks are the difficulties of achieving good dispersion and strong interfacial adhesion between the hydrophilic wood and the hydrophobic polymers which leads to composites with rather poor durability and mechanical properties [8, 9]. Many different modifications of thermoplastic wood composites have been tested and the basic role of these modifications is to reduce wood-wood interactions and increase wood-polymer interactions.

Numerous studies have used graft copolymers of synthetic polymers (e.g., PP and PE), and maleic anhydride (MA) as coupling agents for thermoplastic wood composites [9-11]. The coupling agent (MA-PP or MA-PE) can modify the interface by interacting with both the filler and the matrix, thus forming a link between the components [12]. Kokta et al [8] and Raj et al [13] studied the use of polymethylene-polyphenyl-isocyanate (PMPPIC) as a coupling agent in thermoplastic wood composites. The addition of PMPPIC to the composites improved the mechanical properties compared to unmodified composites. Kokta et al [8] and Raj et al [13] also studied the use of silanes as coupling agents with different combination of solvent and additives in thermoplastic wood composites.

In the study of Oksman and Clemons [14] different modifiers (compatibilizers and impact modifiers) were investigated. Most promising was maleated styrene-ethylene-butadiene-styrene (MASEBS), which was found to act, not only as compatibilizer but also as impact modifier. Another way of modifying thermoplastic wood composites is crosslinking. Janigova et al [15] showed improved adhesion in peroxide crosslinked composites of wood flour filled low density polyethylene (LDPE) compared to non-crosslinked ones. The improved adhesion was explained as a result of covalent bonding between the wood and the LDPE matrix. The bonding was believed to be created as a result of recombina-

tion of radicals formed at the filler surface (after attack of peroxide oxy radicals) and polyethylene macroradicals. SEM-pictures showed a clear sign of de-wetting on the filler surface for non-crosslinked composites while patterns of fracture through the filler were visible for crosslinked composites.

Sapieha et al [16] proposed the same mechanism responsible for improved adhesion in crosslinked composites of low density polyethylene (LLDPE) and bleached hardwood pulp. Sain and Kokta [17] studied composites of polypropylene (PP) and thermosetting resin (epoxy and phenolic)-coated cellulosic fibers. Maleic anhydride graft-PP was used as compatibilizing agent. Trimethylolpropane triacrylate (TMPTA) which is a typical multifunctional low viscosity, low volatility liquid monomer, offers a fast cure response and low volatility during free-radical polymerization. It also favors the property of resistance against weather, chemical, water and abrasion. Choi et al [18] used mixture of styrene and TMPTA as binder for rice husk-plastic composite. They reported a decrease in the water absorption and increase in the flexural strength of the composite.

TMPTA have been extensively used as an initiator for crosslinking in many of the polymer applications and reported by many researchers [19-21]. Such compatibilized thermoplastic-thermoset composites were found to have tensile strength higher than that of unfilled PP and tensile toughness about as good as that of PP. In this study, the possibility of using TPMTA in crosslinking composites of Polypropylene-EFBB and Polypropylene-cellulose has been investigated.

2. Materials

Homopolymer polypropylene (PP) grade 600G (Melt index 11 g/10 min, density 900 kg/m³) was supplied by Petronas Polymers Marketing & Trading Division Malaysia, whereas TPMTA was purchased from UCB Asia Pacific, Malaysia. Empty fruit bunch fiber (EFBF) was purchased from Malaysian Palm Oil Board (MPOB). The cellulose was extracted from EFBF at lab scale by chlorination method (ASTM D1104).

3. Method

3.1. Preparation of raw materials

The EFBF were first washed thoroughly with 2.0% detergent water to remove the adhered oil and contaminants, and dried in an air oven at 100°C for 24 h. 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 h in a hot air oven at 105°C in order to remove the moisture content. The dried EFBF and cellulose were cut using Retsch Muhle cutter and were passed through 25 μ sieves to obtain uniform size of the filler.

3.2. Formulation

The PP-cellulose and PP-EFBF biocomposites were prepared by blending PP pellets with cellulose and EFBF in a fixed ratio of 70:30 (wt/wt). The concentra-

tion of compatibilizer was varied from 2.0 to 7.0 wt%. The biocomposites without the compatibilizers were used as control.

3.3. Compounding technique

The compounding of polypropylene, TMPTA, cellulose and EFBF was carried out by using a Brabender Plasticorder (PL2000-6, Germany) having a mixing cam attached at 180°C for 20 min. Roller speed used was 50 rpm. The compositions of biocomposites are given in Table 1. The blended melt were then cut into small pieces for compression molding.

Table 1. Composition of PP-Cellulose and PP-EFBF Biocomposite with Coupling Agent.

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

3.4. Compression molding

The cut pieces of the biocomposite melt were placed between a two-piece copper molding set and was hot pressed with hydraulic press at 190°C for 5.0 min of preheating under a pressure of 4.0 MPa followed by 3.0 min of complete pressing at a pressure of 14.7 MPa. This is followed by immediate cooling at 25°C for 3.0 min under pressure equipped with chiller facilities. Molded sheets of 1.0, 2.0 and 3.0 mm thickness were prepared for tensile, flexural, and impact testing, respectively.

3.5. Mechanical testing

Four important mechanical properties, tensile strength (Ts), flexural modulus (Fm), impact strength (Is) and Rockwell hardness (Rh) were tested. All test specimen dimensions were according to the respective ASTM standards. All tests were performed at room temperature. Seven specimens of each type were tested and five replicate values were taken as an average of tested specimens.

3.6. Tensile test

The tensile testing specimens were cut into dumbbell shape and the tests were conducted according to ASTM 1822L using INSTRON (Model 4301) Universal Testing Machine with load cell of 1.0 kN, using a crosshead speed of 50 mm/min.

The cross-head speed during the tension was 50 mm/min with load cell of 1.0 kN, and each test was performed until tensile failure occurred.

3.7. Flexural modulus

The flexural samples were cut into rectangular specimens and the testing was done according to ASTM D790-97 standard, using an INSTRON (Model 4301) universal testing machine. Three point bend method was implied for the test, cross-head speed during the bending was 1.3 mm/min with load cell of 1.0 kN, and each test was performed until failure occurred.

3.8. Impact strength

The impact tests were conducted according to ASTM D256 standard. The Izod method was carried out using notched samples by Impact Pendulum Tester (Model Ceast CE UM-636), using a 4 Joule hammer. Rectangular bar shaped specimens are tested for each composition with a thickness of 3 mm and their average values were calculated.

3.9. Rockwell hardness

The Rockwell hardness tester (Model HA-101) was used for measuring the relative hardness of soft materials. The test was done according to ASTM standard D785. Rockwell hardness was measured using a 12.7 mm ball and 60 kgf (588.4 N) of indent force (Rockwell scale L). Specimens were conditioned at 25°C ±50 % relative humidity (RH) prior to hardness testing.

4. Results and Discussion

4.1. Tensile testing

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. 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 polymer matrix and the interfacial bond strength.

Figure 1 shows the effect of TMPTA on the tensile strength of PP-biocomposites. It is apparent from Fig. 1 that TMPTA has more prominent effect on the tensile strength of PP-cellulose biocomposites at 2.0 wt%. This significant increase in the tensile strength of PP-cellulose compared to control PP-cellulose biocomposite is believed to be due to crosslinking at the surface of cellulosic sites between the active hydroxyl groups and the multifunctional TMPTA compatibilizer. More interesting is the significant increase in tensile strength with the TMPTA content. Without interfacial adhesion, between the fiber and the

matrix, the tensile strength would decrease with increasing in the filler content, as reported by many researchers [3, 15].

However, when crosslinking by TMPTA the polymer is in its solid state, and the crosslinks are located mainly in the amorphous regions and the crystalline structure is maintained [22]. Crosslinking of the amorphous regions of the polymer leads to a stronger material. In contrast, marginal increase is observed in PP-EFBB biocomposite. This demonstrates that the cross linking is hindered by the lignin, hemicellulose, waxes and other impurities present in the EFBB. Further increase in the concentration of TMPTA leads to plasticizing effect which gradually decreases the tensile strength of both biocomposites.

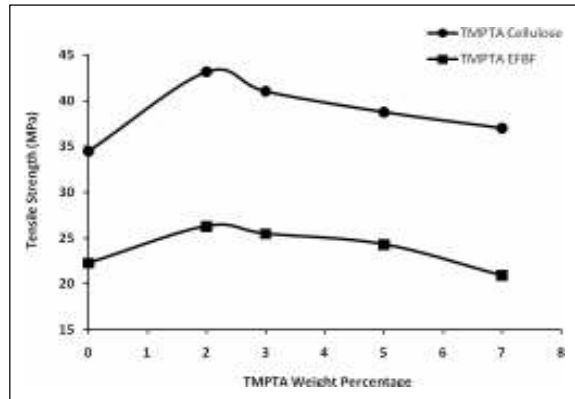


Fig. 1. Effect of TMPTA on Tensile Strength of PP-Biocomposites at 30 wt % Filler Loading.

4.2. Flexural modulus

Figure 2 shows the effect of TMPTA on the flexural modulus of PP-EFBB and PP cellulose biocomposites. It is clear from Fig. 2 that 2 wt % TMPTA is sufficient to improve the flexural properties of PP-cellulose biocomposite. Further addition of TMPTA cause decrease in the flexural modulus as observed to the tensile strength results. No significant changes were observed in the case of PP-EFBB biocomposite, suggesting that the interaction between TMPTA and lignin is of poor quality and this may cause poor wettability of the EFBB by PP hence, reduced stiffness. Moreover, the modulus is more or less independent of the presence of compatibilizers.

Flexural modulus is mainly dependant on the initial strain of the compound and is measured as the slope of the stress–strain curve at the initial stage and is practically not much influenced by the interfacial strength between the fiber and the matrix and the orientation of the filler Maldas et al [23].

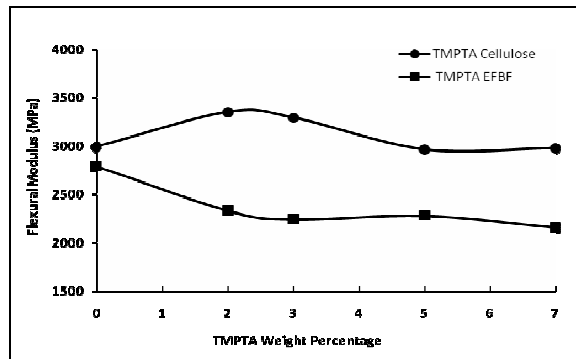


Fig. 2. Effect of TMPTA on Flexural Modulus of PP-Biocomposites at 30 wt % Filler Loading.

4.3. Impact strength

Figure 3 shows the effect of TMPTA on the impact strength of the notched PP-cellulose and PP-EFBF biocomposite where notch determines the crack initiated, as it is the predominant stress concentrated region and the impact strength reflects the energy required for the propagation of the existing crack. Notched impact strength of the PP-cellulose and PP-EFBF biocomposite show an increase in impact strength at 2.0 wt% TMPTA content. The enhancement in impact strength of both the biocomposites with the incorporation of TMPTA can be attributed to the more homogeneous dispersion of the fiber and, also due to the increased chain mobility of the polymer, which has improved the ability of the biocomposites to absorb the energy during fracture propagation. This leads to more uniform distribution of the applied stress which requires more energy for the fiber debonding and subsequent fiber pull out.

Further increase in the compatibilizer content tends to decrease or level the impact strength of the biocomposite. Moreover, too much interaction between the fiber and the matrix, as well as very poor interaction between them, leads to poor impact strength, as the earlier one leads to catastrophic brittle failure and the latter leads to easy fiber pull out [24]. This can be seen in the both cases where, the strong adhesion between fibers and PP matrix cannot stop the crack growth propagating through the matrix, and the crack can easily penetrate into fibers leading to catastrophic brittle failure. Therefore, an optimum interaction between the fiber and the matrix is essential to have good impact strength.

4.4. Rockwell hardness

Figure 4 presents the Rockwell hardness of the biocomposites. It is apparent from the figure that the hardness value of PP-cellulose biocomposites increases with increase in the TMPTA concentration, confirming the crosslinkage between PP and cellulose fibers. It was seen that the composites containing coupling agents with higher molecular weight will give higher hardness values [25]. However, no significant changes were observed in PP-EFBF biocomposite showing the poor compatibility of fiber with the TMPTA and PP matrix.

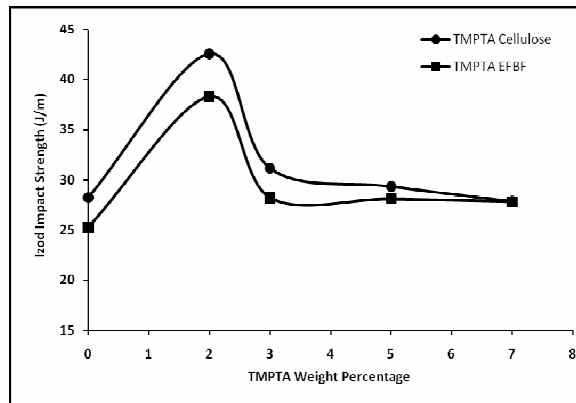


Fig. 3. Effect of TMPTA on Impact Strength of PP-Biocomposites at 30 wt % Filler Loading.

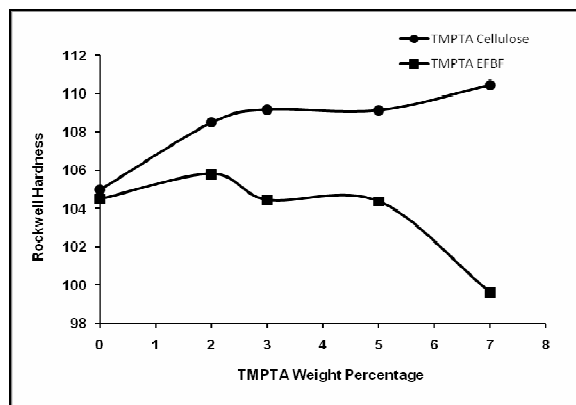


Fig. 4. Effect of TMPTA on Rockwell Hardness of PP-Biocomposites at 30 wt % Filler Loading.

5. Conclusion

TMPTA showed significant influence on the mechanical properties of the PP-cellulose biocomposite at only 2.0 wt% loading. In general, results revealed that the toughness of the both biocomposite is significantly improved by the addition of TMPTA. However, PP-cellulose biocomposite remains the better choice than PP-EFBF biocomposite as the tensile strength, flexural modulus, impact strength and Rockwell hardness showed better properties with the addition of 2 wt% TMPTA. Finally it can be postulated that the content of compatibilizer in the biocomposite depends on the application area and the economic aspects.

Acknowledgments

The author would like to thank the staff of Malaysian Nuclear Agency and Universiti Putra Malaysia for their support to carry out this research.

References

1. English, B., Chow, P., and Bajwa, D. S. (1997). Processing into composites. In: Rowell, R. M., Young, R. A., Rowell, J. K., editors. *Paper and Composites from Agro-Based Resources*. New York: CRC Press.
2. Oksman, K and Selin, J. F. (2004) Plastics and composites from polylactic acid. In: Wallenberger, F. T., Weston, N. E., editors. *Natural Fibers, Plastics and Composites*, Vol. 1. Norwell: Kluwer Academic Press.
3. Bledzki, A. K. and Gassan, J. (1999). Composites reinforced with cellulose based fibers. *Progress in Polymer Science* 24 (2), 221-274.
4. Plackett, D., Logstrup Andersen, T., Batsberg Pedersen, W. and Nielsen, L. (2003). Biodegradable composites based on l-poly lactide and jute fibers. *Composites Science and Technology*, 63(9), 1287–1296.
5. Mohanty, A. K., Misra, M. and Drzal, L. T. (2002). Sustainable biocomposites from renewable resources: Opportunities and challenges in the green materials world, *Journal of Polymers and the Environment*, 10(1), 19-26.
6. Premalal, H. G. B., Ismail, H. and Baharin, A. (2002). Comparison of the mechanical properties of rice husk powder filled polypropylene composites with talc filled polypropylene composites. *Polymer Testing*, 21(7), 833-839.
7. Oksman, K., Skrifvars, M. and Selin, J. F. (2003). Natural fibers as reinforcement in polylactic acid (PLA) composites. *Composites Science and Technology*, 63(9), 1317-1324.
8. Kokta, B.V., Raj, R. G. and Daneault, C. (1989). Use of wood flour as filler in polypropylene: studies on mechanical properties. *Journal of Polymer Plastic Technology and Engineering*, 28(3), 247–59.
9. Lai, S. M., Yeh, F. C., Wang, Y., Chan, H. C. and Shen, H. F. (2003). Comparative study of maleated polyolefins as compatibilizers for polyethylene/wood flour composites. *Journal of Applied Polymer Science*, 87(3), 487–96.
10. Kazayawoko, M., Balatinecz, J. J. and Matuana, L. M. (1999). Surface modification and adhesion mechanisms in wood fiber-polypropylene composites. *Journal of Material Science*, 4(24), 6189–6199.
11. Maldas, D. and Kokta, B. V. (1994). An investigation of the interfacial adhesion between reclaimed newspaper and recycled polypropylene composites through the investigation of their mechanical properties. *Journal of Adhesive Science and Technology*, 8(12), 1439–1451.
12. Felix, J. M. and Gatenholm, P. (1991). The nature of adhesion in composites of modified cellulose fibers and polypropylene. *Journal of Applied Polymer Science* 42, 609-620.
13. Raj, R. G., Kokta, B. V., Maldas, D. and Daneault, C. (1989). Use of wood fibers in thermoplastics. VII. The effect of coupling agents in polyethylene-wood fiber composites. *Journal of Applied Polymer Science*, 37(4), 1089–1103.
14. Oksman, K. and Clemons C. (1998). Mechanical properties and morphology of impact modified polypropylene-wood flour composites. *Journal of Applied Polymer Science*, 67(9), 1503–1513.

15. Janigova, I., Lednický, F., Nogellova, Z., Kokta, B. V. and Chodak, I. (2001). The effect of crosslinking on properties of low-density polyethylene filled with organic filler. *Macromolecular Symposium*, 169, 149–58.
16. Sapiuha, S., Allard, P. and Zang, Y. H. (1990). Dicumyl peroxide-modified cellulose/linear LDPE composites. *Journal of Applied Polymer Science*, 41(9):2039–2048.
17. Sain, M. M. and Kokta, B. V. (1993). Toughened thermoplastic composite. I. Crosslinkable phenol-formaldehyde and epoxy resins-coated cellulosic-filled polypropylene composites. *Journal of Applied Polymer Science*, 48(12), 2181–2196.
18. Choi, N. W., Mori, I and Ohama, Y. (2006). Development of rice husks–plastics composites for building materials. *Waste Management* 26: 189–194.
19. Han, D. H., Shin, S. H and Petrov, S. (2004). Crosslinking and degradation of polypropylene by electron beam irradiation in the presence of trifunctional monomers. *Radiation Physics and Chemistry* 69: 239–244.
20. Ratnam, C.T., Nasir, M and Baharin, A. (2001). Irradiation crosslinking of unplasticized polyvinyl chloride in the presence of additives. *Polymer Testing* 20: 485–490.
21. Ratnam, C. T., Nasir, M., Baharin, A and Zaman, K. (2000). Electron beam irradiation of epoxidized natural rubber. *Nuclear Instruments and Methods in Physics Research B* 171: 455-464.
22. Hjertberg, T., Palmlof, and Sultan, B.A. (1991). Chemical reactions in crosslinking of copolymers of ethylene and vinyltrimethoxy silane. *Journal of Applied Polymer Science*, 42(5), 1185–1192.
23. Maldas, D. and Kokta B. V. (1994). Role of coupling agents on the performance of wood flour-filled polypropylene composites. *International Journal of Polymeric Materials*, 27(1), 77–88.
24. Sain, M., Suhara, P., Law, S., and Bouilloux, A. (2005). Interface Modification and Mechanical Properties of Natural Fiber–Polyolefin Composite Products. *Journal of Reinforced. Plastic Composite*, 24, 121-130.
25. Sombatsompop, N., Yotinwattanakumtorn, C. and Thongpin, C. (2005). Influence of type and concentration of maleic anhydride grafted polypropylene and impact modifiers on mechanical properties of PP/wood sawdust composites. *Journal of Applied Polymer Science*, 97, 475–484.