



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Oil Palm Bio-Fiber Reinforced Thermoplastic Composites-Effects of Matrix Modification on Mechanical and Thermal Properties

¹S.S. Suradi, ¹R.M. Yunus, ¹M.D.H. Beg, ¹M. Rivai and ²Z.A.M. Yusof

¹Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Kuantan, Pahang Darul Makmur, Malaysia

²Department of Polymer Technology, UniKL MICET, Lot 1988 Taboh Naning, Kaw. Perindustrian Bandar Vendor, 78000 Alor Gajah, Melaka, Malaysia

Abstract: The incorporation of lignocellulosic materials as a reinforcing component in polymer composites has received increased attention, particularly for price driven and high volume applications. This development reflects several advantages of lignocellulosic fibers over their inorganic counterparts, including lower density, reduced abrasiveness to expensive moulds and mixing equipment, as well as being less expensive. Moreover, lignocellulosic based fibers are derived from renewable resources. The major challenge for natural fiber composites is their inherent poor adhesion between fiber and the matrix, high moisture absorption and UV degradation. Lignin and hemicelluloses are the components of natural fiber which are mostly responsible for moisture absorption and UV degradation. In this study, the lignocelluloses (Oil Palm Empty Fruit Bunch) were treated with alkaline peroxide to remove lignin and hemicelluloses. Composites were produced with treated and untreated fiber using up to 50% fiber with polypropylene (PP) matrix using twin-screw extruder followed by injection molding. Composites were characterized using tensile and flexural testing, SEM and TGA. The tensile and flexural modulus were found to be higher for alkaline peroxide treated fiber composites compared to untreated fiber composites. To improve interfacial bonding, additional of coupling agents also found to provide higher strength and modulus of composites. The treated fiber and their composites provided higher thermal stability compared to untreated fiber and their composites, respectively.

Key words: Lignocellulose, alkaline peroxide, oil palm empty fruit bunch fiber, composites

INTRODUCTION

Nowadays, enormous studies were developed on potential of natural fibers as reinforcement in thermoplastics which has been shown in important industries such as automotive, construction or packaging industry. 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 are comparable to those of inorganic fibers (Habibi *et al.*, 2008; Arib *et al.*, 2006). There are many fibers that has been explored as reinforcement for polymer matrix. Oil palm biomass is considered a potential source of biofiber; based on Zain *et al.* (1994), almost more than 30 million metric ton of entire oil palm production in the world is considered by product or agriculture material and about 8 million metric ton is empty fruit bunch materials.

The main disadvantage of natural fibers/plastic composites is the poor compatibility between the mainly hydrophobic polymer-matrix and the hydrophilic fibers. This leads to the formation of a weak interface, which results in poor mechanical properties; where the stress transfer at the interface between two different phases is determined by the degree of adhesion. A strong adhesion at the interfaces is needed for an effective transfer of stress and load distribution throughout the interface. Thus, enhanced interfacial adhesion for composites containing natural fibers would provide higher mechanical properties that can be achieved either by fiber and matrix modification with chemical/physical treatments or by use of interfacial additives such as delignification, bleaching and chlorination (Spoljaric *et al.*, 2009; Khalid *et al.*, 2008).

Due to the utilization of chlorine and chlorine derivatives in conventional bleaching processes, large amounts of chlorinated organic compounds are generated,

which presents serious environmental problems. Therefore, the use of chlorine-free bleaching processes has become increasingly important. A few studies have been performed on delignification of lignocelluloses materials with alkaline hydrogen peroxide (Bengtsson *et al.*, 2007; Rozman *et al.*, 2003).

The purpose of this study was to investigate the mechanical properties of composite based on untreated and treated fibers with addition of coupling agent. The present paper is focused on study of new fabrication method of fibers by alkaline peroxide treatment. Within the framework, the role interfacial morphology and thermal stability of fiber and composites were analyzed by means of Thermo Gravimetric Analyzer (TGA) and Scanning Electronic Microscopy (SEM) including mechanical properties of prepared composites.

MATERIALS AND METHODS

Materials: Homopolymer polypropylene (PP) grade G452 (Melt flow Index 45 g/10 min, density 0.90 g cm⁻³) was supplied by MTBE (M) Sdn Bhd, Empty Fruit Bunch Fibers (EFBF) was obtained from Felda Palm Oil Berhad and other chemicals supplied from Merck.

Methods

Alkaline peroxide pre-treatment of Empty Fruit Bunch (EFB): Generally, preparation of EFB was carried out in two stages. The first stage is physical treatment where empty fruit bunch was dried for minimum three days, then were cut using hammer mill and crusher machine and was passed through 500 µm sieve to obtain uniform size of empty fruit bunch fiber. After that, untreated fibers were soaked with hot distilled water at 70°C at least for 4-6 h to remove impurities and large particles. Then, fiber was treated with alkaline peroxide by placing about 25 g fibers in 500 mL Erlenmeyer flask of distilled water containing 15% (w/v) of sodium hydroxide (NaOH) solution. These delignified fibers were then soaked and maintained at 75°C about 3 h to active the OH group of the cellulose. The fiber treatment method is commonly known as mercerization. After 2 h treatment, EFB fibers were taken out and washed with distilled water. Then, was treated with 2% of Hydrogen peroxide (H₂O₂) solution in water bath at 45°C with a speed of 50 rpm for 8 h. The excess NaOH present in treated fiber residue was neutralized by using 10% (v/v) acetic acid (at room temperature) for 30 min. Then, the treated fiber was dried in an oven at 70°C for 48 h.

Preparation of composite: The compounding of polypropylene with untreated and treated EFB fibers, with and without additional of coupling agent (MAPP) was

carried out using twin screw compounder Scientific (MODEL: LTE26-40) at 180°C at a roller speed around 50 rpm and pressure about 48 bar. Coupling agent (MAPP) was added as 10:1 fiber to MAPP ratio. Composite was molded into tensile and bending test specimen, respectively by using injection molding machine (Toshiba, MODEL: IS 80 EPN) at 190°C. After molding, test specimens were conditioned at 23±2°C, with 50 % relative humidity for at least 40 h according to ASTM D618-99.

Characterizations

Fibers and composites: The surface and thermal characteristics were determined by using SEM and TGA. Surface of fibers before and after pre-treatment as well as fracture surface of composites was observed with a scanning electron microscope (SEM) (Model OXFORD). Samples of air-dried cellulose fibers were fixed to a metal-base specimen holder using double-sided sticky carbon tape and then coated with gold using a vacuum sputter-coater to make them conductive prior to SEM observation.

TGA analysis was carried out using thermogravimetric analyzer (TA instruments, TGA Q500). Each specimens (weighed about 10 mg) were run at scanning temperature range of 25-600°C and heating rate of 10°C min⁻¹. TGA was conducted with the compounds placed in platinum crucible in nitrogen atmosphere at flow rate of 40 mL min⁻¹ to avoid unwanted oxidation.

Mechanical properties of composite: The mechanical properties of composite were characterized using tensile, flexural and impact tests. The tensile tests were conducted according to ASTM D638-03 using SHIMADZU (MODEL AG-1) Universal Testing Machine with load cell of 5 kN, using crosshead speed of 10 mm min⁻¹ and with a gauge length of 115 mm. Test was performed until tensile failure occurred. The flexural test was carried out using SHIMADZU (MODEL AG-1) Universal Testing Machine in accordance with ASTM D790-97 standard. The support was 51 mm while the crosshead speed utilized was 1.26 mm min⁻¹. Eight specimens were tested and at least five replicate specimens were presented as an average of tested specimens for all batches. These tests were carried out at 25°C.

RESULTS AND DISCUSSION

Characterization of fibers before and after alkaline-pretreatment

Scanning Electron Microscope (SEM-EDS): Based on Fig. 1a, the rough surface of lignocelluloses EFB can be seen which may be due to high residual of lignin content.

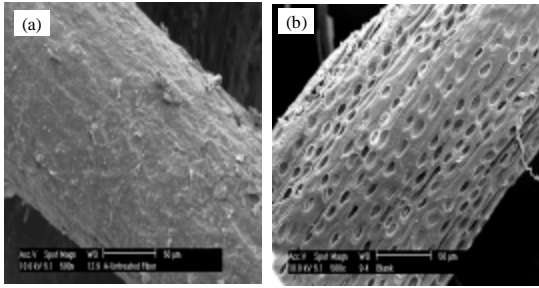


Fig. 1: Fiber surface before (a) and after (b) pre-treatment

While, by applying alkaline peroxide treatment, residual lignin was eliminated as per Fig. 1b.

Alkaline peroxide treatment can improve adhesion characteristics between fiber-PP matrix by removing surface impurities such as lignin content. Then, breakdown the fiber bundles led increasing of porosity, the effective surface area and surface charge exposed further hydroxyl and carboxyl groups, thus exposing micro-fibrils which tend better packing of cellulose chain (Pracella *et al.*, 2006). Furthermore, some researchers reported on the change in the crystallinity through alkaline treatment on sugarcane, coir and flax (Bledzki and Gassan, 1999). The percentage crystallinity index of alkali peroxide treated fibers might be increased because of the removal on the cementing materials, which leads to better packing of cellulose chain (Sun *et al.*, 2004). In addition, treatment with NaOH leads to decrease in the spiral angle, i.e., closer to fiber axis and increase in the molecular orientation. A fair amount of randomness is introduced in the orientation of the crystallites due to non-cellulosic matter. Moreover, the mechanical properties of composites shown to be increased through alkalization peroxide (Averous and Le Digabel, 2006; Le Digabel and Averous, 2006; Bengtsson *et al.*, 2007) due to the improved fiber-matrix bonding.

Thermogravimetric analysis (TGA): The thermogravimetric analyses (TGA) are shown in Fig 2. The onset of thermal degradation can be identified by dramatic decrease in sample weight and increase in the temperature different due to exothermic combustion reaction. The thermal degradation of untreated EFB fiber begins around 217.90°C, while treated EFB fiber starts at around 229.19°C. Untreated fiber degrades at lower temperature due to presence of thermally unstable fiber constituents such as hemicelluloses, holocelluloses, lignin, whereas the treated fiber is more stable due to the removal of these constituents (Beckermann and Pickering, 2008).

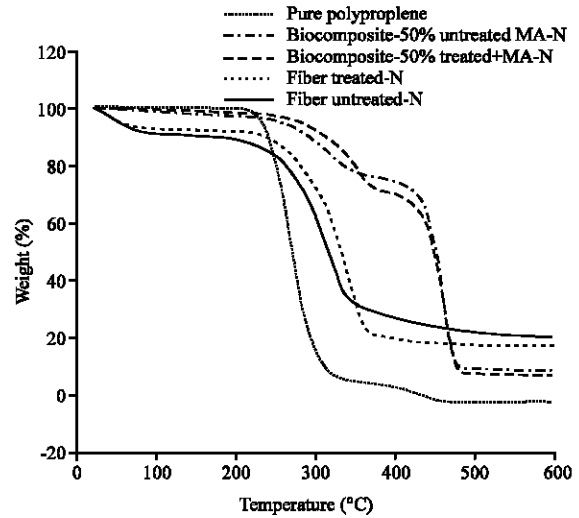


Fig. 2: TGA thermograms of (a) Pure polypropylene, untreated and treated composite with MAPP samples

There are interactions between these fractions to identify the multiple exothermic degradation reaction of cellulose, hemicelluloses and lignins. The maximum decomposition rate of untreated fiber was found to be at 268°C is mainly attributed to the decomposition of hemicelluloses. This is likely caused by decomposition of cellulose leading to the formation and volatilization of levoglucosan and other volatile products (Beckermann and Pickering, 2008), attributed to quick devolatilization reaction (Spinace *et al.*, 2009). It can be concluded that alkaline treatment increases the thermal stability of EFB than untreated EFB fiber.

Similar TGA pattern was found for composites, however, there was a shifting from low to high temperature compared to fiber alone. Specific interaction between fibers and maleic anhydride can established an association through esterification between the anhydride groups and the hydroxyl groups of the fibers after treatment (Spoljaric *et al.*, 2009) which results in higher thermal stability of composites containing treated fiber.

Characterization of composites

Tensile properties: The most crucial factor that affects the mechanical properties of fiber-reinforced materials is the fiber volume fraction and 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 method and the treatment of the fiber (Gomes *et al.*, 2007; Pracella *et al.*, 2006). In the case of PP-lignocelluloses (EFBF) composite without pre-treatment, adhesion between the two materials was expected to be rather poor than the PP-lignocelluloses (EFBF) composite with

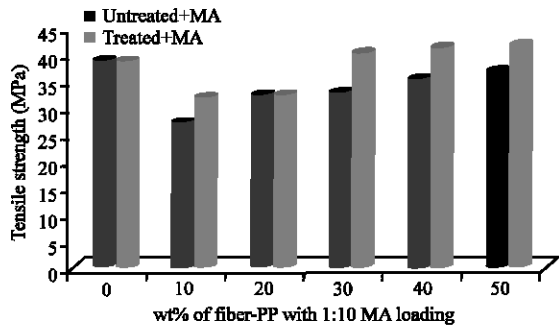


Fig. 3: Tensile strength of lignocellulose based biocomposite

application of treated EFBF. EFBF has polar nature whereas polypropylene is characterized by non-polar groups. Due to the changes in physical structure it was expected for treated lignocelluloses (EFBF) to show some changes in the overall properties. The tensile properties of composites are presented in Fig. 3.

By applying 100% Polypropylene as benchmark, the tensile strength was found to be 38 MPa. The weak bonding between the hydrophilic lignocelluloses filler and the hydrophobic matrix polymer obstructs the stress propagation and causes the tensile strength to decrease as the filler loading increases as explained in many researches (Spoljaric *et al.*, 2009; Habibi *et al.*, 2008; Khalid *et al.*, 2008). Therefore by additional of coupling agent, it enhanced interfacial adhesion between the PP matrix and EFBF filler which treated composite increased significantly rather PP-untreated EFBF composite as per expectation which also can be seen in Fig. 3. These suggests likely due to be attributed to the covalent bonds created between the fiber and the coupling agent and which were ensured by the maleate groups. Moreover, MAPP underwent esterification reaction or hydrogen bonding, at the interface, between the hydroxyl groups of the fibers on one side and the carboxylic groups of the MAPP diffused matrix polymer on the other side (Habibi *et al.*, 2008; Arib *et al.*, 2006; Khalid *et al.*, 2008). Based on Fig. 3 it can be seen that the tensile strength of the MAPP-treated EFBF composite were significantly greater than those of the MAPP-untreated EFBF composite with increasing of fibers till 50 wt% loading. These possible mechanisms have been illustrated in Fig. 4.

It can be seen on Fig. 4 of SEM study that the untreated EFB composite fracture as Fig. 4a had occurred predominantly by transversal fracture in the plane matrix. It is observed that fibers oriented in random arrangement. There are gaps between fibers and matrix which some deep holes left, with more fibers breakage and less pull

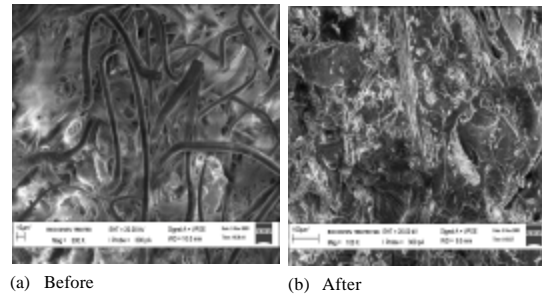


Fig. 4: Biocomposite before (a) and after (b) after pre-treatment with addition of MAPP

out tends weak adhesion and inefficient stress transfer from matrix. Fracture surface of composite with treated fibre (Fig. 4b) showed modification in topographic aspects of the mark developed at matrix surface and clearly improved strong bonding. In addition more of fibers breakage can be seen which indicated improvement adhesion between fiber and matrix. It can be seen in treated composite with MAPP is covered by the layer of matrix material that had been pulled out together with the fiber. This is also a clear indication that treated composite has an effective interaction with PP matrix and have better capability to support stress transfer than the untreated composites from the polymer matrix.

Flexural modulus properties: Modulus (stiffness) is another basic property of composites; the primary intention of filler incorporation is usually to increase the stiffness of the resultant material. The elastic modulus of bulk natural fibers such as wood and hemp are about 1.0 ± 0.5 GPa (Khalid *et al.*, 2008; Luz *et al.*, 2008). Composites with additional MAPP as coupling agent, provided better flexural modulus rather than without coupling agent.

It can be seen as per Fig. 5 that increasing filler content increased the stiffness of composites significantly till loading 50% of fibers. PP-treated EFBF with MAPP composite showed significant increase compared to untreated EFBF till fiber loading is 50wt% which increased from 2.7 to 3.5GPa. There are many factors affecting the modulus of the composites. Those factors are filler content, modulus and aspect ratio. As per expectation, the elastic modulus of fibers, for instance are expected to increase with increasing degree of molecular orientation. Well-oriented cellulosic fibers such as flex have much higher Young's modulus than fibers with medium orientation, such as cotton (Colom *et al.*, 2003).

Not only that, it is may be because alkaline reacts with cementing materials of the fiber, splitting the fibers into sfiner filaments. In addition, combination of alkaline

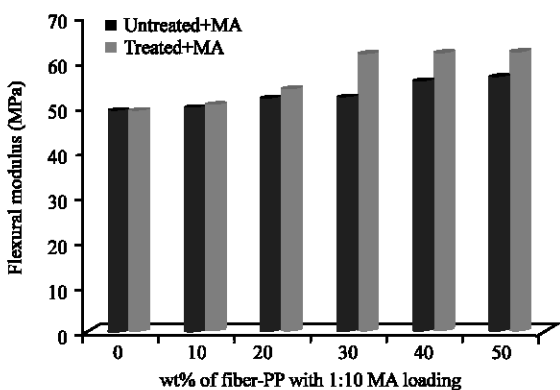


Fig. 5: Flexural modulus of lignocellulose based biocomposite

peroxide enhanced the porosity and pore size on the fiber where improved physical interlocking leading better interfacial bonding between fiber and matrix which illustrated as per Fig. 1a and b. By addition of coupling agent as compatibilizer as per Fig. 4b indicated better interfacial bonding between fiber and polypropylene as matrix which enhanced mechanical properties.

The addition of MAPP with EFBF composite has enhanced the efficiency of stress transfer from matrix to the EFB. This is may come about as the result of better bridging between these two component at interfacial region. It is known that compatibility, in general, between polymer matrix and reinforcing agent is one of the main criteria to produce a good mechanical characteristic of a composite (Bengtsson *et al.*, 2007; Georgopoulos *et al.*, 2005). This bridging may be formed either by Van der Waals Covalent bonding between MAPP which attached to EFBF and PP could be through the opening C = C group in MAPP through radical reaction of dicumyl peroxide (Spoljaric *et al.*, 2009). This can be illustrated in Fig. 4b. Hence, the increased adhesion brought by the C=C group's reaction with the PP matrix, together with other means of enhancing compatibility such as Van der Waals interaction, should be reflected in the mechanical properties. Moreover, due to better compatibility and wetting of MAPP to the PP matrix polymer improved interfacial bonding between the filler and the matrix polymer resulted in good stress propagation and improved the tensile strength.

CONCLUSION

This study showed that addition of coupling agent with pre-treatment of EFB fiber provided better interfacial interaction with polypropylene matrix in term of mechanical and thermal properties. The improvement of

ensile strength was significantly increased by filler loading till 50wt% after addition of coupling agent. Flexural modulus was also indicated that treated EFB composite with coupling agent provides better interfacial bonding chain rather than untreated EFB composite till 50wt% fiber loading. SEM and TGA showed evidence of better adhesion and compatibility between the EFB fibers and the PP after modification matrix with MAPP as coupling agent as well as better thermal stability.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the staffs of Felda Palm Industries Berhad (Felda Lepar Hilir 3), Fiber and Biocomposite Development Centre (FIDEC) and Polypropylene Laboratory of MTBE (M) Sdn Bhd for their technical support to carry out this research.

REFERENCES

- Arib, R.M.N., S.M. Sapuan, M.M.H.M. Ahmad, M.T. Paridah and H.M.D.K. Zaman, 2006. Mechanical properties of pineapple leaf fibre reinforced polypropylene composites. *Mater. Design*, 27: 391-396.
- Averous, L. and F. Le Digabel, 2006. Properties of biocomposites based on lignocellulosic fillers. *Carbohydrate Polymers*, 66: 480-493.
- Beckermann, G.W. and K.L. Pickering, 2008. Engineering and evaluation of hemp fiber reinforced polypropylene composites: Fiber treatment and matrix modification. *Composites Part A: Applied Sci. Manufactur.*, 39: 979-988.
- Bengtsson, M., M.L. Baillif and K. Oksman, 2007. Extrusion and mechanical properties of highly filled cellulose fibre-polypropylene composites. *Composites Part A: Applied Sci. Manufactur.*, 38: 1922-1931.
- Bledzki, A.K. and J. Gassan, 1999. Composites reinforced with cellulose based fibres. *Prog. Polym. Sci.*, 24: 221-274.
- Colom, X., F. Carrasco, P. Pages and J. Canavate, 2003. Effects of different treatments on the interface of HDPE/lignocellulosic fiber composites. *Composites Sci. Technol.*, 63: 161-169.
- Georgopoulos, S.T., P.A. Tarantili, E. Avgerinos, A.G. Andreopoulos and E.G. Koukios, 2005. Thermoplastic polymers reinforced with fibrous agricultural residues. *Polymer Degradation Stability*, 90: 303-312.
- Gomes, A., T. Matsuo, K. Goda and J. Ohgi, 2007. Development and effect of alkali treatment on tensile properties of curaua fiber green composites. *Composites Part A: Applied Sci. Manufactur.*, 38: 1811-1820.

- Habibi, Y., W.K. El-Zawawy, M.M. Ibrahim and A. Dufresne, 2008. Processing and characterization of reinforced polyethylene composites made with lignocellulosic fibers from Egyptian agro-industrial residues. *Composites Sci. Technol.*, 68: 1877-1885.
- Khalid, M., C.T. Ratnam, T.G. Chuah, S. Ali and T.S.Y. Choong, 2008. Comparative study of polypropylene composites reinforced with oil palm empty fruit bunch fiber and oil palm derived cellulose. *Mater. Design*, 29: 173-178.
- Le Digabel, F. and L. Averous, 2006. Effects of lignin content on the properties of lignocellulose-based biocomposites. *Carbohydrate Polymers*, 66: 537-545.
- Luz, S.M., J. Del Tio, G.J.M. Rocha, A.R. Goncalves and A.P. Del'Arco, 2008. Cellulose and cellulignin from sugarcane bagasse reinforced polypropylene composites: Effect of acetylation on mechanical and thermal properties. *Composites Part A: Applied Sci. Manufactur.*, 39: 1362-1369.
- Pracella, M., D. Chionna, I. Anguillesi, Z. Kulinski and E. Piorkowska, 2006. Functionalization, compatibilization and properties of polypropylene composites with Hemp fibres. *Composites Sci. Technol.*, 66: 2218-2230.
- Rozman, H.D., M.J. Saad and Z.A. Mohd Ishak, 2003. Flexural and impact properties of oil palm empty fruit bunch (EFB)-polypropylene composites: The effect of maleic anhydride chemical modification of EFB. *Polymer Testing*, 22: 335-341.
- Spinace, M.A.S., C.S. Lambert, K.K.G. Feroselli and M.A. De Paoli, 2009. Characterization of lignocellulosic curaua fibres. *Carbohydrate Polymers*, 77: 47-53.
- Spoljaric, S., A. Genovese and R.A. Shanks, 2009. Polypropylene-microcrystalline cellulose composites with enhanced compatibility and properties. *Composites Part A: Applied Sci. Manufactur.*, 40: 791-799.
- Sun, J.X., R.C. Sun, X.F. Sun and Y.Q. Su, 2004. Fractional and physico-chemical characterization of hemicelluloses from ultrasonic irradiated sugarcane bagasse. *Carbohydrate Res.*, 339: 291-300.