THE EFFECTS OF MALEIC ACID ON SOME MECHANICAL AND END-USE PROPERTIES OF BAMBOO POWDER FILLED LOW DENSITY POLYETHYLENE COMPOSITES

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ABSTRACT

In all composites, it is necessary to create an adequate interface between the polymer matrix and the fibres (fillers) to generate good stress transfer during loading. When the polymer is non-polar, compatibilizers or coupling agents must be used to improve adhesion between matrix and fibres. In this research work, Maleic acid is the coupling agent used. The effect of Maleic Acid on some mechanical and end-use properties of Bamboo powder filled low density polyethylene composites was studied. Composites of LDPE and bamboo powder (BP) were prepared by melt extrusion using 0, 1, 3, 5 and, 7 % of bamboo powder filler. The process was repeated with the addition of 2 % (of LDPE weight) of maleic acid to each sample before being extruded. The results showed that the composites containing maleic acid showed better mechanical and end-use properties for all filler loadings. The tensile strength and the elongation at break decreased with increasing filler loading for LDPE/BP composites; however, the tensile strength showed substantial improvement in the presence of maleic acid. The addition of maleic acid produced materials with lower void content that decreased the water sorption level with slight increase in the specific gravity of the composites.

Keywords: Low Density Polyethylene (LDPE), Bamboo Powder (BP), Composites, Matrix, Organic Filler, Maleic Acid, Coupling Agent

INTRODUCTION

Composites are combinations of two or more than two materials in which one of the materials, is reinforcing phase (fibres, sheets or particles) and the other is matrix phase (polymer, metal or ceramic). Composite materials are usually classified by type of reinforcement such as polymer composites, cement and metal- matrix composites (Bhatnagar, 2004). Polymer matrix composites are mostly commercially produced composites in which resin is used as matrix with different reinforcing materials. Polymer (resin) is classified in two types thermoplastics (polyethylene (PE), polypropylene (PP), polyether ether ketone (PEEK), polyvinyl chloride (PVC), polystyrene (PS), polyolefin etc.) and thermosets (epoxy, polyester, and phenol–formaldehyde resin, etc.) which reinforces different type of fibre like natural (plant, animal, mineral) and man-made fibre for different application (Cowie, 1991; Crawford, 1998). Natural fibre reinforced thermoplastic composites (NFRTC) represent an opportunity to partially enhance the environmental impacts by integrating biodegradable filler material, such as flax, hemp, wood flour and bamboo, as an alternative for synthetic fillers, such as glass, carbon, or steel and perhaps more critically, the cost of some biodegradable filler materials is better than an order of magnitude less than synthetic reinforcing fibers.

(http://dspace.unimap.edu.my/bitstream/1,2,3,4,5,6,7,8,9/3362/6/introduction.pdf).

Due to increase in population, natural resources are being exploited substantially as an alternative to synthetic materials. Due to this, the utilization of natural fibres for the reinforcement of the composites has received increasing attention. Natural fibres have many remarkable advantages over synthetic fibres. Nowadays, various types of natural fibres (Charier and Rieger, 1974; Espiloy, 1991) have been investigated for use in composites including flax, hemp, jute straw, wood, rice husk, wheat, barley, oats, rye, cane (sugar and bamboo), grass, reeds, kenaf, ramie, oil palm, sisal, coir, water hyacinth, pennywort, kapok, paper mulberry, banana fibre, pineapple leaf fibre and papyrus. The use of the natural fibres, which is a type of organic filler, in polymeric materials especially in the thermoplastic polymer to form composite had been widely developed in order to reduce wastage of the natural fibres (Sapuan and Maleque, 2005; Dahl, 1947).

Natural fibre-reinforced polymer composites have attracted more and more research interests owing to their potential as an alternative for synthetic fibre composites such as glass or carbon fibre composites. Natural fibre composites posses the advantages such as easy availability, renewability of raw materials, low cost, light weight and high specific strength, and stiffness. Thermoplastic resins such as polypropylene, polyethylene, polystyrene and poly (vinyl chloride) soften when heated and harden when cooled. These characteristics allow other materials such as wood to be blended or mixed with the plastic to form a composite product (Adrian et al 2002, Christensen and Waals, 1974).

It is necessary to create an adequate interface between the polymer matrix and the fibres (fillers), in all composites, to generate good stress transfer during loading. Chemical polarity of the matrix will favour interaction with the fibres (fillers), since cellulose has a large number of –OH groups on the surface. When the polymer is non-polar, such as PP and PE, compatibilizers and coupling agents must be used to improve adhesion between matrix and fibres. They are bifunctional molecules that can interact or even react with both the non-polar matrix and with the very polar fibre (filler). Another alternative is to promote chemical attack of the fibre (filler) surface, rendering it more irregular to facilitate adhesion to the polymer matrix. Among these the use of compatibilizer has shown to be more efficient in improving interface adhesion.

A number of investigations have been carried out to explore the capability of additives to enhance adhesion and improve properties such as tensile strength, flexural strength and others. (Patil, et al, 2000; Chand, and Dwivedi, 2006).

The coupling agent is chosen to form chemical bonds between the cellulose chains in the fibres and polymer matrix. There has been a lot of research over the past decades on different types of coupling agents to improve the adhesion between the cellulose and the plastic. The most commonly used coupling agents are maleate polyolefin. Generally, coupling agent has improved significantly the toughness of the cellulose based plastic composite. (Patill, et al, 2000; Chand, and Dwivedi, 2006). Maleic acid (also called cis-butenedioic acid), a white crystals easily soluble in water, acetone, and alcohol, is an unsaturated organic dibasic acid which carboxylic acid groups are next to each other in the cis form. Its trans form isomer is fumaric acid; both are used in making polyesters, alkyd resins, plasticizers and lubricating oils. Maleic acid is used in the preparation of fumaric acid by catalytic isomerization and other chemical products as a carboxylating agent. It is used as an oil and fat preservative and food acidulant, some researchers has used it as coupling agent in polymer/fibre composites. (James, and Williams, 1974; http://oru.edu/cccda/sl/solubility/all sovent.php?Solute = maleic % 20 acid; Kwesi, 1948).

EXPERIMENTAL

Materials

In this research, Low Density Polyethylene (LDPE) and Bamboo (Dendrocalamus strictus) Powder were used. The LDPE has a density of $0.923g/cm^3$, and melt flow index of 2.25g/min and was obtained from Eleme Petrochemical Company, EPCL (now known as INDORAMA), Port Harcourt, Rivers State, Nigeria. The density of the Bamboo is $0.649g/cm^3$. The maleic acid used in this study was made by J.T. Baker, a division of Mallinckrodt Baker Inc., Philipsburg, USA and supplied by Rovet Scientific Limited, 1 Wire road, Benin City, Edo State, Nigeria.

The processing equipment used includes Mesh sieve (0.3mm), Cutlass, Laboratory Size single screw extruder, Instron machine (Universal Testing Machine),Electronic weighing balance, Shredding machine, Permanent marker (Ink), Grinding Machine, Personal Protective Equipment (PPE).

Preparation of Low Density Polyethylene Composites

The bamboo stem was shredded and the dust from the shredded bamboo stem was collected, sun-dried for three days to remove moisture from it. Then a home-made grinder was used to manually grind the bamboo dust to powder. The bamboo powder was later sieved at the Erosion Control Laboratory, FUTO.

The low density polyethylene composites of the bamboo powder filler of particle size 75um (0.3mm size) were prepared by thoroughly mixing 200g of low density polyethylene with appropriate filler quantities (0, 1, 3, 5 and 7 wt %) loadings. The prepared blend compositions were each extruded at the same temperature (145^0C). The process was repeated with the addition of 2 % (of LDPE weight) of maleic acid to each sample before being extruded.

Measurement of Mechanical Properties

Tensile properties of the composites were determined by an Instron Electromechanical Universal Testing Machine (UTM) - LR10K, model 3 type; using ASTM D5323 test method. 5 identical dumb bell samples for each composite were used to determine the tensile properties. Tensile Strength, Elongation at Break and Young's Modulus were recorded and calculated automatically by the instrument's software.

Water Sorption Test

The extruded samples sheet was cut into identical average dimension of about 12mm * 15mm *2mm.Then the cut samples were weighed with electronic weighing balance and it is recorded as the initial weight. The test piece was loaded into a container (sample bottles) filled with water and they were immersed in water for 24 hours (one day) at 32^oC (room temperature).The test piece was then removed from their container, dried with filter paper to remove excess of water and weighed. The percentage of water sorption (24hours) was calculated using the expression:

Water Sorption (%) = $\underline{W_{f\,\text{-}\,}W_i}$ x 100 ……………………………….. (1)
$\qquad\qquad\qquad W_i$

Where W_i is the initial dry weight of the sample and
W_f is the final weight of the sample after 24hours of immersion in water.

Specific Gravity Test

An analytical weighing balance was used for specific gravity estimation. A beaker is used as an immersion vessel. A light thread was used in suspending the specimen in air, and water

during weighing. A test specimen (filled or unfilled low density polyethylene) was first weighed in air (n), and later in water (m).The specific gravity of filled or unfilled low density polyethylene was calculated using the expression:

Specific Gravity (S.G.) = $\dfrac{n}{m}$ …………………………………………… (2)

Where n = weight of specimen in air
    m = weight of specimen in water.

Flammability Test

A modification of ASTM D4804 method was used here. Since low density polyethylene filled or unfilled is a thermoplastic, flame spread is regarded as the rate of melt-burn, i.e. the rate at which the original length of the specimen decreases as flame/heat is applied or plays among the specimens.

A 6mm mark was made on each of the sample specimen. The specimen was then clamped horizontally in a retort stand with the mark 6mm distance protruding out of the clamp. The free end of the sample was ignited using a cigarette lighter, and the time taken for the sample to ignite was recorded as the ignition time (I_t). The sample was allowed to burn to the 6mm mark (D_p).

The relative rates of burning for the different samples were determined using the expression:

Rate of burning (mm/s) = $\dfrac{D_{p\ (mm)}}{P_t - I_t\ (s)}$ …………………………………… (3)

Where D_p = Propagation distance measured in millimeter
    P_t = Flame propagation time measured in seconds
    I_t = Ignition time measured in seconds.

RESULTS AND DISCUSSION

Mechanical Properties

Table 1. Some mechanical properties of bamboo powder filled LDPE composites as a function of filler and coupling agent content

Sample	Wt. % of Filler	Wt. % of Coupling Agent	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
1	0	0	7.788	1169.372	5.304
2	1	0	5.007	1032.825	8.098
3	3	0	4.531	78.092	15.665
4	5	0	4.028	63.749	15.980
5	7	0	3.441	58.490	16.219
6	1	2	5.320	1001.419	6.639
7	3	2	5.022	56.769	8.583
8	5	2	4.093	35.825	8.664
9	7	2	3.952	28.952	8.767

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Tensile Strength

The effect of filler loading on the tensile strength of BP-filled LDPE composites can be seen in Table 1. The tensile strength for the composites decreases with increasing filler loading. This result, as shown in Figure 1, is similar to reports by Garg et al (2007). According to Salmah et al (2005), the decrease in tensile strength is due to the poor adhesion of the filler-matrix and the agglomeration of filler particles. Since the filler particles are very small, a high interfacial surface exists between the polar filler and the apolar matrix. The presence of voids obstructs stress propagation when tensile stress is loaded and induces increased brittleness (Yang et al, 2004). Bamboo powder filler is known for easy agglomeration. The presence of agglomerates can generate flaws and create additional voids between the filler and the polymer matrix thus diminishing tensile strength (Chand and Dwivedi, 2006). Figure 1, also shows the relationship between the tensile strength and the filler loading in the presence of the coupling agent. The tensile strength for LDPE filled with BP and Maleic acid (LDPE/BPMA composites) is higher than that for LDPE/BP composites. This is probably because of a better interfacial adhesion between the filler and the matrix after chemical modification by the addition of maleic acid as coupling agent. Strong adhesion between filler and matrix interface can cause better stress transfer from matrix to filler leading to a higher tensile strength (Morreale, et al, 2007). Maleic acid which has a hydrophilic side that is compatible with the filler and a hydrophobic side that is compatible with the LDPE, react with the surface of the inorganic and to form bonds. Without the maleic acid (coupling agent) there is simple adhesion of the polymer to the filler through weak bonding, i.e. Van der Waals or induction interactions (Baron, and Scmidth, 2005, Christensen, 1976; Elias, 1977). Addition of 2 wt % maleic acid (with respect to the polymer content) showed increase in the tensile strength of the composites for all filler loading indicating that it can be efficiently used as coupling for these LDPE/BP composites.
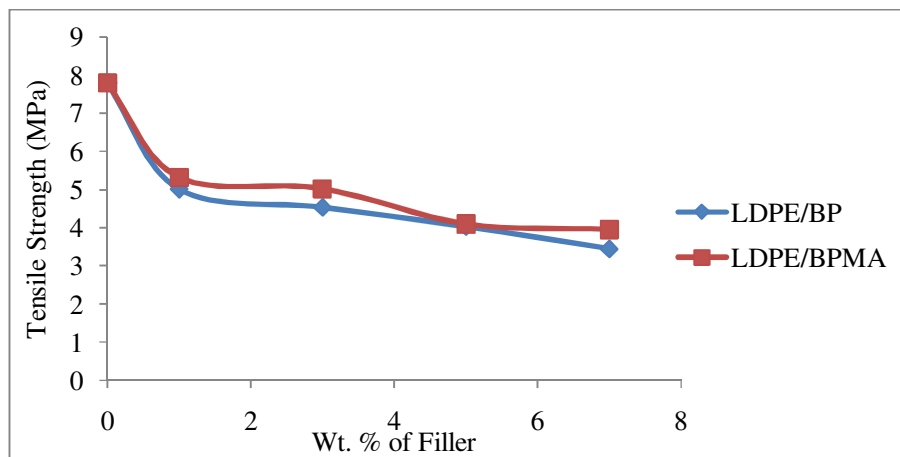

Figure 1. Effect of Filler Loading on the Tensile Strength of Bamboo Powder / Low Density Polyethylene Composites

Elongation at Break

From Figure 2, it can be seen that the elongation at break for the composites decreases with increasing filler loading. Increased filler loading in the LDPE matrix resulted in the stiffening and hardening of the composites. This reduced its resilience and toughness, and led to lower elongation at break (Jacob et al, 2004; Challa, 1993).The reduction of the elongation at break with increasing filler loading indicates the incapability of the filler to support the stress transfer from the filler to the matrix. It can also be seen from Figure 2 that the elongation at break for the LDPE/BP composites is slightly higher than that of the LDPE/BPMA

composites. This is due to the addition of maleic acid in the composites. The stiffness of the composites increased gradually with associated decrease in the elongation at break.
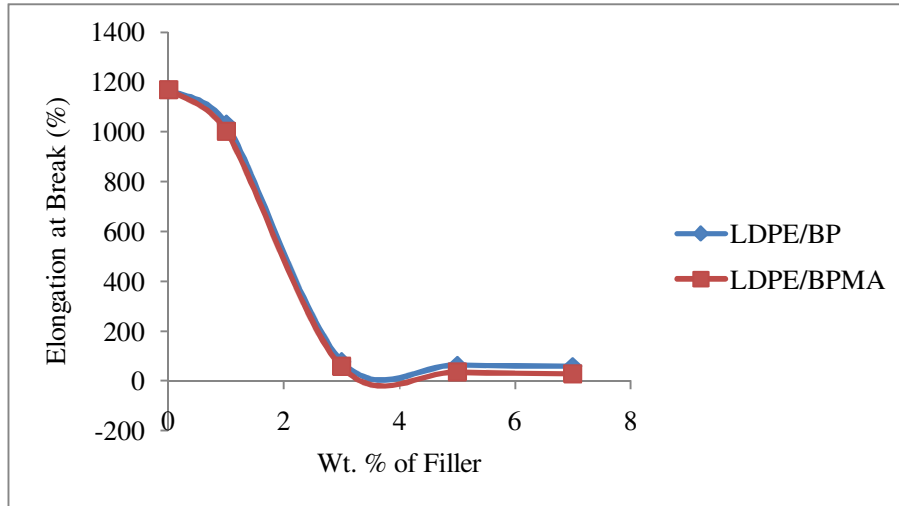

Figure 2. Effect of Filler Loading on the Elongation at Break of Bamboo Powder / Low Density Polyethylene Composites

Young's (Tensile) Modulus

Figure 3, shows that the Young's modulus for the composites increases with increasing filler loading. The increase in the modulus corresponds to more filler where its intrinsic properties as a rigid agent exhibit high stiffness (modulus) compared to polymeric material (Jacob et al, 2004). This is a common behaviour when rigid fillers are incorporated into softer polymer matrices (Elias,1977).Natural lignocellulosic fillers have been found as having elastic modulus higher than PE, PP, and some other polymer materials (Wang et al, 2006). Because of this, the rigidity of its composites tends to strongly increase with addition of these fillers (Chui and Qing, 2008). It can be seen also from Figure 3 and Table 1that the young's modulus for LDPE/BPMA composites is lower than that of LDPE/BP composites for all filler loadings, due to the presence of maleic acid, which toughens the composites and thus decreases the Young's modulus.
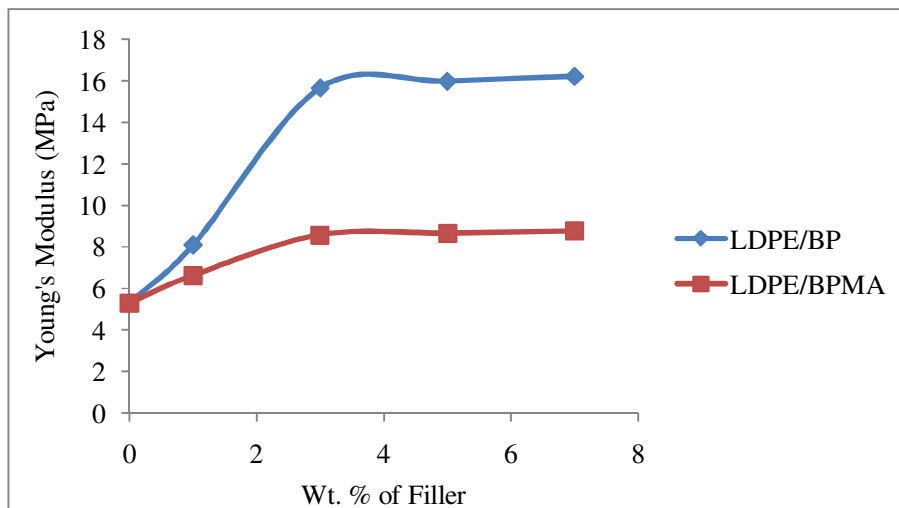

Figure 3. Effect of Filler Loading on the Young's Modulus of Bamboo Powder/Low Density Polyethylene Composites

Table 2. Some end-use properties of bamboo powder filled LDPE composites as a function of filler and coupling agent content

Sample	Wt. % of Filler	Wt. % of Coupling Agent	Water Sorption (%)	Specific Gravity	Flame Propagation rate (mm/s)
1	0	0	0.75	0.938	0.35
2	1	0	1.99	1.020	0.30
3	3	0	2.34	1.220	0.27
4	5	0	2.48	1.267	0.23
5	7	0	2.67	1.311	0.18
6	1	2	1.82	1.211	0.27
7	3	2	2.17	1.272	0.22
8	5	2	2.36	1.294	0.19
9	7	2	2.44	1.398	0.16

Water Sorption

The percentages of water sorption (for 24 hours) for the LDPE/BP composites with different filler loading can be seen in Table 2. Composites with higher BP loading show more water sorption as shown in Figure 4. This is due to the higher contents of filler loading in the composites that can absorb more water. As the filler loading increases, the formation of agglomerations increases due to the difficulties of achieving a homogeneous dispersion of filler at higher filler loading (Wang et al, 2006).

The agglomeration of the filler in composites increases the water sorption of the composites. Figure 4 also showed that the addition of the coupling agent (maleic acid) decreased water sorption as expected. It can be proposed that the chemical reaction between the maleic acid (coupling agent) and the filler reduced the number of available hydrophilic groups. The BPMA has better adhesion between the matrix and the filler, reducing the formation of agglomerates. This can reduce the percentage of water sorption. Apart from this, the formation of an interfacial layer over the surface of the dispersed particles could prevent penetrating interior.
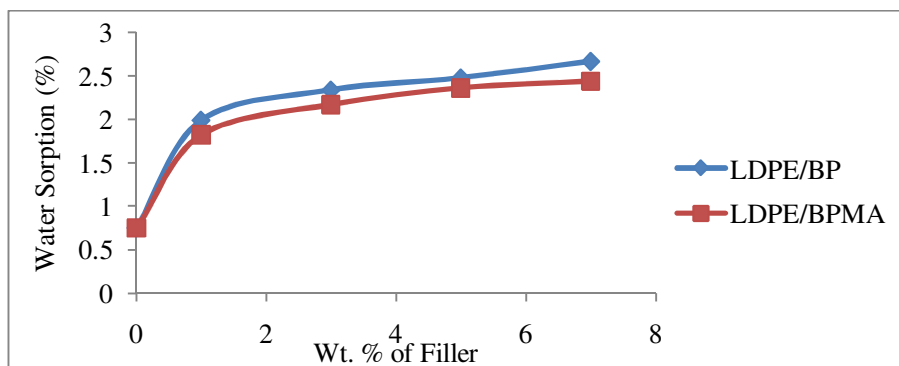

Figure 4. Effect of Filler Loading on the Water Sorption of Bamboo Powder/Low Density Polyethylene Composites

Specific Gravity

Table 2 shows that there was a continuous increase in the specific gravity for all the composites in comparison to that of LDPE. In solid-like composites, the specific gravity of natural fibres is a key for determining the specific gravity of the composites (Shibata et al, 2006).

From Figure 5 it seems that there is a slight tendency of increasing specific gravity with increasing bamboo powder concentration. The addition of the coupling agent (maleic acid) produced a slight more increase in the specific gravity that could be explained by a higher compatibility among the filler and the polymer matrix thus diminishing the presence of voids in the materials.
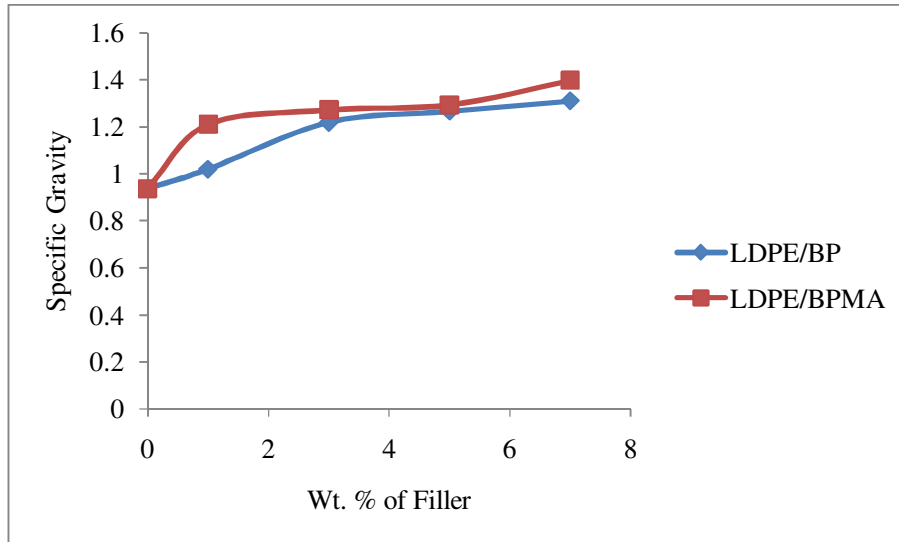

Figure 5. Effect of Filler Loading on the Specific Gravity of Bamboo Powder / Low Density Polyethylene Composites

Flame Propagation

It can be observed that the rate of flame spread of the composites decreases with increase in filler loading for all the composites as can be seen in Table 2.
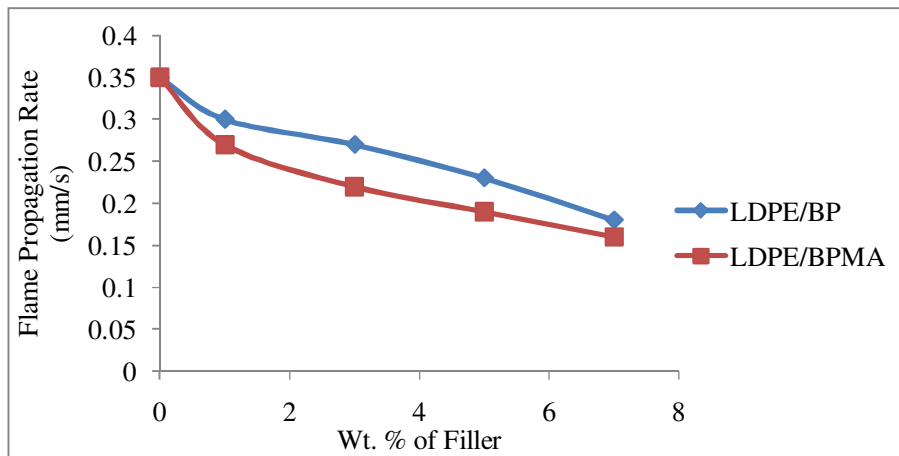

Figure 6. Effect of Filler Loading on the Flame Propagation Rate of Bamboo Powder/ Low Density Polyethylene Composites

The results indicate that the flame retardant property of LDPE is enhanced by bamboo powder filler. Thermo plasticity is observed as shrinkage and softening or melting when such materials are subjected to heat. Both melting and shrinkage have the effect of reducing apparent flammability (Morreale et al, 2007). On approaching the ignition source, a thermoplastic material will shrink and even drip away from the flame. This behaviour ensures energy removal, decrease in surface area exposed, and hence, reduction in flame accessibility. The rate of flame spread for the LDPE/BPMA composites is less than that for LDPE/BP composites. From Figure 6, it can be seen that the flame retardant property of LDPE is enhanced by bamboo powder filler and also by maleic acid. The BP and MA in the LDPE is seen as impurities and they need more heat for its constituents to break down before it begins to burn; hence enhancing the flame retardant property of the LDPE.

CONCLUSION

The results obtained from this research showed that it is feasible to use Maleic Acid (MA) as a coupling agent in LDPE/BP composites. For instance, the incorporation of MA into the LDPE/BP composites brought Substantial improvement in the tensile strength of the composites. The composites' stiffness (Young's Modulus) was seen to increase with increasing filler loading but decreased with the addition of MA. The percentage of water sorption by LDPE/BP composites is so small but was further reduced with the addition of MA, making these materials suitable for use in damp environments. Specific gravity determination showed that there was slight increase in the specific gravity of the composites when MA was added. Bamboo powder (BP) enhanced the flame retardant property of the LDPE and the addition of MA further enhanced it.

REFERENCES

Adrian, J. N., Jose, M. K., Maria, M. R., Mirta, I. A. & Norma, E. M. (2002. Thermal and Dynamic Mechanical Characterization of Polypropylene-Wood Flour Composites, *Polymer Engineering and Science, 42*(4), 733-742.

Baron, J. R. & Scmidth, W. F. (2005). Polyethylene reinforced with Keratin fibres obtained from chicken feathers:*Composites science and Technology, 65*, 173 - 181.

Bhatnagar, M. S. (2004). A Textbook of Polymers: Chemistry and Technology of polymers - *Processing and Applications, II* , 1 – 86.

Challa, G. (1993). Polymer Chemistry: *An Introduction.Ellis Horwood Series in polymer Science*.

Chand, N. & Dwivedi, U. K. (2006). Effect of compiling agent on abrasive wear behaviour of Jute-PP composites, *Wear 261 (Jan),* 1057-1063.

Charier, J. M. & Rieger, J. M. (1974). *Fibre Sci. Technol, 7,* 161-71.

Christensen, R. M. (1976). Int. *J. Solids Structures, 12*, 537.

Christensen, R. M. & Waals, F. M. (1972). *J. Comp. Mater, 6*, 578.

Chui, G. G. & Qing, W. W. (2008). Influence of m-iso Propyl-dimethylbenzy Isocyanate Grafted Polypropylene on the Interfacial Interaction of Wood flour/Polypropylene Composites, *J. Appl. Polymer Science, 109*, 3080-3086.

Cowie, J. M. G. (1991). *Polymers: Chemistry and Physics of Modern Materials*, 23-51.

Crawford, R. J. (1998).*Plastic Engineering*, 1-18.

Dahl, W. S. (1947). *Brit. Plastics*, 19, 114.

Elias, H. G. (1977). *Macromolecules*. New York: Plenum Publishers.

Espiloy, E. B. (1991). *Effect of age on the physico- mechanical properties of some Philippine bamboo*, Intern Bamboo worksh Chiangmai, 4.

Garg, S. & Jana, A. S. (2007). Studies on the properties and characteristics of starch-LDPE blend film using cross-linked and glycerol modified starch. *European Polymer Journal, 43*, 3976-3987.

http://dspace.unimap.edu.my/bitstream/123456789/3362/6/introduction.pdf ; 07/05/2009.

http://oru. edu/cccda/sl/solubility/ all solvents php? Solute= maleic % 20acide, 6/20/2009.

Jacob, M., Thomas, S. & Varughese, K. T. (2004). Mechanical properties of sisal oil palm hybrid fiber reinforced natural rubber composites. *Composite Science and Technology,* 64, 55-965.

James, M. N. G & Williams, G. J. B. (1974). A Refinement of the crystal structure of maleic acid, *Acta Crystallographica* B30 (5): 1249-1275.

Kwesi, A. (1948). Catalytic Hydrogenation of Maleic Acid at Moderate Pressure," A laboratory Demonstration, *Journal of Chemical Education,* 84(12).

Morreale, M., Scaffaro, R., Maio, A. & La Mantia, F. P. (2007). Effect of adding wood flour to the physical properties of a *biodegradable polymer composite*, 42, 214.

Patil, Y. P., Garre, B., Dusane, D., Chavan, S. & Mishra, S. (2000). Effect of maleic Anydride Treatment on steam and water Absorption of Wood polymeric composites prepared from wheat straw, Cane Bagasse and Teak wood sawdust using Novolac as matrix: *J. Appl Polymer Science*, 77, 2963-2967.

Salmah, H., Ismail, A. & Baker, A. (2005). Dynamic vulcanization of sludge filled polypropylene (PP) ethylene propylene diene terpolymer (EPDM). *Malaysian Journal of microscopy*, 2, 15-22.

Sapuan, S. M. & Maleque, M. A. (2005). Design and fabrication of natural woven fabric reinforced epoxy composite for household telephone stand. *Mat. Des.* 65-71.

Shibata, S., Cao, Y. & Fukumoto, I. (2006). Light weight laminate composites made from Kenaf and Polypropylene fibres. *Polymer Testing*, 25(2), 142-148.

Wang, W., Sain, M. & Cooper, P. A. (2006). Study of moisture absorption in natural fiber plastic composites. *Composites Science and Technology*, 66(3-4), 379-386.

Yang, H. S., Kim, H. J., Son, J., Park, H. J., Lee, B. J. & Twang, T. S. (2004). Rice-husk flour filled polypropylene composites; mechanical and morphological studies. *Composite Structures, 63*(3-4), 305-312.