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Full Length Research Article

EFFECT OF BENZOYL CHLORIDE TREATMENT ON THE MECHANICAL AND VISCOELASTIC PROPERTIES OF PLANTAIN PEEL POWDER - REINFORCED POLYETHYLENE COMPOSITES

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ABSTRACT
Mechanical and dynamic mechanical analysis of plantain peel powder (PPP) reinforced polyethylene composites has been investigated. The PPP was treated with benzoyl chloride to reduce potential surface hindrances and bring about adhesion. The percentage fibre loading was varied from 0-25 % (0, 5, 10, 15, 20 and 25) respectively. Ultimate tensile strength, elastic modulus and hardness test data showed an improvement in mechanical properties of the treated fibre composites. Water absorption results indicated that benzoyl chloride treated PPP-recycled polyethylene composites have lower rate of water absorption than the untreated samples. Dynamic mechanical properties results showed that the storage modulus (E') of all the composites increase with increase in fibre loading and decrease with increase in temperature; composite containing 25 % (A25) PPP having the maximum E' value of 678 MPa compared to 576 MPa of the control sample. The results indicated that incorporation of plantain peel powder actually improved the thermal stability and the load bearing capacity of the recycled polyethylene composites.

Keywords: Dynamic mechanical analysis, plantain peel powder, polyethylene composites, recycled low density polyethylene

INTRODUCTION

Polyethylene (PE) is one of the most versatile and widely used thermoplastics in the world because of its excellent properties like toughness, near-zero moisture absorption, excellent chemical inertness, and low coefficient of friction, ease of processing and unusual electrical properties (Khanam and Al Maadeed, 2015). PE is classified based on the precise degree of crystallinity and density as low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), and ultra-high molecular weight polyethylene (UHPE) (Kurtz, 2009).

Low density polyethylene (LDPE) is a low cost material with good processability, excellent electrical insulation properties, chemical resistance, high toughness and flexibility even at low temperature (Ferreira *et al.*, 2005). These properties makes LDPE the most widely used class of PE in various packaging and functional applications. LDPE currently enjoys ubiquitous application in packaging of sachet water popularly known as pure water in Nigeria, resulting in large volume of waste.

Efforts made to prevent indiscriminate disposal of polymeric waste such as recycled low density polyethylene have been inefficient as it is non-biodegradable as attested by many workers (Otake *et al*., 1995; Roy *et al*., 2008). Therefore, attention has recently shifted to the fabrication and investigation of the properties of natural fibre reinforced materials. Low cost, readily available, easy to use, biodegradability and eco- friendly are some of the advantages of natural fibres that have attracted the interest of researchers both in the academia and in the industries.

Dynamic mechanical analysis (DMA) is one of the most widely used techniques for characterizing the thermal properties of natural fibres which are important in selecting processing conditions and applications field. Many researchers have reported studies on the dynamic mechanical properties of natural fibre reinforced polymer composites, and highlighted that these composites have acceptable mechanical properties for many industrial applications (Zhang *et al*., 2017; Palanivel *et al.,* 2017; Gupta, 2018).

The automotive and aerospace industries have both demonstrated an interest in using more natural fibre reinforced composites: For example, in order to reduce vehicle weight, attention has expunge already shifted from steel to aluminium and recently from aluminium to natural fibre based composites for different applications. This has led to predictions that in the near future, plastics and polymer composites will comprise approximately 15 % of total automobile weight (Zampaloni *et al*., 2010; Mohanta, 2016). Several works have been carried out on development and characterization of natural fibre composites. The effect of groundnut shell powder on the mechanical properties of recycled polyethylene and its biodegradability was studied by (Usman *et al*., 2016). It was reported that alkaline treated groundnut shell powder has been shown to improve the mechanical properties of recycled PE composites. Salasinska *et al*. (2017) investigated the mechanical and dynamic thermal mechanical analysis (DTMA) of epoxy composites modified with walnut shell waste as filler. The results obtained indicated an increased stiffness and hardness in comparison to the unreinforced resins. Thermo-mechanical characterization of banana particulate reinforced PVC composite as piping material has been reported by Dan asabe (2016). Through dynamic mechanical analysis, the composition with optimum mechanical property of 42 MPa was estimated to have a long term stress value of 25 MPa corresponding to 40% loss in strength over a period of 32 years.

Plantains (*Musa paradisiacal* L) are plants producing fruits that remain starchy at maturity (Marriot and Lancaster, 1983; Robinson 1996) and need processing before consumption. Nigeria is one of the largest plantain producing countries in the world (FAO, 2006). Despite its prominence, Nigeria does not feature among plantain exporting nations because it produces more for local consumption than for export (IITA, 2014). The consumption of plantains has risen tremendously in Nigeria in recent years because of the rapidly increasing urbanization and the great demand for easy and convenient foods by the non-farming urban population (Akinyemi *et al*., 2010).

Plantain requires humid regions and hence its production in Nigeria is basically in the southern part of the country. Plantains contain more starch and less sugar than dessert bananas and are therefore usually processed before being eaten. They are always cooked or fried when eaten green. At this stage, the pulp is hard and the peel often stiff that it has to be cut with a knife to be removed. Mature plantains can be peeled like dessert bananas. Peel from unripe plantain is obtained when the pulp is used for next production process as starch isolation or dry flour. Plantain peel flour has chemical composition of dietary fibre, poly phenol content, and antioxidant capacity e t c (Agama-Acevedo *et al*., 2016). In Nigeria, plantain peels are used as feed for livestock; while the dried peels are used for soap production (ASTM D638, 2014). The use of plantain peel as a source of dietary fibre has also been reported (Agama-Acevedo *et al*., 2016).

Plantain peel, like banana peel is a lignocellulosic waste which could be utilized as fillers in the reinforcement of polymer composites. Therefore, the need to incorporate this readily available agricultural waste in to recyclable plastics to produce economically viable materials suitable for structural and non-structural applications becomes expedient.

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MATERIALS AND METHOD

Materials

Waste water sachets were collected from refuse dumps in Ahmadu Bello University Samaru, Zaria environs. They were washed; dried and shredded to smaller sizes using shredding machine. This constitutes the recycled (RLDPE) matrix. Fresh unripe plantain peels (*Musa paradisiacal L*) were collected from local vendors in Zaria. Peels were washed and air-dried for 172 hours and finally sun-dried for 3 days. The plantain peels were finally pulverized into powdery form and sieved to 150 µm particle size

Methods

Modification of plantain peel powder (PPP)

The PPP was initially alkaline pre-treated by suspending the fibres in 10 % NaOH for 5 hours and then benzoyl chloride for 15 minutes. This is done in order to activate the hydroxyl groups of the cellulose and lignin in the fibre. The isolated fibres were then soaked in ethanol for 1 hour to remove the excess benzoyl chloride and finally washed with distilled water and dried in oven at 80 °C for 5 hours

Preparation of PPP-Recycled low density polyethylene composites

The recycled low density polyethylene composites were prepared by melt mixing and compression moulding on a two roll mill at the Polymer recycling Laboratory, Department of Polymer Technology, Nigerian Institute of Leather and Science Technology (NILEST), Zaria. The composite samples were produced by compounding process achieved by the addition of the shredded recycled LDPE while the rolls were in counter clockwise motion for a period of 10 minutes at a temperature of 150 ℃, upon achieving a paste like matrix, the filler material (plantain peel powder) was introduced by gently applying manually as the rolls rotate at a rate of 500 rpm. The percentage fibre loading was varied from 0-25 % (0, 5, 10, 15, 20 and 25 %) respectively. The 0 % in this case denotes the control sample. The compounding was carried out at a temperature of 160 ℃. The compounded samples were then inserted into metal moulds of dimensions 120 x 120 x 5 mm, and finally cured in an electrical hydraulic press at a temperature of 150 ℃, pressure of 4 Pa for 5 minutes. Sectioning according to ASTM standards for physical and mechanical test was then performed on the samples

Mechanical property test

Tensile Test

The tensile testing of the samples was done at Engineering Materials Development Institute, Akure, Ondo State, Nigeria in accordance with (ASTM D638, 2014) standard. The samples were machined to dumbbell shape and then placed in Instron universal tensile testing machine 3369 model and the tensile strength and elastic modulus were evaluated

Hardness Test

The hardness test of composites is based on the relative resistance of its surface to indentation by an indenter of specified dimensions under a specified load. Samples of 30 mm x 30 mm x 4 mm were tested for shore hardness values with a durometer Shore 'A' at the Materials laboratory, Nigerian Institute of Leather and Science Technology (NILEST), Zaria-Nigeria. Five measurements were performed on the sample at different spots and the average of the values was taken as the hardness of the sample.

Characterization

Dynamic Mechanical Analysis (DMA)

DMA was carried out using DMA 242E machine in strength of materials laboratory, Mechanical Engineering Department, ABU Zaria according to (ASTM D7028, 2015).The test parameters: E', E'' and tangent of delta (Tan ∂) were first configured via the proteus software using personal computer. Instrument set up included the sample holder (3-point bending), furnace temperature range of 30-110 ℃, dynamic load of 4 N, frequency range of 1 Hz and heating rate of 3 K/min were configured. Sample dimension of 60 x 12 x 5 mm were produced for each test. The test specimens were loaded into the machine using a three- point bending and locked into the furnace.

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Table 1: The designation of symbol and their meaning as used in this work

Symbol	Meaning
A0	unreinforced LDPE (control)
A5	5 wt % plantain peel powder reinforced polyethylene composite
A15	15 wt % plantain peel powder reinforced polyethylene composite
A25	25 wt % plantain peel powder reinforced polyethylene composite
BC-PPP	benzoyl chloride treated plantain peel power reinforced composite
UPPP	untreated plantain peel powder reinforced composite

RESULTS AND DISCUSSION

Mechanical Property Test

Tensile Test

Figure 1 shows the variation of ultimate tensile strength (UTS) with PPP fibre loading. It was observed that the UTS of the PPP-recycled low density polyethylene composites increase with increase in fibre loading and decreases at 25 % fibre loading. This could be attributed to weakening of the interfacial adhesion of the composite as the fraction of RLDPE is reduced with increasing weight of reinforcement. Furthermore, benzoyl chloride treated PPP-recycled LDPE composites were found to have higher UTS as compared to untreated samples. This is because the treated samples have higher interfacial bonding which occurred as a result of decrease in the hydrophilicity of the PPP. Similar results have been reported by other authors (Mohanty *et al.,* 2000; Marques *et al.*, 2015 and Usman *et al.,* 2016).

Figure 2 depicts the elastic modulus of the control, untreated and treated PPP-RLDPE composites with increasing fibre loading. The trend of the modulus of elasticity (stiffness) of the composites increases from 29.6 MPa to 53.1 MPa for the treated composites. However, it was observed that benzoyl chloride treated samples have higher values of elastic modulus than the untreated samples, the highest being 45 MPa at 25 % weight fraction of reinforcement. This is expected, as chemical modification of the PPP resulted to increase in the roughness of the fibre, hence increased contact area with the RLDPE matrix. It has been reported that removal of cementing materials such as lignin and natural oils from the fibre surface led to better packing of cellulose chains, and therefore improve mechanical properties of the composites (Aminu *et al.,* 2014). A similar result was reported by (Dan asabe, 2016). An increase in stiffness with fibre loading was also observed for the untreated samples.

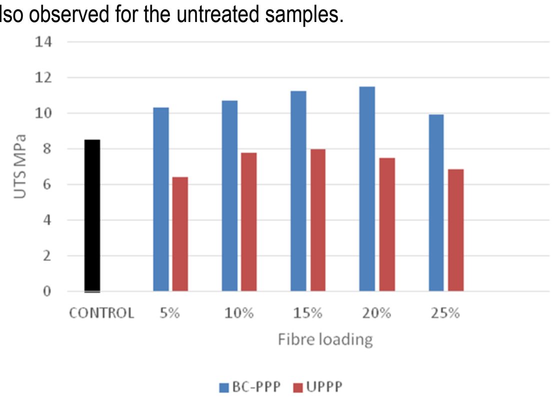

Figure 1: Effect of plantain peel powder on the UTS of recycled LDPE composite

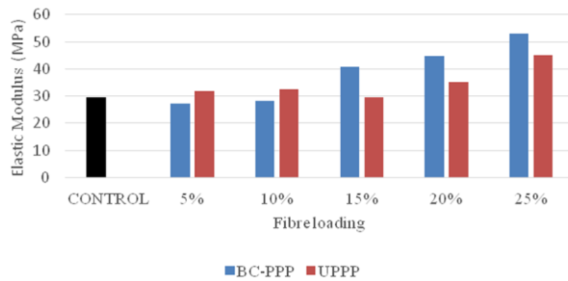

Figure 2: Effect of plantain peel powder on the elastic modulus of recycled LDPE composite

Hardness

Figure 3 depicts the hardness values (Shore A) of PPP-recycled polyethylene composites and the control sample. The treated sample with 25 % reinforcement has the maximum hardness value of 85.6 shores A. This is because there is better interfacial adhesion between the PPP and the RLDPE matrix as well as good particle distribution in the matrix.

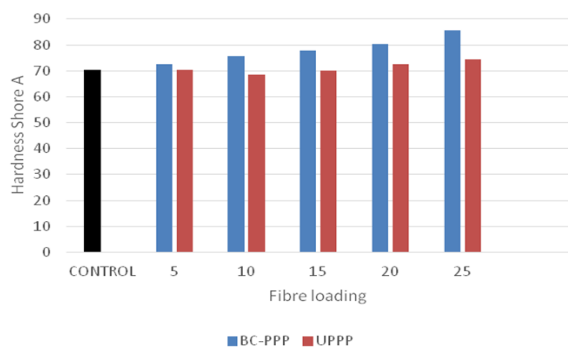

Figure 3: Hardness of PPP-recycled polyethylene composite on Shore scale A

Water Absorption

Figure 4 depicts the rate of water absorption of the composites for the treated, untreated and control samples. The percentage of water absorption of the composite increases as the weight fraction of the fibre is increased. As expected, water absorption was observed to be higher in the untreated samples due to hydrophilic nature of the reinforcing fibre. Furthermore, treated samples had lower rates of water absorption suggesting that fibre treatment gives rise to lower rate of water absorption and better mechanical properties (Gassan and Bledzi, 1997).

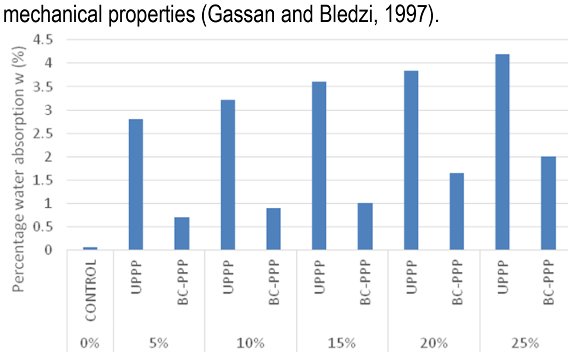

Figure 4: Percentage water absorption of PPP-recycled low density polyethylene composite

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Dynamic Mechanical Properties

Storage Modulus

Storage modulus (E') of polymeric materials depicts their stiffness (Gupta, 2018). In other words, it describes the energy stored in the system which depicts the elastic portion. The variation in the storage modulus as a function of temperature for the studied composites is given in figure 5.As the temperature increases, storage modulus decreases for all composites and this can be attributed to the increase in the molecular mobility of the polymer chains (Palanivel *et al.,* 2017)An increase in storage modulus of the composites in the elastomeric region was observed with incorporation of the fibres due to an increase in stiffness of the matrix with the reinforcing effect imparted by the fibres. With the higher content of PPP, the RLDPE dispersion in the composites was more homogeneous and the energy of the storage modulus is increased. Similar observation has been reported by other authors (Zhang *et al*., 2017; Palanivel *et al*., 2017). Furthermore, the highest value of E'(678 MPa) was shown by composite A25 while its lowest value (576 MPa) was shown by A0; this implies that the incorporation of PPP into RLDPE matrix increases its thermal stability.

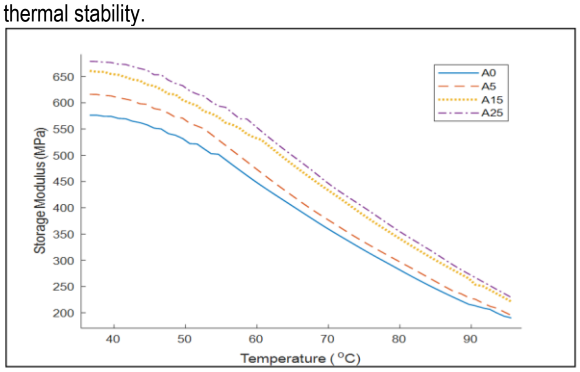

Figure 5: Variation of storage modulus with temperature of treated PPP- RLDPE composites at 1 Hz

Loss Modulus

Loss modulus (E") is defined as the maximum energy dissipated by composite materials during deformation. It represents the viscous response of the materials which depends upon motion of polymeric molecules in the composites (Jawaid *et al*., 2013). The variation in loss modulus of PPP composites as a function of temperature at 1 Hz frequency is shown in figure 6. It was observed that the unreinforced composite (A0) has the highest loss modulus followed composite A5. Composite A25 has the least loss modulus. The sharp increase in temperature to a peak of 50 - 60 °C indicates that at these temperatures, the energy dissipation by the material was rapid. It is also pertinent to note that the glass transition temperature of the composite with optimum thermal property (A25) was higher than the control sample. This implies that the incorporation of PPP into RLDPE increases its thermal stability. Similar observations have reported by other authors (Palanivel *et al.,* 2017; Gupta, 2018). However, the loss modulus was found to decrease with increase in temperature.

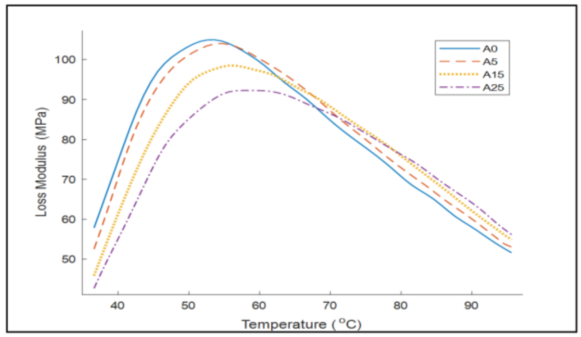

Figure 6: Variation of loss modulus with temperature of treated PPP- RLDPE composites at 1 Hz

Damping

Tan delta (Tan ∂) or damping is the ratio of loss modulus to storage modulus which is related to impact resistance of materials (Gupta, 2018). Figure 7 shows the temperature dependence of the tan ∂ of the unreinforced sample and the composites at 1 Hz frequency. Improvement in interfacial bonding in composites occurs as observed by lowering in tan ∂ values. This indicates that the flexibility of the matrix is increased by molecular mobility of the polymer's molecular chain. Among the composites, the damping factor of sample A25 was the lowest. This could be due to better compatibility and reinforcing effect of PPP in the polymer matrix. Lower value of damping shows the good load bearing capacity of the composites.

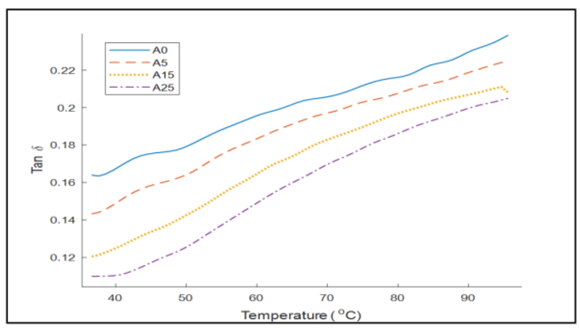

Figure 7: Variation of tan ∂ with temperature of treated PPP- RLDPE composites at 1 Hz**.**

Conclusion

In this work, benzoyl chloride treated recycled low density polyethylene was developed with improved mechanical properties. The optimum mechanical properties were shown by composites having 20 % and 25 % fibre loading respectively. The treated sample has a lower rate of water absorption which implies that benzoyl chloride treated PPP composites are better materials for their intended applications. Similarly, dynamic mechanical properties were found to improve with incorporation of plantain peel powder into RLDPE matrix with the chemically treated sample having the maximum storage modulus value of 678 MPa.

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