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Properties of Reactive Compatibilized Dika Nutshell Powder filled Recycled Polypropylene (PP)/Polyethylene Terephthalate (PET) Biocomposites using Maleated Polypropylene and Epoxy Resin Dual Compatibilizers.

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Abstract: Dika nutshell powder (DNS) filled – recycled polypropylene (PP)/polyethylene terephthalate (PET) biocomposite was prepared by reactive compatibilization using maleic anhydride-grafted-polypropylene (MAPP) and epoxy resin (EPR) as dual compatibilizers. The mechanical and rheological properties, as well as sorption behavior of the compatibilized biocomposites were studied at filler loadings of 0, 2, 4, 6, 8, and 10 phr (parts per hundred parts of resin). PP/PET composition was fixed at 30/70 wt. %. The results show that when MAPP alone was used as compatibilizer, property improvements were not substantial due to the low reactivity between MAPP and PET, which produces insignificant amount of copolymers as coupling agent at the interfaces. Effective compatibilization was achieved by adding epoxy resin (EPR) as suggested by impressive improvement in the properties investigated. Outstanding property improvements, especially oil resistance, tensile and impact strengths (higher values), and elongation at break (lower value) were obtained with increases in EPR and filler loadings.

Keywords: Biocomposite, compatibilization, dika nutshell powder, polyethylene terephthalate, polypropylene, recycling.

I. INTRODUCTION

Polypropylene (PP) and polyethylene terephthalate (PET) have been widely used in packaging applications and are frequently encountered in urban and industrial plastics wastes. Recycling offers an alternative solution for handling plastic wastes. Although there exist, easy and inexpensive separation methods for these plastics, yet a mechanical recycling method which involves blending of the plastics gives rise to secondary materials with interesting properties. It has been reported that blends of polyolefins (particularly polyethylene (PE) and PP) and PET can display good mechanical and permeation characteristics [1]. However, PP and PET are incompatible and immiscible leading to poor interfacial adhesion and mechanical properties, and this has greatly limited the search for PP – PET blend [2]. Compatibilization through a third component, acting as a bridge between the two incompatible phases, becomes necessary to stabilize the blend and to improve its mechanical performance. Two procedures have proved successful in compatibilization of immiscible blends: (1) addition of a block copolymer (BC) or a graft copolymer, which tends to migrate and concentrate at the interface as an interfacial emulsifier and (2) use of functionalized polymers or reactive compatibilizers to form chemical bonds between the blend components [3]. The choice of a block or graft copolymer is based on the miscibility of its segments with the blend components, and such copolymers usually require a separate preparation step, and some of them are difficult to synthesize. Besides, these copolymers may not have enough time to migrate and reside at the interface under a typical melt processing condition [4].

In recent times, the in-situ-formed compatibilizers in blend systems have been used as an alternative to replace the conventional block or graft copolymers. The in-situ reaction occurs during melt processing to form block or graft copolymers at interfaces. These in-situ-formed copolymers tend to reside along the interface to reduce the interfacial tension at melt and increase interfacial adhesion at solid state, thus resulting in substantial improvement in the physico-mechanical properties of the resultant blend [5]. The reinforcement of polymeric materials is expressed by enhancement of certain processing and end-use properties. The past decades have witnessed a growing interest in the use of renewable resources as reinforcements in polymer composite systems. This is due to strong environmental regulations and increased interest in the proper utilization of renewable natural resources to develop eco-friendly components. Numerous studies have been carried out on the utilization of bamboo [6] and wood [7] or products like rice husk [8, 9], chitin [10], coir [11] and numerous natural fibers [12, 13] as reinforcement materials. Benefits of these natural fillers include abundance and low cost, light weight, biodegradability and so on [14, 15]. These advantages led to the use of natural fillers as potential replacement for traditional reinforcement materials such as glass fiber in composite systems [16]. However, the compatibility or miscibility of natural fillers in polymeric materials is often in doubt due to the non-polar and hydrophobic nature of most polymeric materials when compared with the polar and hydrophilic lignocellulosic filler material due to the presence of hydroxyl groups in cellulose [17]. To address this problem, studies have been conducted on surface modification of natural fibers for the purpose of making the hydrophilic surface more compatible with hydrophobic polymers by using coupling agents [18]. Excellent reports exist in the literature on chemical treatment of fiber surface and use of coupling agents to improve the compatibility between hydrophobic polymer matrices and hydrophilic fillers [18-20]. There are experimental results in the literature supporting polymeric systems as effective in-situ reactive compatibilizers for polymer blends [18, 21]. Onyeagoro [21] used maleic anhydride-grafted-polyisoprene and epoxy resin as reactive compatibilizers in natural rubber/carboxylated nitrile rubber blends and reported improvements in cure characteristics and mechanical properties in the blends. Ming-Yih Ju et al. [22] reported that a combination of styrene-maleic anhydride random copolymer (SMA – 8wt % MA) and tetra-glycidyl ether of diphenyl diamino methane (TGDDM) (epoxy resin) is able to compatibilize PET – Polystyrene (PS) blends. The authors revealed finer phase domain size of the dispersed phase in the compatibilized blends. Improvements in tensile and impact properties were also reported. It is well known that PET carboxyl terminal groups do not react with the anhydride of maleic anhydride-grafted-polypropylene (MAPP), while the reaction between hydroxyl groups of PET and dika nutshell powder (DNS) filler (a cellulosic filler) is insignificant without the presence of a catalyst. However, many researchers [22-24] have shown that epoxy is able to react with polyester terminal carboxyl group to compatibilize effectively many polyester-related blends. Epoxy is also well known to react with anhydride readily. Thus, the presence of epoxy in the PP/PET/MAPP blend is capable of producing PET-co-epoxy-co-MAPP copolymer at the interface, which is able to function as an effective compatibilizer.In the present study, the effect of epoxy resin on mechanical properties, water absorption, and sorption behavior of compatibilized biocomposites of PP/PET/MAPP/DNS is investigated. The use of DNS as filler for polymer systems has been reported in the literature. Thus, Onyeagoro [25] investigated the influence of carbonized dika (Irvialgia Gabonensis) nut shell powder on the vulcanizate properties of natural rubber/acrylonitrile-butadiene rubber blends. The author found that the synchronous use of carbon black and carbonized dika nutshell powder obtained at a carbonization temperature of 600^0C brought significant improvements in the vulcanizate properties of the blends at filler loading of 10 phr, and suggested that carbonized dika nutshell powder could serve as potential substitute filler for carbon black in the rubber industry, especially in the production of low-cost/high volume rubber products where strength is not critical. Similarly, the sorption characteristics of dynamically vulcanized polypropylene/epoxidized natural rubber blends filled with carbonized dika nutshell (Irvialgia Gabonensis) were studied by Onyeagoro and Enyiegbulam [26]. The authors revealed that resistance to toluene sorption increased with dynamic vulcanization and also with increase in the filler carbonization temperature. Furthermore, studies on reactive compatibilization and dynamic vulcanization of polypropylene/epoxidized natural rubber blends filled with carbonized dika nutshell powder were carried out by Onyeagoro and Enyiegbulam [27]. The authors reported outstanding improvement in tensile and impact properties (higher values) and elongation at break (lower values) with increase in filler loading. Dika is a tropical nut grown in Nigeria and most tropical African countries [25]. Nigeria produces about 150,000 tonnes of dika annually [25-27]. The shell which is a by-product of dika nut processing is presently discarded as waste and could be found littering waste bins in our big cities and farm yards in most localities. Presently, it does not have any known domestic/industrial applications. The only existing practice of utilizing them as fuel by some oil processing mills in the country constitutes a great environmental hazard to the host communities and the practice has been discouraged. Therefore, the present study also seeks to harness the potentials of dika nutshells as filler in thermoplastic polymers.

II. EXPERIMENTAL

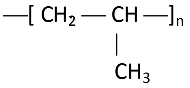
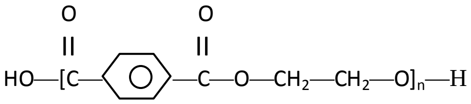
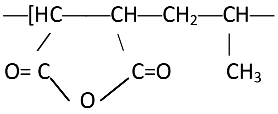
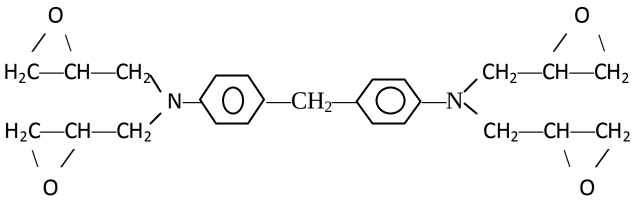
2.1. Materials

The recycled polymers used in this work were two thermoplastics (PP and PET). PP was obtained from industrial scraps. The PET used was obtained from a separate collection of post-consumer bottles (drinking and soft drink bottles). The compatibilizers, maleic anhydride-grafted-polypropylene containing 10 wt% maleic anhydride (Samsung Chemical Co.) and epoxy resin (tetra-glycidylether of diphenyldiaminomethane, TGDMM) with the trade mark of NPEH-434 (Nan Yea Plastics Co. of Taiwan) were purchased from Rovet Chemicals Ltd, Benin City, Nigeria. Dika nutshells were sourced from different farm yards in Auchi, Edo State, Nigeria. The repeating units of the polymers used in this work are given in Table 1.

2.2. Preparation of Dika nutshell Powder

Dika nut shells were thoroughly washed to remove sand particles and other earthy materials. Dika nutshell powder (DNS) was produced by milling Dika nutshells to fine powder. The powder was sieved at a particle size of 150µm, dried at 110^{0}C for 24 hours in a vacuum oven and then kept in a dessicator until required.

Table 1. Repeating units of each component

Component	Repeating unit
PP	 $-[CH_2-CH(CH_3)-]_n$
PET	
MAPP	
EPR	

2.3. Preparation of Composite Samples

Formulations of DNS powder filled recycled PP/PET bio-composites are given in Table 2. Blend composition of PP/PET was fixed at 30/70 parts per hundred parts of resin (phr) concentration, while varying filler (DNS) loadings of 0, 2, 4, 6, 8, 10 phr were used. Prior to the extrusion compounding technique employed, PET was dried at 120^{0}C, and PP and MAPP were dried at 90^{0}C for over 24 hours in separate vacuum ovens. The epoxy resin (EPR) was dried at 60^{0}C for 2 hours before using. The compounding ingredients, excluding DNS powder were charged into the extruder. All composites were prepared by dry-mixing first, followed by melt-mixing in a 30mm co-rotating intermeshing twin-screw extruder with a 7:1 length-to-diameter screw operated at a rotational speed of 250rpm. The temperature of the melt ranged from 255 to 265^{0}C. After 6 minutes of mixing, DNS powder was then added into the molten mixture and the composite mixture extruded as pellets. The extruded pellets were dried in a vacuum oven and compression molded using a hot press into standard ASTM specimens for mechanical property testing [9].

Table 2: Compounding recipe for recycled PP/PET/DNS bio-composites.

Ingredients (phr)	Uncompatibilized	Compatibilized			
	MAPP/EPR = 0/0	MAPP = 2.0	MAPP/EPR = 2.0/0.1	MAPP/EPR = 2.0/0.3	MAPP/EPR = 2.0/0.5
PP	30	30	30	30	30
PET	70	70	70	70	70
MAPP	0	2.0	2.0	2.0	2.0
EPR	0	0	0.1	0.3	0.5
DNS	0, 2, 4, 6, 8, 10				

2.4. Measurement of Rheological Properties

Rheological properties of the composites were carried out on a rheometric dynamic spectrometer using a parallel- plate geometry (R = 25 mm) at 230^0C [30]. For strain sweep measurements, a strain range of 0.1 to 300% and an angular frequency of 7.5 rad/s were used. Measurements with frequency sweep were done at a constant strain of 2.5% and a frequency range of 0.1 to 100 rad/s.

2.5. Measurement of Mechanical Properties

Tensile tests were conducted at room temperature (270C) using a Monsanto Tensile Tester (Model1/m) using dumb bell test pieces measuring 45mm x 5mm x2mm according to ASTM D412-87 method A. The crosshead speed was 500mm min-1. Tensile strength, tensile modulus, and elongation at break of each composite sample were obtained from the average of five specimens with their corresponding standard deviations. Impact strengths were measured by carrying out Izod impact tests. All specimens for Izod impact test were stored in a dessicator until required for test to avoid moisture absorption. Izod bars of composite samples were notched and tested at room temperature (27^0C) according to the ASTM D256 method. The value of impact strength of each specimen is the average of 5 runs.

2.6. Water Absorption Test

The water absorption test was carried out by immersing the composite samples in distilled water at room temperature (27^0C). The samples were removed at specified time intervals and gently blotted with tissue paper to remove the excess water on the surface. The weight of each swollen sample was recorded. The sample was then dried at 40^0C until a constant weight was achieved. The degree of water absorption (Sw), and degree of weight loss (Lw) were calculated using equations 1 and 2 [28].

$$Sw = \frac{W2 - W1}{W1} \tag{1}$$

$$Lw = \frac{W1 - W3}{W1} X\ 100 \tag{2}$$

Where W1 and W2 are the weights of the sample before and after the water absorption, respectively, and W3 is the dry weight of a sample after water absorption.

2.7. Sorption Test

Sorption test was conducted by immersing composite samples in ASTM No. 3 oil at room temperature (27^0C) for 70 hours according to ASTM D 471-98. The samples were removed at specified time and gently wiped with tissue paper to remove the excess oil on the surface. The weight of each swollen composite sample was recorded. Swelling index was the swelling parameter used to assess the extent of swelling of the composite and was calculated by equation 3 [9].

$$S = \frac{Ws - W0}{W0} X\ 100 \tag{3}$$

where W0 and Ws are the initial dry weight and final (swollen) weights of the composite, respectively.

III. RESULTS AND DISCUSSION

3.1. Rheological Properties

Plot of complex viscosity, η, versus angular frequency, ω, for recycled PP/PET/DNS composites is presented in Fig. 1. It can be seen from the figure that the complex viscosity of compatibilized composite is always higher than that of uncompatibilized composite, at all the frequency levels investigated. The higher complex viscosity observed for compatibilized PP/PET/DNS composite in this study is attributed to the reactive compatibilization arising from chemical reaction between the acid groups of MAPP and PET, and the hydroxyl groups (-OH) of DNS during melt blending. Similar results were obtained in our previous report on reactive compatibilization and dynamic vulcanization of polypropylene (PP)/epoxidized natural rubber (ENR) blends filled with carbonized Dika nutshell [27]. The result of this finding is also consistent with some previous reports on polymer blends which revealed general increases in complex viscosity when there is either a specific interaction between the phases [4, 29], or chemical bonding between the blend components [30]. Such a chemical bond will also induce a strong interaction between the phases. The net effect is that the matrix exhibits greater resistance to flow due to resultant increase in viscosity. On the other hand, in the absence of any such physical interaction or chemical bonding, low viscosity results because the domain can easily be elongated in the matrix. The use of MAPP alone as compatibilizer did not produce any significant increase in complex viscosity. This indicates that MAPP alone cannot effectively compatibilize recycled PP/PET/DNS composites.

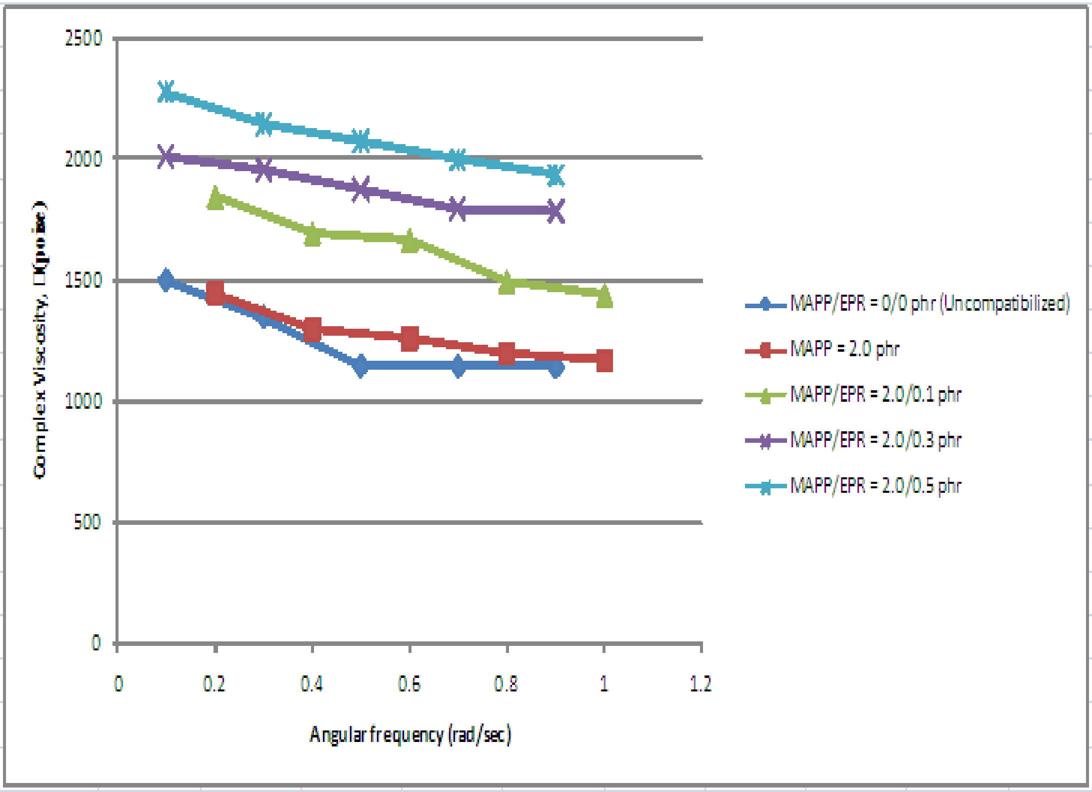


Figure 1: Plot of Complex Viscosity versus Angular frequency for recycled PP/PET/DNS Composites.

Figure 1 also shows that complex viscosity of the composites increased with increase in EPR loading due to the stiffening effect of EPR with increase in EPR loading. This result demonstrates that portion of EPR is able to act as an effective coupler to react with MAPP and PET simultaneously to produce the desired PET-co-EPR-co- MAPP copolymers. As a result of the chemical reaction, these in-situ-formed copolymers tend to anchor along the interface. Other portion of EPR may function as a chain extender to react with only one blend component (PET) to increase the molecular weight of PET. Increasing EPR content increases the concentration of the reactive functional groups of EPR. Thus, increase in EPR content causes light crosslinking of the composite which results to a corresponding increase in complex viscosity. Like the complex viscosity, the higher increase in storage modulus, G, displayed by compatibilized recycled PP/PET/DNS composites over the uncompatibilized composites (Figure 2) is attributed to molecular build-up arising from the chemical reactions that occurred during the melt compounding process [29].

Figure 3 illustrates the effect of epoxy resin (EPR) on maximum torque value of PP/PET/DNS composites. The results show a low value (5.8 Nm) of maximum torque in the absence of MAPP/EPR compatibilizer, which indicates poor physical interaction between PP and PET phases in the absence of the compatibilizer. Again, like the complex viscosity and storage modulus the presence of MAPP alone as compatibilizer (MAPP/EPR = 2.0/0) did not produce any appreciable increase in maximum torque (only 3.0 Nm). This indicates that MAPP alone cannot effectively compatibilize polymer composites of PP/PET/DNS. However, the presence of only 0.1 phr EPR (MAPP/EPR = 2.0/0.1) is able to increase the maximum torque significantly. This result indicates that the coupling and chain extending reactions indeed occur during the melt blending process and produces various PET-co-EPR-co- MAPP copolymers and chain-extended PET in the compatibilized composites. The in-situ-formed copolymers tend to anchor along the interface and, therefore, raise the interfacial friction of the compatibilized composites under shear stress.

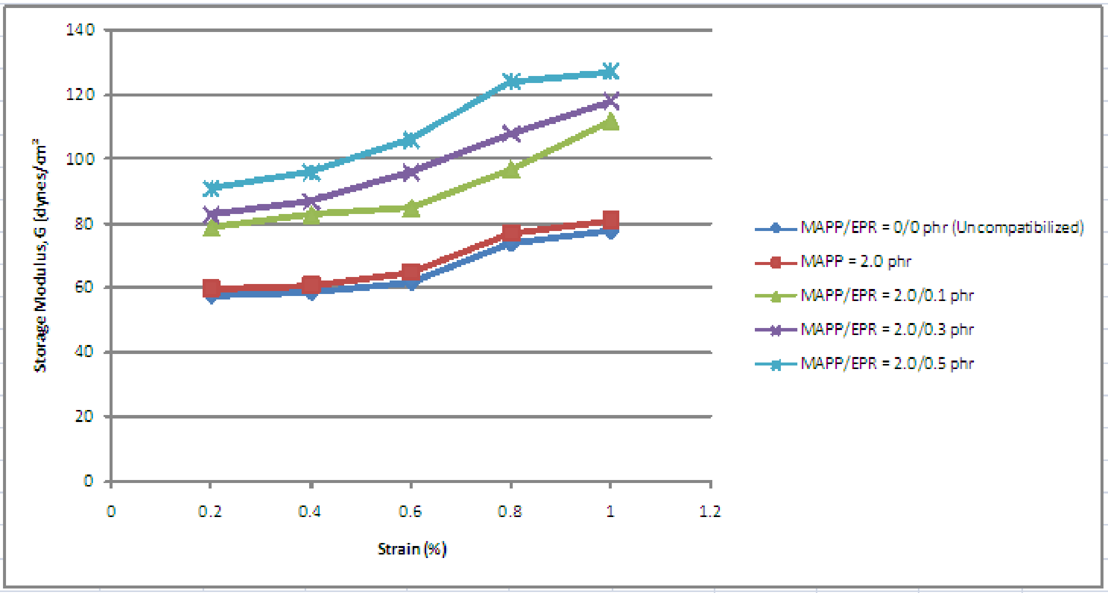


Figure 2: Plot of Storage Modulus versus Strain for recycled PP/PET/DNS Composites.

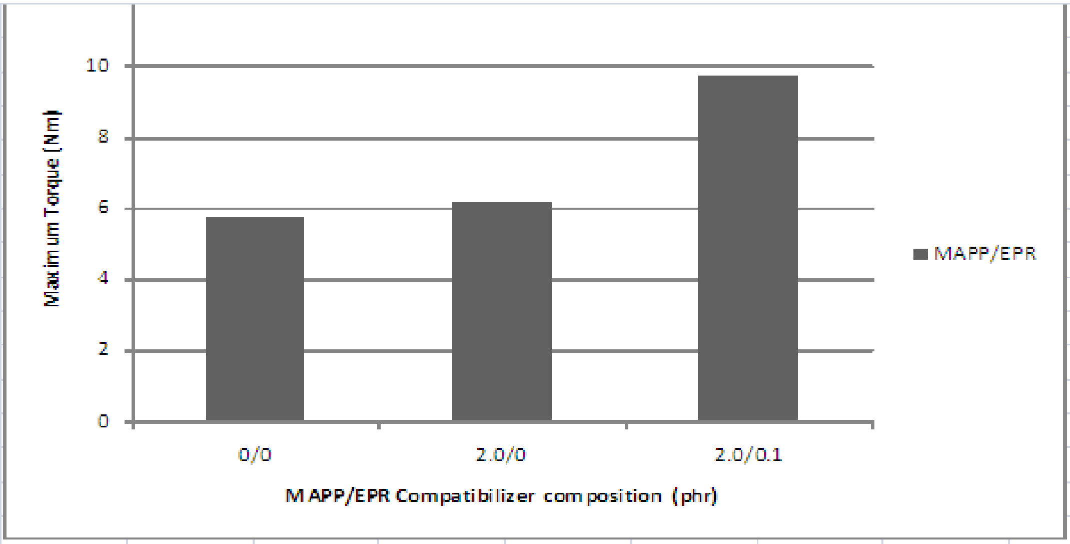
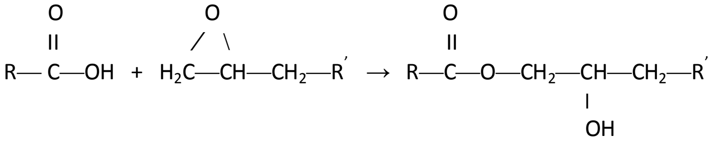


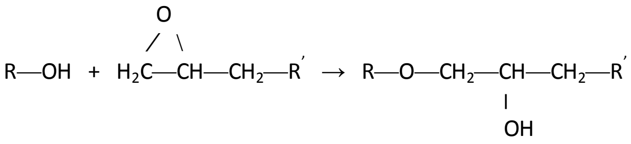
Figure 3. Effect of epoxy resin (EPR) on maximum torque value of Dika nutshell powder filled recycled PP/PET composites.

3.2. Mechanical properties

Figure 4 shows the effect of DNS loading and epoxy resin (EPR) on recycled PP/PET/DNS composites. The result shows that the tensile strength decreased with increase in DNS content. The decreasing trend in tensile strength with increase in DNS content may be due to poor adhesion between polar DNS and non polar PP matrices which makes the DNS incapable of supporting stress and transmitting it to polymer matrix. Figure 4 also shows that at a similar filler loading, the presence of MAPP alone as compatibilizer does not produce any appreciable increase in tensile strength of the composites. This result implies that the expected reaction between anhydride groups of MAPP and hydroxyl groups of PET does not occur or occurs insignificantly during extruder compounding. On the contrary, addition of EPR in the PP/PET/DNS composite leads to a significant increase in tensile strength, indicating improvement in interfacial adhesion which is attributed to the additional chemical reaction between EPR and PET terminal hydroxyl group, as well as the anhydride group of MAPP. The improved interfacial bonding provides better stress distribution which results in increase in tensile strength of the composites when compared with the composite with MAPP alone and the one without compatibilizer. Similar findings were reported by Ju and Chang. [22], whereby higher tensile strength in polymer blend of PET – Polystyrene (PS) was reported with progressive increase in tetra-glycidyl ether of diphenyl diamino methane (TGDDM) (an epoxy resin) using styrene maleic anhydride (SMA) random copolymer and TGDDM as dual compatibilizers. The reaction mechanism between EPR and terminal groups of PET is well elucidated in the literature as the following simplified equations 4 and 5 [31].

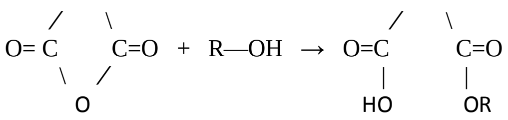


$$R-\overset{\overset{O}{\|}}{C}-OH + \overset{\overset{O}{/\ \ \backslash}}{H_2C-CH}-CH_2-R' \rightarrow R-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-R' \qquad (4)$$

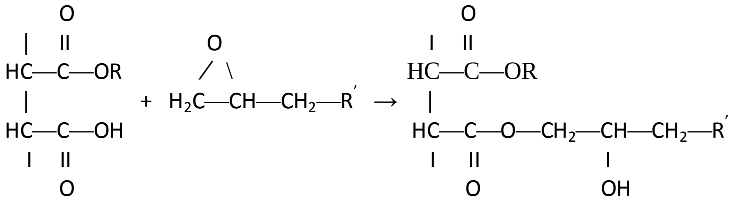


$$R-OH + \overset{\overset{O}{/\ \ \backslash}}{H_2C-CH}-CH_2-R' \rightarrow R-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-R' \qquad (5)$$

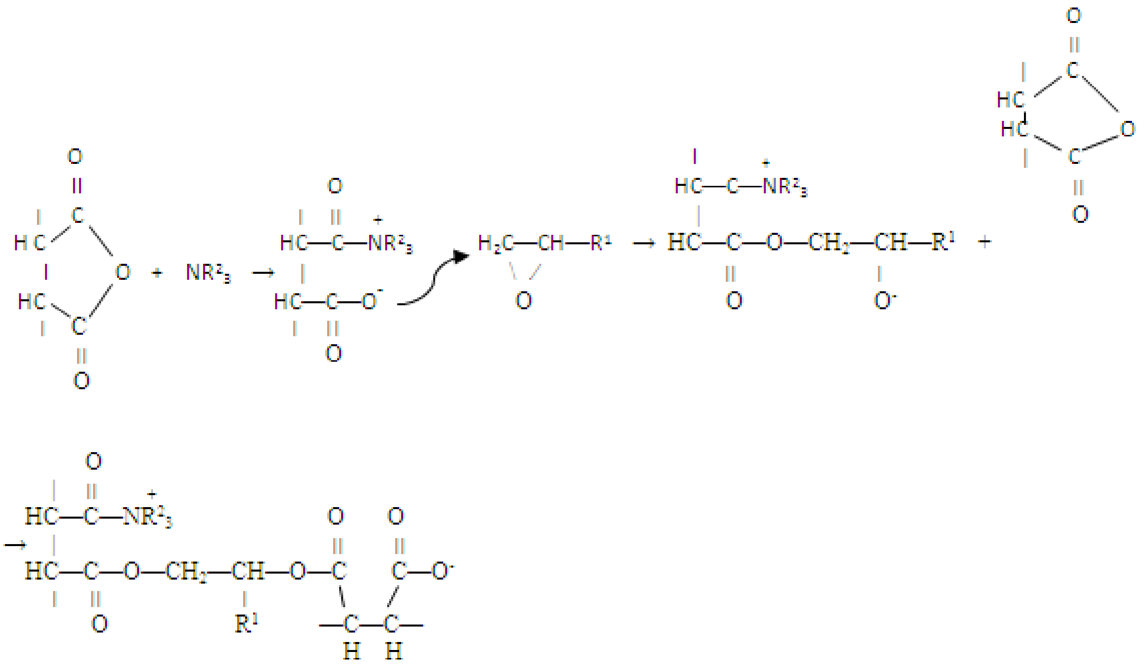
Also, the reaction between epoxy resin and anhydride groups can be initiated by a hydroxyl-containing compound to proceed ring-opening reaction, as illustrated in equation 6 [22]. Furthermore, it has been reported that a hydroxyl-containing compound can be obtained from the reaction between TGDDM and PET or from the terminal group of PET and then, the ring-opened anhydride groups can react with epoxy group as the following equation 7 [22]: Scheme 1 illustrates the simplified reaction mechanism between EPR and anhydride groups catalyzed by a tertiary amine. The tertiary amine on the EPR can act as a catalyst, and the self-catalyzed reaction is able to proceed during the melt blending process [31].



$$\begin{array}{c}-HC-CH-\\ /\qquad\backslash\\ O{=}C\qquad C{=}O\\ \backslash\qquad /\\ O\end{array} + R-OH \rightarrow \begin{array}{c}-HC-CH-\\ /\qquad\backslash\\ O{=}C\qquad C{=}O\\ |\qquad\quad |\\ HO\qquad OR\end{array} \qquad (6)$$



$$\begin{array}{l}\quad\ \ O\\ |\ \ \ \|\\ HC-C-OR\\ |\\ HC-C-OH\\ |\ \ \ \|\\ \quad\ \ O\end{array} + \overset{\overset{O}{/\ \ \backslash}}{H_2C-CH}-CH_2-R' \rightarrow \begin{array}{l}\quad\ \ O\\ |\ \ \ \|\\ HC-C-OR\\ |\\ HC-C-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-R'\\ |\ \ \ \|\\ \quad\ \ O\end{array} \qquad (7)$$



Scheme 1: The simplified reaction mechanism between EPR and anhydride catalyzed by tertiary amine.

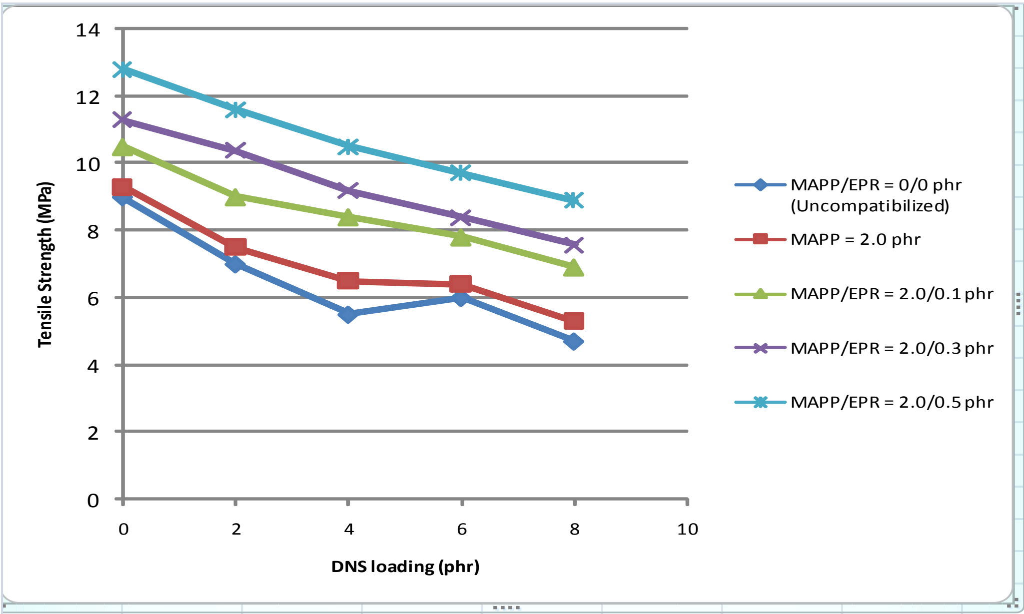


Figure 4: Effect of DNS loading and epoxy resin (EPR) on tensile strength of recycled PP/PET/DNS composites.

Figure 5 shows that increase in DNS loading produces increases in tensile modulus of composites with and without compatibilizer. The incorporation of DNS filler into the recycled PP/PET matrices increases the stiffness of the composites. This reduces the PP/chains mobility, consequently producing more rigid composites. At a similar filler loading, the composite obtained with MAPP compatibilizer alone did not produce significant increase in tensile modulus. However, the incorporation of only 0.1phr EPR compatibilizer exhibited appreciable increase in tensile modulus, which increased further with increasing amount of EPR compatibilizer. This is attributed to significant coupling and chain-extending reactions which occur on addition of EPR during the melt blending process, producing various PET-co-EPR-co-MAPP copolymers and chain-extended PET in the compatibilized composites. Similar findings were reported by Ismail et al. [35], whereby higher rigidity of rice husk powder filled polypropylene/recycled acrylonotrile butadiene (PP/NBRr/RHP) biocomposites produced higher tensile modulus due to better interaction between the matrix and filler in the presence of a silane coupling agent. Similarly, Liu et al. [32] who worked on mechanical properties of poly (butylenes Succinate) (PBS) bio-composites reinforced with surface modified jute fiber reported increases in tensile modulus, which the authors attributed to better interaction between the PBS matrix and silane coupling agent-modified jute fiber.

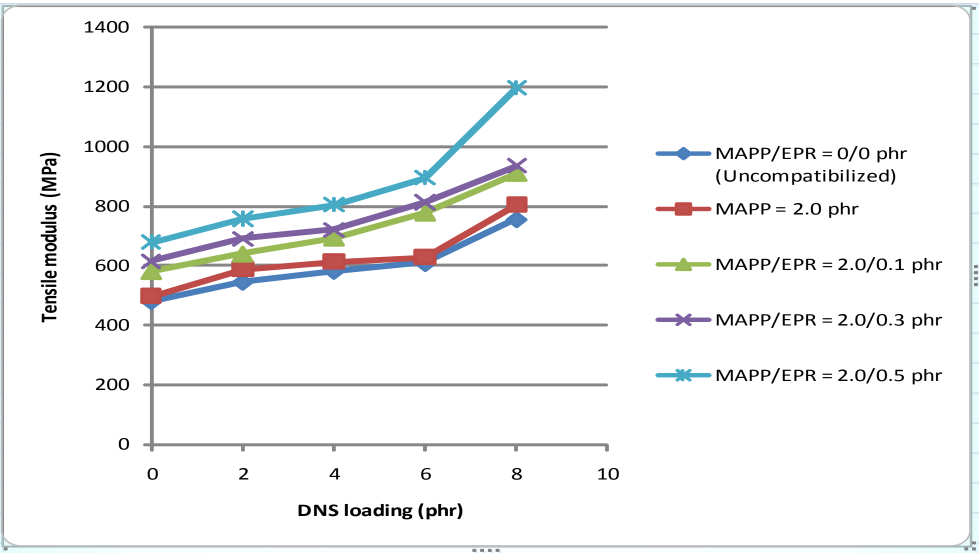


Figure 5. Effect of DNS loading and epoxy resin (EPR) on tensile modulus of recycled PP/PET/DNS composites.

The elongation at break of PP/PET/DNS composites with and without compatibilizer is shown in Figure 6. Clearly, the incorporation of DNS into the PP/PET matrices resulted in a reduction of elongation at break. The decreasing trend in elongation at break at higher DNS loading may be due to increase in stiffness and brittleness of the composites. The uncompatibilized composite produced the highest elongation at break. The decrease in elongation at break caused by MAPP compatibilizer alone is insignificant. However, addition of only small amount of EPR (0.1phr) compatibilizer in the composite is able to cause noticeable decrease in elongation at break, which decreased further with increasing amount of EPR in the composite. As explained earlier, this may be due to significant coupling and chain-extending reactions which occur on addition of EPR, which enhances the matrx-filler interaction resulting in lower elongation at break. This result is consistent with the findings of Hong et al. [33] who reported that silane-treated jute fibres yield a stronger interfacial adhesion, resulting in low elongation at break in silanized/polypropylene composites.

Figure 7 presents the effect of DNS loading and epoxy resin (EPR) on the impact strength of recycled PP/PET/DNS composites. The trend of impact strength for the composites with and without compatibilizer is consistent with corresponding tensile strength. EPR compatibilizer exhibits a significant effect on the enhancement of impact strength for PP/PET/DNS composites, which can be attributed to the in-situ-formed PET-co-EPR-co-MAPP copolymer molecules which anchor along the interface. A greater number of in-situ copolymer molecules are produced with increasing amount of EPR content as shown by progressive increase in impact strength.

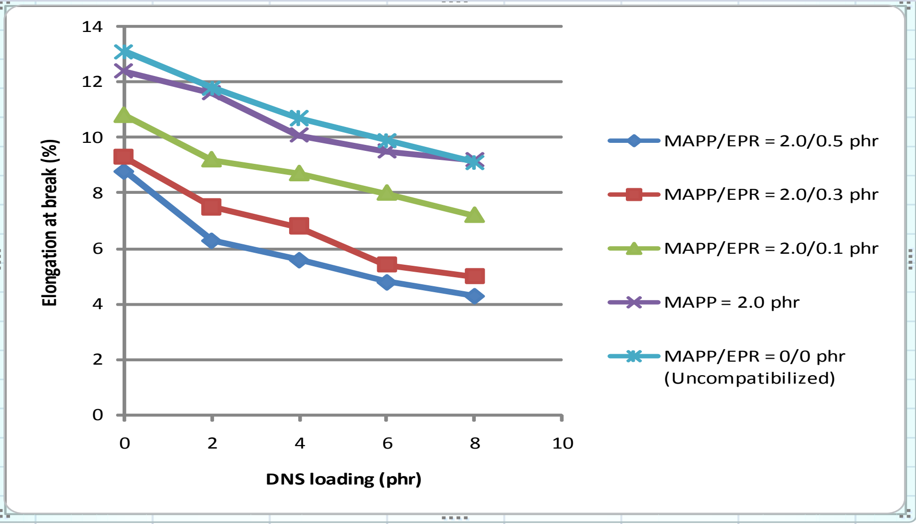


Figure 6. Effect of DNS loading and epoxy resin (EPR) on elongation at break of recycled PP/PET/DNS composites.

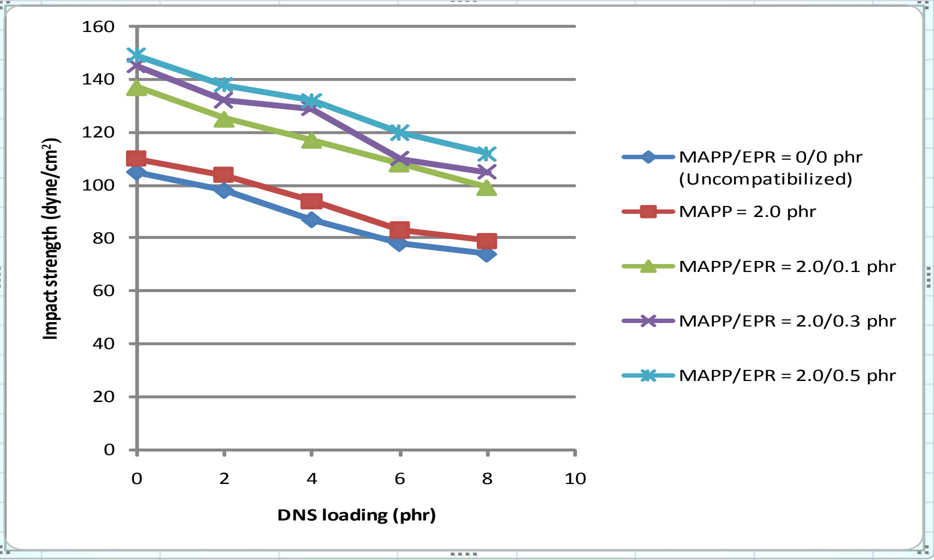


Figure 7. Effect of DNS loading and epoxy resin (EPR) on impact strength of PP/PET/DNS composites.

3.3. Water absorption Test

Figure 8 shows the effect of DNS loading and EPR compatibilizer on water uptake of recycled PP/PET/DNS composites. The results show that water uptake increased as DNS filler content increased. Natural fibers and fillers are highly hydrophilic due to hydroxyl (-OH) groups of polysaccharides found in cellulose, which are able to form hydrogen bonds between water and the DNS filler. As filler loading increases, the number of hydrogen bonds between organic components and water molecules also increases. This is due to the fact that as the filler loading in composite increases, the number of free OH groups on the lignocellulosic filler increases. Free OH groups come in contact with water through hydrogen bonding, which results in water uptake and gain in the composites. Similar findings have been reported by other researchers (Razavi et al. [34]; Ismail et al. [35]). At similar filler loading, it can be seen that the composite with MAPP compatibilizer alone showed a lower water uptake when compared to the composite with MAPP/EPR dual compatibilizers. Water uptake decreased further with increasing EPR content. This provides an indication that EPR enhances the filler-matrix interaction at the interface, thus decreasing the amount of equilibrium water uptake by the composites. This observation is consistent with the findings of Ismail and Mega. [18] in their study on the effect of a silane coupling agent on the properties of white rice ash-polypropylene/natural rubber (PP/NR/RHP) composites. The authors revealed lower water uptake by PP/NR/silane-treated RHP composites, and attributed this observation to the ability of silane coupling agent to form a protective layer at the interfacial zone and consequently prevent the direct diffusion of water molecules into the silane-treated filler composites.

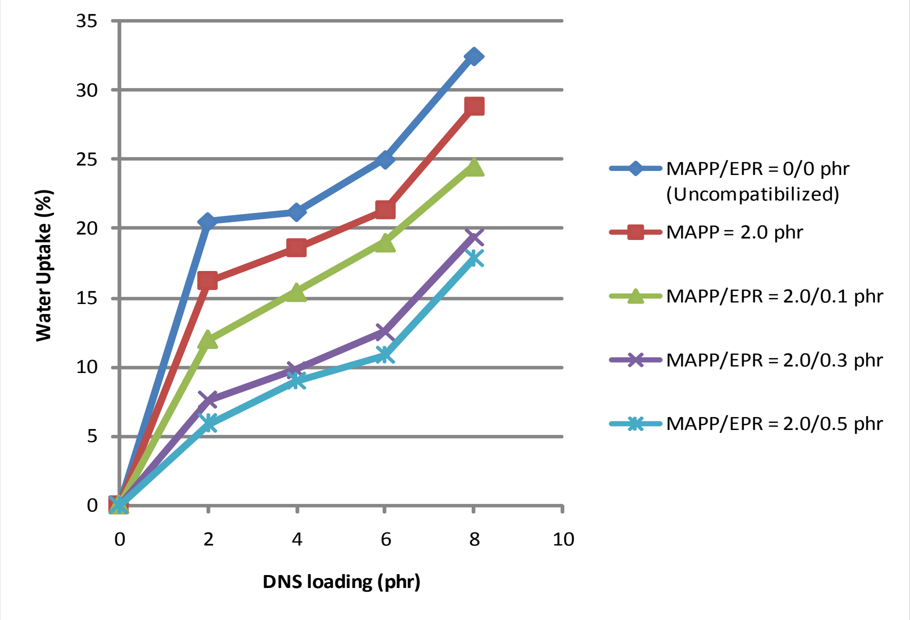


Figure 8. Effect of DNS loading and epoxy resin (EPR) on water uptake of recycled PP/PET/DNS composites.

3.4. Oil Sorption Test

Inhibition of oil uptake is primarily associated with the level of filler-matrix adhesion. Thus, oil sorption test was carried out to evaluate the degree of oil uptake in the composites. Figure 9 presents the variation of % swelling index of PP/PET/DNS composites with DNS loading and EPR content at room temperature (27^0C) for 70 hours. The results show that the % swelling index decreased with increasing DNS loading. This is attributed to the hydrophilic character of DNS filler due to the OH groups found in the lignocellulosic DNS filler. Oil resistance (decrease in % swelling index) is expected to increase with increase in polarity [16]. Thus, the higher the DNS filler loading (increased polarity) the lower the % equilibrium oil absorption (lower % swelling index). The findings of this study are also in agreement with the work of Mathew et al. [36], who reported decreases in equilibrium solvent uptake of isora fiber filled natural rubber composites with increases in fiber loading. The authors attributed this observation to increased hindrance exerted by the polar fibers at higher fiber loading.It can also be seen that compatibilization by MAPP alone leads to insignificant degree of oil resistance by the composites. However, compatibilization by MAPP/EPR dual compatibilizers produced greater degree of oil resistance, which also indicates increases in ol resistance with increasing EPR content in the composite. This is probably due to adequate interfacial adhesion at phase boundaries by the compatibilizing effect of MAPP/EPR dual compatibilizers.

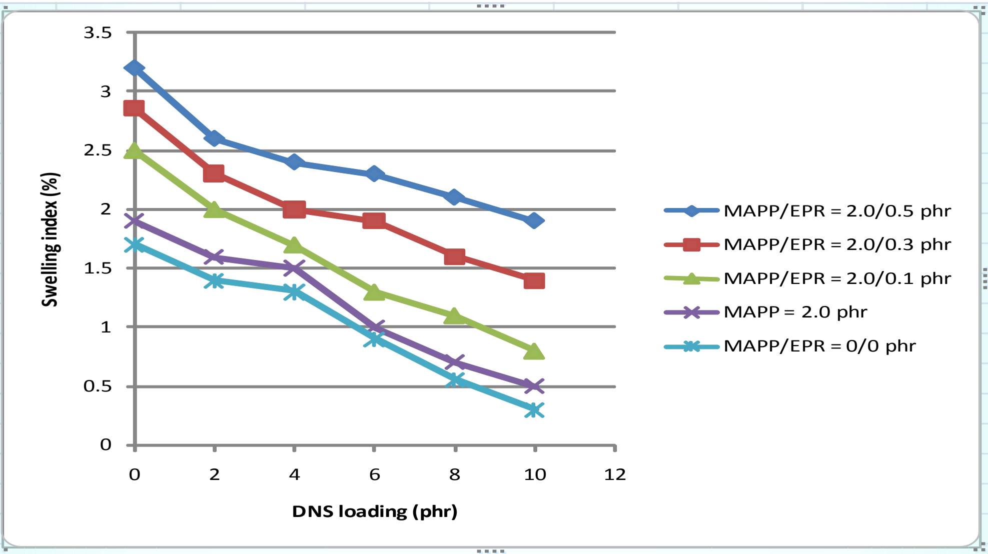


Figure 9. Variation of % Swelling index of PP/PET/DND composites with DNS loading and epoxy resin (EPR) at room temperature (27ºC) in ASTM No. 3 oil.

IV. CONCLUSION

The following conclusion can be drawn from this study:

1 Dika nutshell powder (DNS) filled recycled polypropylene (PP)/polyethylene terephthalate (PET) biocomposites were prepared by reactive compatibilization using maleic anhydride-grafted-polypropylene (MAPP) and epoxy resin (EPR) as dual compatibilizers. The effects of DNS loading and EPR content on mechanical and rheological properties as well as water absorption and sorption behavior of the compatibilized bio-composites were investigated. Blends of PP and PET (and in general blends of polyolefins and polyesters) result in materials with inferior mechanical properties because of the incompatibility between the two phases. The problem is compounded when a third component, such as dika nutshell powder is added to produce composite material due to the high polarity of the lignocellulosic filler when compared with the non-polar PP. Thus, compatibilization is necessary in order to improve the mechanical performance of the resulting composite for commercial applications. Maleic anhydride-grafted-polypropylene (MAPP) alone is not an effective compatibilizer for PP/PET/DNS composites due to low reactivity between MAPP and PET without the presence of catalyst leading to the formation of insignificant quantity of PET-co-MAPP copolymer during the extrusion melt blending. Consequently, property improvement of the compatibilized composite is not substantial. However, upon addition of epoxy resin (EPR), the properties of the composite are strongly modified and the resulting materials show good mechanical performance. Thus, compatibilization improved with addition of EPR, which act as a coupling agent to produce PET-co-EPR-co-MAPP copolymers at the interface. These interfacially formed copolymers tend to anchor along the interface and act as effective emulsifiers. Consequently, the compatibilized composite gives greater interfacial adhesion with impressive improvement in the properties investigated.

2. Dika nutshell powder (DNS) used as particulate filler in this study is a biodegradable agricultural waste obtained from a cheap renewable resource. Thus, when used as filler in PP/PET blend, DNS confers biodegradability to the resulting composite. It also represents an environmentally friendly alternative to conventional non-biodegradable reinforcing fibres. This is in consonance with growing global environmental concerns as well as new environmental regulations which have forced the search for materials that are compatible with the environment.

3. PP and PET are frequently encountered in urban and industrial waste and are recycled after separating the polymers by flotation. Though, the separation may be quite easy and inexpensive, yet the heterogeneous recycling of these two thermoplastics can give rise to secondary materials, especially composites with good mechanical and permeation characteristics which can serve many application areas.

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