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Compatibilized recycled polymers/clay as a matrix for rice husk composites: mechanical and physical properties

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Abstract. The growing green technological trend towards waste utilization and cost reduction has gained the industrial attention in the use of agricultural waste as a value added filler material. This research addresses a simple fabrication of greenly bionanocomposites made from polyethylene (rHDPE), recycled polyethylene terephthalate (rPET), nanoclay and rice husk (RH), with and without ethylene-glycidyl methacrylate (E-GMA) or maleic anhydride polyethylene (MAPE) compatibilizer, using a two-step twin-screw extrusion followed by hot/cold pressing. Results showed the positive effect in elongation at break and impact strength upon the reinforcement of nanoclay with the aids of compatibilizer as compared to the neat polyolefin blend. By adding RH, the flexural properties were found to increase remarkably up to 3.6 times than the blend matrix. It was found that the addition of compatibilizer, especially E-GMA, lowered the water absorption and thickness swelling of bionanocomposites. Scanning electron microscopy confirmed the improved compatibility of nanoclay with polymer blend upon the addition of compatibilizer. It can be concluded that the synergy effects of hybrid reinforcements of rice husk fibre and nanoclay in the recycled polymer blend have achieved while maintaining environmental appeal.

1. Introduction

Rice husk (RH) is well established as the agricultural by-product which was estimated for approximately 20 % of the total production of rice during milling process. The introduction of RH fibre into plastic wastes makes the resultant composites viable from performance, environments and economic aspects, including lower materials cost, lighter product weight, and better properties those are enhanced modulus and stiffness, acoustic and thermal stability [1]. In the manufacture of RH-reinforced composite panels, there is a poor interaction and adhesion between the (hydrophobic) polymer matrix and (hydrophilic) RH [2], which resulting in deterioration of composite performance [3].

Recently, hybrid material, especially polymer matrix nanocomposites represents a new class of materials which becomes a great attraction in research area. The interest in organic-inorganic material system is attributed to the fact that the dispersion of the nanoscale fillers as well as the polymer-fillers interactions which resulted in a noteworthy improvement of properties in comparison to micro or macro composites [4]. The reinforcement of nanofillers such as clay in polymer composites is beneficial in terms of mechanical, optical clarity, gas barrier, thermal and fire properties, which are desired in automotive, civil, aerospace and packaging industries [5]. Boujmal et al. reported that the hybrid polymer composites containing clay and graphite presented optimum improvement in thermal stability and tensile modulus as well as could control the raw material costs by optimization of

composition [6]. However, compatibility between the components in hybrid material is inherently low due to the great difference in polarity in which the polyethylene is hydrophobic (non polar), the natural fibres and clay particles are hydrophilic (high polarity). This shortcoming is proven to be solved in the literature [5, 7] by adding coupling agent or compatibilizer that containing polar functional groups and the same polymer family backbone at two different sides.

Numerous published works proved that the hybridization has contributed a synergistic effect to composite materials. However, the hybridization studies on highly green materials are still limited. In this work, the recycled plastics and high loading of agricultural waste (70 wt%) were used. The aim was to investigate the addition effect of clay, rice husk fibre and compatiblizers (maleic anhydride and glycidyl methacrylate copolymers) on the mechanical, and physical properties, and morphological structure of recycled polyolefin blend nanocomposites.

2. Materials and method

2.1 Raw Materials

Recycled high-density polyethylene (rHDPE) and recycled polyethylene terephthalate (rPET) were used as thermoplastic blend matrix. The rHDPE has a melt flow index of 0.72 g/10 min (190 ℃, 2.16 kg load); whereas, rPET has an intrinsic viscosity of 0.68 dL/g. Organoclay (Cloisite 10A) with CEC = 125 meq/100 g (d spacing = 19.2 Å) was obtained by Southern Clay Products Co. The 100-mesh rice husk (RH) was used as the natural filler. Ethylene-glycidyl methacrylate (E-GMA) and maleic anhydride grafted polyethylene (PE-g-MA) copolymers were used as compatibilizer in this study. E-GMA (Lotader AX8840) has a melt flow index of 5 g/10 min (190 ℃, 2.16 kg load). All the materials, except for clay, were sponsored from Bio Composites Extrusion Sdn. Bhd. The rPET pellet, clay and RH powders were oven-dried at 90 ℃ for 24 h before compounding.

2.2 Extrusion compounding and hot/cold pressing

Melt-mixing of the blend and composite materials was conducted in a Thermo Prism TSE 16 PC co-rotating twin screw extruder with an aspect ratio of 25. Neat rHDPE/rPET polymer blend (PB) was formulated at a composition ratio of 4:3, the composition of clay, PE-g-MA and E-GMA was fixed at 3, 3 and 5 part per hundred resin (phr), respectively. The formulated PB and PB/clay materials (PB, PB/clay, PB/clay/MA and PB/clay/GMA) were manually mixed and extruded at 30 rpm and 190-240-270-250°C. In the preparation of composites containing RH, the pre-extruded granules were compounding with 70 wt% RH via second extrusion with the same rotation speed and a temperature profile 170-215-210-195 °C. The extruded granules were compression molded at 200°C via hot and cold pressing (LP50 machine) to produce composite specimens. The hot and cold pressings were applied at 10 min and 5 min, respectively.

2.3 Characterization

Flexural and tensile tests were done in the Testometric M350-10CT testing machine at a crosshead speed of 5 mm/min in accordance to ASTM D638-03 (type I) and D 790-03, respectively. Izod impact test was carried out at 3.46 ms^{-1} and 2.765 J by using a Ray-Ran Universal Pendulum Impact System based on ASTM D 256-05. Five replicates were done for each formulation. Water absorption test was performed according to ASTM D 570-98. After immersion for 2, 24 and 48 hours, the weight and thickness of the specimens were measured after being removed from water and wiped dry. The percentages of water absorbed (WA) and thickness swollen (TS) were calculated using equations: WA (%) = $(W_t - W_0)/W_0$ x 100 and TS (%) = $(T_t - T_0)/T_0$ x 100 where W_0 and W_t are the oven-dried weight and weight after immersion time t, respectively, T_0 and T_t define the thickness after oven-drying and the thickness after immersion time t, respectively. Scanning electron microscopy (SEM) of tensile-fractured specimen surfaces was performed using VPSEM Philips XL-30 at 10-15 kV. X-ray diffractometer (D8 Advance) was used to determine the intercalation and exfoliation state of silicate layers in the nanocomposites. The samples were scanned at room temperature with a scanning rate of 2°/min using a CuK$_\alpha$ radiation (λ = 0.154 nm, 40 kV, 30 mA).

3. Results and discussion

3.1 Mechanical properties

Figure 1 shows the mechanical properties of the investigated composites (a) flexural strength (b) flexural modulus (c) elongation at break, and (d) impact strength. The neat PB blend (without clay and RH) and PB/RH composites exhibited the lowest mechanical properties due to the incompatibility situation occurred between polar-non polar polymer, polymer-clay, polymer-clay-RH which can be observed in two-phase microstructure shown in SEM micrograph. When 3 phr clay was incorporated into the blend, the flexural, elongation and impact strength values in Figure 1 (a-d) declined by ~25%. There is no significant change was found for elongation at break and impact strength as shown in Figure 1 (b-c). Similar finding was reported in the previous study on polypropylene (PP)/PET blends filled with montmorillonite (MMT) [8]. For the PB/clay/RH composites, the flexural properties increased with higher rate than those of elongation and impact strength. This is ascribed to the role of nano-sized clay in carrying and transferring more loads, and also clay possesses higher stiffness in nature than that of polymers [9]. The inclusion of compatibilizers in the nanoclay-filled blends led to enhancement in mechanical properties, which was higher than that of neat PB blend. This improvement is attributed to the enhanced compatibility between the polymer components (polar PET and non-polar HDPE). Comparing to PE-g-MA, the E-GMA compatibilized blend possessed better mechanical performance as a result of the higher functional reactivity of GMA than MA, as deeply explained in our previous study [10]. The mechanical performance is significantly improved via the reinforcement of fillers in which this is a crucial requirement for structural and engineering applications.
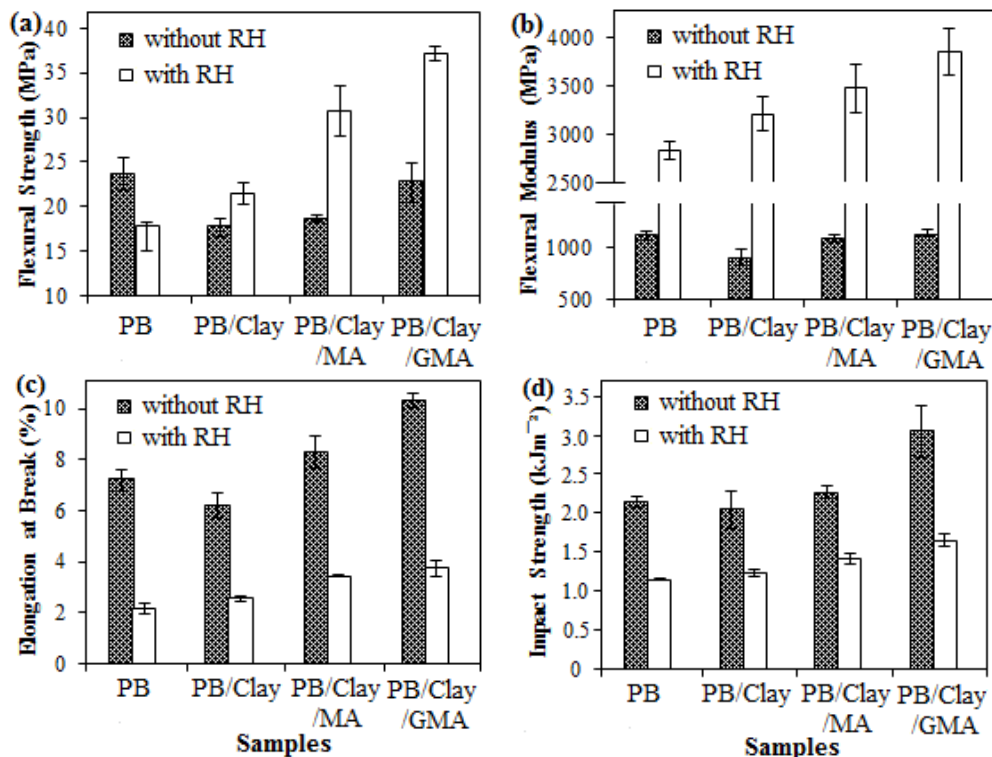

Figure 1. (a) Flexural strength, (b) flexural modulus, (c) elongation at break, and (d) impact strength of the investigated PB-based composites.

3.2 Percentages of water absorbed and thickness swollen

Figure 2 displays the percentage of (a-b) water absorbed and (c-d) thickness swollen of the recycled PB with and without RH nanocomposites after water immersion. Generally, as the times of immersion

increased, all the samples include PB, PB/clay and PB/RH/clay nanocomposite systems were becoming physically (dimensionally) instable as evidenced by the increased absorbed water (Figure 2 a-b) and thickness swollen (Figure 2 c-d). A striking observation is shown that the percentages of water absorbed and thickness swollen are in different levels for samples with and without RH fibres. In which the RH composites (Figure 2 b and d) exhibited higher percentages of water absorbed (~ 8-12 % after 48 hours immersion) and thickness swollen (~7-8 % after 48 hours immersion) as compared to negligible or comparatively low results for samples without RH. This is a logical trend for natural fibre composites [3, 11]. In the case of without RH fibres, the low percentages of water absorbed (< 0.06 %) and thickness swollen (< 2 %) in PB were ascribed to the hydrophobic HDPE-rich (major phase) matrix. By incorporating clay into PB, although in a low loading at 3 phr, the water absorbed and thickness swollen increased one-third for the system without RH, as displayed in Figure 2 a and c. This could be explained by the hydrophilic characteristic of layered silicate [4] which allows the water molecules absorbed into the composite material. Nevertheless, the modification of PB sample with the aids of compatibilizer (i.e. MA or GMA copolymers) was shown to promote good impact to dimensional stability behaviour of PB-based material. This observation can be interpreted by the chemical interaction of oxygen-containing functional groups (anhydride group of MA and epoxide group of GMA) with hydroxyl groups of hydrophilic fillers (clay and RH) [7]. The lowering of water absorbed and thickness swollen is greatly desired in natural fiber composites because this characteristic could improve the durability and performance of the material as well as could be used for outdoor applications such as building and construction.
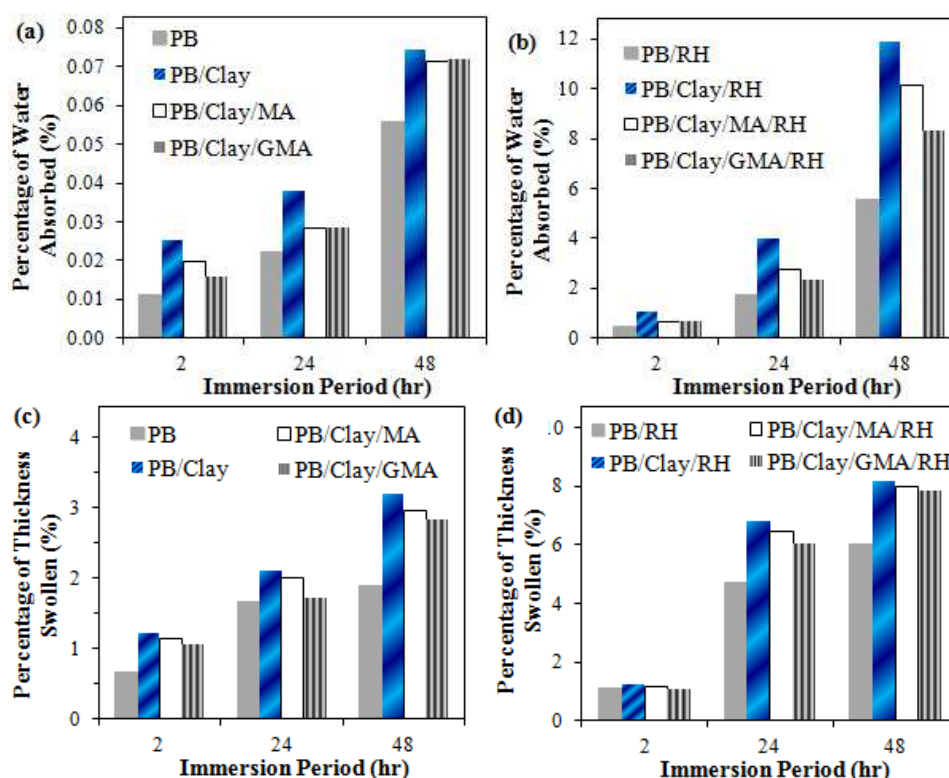

Figure 2. The percentage of (a-b) water absorbed and (c-d) thickness swollen of the investigated PB-based composites after a certain period of immersion in distilled water.

*3.3 Molecular structure and interaction of polymer-clay-rice husk*
Figure 3 demonstrates the morphological structure observations of PB/clay and PB/clay/RH nanocomposites with and without the presence of GMA. In PB/clay nanocomposite, it was clearly visible that the separated-phase microstructure where there were equally distributed spherical phase within another continuous phase, which strongly implying none of interaction occurred between these two phases. This is due to major component (97 wt%) of immiscible polymer blend of HDPE and PET

[10]. However, it is interesting to find that the addition of compatibilizer improved the compatibility and miscibility of binary blend as shown by the one-phase morphology structure. This can be also proven by a slight improvement in dispersion state of layered silicate (Figure 4), which was a small positive effect on the degree of exfoliation as indicated by the lower intensity of the peak but negligible changes in the degree of intercalation as represented by the similar peak position [5]. For the samples with the presence of RH, the SEM micrographs display much finer morphology structure as compared to those without RH, besides the existance of many large rectangular sheets that having external bumpy surface in which this structure is representing the RH fibres [1]. Without compatibilizer, the SEM micrograph of PB/clay/RH nanocomposite shows a uniform distribution of RH fillers within the PB/clay matrix but the RH surface, either internal (flat parallel scratch) or external (bumpy) was quite smooth and there was a lot of clear gaps between the RH-RH and RH-polymer. These observations suggest that the extrusion process could distribute the high loading RH in polymer matrix, however, the interaction and chemical bonding between the polymer-filler are limited if the compatibilizer was absent. When the compatibilizer (GMA in this case) was added, the PB/clay/GMA/RH nanocomposite exhibited a more compact and rougher morphology structure in comparison to the earlier. This can be ascribed to the improved adherence and interaction of RH surface with polymers. This finding has been commonly reported in previous natural fiber composites coupled with coupling agent [12].
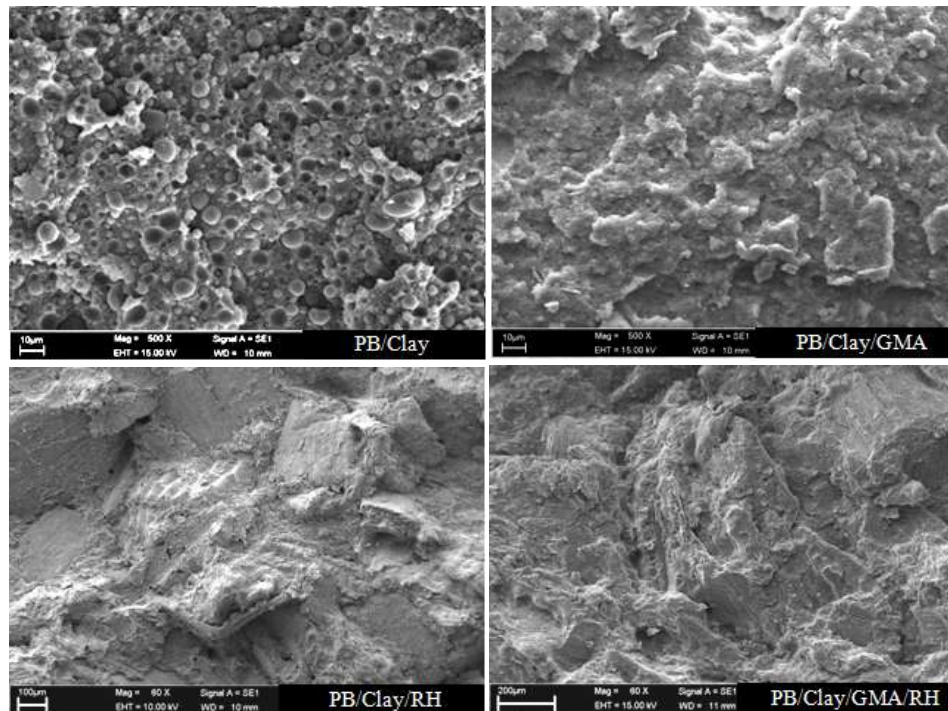
Figure 3. SEM micrographs of PB/clay with the presence and absence of compatibilizer (GMA) or/and RH nanocomposites.
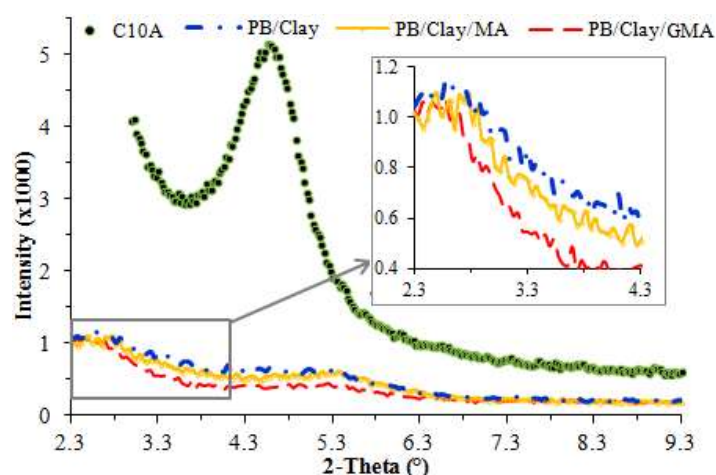
Figure 4. XRD patterns of raw clay and PB/clay nanocomposites with the presence and absence of compatibilizer (GMA).

4. Conclusion

The rHDPE/rPET/clay blends and RH fibre-reinforced rHDPE/rPET/clay composites were prepared via melt-blending process. The effect of the presence of fillers (micro- and nano-sized RH and clay, respectively) and compatibilizers (MAPE or E-GMA) on the mechanical and physical properties, and morphological structures were investigated. It was found that the maximum properties such as flexural strength (37 MPa), flexural modulus (3856 MPa), and resistance to water absorption (8.2%) and thickness swelling (7.8%) for E-GMA compatibilized PB/clay/RH composites. This composite could be act as a potential candidate to replace wood-based composites.

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