

Full Length Research Paper

Mechanical, thermal and barrier properties of unsaturated polyester Nanocomposite based on pet-waste for polymer concrete

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Unsaturated polyester (up) resin based on recycling pet is widely used for the matrix of composites such as fiber reinforced plastic (frp) and polymer concrete (pc). Consequently, inexpensive and high performance resins are important for the future of polymer composites. One recent method for enhancing the performance of polymer composites are the manufacture of MMT (montmorillonite)-UP nanocomposite synthesized by intercalating the UP resin into the silicate layers of MMT. This study investigates the mechanical and thermal properties of UP-MMT nanocomposites. The structures of UP-MMT nanocomposite were investigated by X-ray diffraction and transmission electron microscopy (TEM). Test results indicate that the mechanical properties and thermal stability of UP-MMT nanocomposites are better than those of pure UP. The glass transition and main chain decomposition temperatures of the UP-MMT nanocomposite exceed those of pure UP. The tensile strength, toughness and young's modulus of UP-MMT nanocomposites exceeded those of pure UP. Decrease of water permeability of The UP-MMT nanocomposite. improved performance of UP is very important for polymer concrete.

Keywords: Nanocomposites; Recycling; Polymers; Mechanical properties; Polymer concrete Transmission electron microscopy (TEM)

INTRODUCTION

Polymer nanocomposites, especially polymer-layered silicate nanocomposites, represent a rational alternative to conventionally filled polymers. Because of their nanometer scale dispersion, nanocomposites exhibit markedly improved properties when compared with the pure polymers or conventional composites (Giannelis, 1998). Polymer-layered silicate nanocomposites possess several advantages such as: (a) a lighter weight compared to conventionally filled polymers, because high degrees of stiffness and strength can be realized with far less high-density inorganic material; (b) mechanical properties that are potentially superior to fiber-reinforced polymers; and (c) their outstanding diffusional barrier properties without requiring a multipolymer layered

design (Kirshnamoorti et al., 1998). The performance of unsaturated polyester (UP) resin has relatively poor mechanical properties, thermal stability, and fire retardant properties, which limits its use in advanced composites. The modification of polymers is of considerable significance from a material science and engineering point of view. The performance of unsaturated polyester (UP) resin may be enhanced by the addition of inorganic fillers (Okada et al., 1995; Kornamann et al., 1998). Conventional particulate polymer composites, often called filled polymers, are of significant commercial importance as materials in industrial applications. Polymer nanocomposites are a new class of composites derived from nano-scale inorganic particles. Their dimensions typically range from 1 to 1000 nm and they are homogeneously dispersed in the polymer matrix. Owing to the high aspect ratio of the fillers, the mechanical, thermal, flame retardant and barrier properties of polymers may be enhanced without a

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significant loss of clarity, toughness or impact strength. The layered silicate is generally made organophilic by exchanging the inorganic cation, which is located between the layers (d-spacing), with an organic ammonium cation. Clay-polymer composites can be classified into three types: conventional composite, intercalated nanocomposites and exfoliated nanocomposites.

Conventional Composites: If the clay layers and polymer are not compatible, the surface energies are incompatible for wetting, and consequently no polymer will penetrate the gallery layer. There will be no, or very little, bonding between the clay and the polymer; therefore, the clay will provide little mechanical reinforcement.

Intercalated Nanocomposites: An intercalated nanocomposite is formed when the clay layers are separated by a fixed amount. The clay layers will reinforce the polymer, although the fixed layer separation is unable to provide the optimum level of reinforcement.

Exfoliated Nanocomposites: An exfoliated nanocomposite is formed when the clay layers are dispersed in the polymer with random separation and orientation. The clay layers will be sufficiently separated and randomly orientated to allow full interfacial bonding and to contribute all their strength to improve the properties of the nanocomposite (Aranda and Ruiz-Hitzky, 1992; Alexandre and Dubois, 2000).

Montmorillonite (MMT) is a layered aluminosilicate mineral most often present in clays and most often used in polymer nanocomposite preparation. The surface of MMT is hydrophilic and therefore not suitable for preparation of nanocomposites with most of commercial polymers. To ensure good intercalation the surface of MMT platelets has to be modified. There are several ways of modifying MMT but the most common method is a cation exchange with organic ammonium salts (onium-salt), which differ in a number, length and structure of long chains (Bergaya and Lagaly, 2001). Quaternary ammonium salts or amine hydrochlorides, having one or more long alkyl chains bound to amine, are most commonly used (Lee and Lee 2004; Yang et al., 1999). The role of the modification of MMT with ammonium salts is to increase the interlayer spacing, reduce interactions between the MMT platelets, and improve the interaction between the clay and the polymer matrix. When a proper combination of modifier and polymer is chosen, fully exfoliated nanocomposites can be obtained; otherwise only intercalation of polymer chains within the clay platelets is observed (Zheng et al 2004). The interlayer spacing in intercalated nanocomposites also depends on the type of modifier, which strongly influences the nanocomposite's mechanical properties i.e. mechanical properties are not always improving with increasing interlayer expansion (Barber et al., 2005).

General, there are two methods of making nanocomposites, melt intercalation and in situ

intercalative polymerization of monomers. Melt intercalation of high polymers is a powerful new approach for synthesizing polymer-layered silicate nanocomposite. This method is quite general and is broadly applicable to many commodity polymers, from essentially non-polar polystyrene, weakly polar PET to strong polar nylon (Giannelis, 1998). The nanocomposites of thermoset polymer can be prepared by the in situ intercalative polymerization method (Akelah and Moet, 1996); phenol resins, epoxy resins Lan et al., 1995; Lee and Jang, 1998 and unsaturated polyester resins are included in this category. These thermosetting nanocomposite materials are prepared by first swelling the various organo-modified montmorillonite (MMT) with the proper polymerizable monomers, followed by crosslinking reactions.

The objective of this study is to enhance the performance of polymer composites using unsaturated polyester (UP) resin based recycled PET (poly ethylene terephthalate) prepared in our previous work (Shimaa et al., 2009). Therefore, this work investigates the mechanical properties and thermal stability of UP-MMT nanocomposites. The results are supported by mechanical testing, X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and thermo gravimetric analysis (TGA).

Experiments

MATERIALS

Two different kinds of MMT were used unmodified Na-MMT and modified Cloisite 30B (Southern Clay Products Inc., USA). The unmodified MMT was treated in our lab with dodecyl methyl ammonium chloride by accepted procedures (Hasegawa et al., 1998; Oh et al., 1998). First, 20g of MMT was dispersed into 400ml of water. Dodecyl methyl ammonium chloride (8.82g) was then dissolved in 100ml of water and in 100ml of ethanol. It was poured into the MMT-water solution with vigorous stirring for 5–6h at 50–70°C. The precipitates were collected and redispersed for 1h. The solution was then filtered and freeze-dried to yield an organophilic modified MMT-D. Cloisite 30B is a montmorillonite modified with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride.

The unsaturated polyester resin based on recycled plastic (PET) was used as the matrix in our previous work (Shimaa et al., 2009). Aminolysis of PET waste materials with ethanol amine (EA) of molar ratio of 1:6 under reflux in the presence of 0.1 wt % sodium acetate (with respect to the weight of PET) for various time periods up to 8h. At the end of the reaction, distilled water was added handily in excess to the reaction mixture with vigorous agitation to precipitate out the product, bis (2-hydroxyl ethylene) terephthalamide (BHETA). The UP resins were prepared

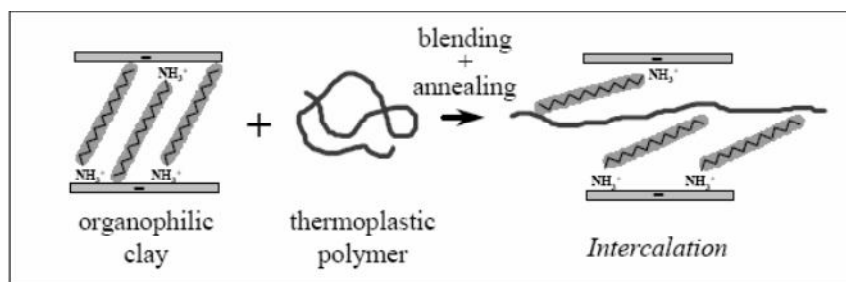


Figure 1. The melt intercalation method

by the reaction of 1.1mol of BHETA with 0.5mol of maleic anhydride (MA) and 0.5mol of saturated aliphatic acids, Decanedioic Acid (DA). The esterification reaction carried out in reactor equipped with a stirrer, a thermometer, a Dean–Stark side arm, and a nitrogen inlet. The reactants were heated from room temperature to 180OC in a nitrogen atmosphere for 1.5h and held at this temperature for 4 h. Finally, the temperature was raised and kept at 200OC for 1h. The reaction product was permitted to cool to 60OC, and hydroquinone (0.1 wt%) was added as an inhibitor to avoid the polymerization of the product. To start the curing process, methyl ethyl ketone peroxide (MEKP) and cobalt octoate (Co) were used as the initiator and activator, respectively. MEKP was supplied as a 50% paste in dimethylphthalate. Co was a 10% solution in styrene. A styrene content of 40% in unsaturated polyester was chosen for its low viscosity and to achieve improved resin diffusion into the galleries of the MMT.

The following optimum and fine inorganic aggregates were used in the experimental study of polymer concrete: 10 mm pea gravel; river sand and fly ash (fly ash makes the mix both more workable and stronger). The aggregate was oven-dried for a minimum of 24 h at 200OC to reduce its moisture content to less than 0.3% by weight, thus ensuring a perfect bond between the polymer matrix and the inorganic aggregates.

Measurements

X-ray diffraction (XRD) patterns were obtained using a Rigaku X-ray diffractometer equipped with CuK α radiation and a curved graphite crystal monochromator. Samples were prepared by applying the pre-intercalated mixture and nanocomposite of UP-MMT in sheet form on a slide. All XRD data were collected with an X-ray generator ($\lambda = 1.5406 \text{ \AA}$). Bragg's law ($\lambda = 2d/\sin\Theta$) was used to compute the crystallographic d-spacing. In order to evaluate the change in the glass transition temperature, T_g , associated with increases in the MMT content, a differential scanning calorimeter (DSC) analysis was

carried out using a General V4.1C DuPont 2000. The measurement was carried out from 50OC to 300OC using a heating rate of 10OC/min in a nitrogen atmosphere. The thermal behavior was determined with a thermogravimetric analyzer (TGA). Microscopic investigation was performed with a transmission electron microscope (TEM) with an acceleration voltage of 100 kV. The mechanical characteristics of the cured UP-MMT nanocomposite under investigation, represented by Young's modulus (EY), tensile strength, and toughness were measured with a Shimadzu universal testing machine (series UH-A model 2000 KN computer-controlled hydraulic servo system). Testing of the mechanical properties was carried out according to ASTM D 695-44T.

Preparation of unsaturated polyester silicate nanocomposite

There are two procedures for manufacturing the UP-MMT nanocomposite. The first step is the mixing process. In other words, the UP linear chains are mixed with styrene monomers and layered silicate (melt process) figure (1). The second step is the curing process. The crosslinking reaction starts by decomposing the initiators in the curing process.

The unsaturated polyester chains, styrene monomers and nano-MMTs were mixed for 3h at 60OC. The weight percentages of MMT in UP-MMT nanocomposite used were 2%, 5%, 8% and 10%, respectively. The mixture was then cooled to room temperature. 1% by weight of initiator (MEKP) was added and the mixture was stirred for 2min. The mixture was poured into molds, cured at room temperature for 12h and post-cured at 120OC for 4h.

Preparation of polymer concrete using up-mmt-30b nanocomposites

The mix design of polymer concrete, proportioned by

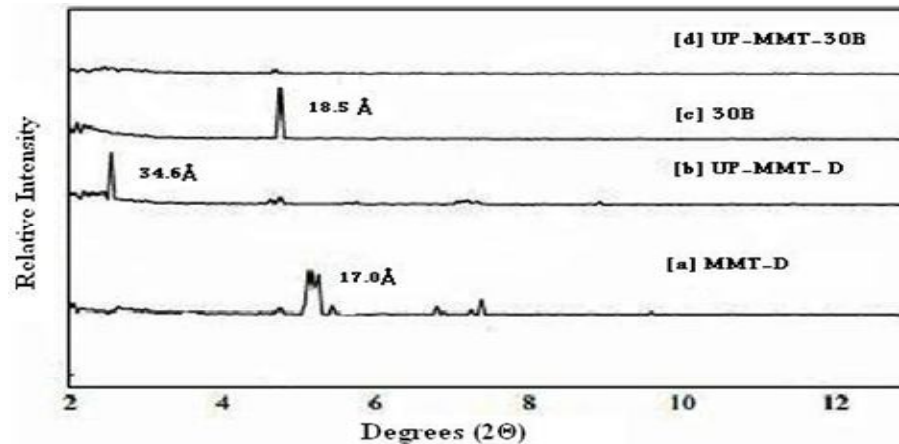


Figure 2. XRD data for UP-MMT nanocomposites with MMT contents of 5%: (a) MMT-D, (b) UP-MMT-D composite; (c) Cloisite 30B (d); UP-MMT-30B composite.

weight, was as follows: 11% resin (MMT-UP), 45% oven-dried optimum aggregate, 33% oven-dried sand, and 11% fly ash. Flexural specimens were mixed and compacted in a steel mold with dimensions of 50x50x305-mm. The beams were loaded in third-point loading at a uniform rate of 2225 N/min. The specimens were cast, cured, and tested at room temperature. Testing of the specimens was performed at 7 days. Tests were performed to determine the effect of temperature on the PC compressive strength, splitting tensile strength, modulus of elasticity, and flexural strength. After curing, specimens were put in an environmental chamber at the desired temperature for a period of 2 days prior to testing. Selected temperatures were -15°C, 25°C, and 65°C. Actual testing was performed at room temperature immediately after removing the specimens from the environmental chamber.

Tensile tests were performed according to ASTM D638M-91a at a crosshead speed of 5 mm/min. The polymer concrete cylinders used for compression and splitting tensile tests were 76mm in diameter and 152mm in length. Specimens were tested in a hydraulic load machine at a constant loading rate of 44,500 N/min.

RESULT AND DISCUSSION

Two complementary techniques are generally used to characterize the structures of nanocomposites: XRD and transmission electron microscopy (TEM) [Alexandre and Dubois, 2000; Ray and Okamoto, 2003]. Due to its ease of use and availability, XRD is most commonly used to probe the nanocomposite structure and occasionally to study the kinetics of polymer melt intercalation (Ray and Okamoto, 2003). This technique allows the determination of the spaces between structural layers of the silicate utilizing Bragg's law ($\lambda = 2d/\sin\theta$), where λ corresponds

to the wave length of the X-ray radiation used in the diffraction experiment, d the spacing between diffractive lattice planes and θ is the measured diffraction angle or glancing angle (Alexandre and Dubois, 2000; Porter et al., 2000).

XRDs of MMTs revealed different peaks with the surface modifiers as shown in Figure (2), the XRDs of MMTs and MMT-UP composites investigated different peak with the types of MMTs. The peaks for MMT-D, MMT-30B and UP-MMT-D composite are shown at 5.2 θ , 3.5 θ and 2.6 θ , respectively. These 2θ values correspond to interlayer spacing of 17.0, 18.5 and 34.6Å, respectively. Whereas, for UP-MMT-30B composite, the peak at the lower angle disappeared, verifying that the silicate layer platelets was exfoliated in the polymer matrix and also disappeared because the spacing between the layers was too large. It is important to note that polymerization of UP-MMT-D nanocomposite led only to an intercalated structure, while UP-MMT-30B promoted the delamination process of layered silicates to achieve exfoliation. May be due to the interlayer spacing of the MMT-30B is larger than that of the MMT-D; this is because the MMT-30B contains the two longer alkylammonium chains as organic modifiers.

On the other hand, TEM allows a qualitative understanding of the internal structure and can directly provide information in real space, in a localized area, on morphology and defect structures (Ma et al., 2003; Morgan and Gilman, 2003). Since the silicate layers are composed of heavier elements (Al, Si and O) than the interlayer and surrounding matrix (C, H and N), they appear darker in bright-field images. Therefore, when nanocomposites are formed, the intersections of the silicate sheets are seen as dark lines which are the cross sections of the silicate layers, measuring 1 nm thick. However, special care must be exercised to guarantee a representative cross-section of the sample (Porter et al.,

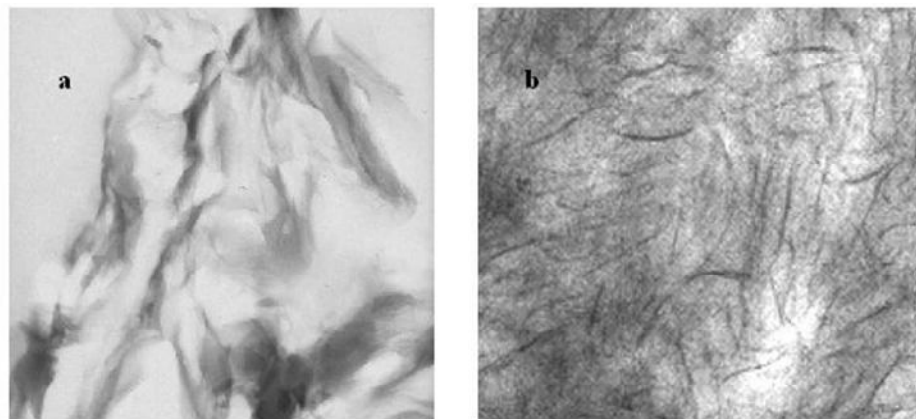


Figure 3. Transmission Electron Micrographs (TEM) of UP-MMT nanocomposite: (a) UP-MMT-D, (b) UP-MMT-30B.

Table 1. Mechanical Test of UP-MMT Nanocomposites

Samples	UP-MMT content (%)	Young's modulus (GPa)	Tensile strength (MPa)	Toughness(MPa)
Pure UP	0	22.210	130.201	1616
	2	21.221	153.241	2361
	5	20.673	176.523	3034
UP-MMT-D	8	21.565	165.231	2388
	10	23.212	160.540	2104
	2	21.901	173.578	2541
UP-MMT-30B	5	17.568	195.214	3446
	8	19.214	183.247	2610
	10	21.020	175.214	2215

2000; Ma et al., 2003). Figure (3) shows the TEM micrographs obtained for an intercalated and an exfoliated nanocomposite. As already mentioned, besides these two well defined structures other intermediate organizations can exist presenting both intercalation and exfoliation. In this case, a broadening of the diffraction peak is often observed and one must rely on TEM observation to define the overall structure (Alexandre and Dubois, 2000) so more direct evidence for the formation of a nanocomposite is provided by TEM. The TEM of image UP-MMT-30B in Figure (3a) display individual silicate layers apparent as dark lines. However, the UP-MMT-D in Figure (3b) layers have some irregular dispersions of the silicate layer maintained their original ordering.

With the addition of the MMT, the tensile strength of the composites shown in Table (1) increases up to 5% loading since MMT is more rigid than the pure UP resin.

Mechanical and thermal properties

The tensile strength of the UP-MMT-30B composites exceeds that of UP-MMT-D composite owing to their higher degree of exfoliation and better adhesion at the

UP-MMT interface. Above 5% MMT content, the tensile strength starts to decrease with MMT content in both types of composites, due to a lower degree of exfoliation and a lower degree of polymer–MMT surface interactions at higher MMT content as demonstrated in Table (1). Also, the cross-link density might be lower with a higher MMT content, leading to a lower tensile strength i.e. indicating that the crosslinking density is inversely proportional to the degree of exfoliation (Chang and Kim,2004). The increase in tensile strength associated with increases in MMT content is demonstrated in Table (1).

It was evident that with the addition of small amount of montmorillonite (5%) to UP, the tensile strength significantly increased while the young's modulus (elasticity) decreased. i.e. composites became more rigid exhibiting higher resistance to deformation. The toughness follows the same trend as tensile strength that is, increased with increasing MMT contents up to 5%. The results indicated the reinforcing effect of MMT to enhance the mechanical properties of the composite.

Work done on the thermal properties of polymers has shown that the glass transition of polymer–MMT nanocomposites increases with increasing MMT content. The effect of UP-MMT-30B content on the Tg is shown in

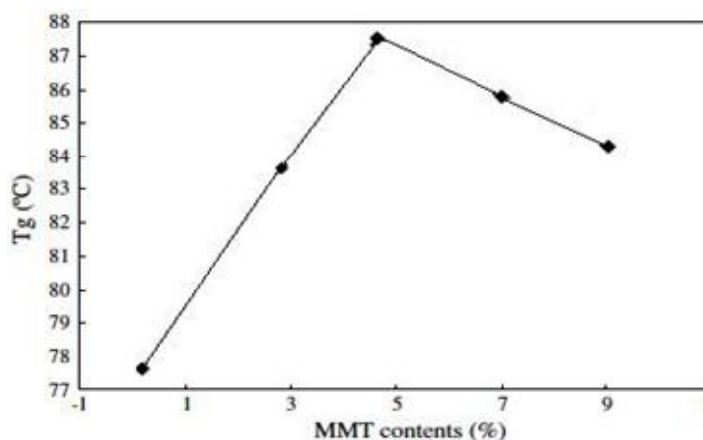


Figure 4. Glass transition temperature of UP-MMT-30B- nanocomposite.

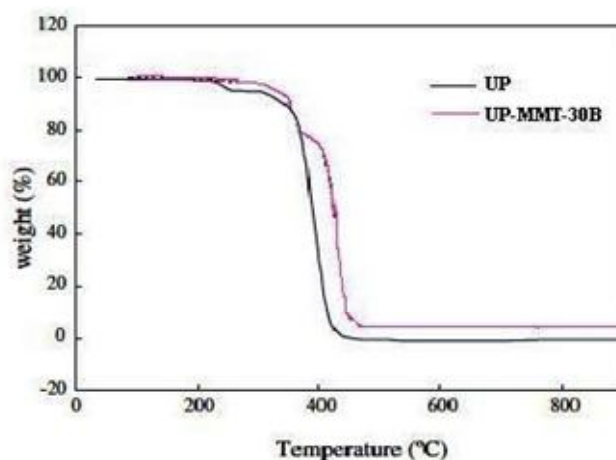


Figure 5. TGA thermal degradation for UP-MMT-30B nanocomposites (5%) and pure UP.

Figure (4). The T_g increases with increasing of MMT (Cloisite 30B) content. This implies improved adhesion between the UP and MMT surfaces. Also, the UP-MMT prevents segmental motions of the polymer chains.

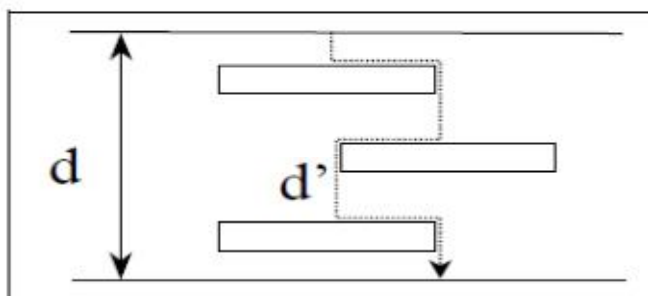
TGA curves of the pure UP and the UP-MMT-30B nanocomposite are shown in Figure (5) and have three steps. The first is the decomposition of relatively weak linkages, impurities, and styrene monomers in the UP. The second is the decomposition of the UP chain-end, and the third is the decomposition of the UP main chains. The three degradation steps occurred at 170°C, 285°C, and 342°C in the pure UP and at 232°C, 341°C, and 420°C in the MMT-UP nanocomposite. It is reported that the thermal stability of UP-MMT-30B nanocomposites gradually increases with increasing MMT, up to a loading of 5 wt.%. The temperature of the main chain decomposition of the UP-MMT-30B nanocomposite exceeds that of the pure UP by about 100°C. Pure UP is

completely decomposed at 400°C. The nanocomposites show slower degradation above 500°C.

Barrier properties

Permeability

The substantial decrease of permeability brought by nanocomposite structure is also a major advantage of polymer-clay nanocomposite. It was first reported by the Toyota researchers (Okada et al., 1990) that their polyamide-6-clay hybrid had a rate of water absorption reduced by 40% as compared with the pristine polymer. In our work, we are observed a dramatic decrease of water permeability with UP-MMT-30B nanocomposite, up to 80% with only 5 vol% of clay. Until recently, the impressive decrease of permeability was attributed to the



Model describing the path of the diffusing gas through the nanocomposite

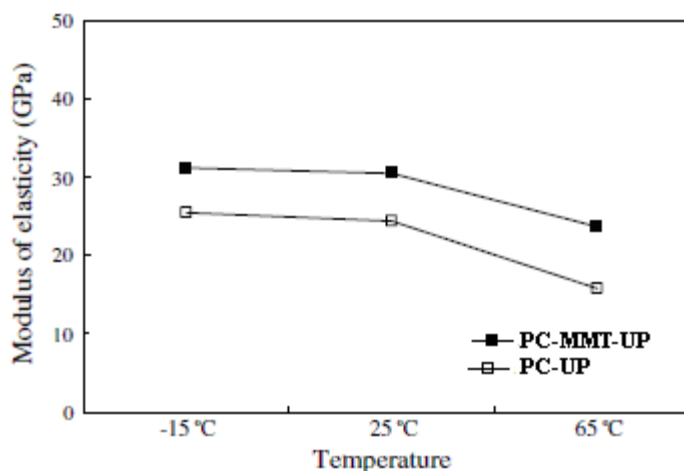


Figure 6. Elastic modulus of polymer concrete using UP- MMT-30B nanocomposite.

large aspect ratio of the clay layers which should increase the tortuosity of the path of the gas as it diffuses into the nanocomposite.

Solvent Resistance

The better barrier properties of polymer-clay nanocomposites also increase solvent resistance. In our study performed on UP-MMT-30B nanocomposite that offer a better resistance to organic solvents (alcohol's, toluene, and chloroform), particularly when the solvent molecules are small enough to penetrate into the polymer network and large enough so that once they are absorbed, they cause molecular damage to the polymer matrix, as with propanol or toluene.

Effect of up-mmt-30b nanocomposites on polymer concrete

Effect of temperature on mechanical testing

The strength of polymer concrete specimens cast with UP-MMT-30B nanocomposite containing 5% MMT content was estimated.

The effects of temperature on the compressive strength, modulus of elasticity, and splitting tensile and flexural strength of the polymer concrete using UP-MMT nanocomposite are shown in Figure (6-8). The modes of failure of polymer concrete differed depending on the temperature at which the materials were tested. Compression cylinders had a sudden, brittle failure when tested at -15OC and 25OC. Conversely, cylinders tested

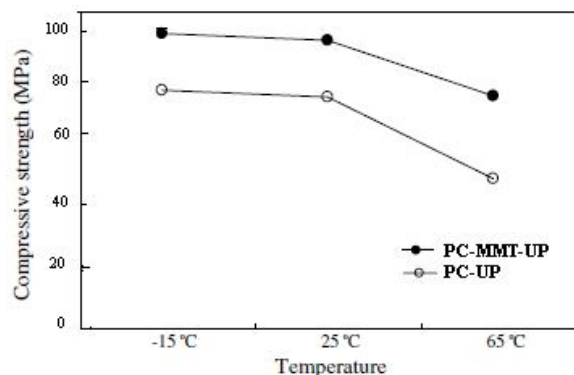


Figure 7. Compressive strength polymer concrete using UP-MMT-30B nanocomposite

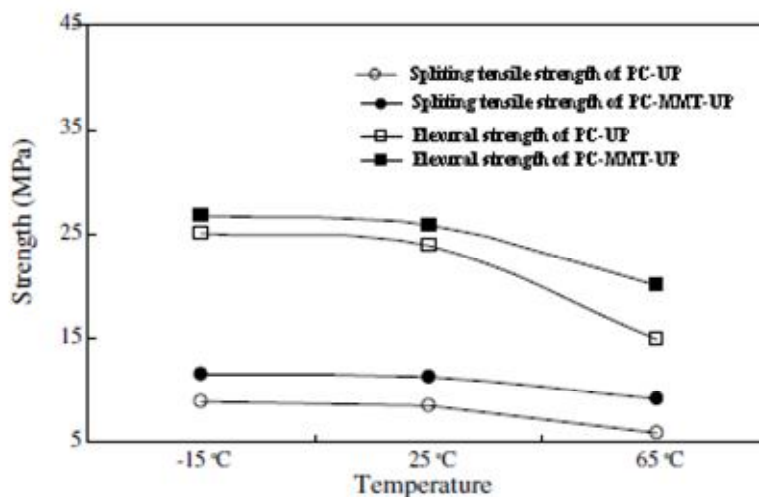


Figure 8. Splitting tensile and flexural strength of polymer concrete using UP-MMT-30B nanocomposite.

at 65OC had a slow, flexible failure resulting in an excessive bulging of the specimens. This behavior arises from decreases in the modulus of the resin in the polymer concrete specimens under increasing temperature. That is, the modulus of the polymer concrete specimen decreases with increases in temperature, as shown in Figure (6 and 7). Increase in temperature affected a loss in strength and modulus of elasticity in the polymer concrete specimens because the resin decreased in strength with an increase in temperature. In the case of the polymer concrete specimens using pure UP, an increase in temperature from -15OC to 65OC decreased the compressive strength by about 33%, modulus of elasticity by about 36%, splitting tensile strength by about 31%, and flexural strength by about 38%. In the case of the polymer concrete specimens using UP-MMT nanocomposite, an increase in temperature from -15OC to 65OC decreased the compressive strength by about 18%, modulus of elasticity by about 22%, splitting tensile strength by about 18%, and flexural strength by about

22%. This result demonstrates that the polymer concrete made with MMT-UP nanocomposite has mechanical properties that are better than those of pure UP. The improved performance of UP is very important for the future of polymer concrete. Therefore, the enhancement of the mechanical and thermal performance of polymer concrete afforded by the use of nano-MMT is remarkable.

CONCLUSIONS

Unsaturated polyester resins based on aminolized PET waste and nano-MMT may be used to greatly enhance the performance of polymer composites at a relatively low cost.

The mechanical and thermal properties of UP-MMT nanocomposite, which have their maximum tensile strength, toughness and Tg with 5% nano-MMT, were greatly improved by the addition of nano-MMT dispersed in the polymer matrix. Also, the elastic modulus of MMT-

UP nanocomposite was enhanced by the addition of nano-MMT. However, beyond a certain MMT content (approximately in the range of 5–7%), the mechanical and thermal performance of the composites decreased with increasing nano-MMT content.

The mechanical and thermal properties of UP-MMT-D did not show a significant change because the degree of exfoliation is less than that of UP-MMT-30B nanocomposites.

The compressive strength, elastic modulus, and splitting tensile strength of polymer concrete using exfoliated UP-MMT-30B nanocomposite exceeded the corresponding properties of polymer concrete using pure UP.

The use of exfoliated UP-MMT nanocomposite enhances polymer concrete strength. It is important to note that the exfoliated MMT-UP nanocomposite greatly affects the performance of the polymer concrete.

The strength and elastic modulus of polymer concrete was found to be positively correlated with the tensile strength and tensile modulus of the PC-MMT-UP nanocomposite.

Polymer concrete that exhibits excellent mechanical and thermal performance.

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