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Processing and Mechanical Characterization of Graded and Non-graded Nanoclay Composites

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Abstract

In this research, nanoclay reinforced polyester nanocomposites were developed with a semi-commercial process. Two types of nanoclays viz. graded and non-graded nanoclay were used as reinforcements. Each of the nanoclay was added 1 wt. % in polyester separately and the effects of the addition of nanoclay on the polyester were studied by mechanical characterization. Tensile and flexural strength were measured by using an Instron Universal Testing Machine. Hardness of the developed nanocomposites was measured by a Shore Hardness Tester. The fracture surfaces were investigated by Scanning Electron Microscope (SEM). It is found that the modulus and strength of graded nanoclay reinforced nanocomposite is higher than that of the unreinforced polyester and non-graded nanoclay reinforced nanocomposite. The flexural strength is also found to be higher in the graded nanoclay composites as compared to the unreinforced polyester and non-graded nanoclay reinforced nanocomposite. The hardness of unreinforced polyester and both the nanocomposites are almost same. The fracture morphology of the unreinforced polyester and reinforced nanocomposites and its correlation with mechanical properties are also discussed.

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1. Introduction

Nanocomposites have courted and enticed attention in recent years because of improved mechanical, thermal, solvent resistance and fire retardant properties compared to the pure or conventional composite materials. Therefore, much work has focused on developing polymer/clay nanocomposites using various polymers which add to the lure of advancement of modern materials. In the simplest case, appropriately adding nanoparticulates to a polymer matrix can enhance its performance, often dramatically, by simply capitalizing on the nature and properties of the nanoscale filler [1]. This strategy is particularly effective in yielding high performance composites, when good dispersion of the filler is achieved and the properties of the nanoscale filler are substantially different or better than those of the matrix. An example of this would be reinforcing a polymer matrix by much stiffer nanoparticles of ceramics, clays, or carbon nanotubes [2-3]. By the addition of the nanofillers, the improvement in mechanical properties not only is limited to stiffness or strength, but it is also extended to improve the time-dependent properties [4]. Alternatively, the enhanced crystallization behaviour under flow conditions and other physical properties of high performance nanocomposites is mainly due to the high aspect ratio and/or the high surface area of the fillers, since nanoparticulates have extremely high surface area to volume ratio when good dispersion is achieved [5-7]. Nanoparticle dispersion in the polymer matrix is a key issue, which limits the applicable particle volume fraction and therefore also the multi-functionality of the composite material.

Nanoclay is one of the most affordable materials that have shown promising results in polymers. The clays used for the preparation of nanoclays or organoclays belong to smectite group or montmorillonite clays. Organophilic clay (nanoclay) can be obtained by simply the ion-exchange reaction of hydrophilic clay with an organic cation such as an alkyl/aryl ammonium, phosphonium or imidazolium cations in aqueous solution or in the solid state. The inorganic ions are exchanged with more voluminous organic onium cations. When the solubility of quaternary salts is low, water-alcohol mixtures are often used as a solvent. The ion exchange reaction has two consequences; first, the gap between the single sheets is widened, enabling organic cations chain to move in between them and second, the surface properties of each single sheet are changed from being hydrophilic to hydrophobic or organophilic [8-9]. Montmorillonite consists of ~ 1 nm thick aluminosilicate layers surface-substituted with metal cations and stacked in ~ 10 µm-sized multilayer stacks. The stacks can be dispersed in a polymer matrix to form polymer-clay nanocomposite. Within the nanocomposite, individual nm-thick clay layers are fully separated to form plate-like nanoparticles with very high (nm x µm) aspect ratio. Even at low nanoclay loading (a few weight %), the entire nanocomposite consists of interfacial polymer, with majority of polymer chains residing in close contact with the clay surface. Potential benefits include increased mechanical strength, decreased gas permeability, superior flame-resistance, and even enhanced transparency when dispersed nanoclay plates suppress polymer crystallization [10]. Thus the present study has therefore been taken to study the effect of graded and non-graded nanoclay on polyester.

2. Experimental Procedure

The materials in this experiment were pure polyester, graded nanoclay (nanoclay nanomer 1.31 PS, montmorillonite clay surface modified with 15-35 wt% octadecylamine and 5 wt% aminopropyltriethoxysilane), non-graded nanoclay which is basically non-processed and non-modified clay collected from local areas and a hardener which is methyl ethyl ketone peroxide hardener (molecular formula: $C_8H_{18}O_6$, molar mass: 210.22 g mol^{-1}, appearance: colorless liquid, density: 1.170 g cm^{-3}).

First of all, raw samples of non processed clay were obtained from Chuyadanga local areas for the accomplishment of non-graded nanoclay. This kind of clay contains nano-size particles as well as micro-sized particles and even larger particles. So it was a necessity to have them refined and separated. The clay was then processed in a semi-commercial technique for it to be at an approximate nano level. A portion of the lumps of clay was taken in a funnel and appropriate amount of water was added in the clay. Then significant time was allowed for the large size clay to settle. The small size clay was then filtered through a 100 micron sieve and those that passed through the sieve were collected in a bucket. The particles passing through the sieve means that they are finer and therefore collected. The procedure was then repeated with the collected clay-water mixture so that finer and finer

clay particles can be obtained. The whole process was then repeated for other portions of the lumps of clay. After 3-4 days the prepared non-graded nanoclay was collected from the bucket and was kept a drying oven at 110°C for 24 hrs. The clay was then taken out of the oven and ground in a mortar for ensuring finer particles. The non-graded clay was then stored in an air tight container.

Liquid polyester was selected as matrix material for this study and collected from local market. The dimension of the casting dies were 100 mm in diameter and 6 mm in thickness. First of all, pure polyester samples were produced for standard comparison. Usually air/gas remains dissolved into the liquid polyester. Before casting the liquid polyester and the nanoclay into the dies was made gas/air free by a vacuum process. Then hardener (methyl ethyl ketone peroxide) of required proportion was added inside the gas free liquid polyester and stirred properly for obtaining a uniform mixture. The mixture was again evacuated putting the beaker inside the vacuum chamber for removing air and the beaker was taken from the chamber, and the pasty mass was cast into die of required shape. For preparing nanocomposites, 1 wt.% of graded and 1 wt.% non-graded nanoclay was added to the polyester separately and the mixture was stirred properly to get uniform distribution of the reinforcing particles.

More than eight samples of pure polyester and each group of composites were made through die cast method. The rectangular samples were then machined as ASTM standard tensile test samples. The final dimensions of the tensile test samples were 100 mm x 12 mm x 6 mm with gauge length 30 mm. For performing bend test, casting samples were machined to produce a rectangular shape of dimensions 5 mm thickness, 13 mm width with span length of 80 mm.

After tensile tests, fracture surfaces were cut for fractographic analysis under the Field Emission SEM. To avoid charging effect, the fracture surfaces of all samples were coated by gold sputtering technique. Under SEM, various fracture features were investigated.

3. Results and Discussion

Tensile properties of pure polyester (P), polyester reinforced with non-graded nanoclay (P+NGNC) and polyester reinforced with graded nanoclay (P+GNC) are shown in Table 1. It is observed that the tensile strength and modulus of pure polyester decrease by about 30% with the addition of non-graded nanoclay. The reason behind the decrease in strength of polyester with the addition of non-graded nanoclay may be attributed due to the agglomeration of nano particles and also due to the inhomogeneous mixture between agglomerated clay particles and polyester. However, an opposite result has been achieved when graded nanoclay was added to pure polyester as reinforcement. The maximum tensile strength and modulus has increased by about 10% compared to that of pure polyester. This is because all the clay particles are of same size at a nano level as they are graded and processed in a commercial way. Therefore, this has resulted in a larger surface area than that of any other reinforcement and therefore leading to a very efficient stress transfer mechanism, hence resulting in a higher strength and modulus. The trend is consistent with the results reported by others. According to Kojima et al., a region where the polymer chains are restricted in mobility contributes to the improvement of the tensile modulus in a polymer–clay hybrid [11].

Table 1: Tensile properties of pure polyester, polyester reinforced with non-graded nanoclay and polyester reinforced with graded nanoclay.

Samples	Maximum tensile strength (MPa)	0.2% offset yield strength (MPa)	Modulus (MPa)
P	47.9	32.6	4728
P + NGNC	32.8	23.1	3181
P + GNC	52.7	29.3	5342

Table 2 shows flexural strength of polyester, polyester reinforced with non-graded nanoclay and polyester reinforced with graded nanoclay. From the table, it can be observed that the flexural strength of pure polyester decreases by about 5% with the addition of non-graded nanoclay in polyester. According to the type of the filler, it can be suggested that the hydrophilic unmodified nanoparticles cannot be dispersed appropriately and generally agglomerates in the resin phase. This phenomenon causes the stress to be concentrated on particular points in the

resin phase and the crack to spread easily through the unfilled parts of matrix resin. This can be the main reason for crack propagation that leads to matrix fracture and reduction in flexural strength.

But when graded nanoclay is added in pure polyester as reinforcing particles, flexural strength is found to increase (about 15%) significantly. This increase may be attributed to the fact that graded nanoclay provides appropriate separation and dispersion of the particles in the resin matrix, especially in nanoscale, which plays an important role in the physical characteristics of resin-based materials. Modifications of nanoparticles can efficiently enhance their dispersion. Swelling of the grafted polymeric chains on the graded nanoclay particles may reduce their density and facilitate their distribution in the resin phase by making them polarized. This uniform dispersion in nanoscale prevents crack propagation and causes a significant improvement in flexural strength properties,

Table 2: Flexural strengths of polyester, polyester reinforced with non-graded nanoclay and polyester reinforced with graded nanoclay.

Samples	Flexural Strength (MPa)
P	82.1
P + NGNC	78.8
P + GNC	94.6

The hardness of pure polyester, polyester reinforced with non-graded nanoclay and polyester reinforced with graded nanoclay are presented in Table 3. From this table, it is seen that the hardness of unreinforced polyester and both the nanocomposites are almost same. This is because the resistance to withstand indentation did not increase upon addition of nanoclay in the polyester.

Table 3: Hardness of polyester, polyester reinforced with non-graded nanoclay and polyester reinforced with graded nanoclay.

Sample	Hardness (Shore)
P	96.1
P + NGNC	97.1
P + GNC	97.4

The fracture surfaces of pure polyester, polyester reinforced with non-graded nanoclay and polyester reinforced with graded nanoclay are shown in Fig. 1. No particles or impurities are observed in pure polyester as it is virgin polyester (Fig. 2a). It is also seen from Fig. 2a that the fracture initiation occurs in the direction of tensile loading and the mode of fracture is ductile type. The fracture surface of non-graded reinforced polyester composite shows that there exists some decohesion or debonding between agglomerated particles and polyester (Fig. 2b). It is thought that this debonding during tensile loading is responsible for the decrease in tensile strength. Fig. 2c shows the fracture surface of graded nanoclay reinforced polyester composite. Nanoclay particles, being too small and well dispersed are not seen under the Scanning Electron Microscope. But it clearly indicates that the nature of the fracture is brittle as there is no debonding or cup and cone observed, rather fracture occurs at a single leap, viz., it is a brittle fracture. The fractography analysis is supportive with the mechanical properties where tensile and flexural strengths have increased upon addition of graded nanoclay.
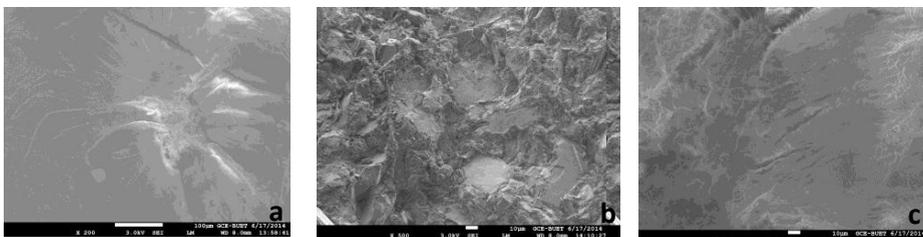

Fig. 1: SEM images of the fracture surface of (a) pure polyester, (b) non-graded nanoclay reinforced polyester composite and (c) graded nanoclay reinforced polyester composite.

4. Conclusions

The present study has been undertaken to investigate the effects of graded nanoclay and non-graded nanoclay on polyester and following conclusions can be drawn.

1. Upon addition of non-graded nanoclay to pure polyester, the tensile strength and modulus decreases from by about 30%.

2. When graded nanoclay was added to pure polyester as reinforcement, the strength and modulus has increased by about 10% compared to that of pure polyester.

3. Flexural strength of pure polyester is higher than that of polyester reinforced with non-graded nanoclay. But when graded nanoclay was used as reinforcing particles, flexural strength has increased by about 15%.

4. According to fractographic analysis, fracture of pure polyester is found to be ductile type while fracture of graded nanoclay reinforced polyester composite is brittle type.

Acknowledgements

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