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Mechanical and thermal properties of unsaturated polyester-silica nanocomposites

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ABSTRACT

Nano silica was synthesized by a sol-gel technique and the size of the particles was confirmed to be of 50-60nm using transmission electron microscopy (TEM). Nanocomposites of unsaturated polyester with silica were prepared by using casting technique. Unsaturated polyesters containing different proportions of nano silica (1, 3, 5, 7 and 9 wt %) was prepared and cured using methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate as initiator and accelerator respectively. The mechanical properties (tensile strength and modulus, flexural strength, hardness and impact strength) and thermal properties were analyzed by using dynamic mechanical analyzer (DMA) and thermo gravimetric analyzer (TGA). Mechanical and thermal properties of nanocomposites were found to be improve with the addition of silica, but decline if the nano silica was the excess of 5 wt%.

KEYWORDS

Nano silica;
Unsaturated polyester resin;
Nano composites.

INTRODUCTION

Nanocomposites are attracting increasing research and market interest because of their potential of providing novel performance. The tremendous interfacial area in polymer nanocomposite helps to influence the composite properties to a greater extent even at rather low filler loading[1]. The mechanical and thermal properties of polymer and composites structure can be improved through the use of various kinds of fillers. Micron size fillers usually cause decrease in strength, impact resistance and processability[2,3]. Nanocomposites show superior physical and mechanical behavior over conventional micro composites[4]. The inorganic nano filler drastically improve the physical, mechanical and microscopic properties of polymers, even though their quantity is less.

Nano sized composite materials are containing two (or) more materials, in which the materials are nano sized (1-100 nm).Thanks to the special structure of nano sized materials, it is possible to change the original physical and chemical properties for a higher degree of strength and toughness[5,6]. Nano sized composite materials are prepared using methods such as hot press method, sol-gel process, molecular composite generation method and ultra fine particle dispersion method.

Unsaturated polyester is available as liquid resin. It is relatively cheap and widely used for structural applications. Exploring the possibility of improving the properties of isophthalic polyester by nano clay incorporation

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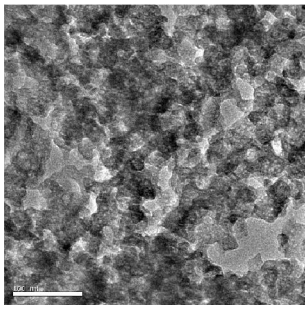

Figure 1 : TEM image of nano silica particles

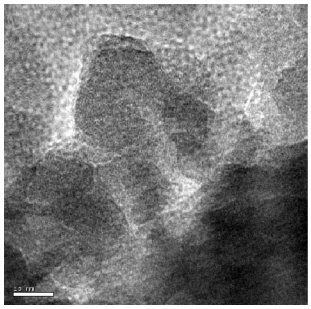

Figure 2 : TEM image of unsaturated polyester / nano silica (5 wt%)

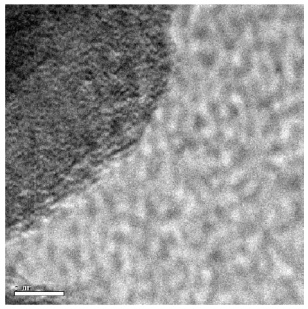

Figure 3 : TEM image of unsaturated polyester / nano silica (7 wt%)

will be useful for both commercial and industrial aspects.

In this study, the nano silica particles were synthesized by an sol –gel technique. The size of the silica particle and formation of nanocomposites have been analyzed by transmission electron microscopy (TEM). The nanocomposites were prepared with nano silica particle as the filler in an unsaturated polyester resin matrix and characterized for mechanical and thermal properties.

EXPERIMENTAL

Materials

The general purpose unsaturated polyester resin, cobalt naphthenate (accelerator) and methyl ethyl ketone peroxide (catalyst) were procured from GVS Agencies, Madurai (Tamilnadu), India. Tetraethoxy orthosilicate and dichloromethane were obtained from Merck chemicals Ltd., Mumbai, (India).

Synthesis of nano silica

The nano silica was synthesized by a sol-gel technique. Water (3mL) and dichloromethane (4mL) were taken in a three nicked round bottom flask and mildly heated for proper mixing. After proper mixing the tetraethoxy orthosilicate (TEOS) (0.76mL) solution was added and the mixture was stirred at room temperature for 10 hours. The precipitate was filtered and dried in a vacuum oven. This material was used for the preparation of the nanocomposites.

Preparation of nanocomposites

Unsaturated polyester resin composites containing different proportions of nano Silica (1, 3, 5, 7 and 9 wt %) were prepared by the procedure given below. Unsaturated polyester resin (400mL) was taken in a clean glass beaker. Then the required quantity of nano silica was added. The resultant mixture was stirred using a mechanical stirrer for 1 h at 1000 rpm followed by ultrasonication for 6 h. Exactly 1mL of 6 % cobalt napthenate solution was added as an accelerator to the above mix and blended thoroughly. To this the catalyst, methyl ethyl ketone peroxide, 4mL was added and stirred. From this, sheets of size $350 \times 350 \times 3mm^3$ were cast using a glass mold. The material was allowed to cure for 24 h at room temperature and post cured at 70°C for 3 h.

CHARACTERIZATION

Transmission electron microscopy

Particle size of silica and silica in the cured unsaturated polyester-silica composites were observed using JEOL 1200 EX transmission electron microscopy (TEM).

Mechanical properties

Tensile test specimens were prepared according to ASTM D 638 and the tests were performed at room temperature using Instron 4301 Universal Testing Machine (UTM) with crosshead speed of 5 mm min^{-1}. Flexural test specimens were prepared according to ASTM D 790. Test was performed at room temperature using Instron 4301 Universal Testing Machine, a three point loading system, support span length was adjusted to 60 mm and the cross head speed was 2 mm min^{-1}. Izod impact properties were evaluated using Frank Impact Testing Machine as per ASTM D 256. The hardness of the nanocomposites were tested as per ASTM D 2240 and the hardness was reported in shore D scale.

Thermal properties

Thermogravimetric analysis (TGA) was carried out

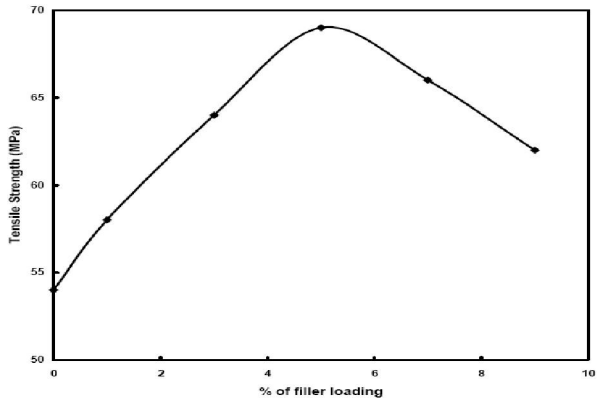

Figure 4 : Tensile strength of unsaturated polyester / Silica nanocomposites

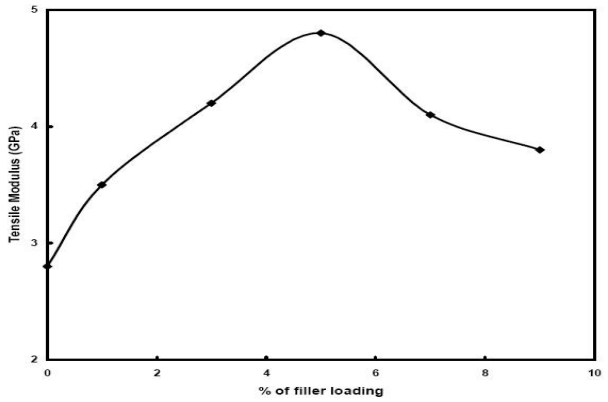

Figure 5 : Tensile Modulus of unsaturated polyester / Silica nanocomposites

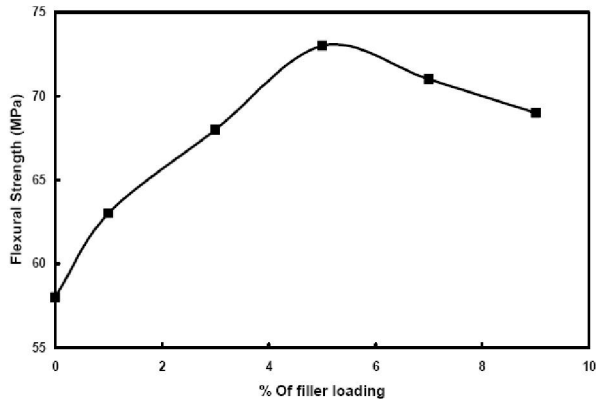

Figure 6 : Flexural strength of unsaturated polyester / Silica nanocomposites

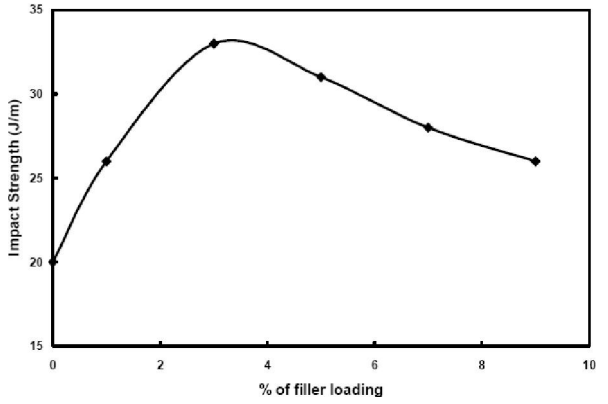

Figure 7 : Impact strength of unsaturated polyester / Silica nanocomposites

using Netzsch STA 409PC thermogravimetric analyzer. Samples were ground to fine powder and placed in alumina sample pan. All samples were heated in nitrogen atmosphere at a heating rate of 10°C min^{-1} from ambient to 600°C. Dynamic mechanical analysis was performed using Netzsch DMA 242C in three point bending mode at a frequency of 10 Hz and amplitude of 120 μm over a temperature range of 20-180°C at a heating rate of 2°C min^{-1}.

RESULTS AND DISCUSSION

Transmission electron microscopy

The TEM image of synthesized silica is presented in figure 1. The sizes of the particles are found to be 59nm and the particles are not showing any agglomeration. In figures 2 and 3, the TEM images of cured unsaturated polyester resin matrix containing 5 and 7 wt% of nano silica are presented respectively. From figure 3, it is obvious that presence of 7 wt% of nano silica in unsaturated polyester resin matrix leads to aggregates.

Mechanical properties

The tensile properties of unfilled cured unsaturated polyester, nano silica based composites are investigated. It is evident that the tensile strength of unfilled cured unsaturated polyester is found to be 58 MPa, which is increased to 69 MPa with the addition of nano silica to the tune of 5 wt%. However, in composites containing high silica content (> 5 wt%), the value of tensile strength decreased (Figure 4).

The tensile modulus of the unfilled polyester is found to be 2.8 GPa. Addition of nano silica shows significant improvement in modulus. A maximum value of 4.8 GPa is observed at a nano silica content of 5 wt% and there after it is decreased (Figure 5). The increment in tensile properties is due to uniform dispersion of nano silica into polymer matrix. The intercalation of the nano particle with polymer matrix increases the degree of cross linking[7]. Higher loading of silica in the resin matrix results more difficult for dispersion, and easier for nano sized particle agglomeration. Since the agglomerated

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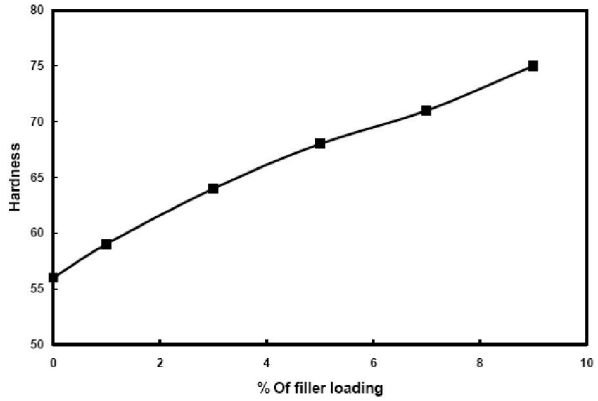

Figure 8 : Hardness of unsaturated polyester / silica nanocomposites

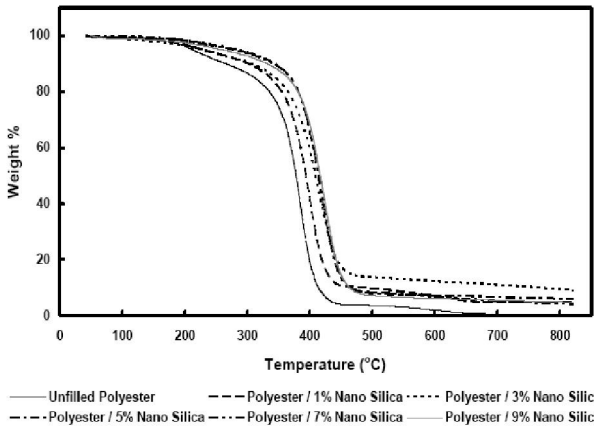

Figure 9 : TGA curve of nanocomposites

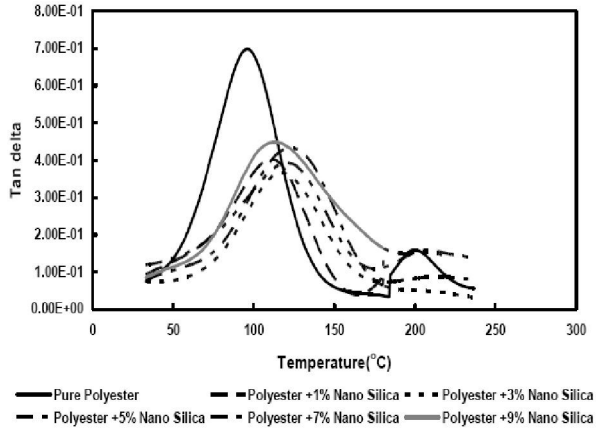

Figure 10 : Loss factor of nanocomposites

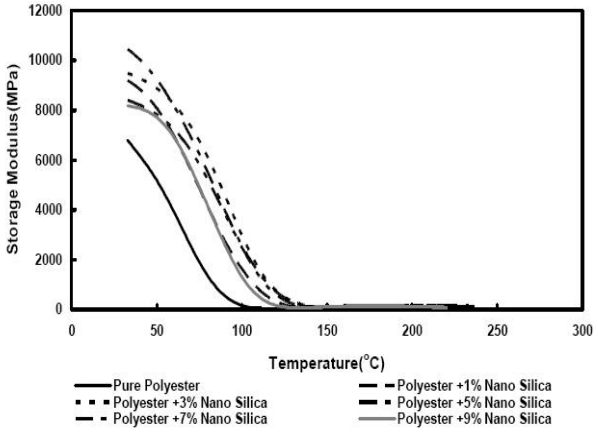

Figure 11 : Storage modulus of nanocomposites

particles makes it possible to generate defects on the material surface, stress concentration will likely occur within the resin, or agglomerated particles will generate slippage within the materials due to external force, resulting in a decreased tensile properties[8].

The flexural strength of nano composites is shown in figure 6. The flexural strength of the nano silica loaded cured unsaturated polyester resin was found to increase with increase in the content of nano silica (< 7 wt %). The better interfacial bonding may occur between silica particles and unsaturated polyester resin, such that the improved surface property of particles and unsaturated polyester resin can help absorb some energy for an increased flexural properties of composites. In the case of excessive silica content (> 5 wt %), it is possible to result in a higher occurrence of agglomeration under the gravitational interaction between silica particles and unsaturated polyester resin substrate. When the materials are bent, silica particles cannot lead to transfer for an enhancement of unsaturated polyester resin, but hinder the extrusion of unsaturated polyester resin's molecular chains. This leads to stress concentration within the materials, so that the bend fracture strength of materials has a declining trend[9].

The impact strength of the unfilled cured polyester sample is found to be 20 Jm^{-1}. Addition of nano silica exhibits significant improvement in impact strength. The maximum improvement in impact strength was observed for nanocomposites prepared using 3 wt% of nano silica (Figure 7). There are two influential factors associated with the impact strength of materials: (1) dispersibility of unsaturated polyester resin against impact energy and (2) absorption degree of inorganic rigid nanosized particles against impact strength[10]. In the case of agglomeration within silica particles, stress concentration is likely to occur. When the impact energy is applied within the materials, the materials can neither uniformly disperse the applied force, nor enable silica particles to fully adsorb the stress within the materials, thus leading to a possible damage[11].

The Hardness of the unfilled polyester sample is found to be 56. Addition of nano silica exhibits signifi-

cant improvement in Hardness. Hardness increases with increase in filler amount (Figure 8)

Thermo gravimetric analysis

The TG curve of nano silica filled unsaturated polyester is shown in figure 9. The degradation temperature of nano silica filled unsaturated polyester nanocomposites increases with the increase in nano silica content of 5 wt%. The onset of thermal degradation temperature at 10 % weight loss increases with nano Silica content (<7 wt%) and it is 304, 314, 347, 346 and 337°C for nano Silica content of 1, 3, 5, 7 and 9 wt% respectively. The maximum decomposition temperature of the matrix polyester resin increased from 267°C to 347°C in the nanocomposites prepared using 5wt% of nano silica. The enhancement in thermal properties is primarily due to restriction of the nano particle on the long range chain mobility of the matrix phase with in the nanocompsites[12].

Dynamic mechanical analyzer

The temperature at which tan δ curve shows a peak maximum is taken as the T_g of the composite. The figure 10 shows that loss factor (tan δ) Vs temperature for unsaturated polyester / silica nanocomposites.The composite up to 5 wt% showed a shift in T_g to the right side, it confirms that well dispersion of nano particle restrict the motion of nanoparticle segmental chain, while the reverse is seen in the case of 7 and 9 wt% nanocomposites.The maximum increase in T_g of 124°C is observed for 5% nano silica., on further addition the T_g value decreased to 123°C and 114°C for 7% and 9 wt% of nano silica respectively. On further increase in silica content (>5wt %), T_g decrease due to poor interfacial bonding and cross linking[13].

Figure 11 shows the effect of nano silica on storage modulus of unsaturated polyester. Pure unsaturated polyester show modulus of 6787 Mpa. It increases continuously up to 5 wt% of nano silica in unsaturated polyester matrix. Unsaturated polymer with 5 wt% of silica shows maximum value storage modulus of 10385 Mpa. On further addition of nano silica, the storage modulus continuously decreases. For unsaturated polyester with 9wt% silica, storage modulus is 8168 Mpa. The composite were prepared with nano filler and matrix filler interaction is responsible for increase in storage modulus.

CONCLUSION

Nano silica-unsaturated polyester composites have been prepared using casting method. Transmission Electron Microscopy analyses confirmed the size of the nano particle and formation of nanocomposites. A significant improvement in tensile strength, tensile modulus, flexural strength, impact strength and hardness were noted. The thermal stability of unsaturated polyester matrix increased with incorporation of nano Silica. The glass transition temperature of nanocomposites showed higher value as compared to pristine polyester. Thus, nanocomposites possess better properties than neat polyester sheets.

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