Effect of Titanate Coupling Agent on the Mechanical, Thermal, Dielectric, Rheological, and Morphological Properties of Filled Nylon 6

Suryasarathi Bose, P. A. Mahanwar

University Institute of Chemical Technology, Matunga, Mumbai 400019, India

ABSTRACT: Fillers are used along with various commodity as well as engineering polymers to improve the properties of polymers. The performance of filled polymers is generally decided on the basis of the interface attraction of filler and polymers. Fillers of widely varying particle size and surface characteristics are responsive to the interfacial interactions with polymers. The present study deals with the effect of a coupling agent, tetra isopropyl titanate (TPT), on the properties of flyash filled nylon 6. It is observed that tensile strength, impact strength, and heat distortion temperature improved with the addition of TPT as compared to without the coupling agent filled nylon 6. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 266–272, 2006

Key words: composites; filler; polyamides

INTRODUCTION

Particle filled polymer composites have become attractive because of their wide applications. Incorporating inorganic mineral fillers into plastic resin improves various physical properties of the materials, such as mechanical strength, modulus, and heat distortion temperature. In general, the mechanical properties of particulate filled polymer composites depend strongly on size, shape, and distribution of filler particles in the matrix polymer and good adhesion at the interface surface. Nylons are one of the most widely used engineering thermoplastics, for example, in automobile, electrical, electronic, packaging, textiles, and consumer applications, because of their excellent mechanical properties.[1–6] However, limitations in mechanical properties, low heat distortion temperature, high water absorption, and dimension instability of pure nylons has prevented their applications to structural components. Hence, numerous efforts have been undertaken to use nylons as matrix resins for composites by adding inorganic fillers, namely, aluminatrihydrate,[6] clays,[6] silica,[6] mica,[7–9] talc,[2,6,10,11] flyash,[12] wollastonite,[2,6,10,13] kaolin,[2,6,13] and so forth. The majority of these fillers or reinforcements are incompatible with a polymer matrix. The fillers/reinforcing materials are required to be modified on the surface to overcome the problem of incompatibility.

In a highly filled polymer system, a major problem is nonuniformity of properties due to poor dispersion of the filler in the matrix.[14] Therefore, the application of some coupling agents in particulate filled polymers has generally been directed to overcome the dispersion problem and to enhance the properties of the composite by improving adhesion across the interface and thus upgrading the performance of the composite. Surface modification is an important step for manufacture of good quality fillers/reinforcing materials.[15] Basically, two types of surface modifications are normally used. The first modification provides a physical bond between the filler and the polymer. Normally, waxes and fatty acids are employed in this type of physical bond. These fillers/reinforcements need chemical bonding at the molecular level. Such a chemical surface modification is achieved by the use of "coupling agents"—special chemicals containing silanes, titanates, or zirconates. All these chemicals are essentially organometallic in nature and contain alkoxy groups that react with fillers. There is also an organo functional group that allows bonding to the polymer matrix by chemical reaction. The organo functional group contains different functional groups to provide bonding to different polymer matrices. The reaction mechanism[16] of the tetra functional organometallic compounds based on silicon and titanium is believed to occur in three steps. First, the alkoxy group in the coupling agent undergoes a hydrolysis process. Water for the hydrolysis comes from the surface humidity of the filler (in the case of silane treatment), and from the surface or in the resin in the case of the titanate treatment. Next, the groups react with the

*Correspondence to:* P. A. Mahanwar (pmahanwar@yahoo.com).

hydroxyl of the filler surface by hydrogen bond formation. Then, Si-O or Ti-O crosslinks are formed between the filler surface and the adjacent functional groups in a condensation reaction with the elimination of water. Converting a typical hydrophilic mineral or inorganic surface into an organofunctional one is somewhat expensive. Because of the expense, surface-modified materials are used for performance, not economics. Although economics can many times be determined by performance rather than price.

Use of flyash as a filler is not new. Flyash is a fine ash byproduct commonly produced by the combustion of coal during the generation of electrical power. The results of many experimental studies conducted with flyash have shown that the addition of flyash filler does increase the stiffness of a plastic formulation, but like most fillers, reduces impact resistance.[17–26] Chand[18] introduced flyash into thermosetting polyesters and found that the impact strength and the ultimate tensile strength decreased with the addition of the flyash. Srivastava and Shembekar[19] also saw a decrease in the tensile strength when flyash was added to epoxy resin, but this was accompanied by an increase in modulus and an increase in fracture strength as the flyash content was increased to 8 vol % flyash, followed by a decrease in the fracture toughness at higher additions. Hundiwale et al.[27] reported improvement in mechanical properties on incorporating flyash. Nabil et al.[28] studied the effect of the titanate coupling agent on the mechanical properties of flyash filled polybutadiene rubber and found improvements in tensile strength and Young's modulus.

This article reports the effect of flyash addition and the effect of a coupling agent on the mechanical, thermal, dielectrical, morphological, and rheological behavior of flyash filled nylon-6 composites.

EXPERIMENTAL

Matrix material nylon 6 (1.16g/cc) was obtained from M/s Nirlon India ltd. (Mumbai, India). Filler additives, namely, antioxidants (Irganox 1076 and Irgafos 168) and the dispersing agent (FinnawaxSS) were obtained from M/s Ciba Speciality Chemicals ltd. (Mumbai, India) and M/s Fine Organics (Mumbai, India), respectively; flyash of different particle sizes was obtained from M/s B.S.Mica Pvt. ltd. (Mumbai, India) and a local supplier, respectively. The titanate cou-
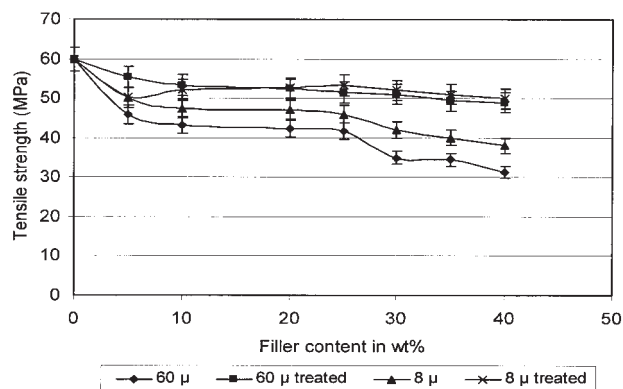
Figure 1 Variation of tensile strength of nylon 6 with wt % of filler (both treated and untreated) content.

pling agent, tetra isopropyl titanate (TPT), was obtained from M/s Dupont (Wilmington, DE). Antioxidants (1 wt % each of Irganox and Irgafos), the dispersing agent (1.5 wt %), the titanate coupling agent (1 wt % of filler), and flyash were added to nylon 6 in 5, 10, 20, 25, 30, 35, and 40% wt/wt ratios. The physical properties of the filler are listed in Table I. The composite granules were prepared by using a twin-screw extruder (M/s APV Baker, UK, and Model: MP19PC). In this process, the temperature profiles in the barrel were 200°C, 220°C, 230°C, 240°C, and 250°C from hopper to die. The screw length to diameter ratio (L/D) was 25, and a screw rotation rate of 60 rpm was used. Tensile, flexural, and Izod impact samples (according to ASTM D-638 M91, ASTM D 790, and ASTM D 256–92, respectively) were prepared using an injection molding machine (M/s Boolani Engineering, Mumbai) with a barrel temperature of 220°C, 250°C, and 260°C. Uniaxial tensile tests were carried out using Universal tensile testing machine LR 50k from Lloyd Instruments Ltd. (UK) at a cross head speed of 50mm per minute. The impact test was carried out at room temperature using an Avery Denison impact tester. The heat distortion temperature (ASTM D 648) was measured using a Davenport Vicat Softening Point Instruments Ltd. (UK). Dielectric strength (ASTM D 149) was measured (using a 2mm thick composite sheet) by Zaran electrical instruments (input: 240V, 50Hz, 1PH; output: 0–50kV; capacity: 100mA; rating: 15 min). The values reported are the average values from at least five samples.

RESULTS AND DISCUSSION

Mechanical properties

Figure 1 shows the variation of tensile strength with filler concentration of flyash. It is observed that the tensile strength decreases with increase in the filler concentration of flyash. The rate of decrease of

TABLE I
Physical Properties of the Filler

| Filler	Average particle size (μ)	Specific surface area (m^2/g)	Density (g/cc)
Flyash	8	1.69	2.3
	60	0.34	1.99
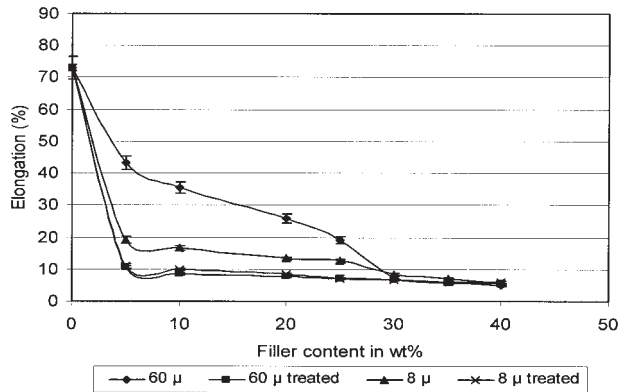
Figure 2 Variation of the elongation at break of nylon 6 with wt % of filler (both treated and untreated) content.

Figure 3 Variation of flexural modulus of nylon 6 with wt % of filler (both treated and untreated) content.

strength was higher when a larger particle size was used, whereas the rate of decrease of strength was lower when the filler was treated with titanates. In the case of treated filler, it is observed that the rate of decrease of strength is high at a lower filler percentage in the case of a smaller particle size as compared to a larger particle size. The extent of reduction in tensile strength is low as compared to untreated filler. It clearly indicates the role of the coupling agent in increasing the interface interaction of the filler and matrix.

As seen from Figure 2, the elongation at break decreases drastically on addition of filler. It is also seen that the rate of change of percentage elongation with varying percentages of filler is higher in the case of a smaller particle size as compared to a larger particle size in the case of untreated flyash filler, whereas the difference between the rate of change of elongation in the treated filler is negligible in the case of both particle sizes. The elongation has decreased on treatment with a higher rate as compared to untreated filler, which clearly supports the assumption of improved interface filler matrix interaction. The presence of filler indicates an interference[29–31] by the filler with the mobility or deformability of the matrix. This interference is created through physical interaction and immobilization of the polymer matrix by imposing mechanical restraints.

Figures 3 and 4 present the variation in flexural modulus and flexural strength with varying concentrations of flyash treated and untreated, respectively. Observation shows that the flexural modulus has increased almost twofold with addition of filler up to 25% loading in the case of a smaller particle size. The rate of increase of flexural modulus with increasing concentration of filler is higher when a smaller particle size of flyash is used. The maxima for flexural modulus is extended and achieved at higher loading when a larger particle size is used as compared to a smaller particle size, but the rate and extent of increase of
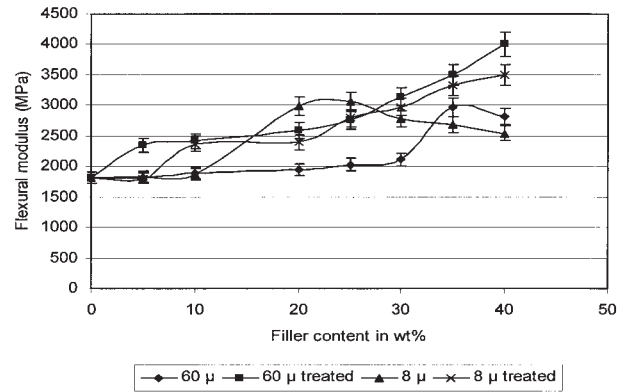
flexural modulus is higher when a smaller particle size of filler is used. It is observed that flexural modulus increases with increase in concentration of the treated filler in the cases of both particle sizes, but the rate of increase of flexural modulus is higher in the case of a larger particle size treated filler than a smaller particle size. This change in phenomenon of variation in flexural modulus of treated and untreated filler composites may be due to increase in the interfacial interaction of the filler and matrix due to incorporation of the coupling agent. It is also seen that flexural strength has increased with increase in concentration of the filler, but the rate of increase in flexural strength is higher in the case of untreated smaller particle size flyash than in untreated larger particle size flyash. The change in flexural strength on addition of the treated filler is higher when a larger particle size filler is being used as compared to a smaller particle size filler. It is clearly observed that smaller particle size will agglomerate faster than larger particle size filler, which disturbs the dispersion of filler particles in the matrix, which increases the flexural strength but decreases the flexural modulus. The agglomeration occurs at the lower con-
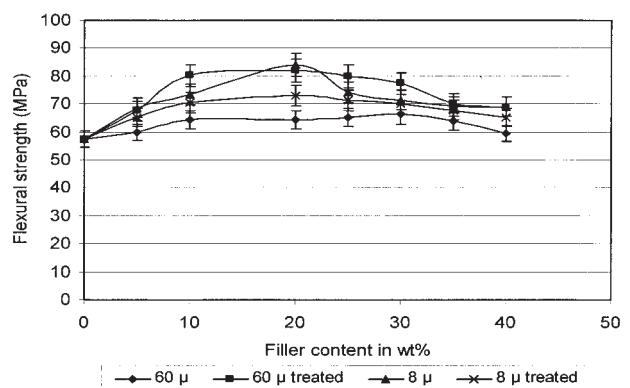
Figure 4 Variation of flexural strength of nylon 6 with wt % of filler (both treated and untreated) content.
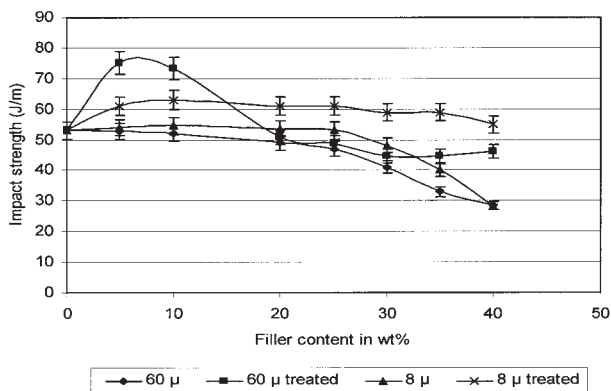
Figure 5 Variation of impact strength of nylon 6 with wt % of filler (both treated and untreated) content.

centration of filler loading in the case of a smaller particle size, which is clear from the maximum in flexural strength of 8 micron filler at 20% loading. The agglomeration is prevented by the addition of the coupling agent, which is clearly observed from Figure 3, where there is no maximum but continuous increase in the modulus.

Figure 5 illustrates the variation of impact strength with filler by weight percentage. It is clear from this Figure that the strength increment at a low weight percentage of filler may be attributed to the formation of small sized crystallites, that is, spherulites, as well as the capacity to absorb more energy by an increased portion of the matrix.[32,33] A further increase in weight percentage reduces the deformability of the matrix, reducing in turn the ductility in the skin area, so that the composite tends to form a weak structure. Without any coupling agent to modify the filler surface characteristic, poor wetting of the particle by the matrix is expected.[34] This gives rise to poor interfacial adhesion between the filler and the polymer matrix, resulting in weak interfacial regions. During the impact test, cracks travel both through the polymer as well as along the weaker interfacial regions. The later cannot resist crack propagation as effectively as the polymer region, hence reducing the impact strength. Increasing the filler content merely increases the interfacial regions that exaggerate the weakening of the composites to crack propagation. For the same weight fraction of the filler material, the smaller the size, the larger will be their surface area; hence, the higher will be the increase in crack length, leading to increase in energy absorption before fracture, which is clearly seen from the Figure.

Thermal properties

Figure 6 illustrates the variation of the heat distortion temperature with varying filler percentages. It is observed that the heat distortion temperature increases with increasing concentration of the filler. The rate of increase of the heat distortion temperature with increase in filler concentration is higher when a larger particle size flyash is used. In the case of a larger particle size, the increase in the heat distortion temperature is higher on addition of untreated flyash at lower concentrations. It is also seen that on addition of the treated larger particle size filler, the heat distortion temperature has attained maxima and then reduced consistently, whereas no maximum has been observed in the case of untreated filler. This may be due to increase in the interfacial interaction of the filler matrix due to addition of the coupling agent and restriction of mobility of the matrix chains. At higher concentrations of the treated fillers, it may be allowing the matrix chains to adjust themselves as per the agglomerated size of the fillers, due to which the heat distortion temperature at higher treated filler loading is lower in the case of both particle sizes.

Dielectric properties

It is clear from Figure 7 that dielectric strength increases with increase in the filler concentration and attains maxima. The maximum value of dielectric strength is attained at a lower filler percentage in the case of a larger particle size; whereas when it is treated, the maximum is extended. In the case of a smaller particle size the dielectric strength is comparable; whereas when it is treated, again the maximum is shifted towards a higher filler percentage. At a higher filler loading, the dielectric strength values remained constant with increase in the filler, but they are higher for treated larger particles as compared to treated smaller particle sizes. This trend in variation of the dielectric strength in flyash was attributed to the total surface available.

Morphology

The effect of the coupling agent on the interfacial interaction between the filler and matrix is shown in
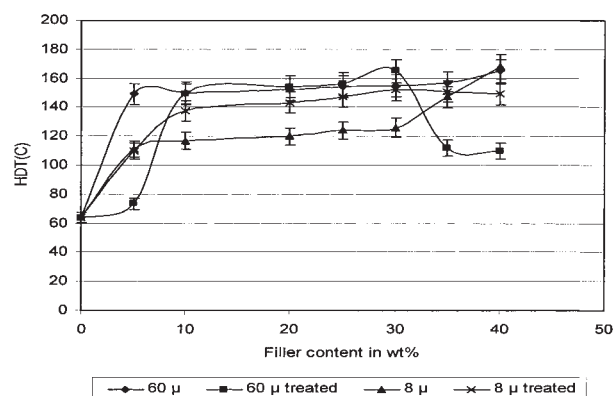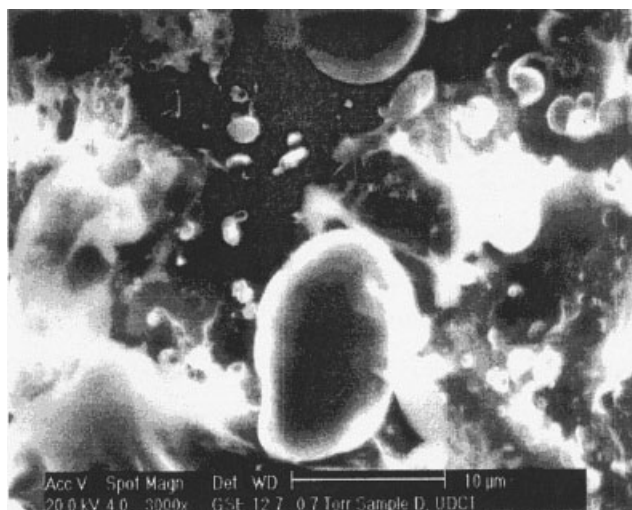

Figure 6 Variation of heat distortion temperature of nylon 6 with wt % of filler (both treated and untreated) content.
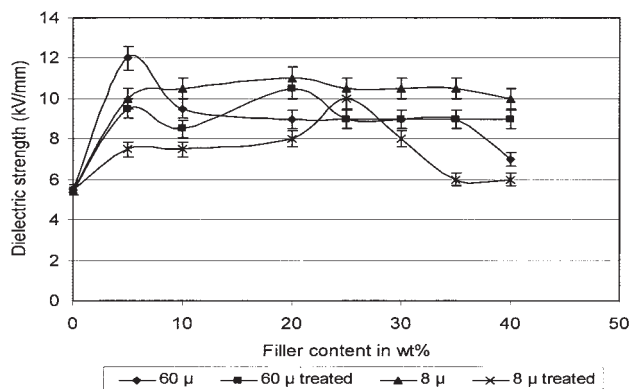
Figure 7 Variation of dielectric strength of nylon 6 with wt % of filler (both treated and untreated) content.

Figure 9 SEM micrograph of a fractured surface of treated 60μ flyash/nylon 6 composite containing 30 wt % flyash.

the SEM micrograph (Figs. 8–11). The micrographs of both particle sizes of flyash filled nylon 6 depict that uncoupled filled nylon 6 exhibits brittle failure at the filler/matrix interface. Brittle failure mode would be contributed to by the formation of voids due to incompatibility of the filler/nylon 6 and the poor dispersive effect of the filler in the matrix. With the incorporation of the titanate coupling agent, in the case of a larger particle size of flyash, it is observed that the fillers were embedded in the matrix, which can be seen from Figure 9. It is, therefore, apparent that the titanate coupling agent has an effect to modify the surface characteristics of the filler. Moreover, in the presence of the coupling agent, the dispersion of filler particles in the polymer phase is enhanced by the replacement of water of hydration at the inorganic surface of the filler/polymer, with organofunctional titanate causing inorganic/polymer interface compatible, thereby eliminating air voids in the system. Consequently, it

results in deagglomeration and more uniform dispersion in melt blending, as seen from the SEM micrographs. In the case of a smaller particle size treated flyash, the composites exhibited sufficient nylon 6 residue on the filler surfaces, which confirmed the strong interfacial bonding between the filler and the matrix, which is clearly seen from Figure 11.

Rheological properties

Figures 12 and 13 illustrate the variation of shear viscosity at 250°C (in Pascal second) with filler concentration for a larger particle size of flyash treated and untreated, respectively. Increase in the viscosity may be attributed to the properties of the filler, such as
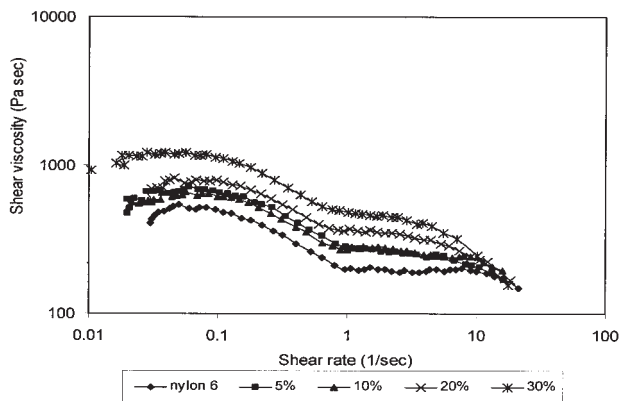

Figure 8 SEM micrograph of a fractured surface of untreated 60μ flyash/nylon 6 composite containing 30 wt % flyash.
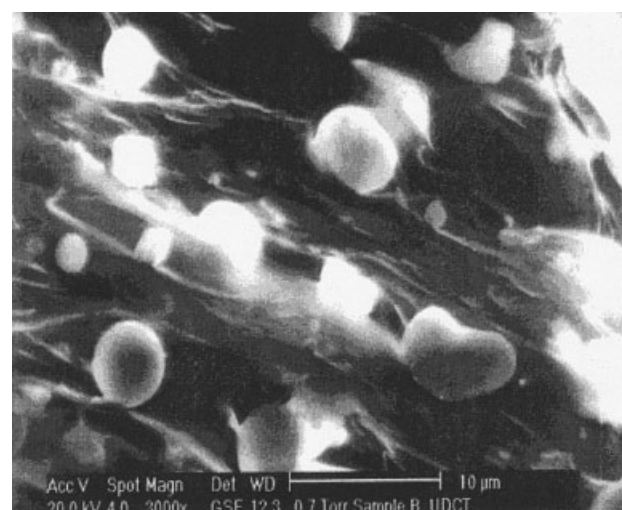
Figure 10 SEM micrograph of a fractured surface of untreated 8μ flyash/nylon 6 composite containing 30 wt % flyash.
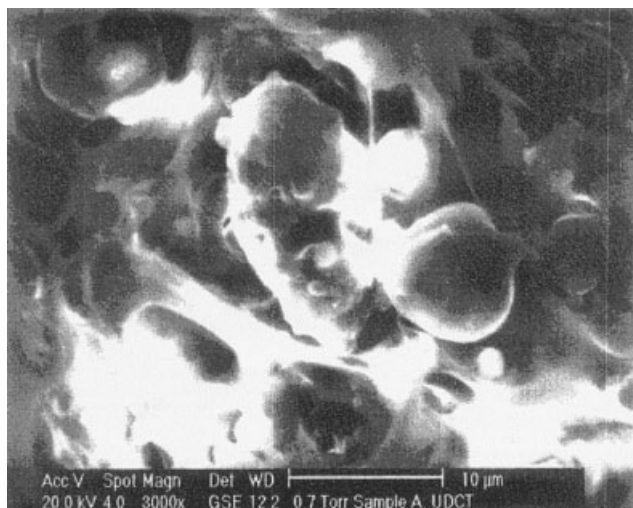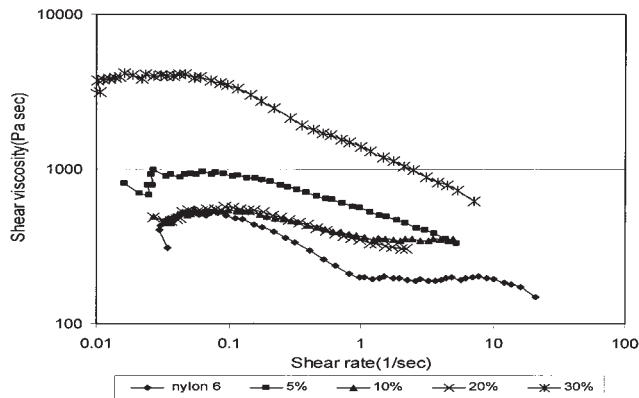
Figure 11 SEM micrograph of a fractured surface of treated 8μ flyash/nylon 6 composite containing 30 wt % flyash.

maximum packing fraction. The rate of increase in the viscosity depends upon the ratio (ϕ / ϕ_{μ}), where ϕ = the vol fraction of the filler and ϕ_{μ} = the max. packing fraction. Increase in the viscosity is also due to the ability of fine particles of the fillers to form a large network, causing tighter packing. The porous and irregular shaped filler particles introduce discontinuity in the base matrix. The extent of discontinuity increases with increase in the filler content in the composite. Thus, it appears that the melt viscosity of the base matrix increases due to increased obstruction produced to the flow by these filler particles. Addition of filler did not alter the pseudoplastic behavior of the polymer matrix. With increase in filler content, the viscosity of the component increases and the rate of increase of viscosity is higher for a treated larger particle size filler. Lower viscosity of the filled compounds may indicate a slip between filler particles and the polymer matrix. In polymer processing, increased
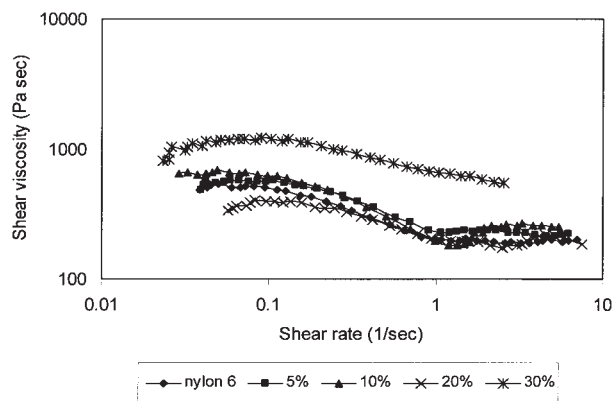

Figure 13 Variation of shear viscosity in nylon 6 with filler content (60 micron flyash treated with titanate coupling agent) in wt %.

viscosity of filled polymers at high shear rates is of interest. Normally, the addition of particulate fillers to a polymeric matrix restricts molecular motion in the matrix, thus imposing resistance to the flow. As a result, it gives higher viscosity as the filler content increases. A decrease in viscosity indicates better molecular motion between polymer chains. Possible reasons for this phenomenon could be molecular chain scission, or it might be a lubricating/plasticating action induced by the coupling agent. In the case of a smaller particle size flyash, as can be seen from Figure 14, the increase in viscosity with increase in the filler content may be due to restricted molecular motion in the matrix due to agglomeration of the particles; but on treating it with the titanate coupling agent, the particles are well dispersed, thereby lowering the viscosity as the chains can move freely as can be, seen from Figure 15.

CONCLUSIONS

- It is apparent that the titanate coupling agent has an effect to modify the surface characteristics of the filler as inferred from the SEM micrographs.

Figure 12 Variation of shear viscosity in nylon 6 with filler content (60 micron flyash) in wt %.

Figure 14 Variation of shear viscosity in nylon 6 with filler content (8 micron flyash) in wt %.
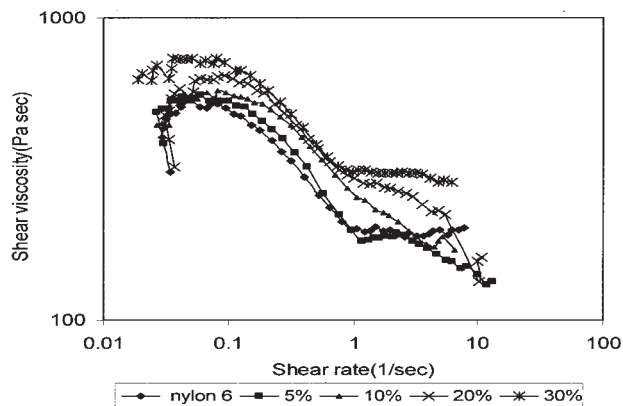
Figure 15 Variation of shear viscosity in nylon 6 with filler content (8 micron flyash treated with titanate coupling agent) in wt %.

- The toughness and elongation at break decreased as particle size and agglomeration concentration increased, which was to some extent reduced by using the coupling agent.
- Inorganic fillers, namely, flyash, added to the polymer improves its rigidity, heat resistance, and dimension stability.
- A significant increase in the heat distortion temperature was found with increase in the filler loading, in the case of both fillers.
- Thus, the mechanical properties of the composite are a function of the particle size, dispersion, particle orientation, and interfacial interaction between the minerals and the polymer matrix.
- The nature of the interlayer between the filler and the polymer matrix, introduced by the titanate treatment, plays a significant role in the effectiveness of improving the mechanical properties of the composite.

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