Mica Reinforced Nylon-6: Effect of Coupling Agents on Mechanical, Thermal, and Dielectric Properties

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ABSTRACT: The effects of applying titanate (TYZOR® TPT) and silane (DYNASYLAN VTMO) coupling agents to wet ground muscovite mica in nylon-6 composites are described. Nylon-6 composites of 5–40 wt % filler loadings were compounded using an APV Baker twin-screw extruder. Mica (25 wt %) brought about an increase in the Young's modulus, flexural strength, and flexural modulus but did not produce significant variations in tensile and impact strength. Hence different coupling agents were employed. It was observed that titanate coupling agent improved the tensile strength and the Young's modulus of the composites much while the impact properties were enhanced by the silane coupling agent. An attempt was made to use ε-caprolactum in improving the interfacial adhesion of the filler and the matrix. It was observed that ε-caprolactum improved the flexural modulus of the composites most. The effect of coupling agents on the dielectric strength, heat distortion temperature, and morphology were also investigated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4074–4081, 2006

Key words: nylon-6; mica; coupling agents; composites

INTRODUCTION

Particulate reinforced thermoplastic composites are designed to improve the properties and to lower the overall cost of engineering plastics. Inorganic fillers ($CaCO_3$, flyash, talc, mica, etc.) are widely used in polymer composites to improve various physical properties of the materials, such as mechanical strength and modulus, rigidity, and heat-resistance. Nylons are one of the most widely used engineering thermoplastics such as in automobile, electrical, electronic, packaging, textiles, and consumer applications because of their excellent mechanical properties.[1–6] However, limitations in mechanical properties, the low heat distortion temperature, high water absorption, and dimension instability of pure nylons have prevented their applications to structural components. Hence numerous efforts have been undertaken to use nylons as matrix resins for composite by adding inorganic fillers such as glass beads,[2,3,7–9] kaolin,[2,3,10,11] aluminatrihydrate,[11] clays,[11] silica,[11] flyash,[12,13] wollastonite,[2,3,11,14] mica,[15–18] talc,[2,3,11,19] calcium carbonate,[11,20] whiskers,[21–23] etc. Flakes or platelets represent a special class of reinforcing fillers for thermoplastics and thermosets.[24] Mica is one such type of filler and is particularly abundant mineral. By virtue of its crystal habit, it may be easily cleaved into thin flakes by ordinary grinding methods and with special care, may be delaminated into very thin flakes. Such flakes when suitably aligned in a plastic matrix, may impart a relatively high degree of reinforcement in terms of strength and stiffness.[24] The commercial delamination of mica may be characterized as wet or dry according to whether the delamination is carried out in a dry state or in the presence of fluid medium such as water. Wet grinding preserves the natural luster and sheen of mica and is normally characterized by clean cut edges, higher aspect ratios, smooth surfaces, and ability to disperse easily.[24] It is often necessary to treat filler by coupling agent such as silane and titanate before usage to improve its dispersing condition in matrix, prevent aggregation, and reinforce the interfacial coherence with resin.[25–28] A coupling agent is just like a molecular bridge between the interface of inorganic filler and organic polymer matrix. The most common type of coupling agents presently used are organofunctional silanes and organotitanates.[29] The coupling agent aforementioned may be simplified to the general formula of R–M–X, where R is the organofunctional group, M is the tetravalent base metal (Ti and Si), and X is a hydrolysable group. The reaction mechanism is described elsewhere.[13] The results of many experimental studies have shown that the addition of mica to a thermoplastic matrix improves the mechanical, dielectric and thermal properties.[30–39] Researchers as Woodhams et al.,[30] Daoji et al.,[31] and Maged et al.[32] have reported that the addition of mica to a polymer system results in significant improvement in tensile strength and modulus. Ruofei et al.[33] and Shepherd et

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al.[34] studied the effect of mica as a filler on polymer systems and found significant improvement in flexural properties. Gupta et al.[35] and Grace[36] reported improvements in dielectric strength on incorporating mica into plastics. Xantos [37] and Pastorini and Nunes[38] saw significant improvements in heat distortion temperature (HDT) and Vicat softening temperature (VST) respectively. Okuno and Woodhams[39] studied the rheological behavior of mica filled thermoplastics and reported that addition of mica increases the melt viscosity. It was also shown that coupling agent improves the mechanical properties of mica filled thermoplastics than their uncoupled counterpart.[40–46] We can mention Susan and Charles[40] who studied the effect of treated mica on polypropylene, Newman and Meyer[41] and Verbeek,[42] who analyzed the effect of treated mica on polyolefins and found that the incorporation of coupling agent led to significant improvement in Young's modulus. Schreiber et al.[43] observed significant changes in rheological behavior on treating mica prior to compounding. Silane and zirconate coupling agent treated mica also showed significant improvements in flexural and dielectric strength, as reported by Collins and Kludt[44] and Pushpa et al.[45] respectively. In this paper, we report our findings on the influence of silane and titanate coupling agents on the mechanical, dielectrical, thermal, and morphological behavior of wet ground muscovite mica filled nylon-6. An attempt has been made to use ε-caprolactum as a coupling agent in improving the filler matrix interaction.

EXPERIMENTAL

Materials

Matrix material nylon-6 with 1.16 g/cm^3 density and relative viscosity of 3.3 (as reported by the supplier) was obtained from Nirlon India Ltd. (Mumbai, India). Filler additives viz. antioxidants (Irganox 1076 and Irgafos 168) and dispersing agent (Finnawax SS) were obtained from Ciba Specialty Chemicals Ltd. (Mumbai, India) and Fine Organics (Mumbai, India), respectively. The coupling agents chosen were TYZOR® TPT (tetra-isopropyl titanate), supplied by Dupont, USA, and DYNASYLAN VTMO (vinyl trimethoxy silane), supplied by Degussa AG, Aerosil and Silanes, Australia. ε-Caprolactum was obtained from a local supplier (Mumbai). The physical properties of the filler are listed in Table I.

TABLE I
Physical Properties of the Filler

Filler	Muscovite mica (wet ground)
Supplier	M/s BS Mica Pvt. ltd., Mumbai, India
Avg. particle size (μm)	75
Particle size distribution (μm)	0.9–180
Specific surface area (m^2/g)	0.191
Density (g/cm^3)	2.5

Compounding

Nylon-6 and mica were predried at 80 °C for 7 h prior to compounding. Fillers were added to nylon-6 in 5, 10, 20, 25, 30, 35, 40% (w/w) ratios. Antioxidants (1 wt % each of Irganox and Irgafos) and dispersing agent (1.5 wt %) were added to the filler prior to the compounding. The composite granules were prepared by using twin-screw extruder (APV Baker, UK; Model, MP19PC). In this process, the temperature profiles in the barrel were 200, 220, 230, 240, 250 °C from hopper to die. The screw length to diameter ratio (L/D) was 25 and screw rotation rate of 60 rpm was used. The extrudates were water cooled at room temperature, pulled, and pelletized. An application technique of the coupling agent was carried out as advised by the manufacturer of the respective coupling agents. The treatment with the silane and titanate coupling agents to which the filler was subjected consisted of the following: the required quantity of coupling agent (to reach 1, 1.5, 2, 2.5, 3, 3.5, 4 wt % compositions with respect to filler) was diluted in a solution consisting of water and methanol in 1:9 ratio, which was sprayed onto the mica as the latter was rotated in a table top tumbler mixer. For the ε-caprolactum the treatment level was as follows: required quantity of ε-caprolactum was dissolved in ethanol to make up a 40% solution. Mica was charged into a table top tumbler mixer and the solution was added slowly over a period of 15 min to ensure uniform distribution of the ε-caprolactum. The following procedure was followed for all the coupling agents: the filler was continuously mixed for 30 min. The treated filler was then dried at 80 °C for at least 2 h. Filler additives and mica were surface treated with silane, titanate, and ε-caprolactum respectively. In the second extrusion step, under the same conditions, 25 wt % mica, treated with different coupling agents mentioned, was mixed with nylon-6 along with the other filler additives.

Injection molding

Test specimens were injection molded in a multicavity mold of tensile, impact, and rectangular bars, using a 1 ton microprocessor-based injection molding machine from Boolani Engineering, Mumbai.

Tensile testing

The dumbbell-shaped tensile strength specimens were injection molded and uniaxial tensile tests were carried out using Universal Tensile Testing Machine

TABLE II
Mechanical Properties of the 75-μm Mica/Nylon-6 Composites

Composition of mica (wt %)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
0	59.8	1369	54.8	57.5	1811	53
5	44.3	1099	7	69.3	2212	95.4
10	52.3	1514	15	71.6	2414	91.4
20	54.7	2084	7	85.8	2555	87.4
25	56.7	2029	9	93.6	3991	75.2
30	57.5	2381	3	97	4272	67
35	59.7	4116	3	98.5	4800	46.7
40	69.9	8406	3	99.2	5335	26.4

The values reported are the average values from at least five test specimens.

(UTM) LR 50k from Lloyd Instruments Ltd. (UK) at a cross head speed of 50 mm/min. Tests were conducted in accordance with ASTM D 638M91.Young's modulus and elongation at break were also recorded.

Flexural testing

Flexural properties were measured using a three-point bending test method and were carried out on UTM LR 50k from Lloyd Instruments Ltd., with rectangular bars of dimensions 125 $\times$ 13 $\times$ 6.5 mm^3. Tests were conducted at a jaw speed of 2.8 mm/min at room temperature.

Notched Izod impact testing

The injection molded samples were notched at room temperature, using a motorized notch-cutting machine (Polytest Model 1, Ray Ran, UK). A total of five specimens were tested for each sample at room temperature to obtain the average impact value. Notched Izod impact tests were performed using a 2.7 J pendulum and a striking velocity of 3.46 m/s on an Avery Denison Impact tester (model 6709), based on ASTM D 256–92. The dimensions of the sample were 63 $\times$ 12 $\times$ 12 mm^3 with a 2-mm notch.

Heat distortion temperature (HDT)

HDT (according to ASTM D 648) was measured using Davenport Vicat Softening Point Instruments Ltd. (UK). The sample position was edgewise, test span was 100 mm and surface stress was 1820 kPa.

Dielectric strength (DS)

The DS, according to ASTM D 149, was measured using Zaran Instruments (India), with a 2-mm-thick composite disc. The voltage was increased slowly and the voltage at which the current penetrates through the sample was noted. The configurations of the instruments were as follows: input, 240 V, 50 Hz, 1 PH; output, 0–50 kV; capacity, 100 mA; rating, 15 min.

Scanning electron microscope (SEM).

SEM studies of fractured tensile samples were carried out on a FEI Quanta 200 HV SEM. The accelerated voltage used was 15 kV. Samples were sputter coated with gold to increase surface conductivity. The digitized images were recorded.

RESULTS AND DISCUSSION

Effect of mica on the properties of nylon-6

Mechanical properties

Table II summarizes the mechanical properties of 75 μm mica/nylon-6 composites. It is observed that as the concentration of filler increases tensile strength values decreases initially and then increases at higher filler concentration. It is also observed that percentage elongation decreases drastically on addition of filler, which indicates interference by the filler to the mobility or deformability of the matrix. This interference must be created through the physical interaction, thereby immobility of the polymer matrix by imposing mechanical restraints. At higher filler loading the interstitial volume has been occupied by smaller particle size filler and there may be insufficient matrix available for contributing the percentage elongation. It is also found that the Young's modulus values increases with increase in filler concentration. At 40 wt % filler loading a sixfold increase in Young's modulus is observed. In this context, it is worthy to mention that agglomerates or flocculated particles at higher filler loading provides higher modulus, since that portion of the matrix which is isolated in the agglomerates is less free to react to stress and strain than the continuous phase at values below the maximum packing fraction.[24] Flexural strength and modulus values increase with increase in concentration of filler load-

TABLE III
Dielectric and Thermal Properties of the 75-μm Mica/ Nylon-6 Composites

Composition of mica (wt %)	Dielectric strength (kV/mm)	HDT (°C)
0	5.5	63.9
5	10.5	154
10	13	158
20	11.5	169
25	10.5	174
30	10	177
35	9	190
40	9	205

The values reported are the average values from at least five test specimens.

ing. Since the filler has platy structure the total surface area increases with increase in concentration of filler which reduces the rate of deformation. Thus it is confirmed that the total area available for deformation stress plays an important role. The flexural modulus increases almost threefold with addition of 40 wt % filler loading. The impact strength values increases significantly at lower filler concentrations. The strength increment at low weight percentage of filler may be attributed as capacity to absorb more energy by increased portion of matrix. 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.

Dielectric strength and heat distortion temperature

Table III reports the dielectric strength and the heat distortion temperature values of 75 μm mica/nylon-6 composites. It is observed that on addition of mica the values of dielectric strength increase drastically but the dielectric strength remain unchanged beyond 20 wt % filler loading. This trend in variation of dielectric strength in mica is attributed to the total surface area available from the filler as well as its continuity. The initial increase in dielectric strength must be due to uniform dispersion of fillers at lower concentration, where as at higher concentration the dispersion of platy structure is impeded and hence the total dielectric strength gets reduced. The heat distortion temperature values increases with increase in concentration of filler, which is expected because inorganic fillers like mica have high thermal stability.

Effect of coupling agents on mica (25 wt %) reinforced nylon-6

From on the aforementioned analysis, it was found that 25 wt% mica brought a significant improvement in Young's modulus, flexural strength, and flexural modulus but at the same time showed a drop in the impact strength compared to a significant improvement at the lower filler loading. Hence different coupling agents mentioned previously were employed.

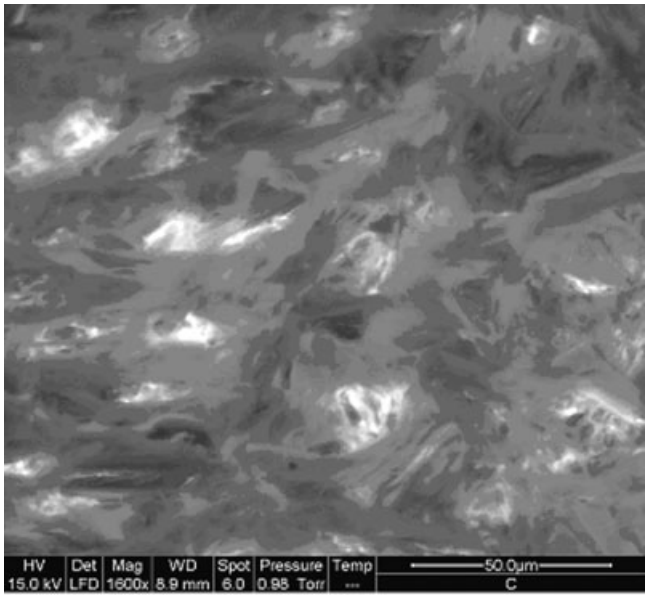

Figure 1 SEM micrograph of 25 wt % mica/nylon-6 composite.

The scanning electron microscope (SEM) micrographs of the composite untreated and treated with different coupling agents can be found from Figures 1–4. The values of tensile strength for the composites with mica treated with the coupling agents at the concentration mentioned before can be found from Figure 5. It is observed that the tensile strength values decreased initially in the case of silane and ε-capro-

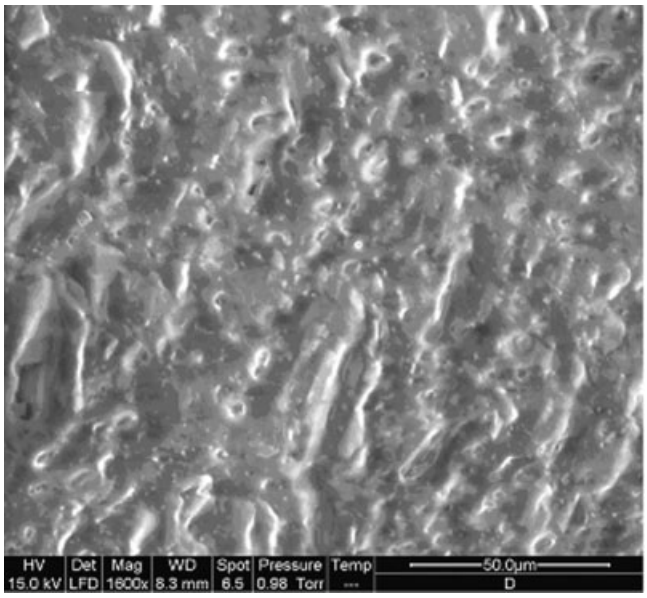

Figure 2 SEM micrograph of silane (3%) treated 25 wt % mica/nylon-6 composite.

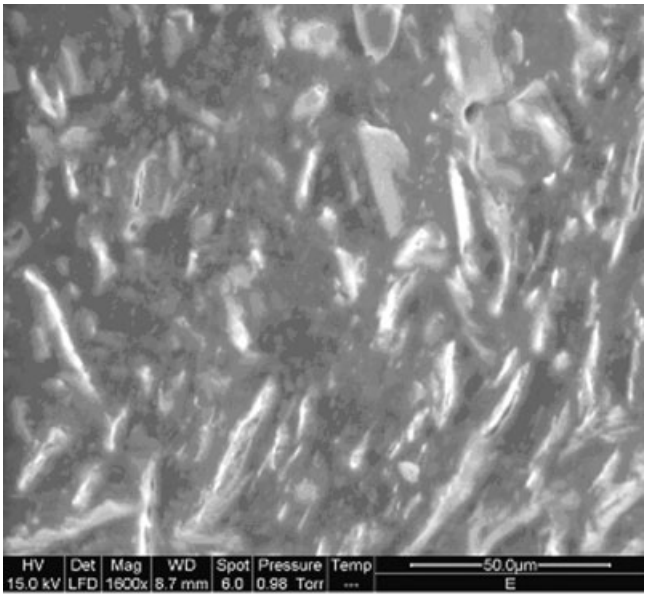

Figure 3 SEM micrograph of ε-caprolactum (3%) treated 25 wt % mica/nylon-6 composite.

lactum but it attained maxima at 3% coupling agent in both the cases. The case is quite reverse with the titanate coupling agent. The values attained maxima at 1 wt % on treating the mica particles with titanate coupling agent, which decreased later. These variations suggest that a flexible interface layer in the composite might have formed owing to their having been treated with silane. The existence of flexible layers could expedite the yielding and plastic deformation of the matrix near the filler surface, resulting in a decreasing tendency in tensile strength. Similar results were obtained by Ying et al.[47] It is also observed from the SEM micrographs that untreated mica/nylon-6 composites showed insufficient quantity of matrix to wet the filler particles and hence resulted in voids thereby increasing the composite porosity; where as sufficient nylon-6 residue can be found when the filler was treated with various coupling agents. Figure 6 depicts the variations in elongation at break on treating mica particles with different coupling agents. It can be seen that elongation at break further reduces on increasing the concentration of coupling agent but this reduction to some extent is controlled by titanate coupling agent. This may be due to what Maiti et al.[48] stated, certain coupling agents have a plastifying action between the filler and the polymer matrix. The values of Young's modulus for the composites with mica treated with the coupling agents can be found from Figure 7. It is observed that the modulus values attained maxima at 3.5 wt % silane and 2.5 wt % in case of ε-caprolactum. A significant improvement in the Young's modulus was observed in the case of titanate treated mica composites. The modulus

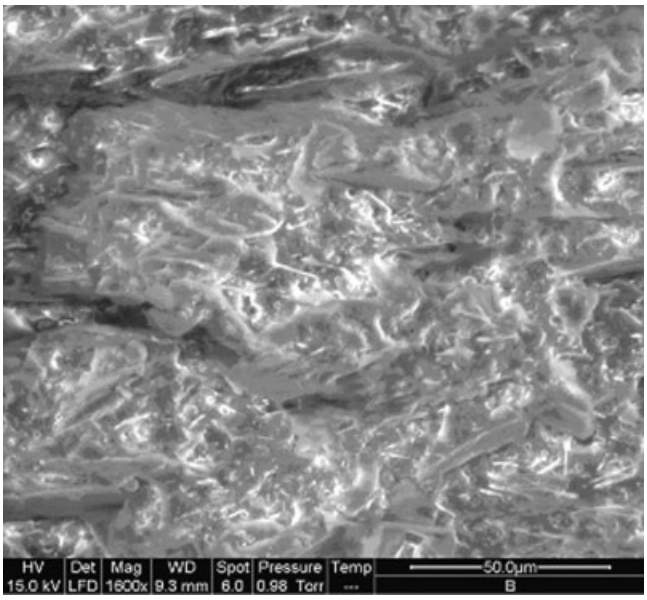

Figure 4 SEM micrograph of titanate (1%) treated 25 w t% mica/nylon-6 composite.

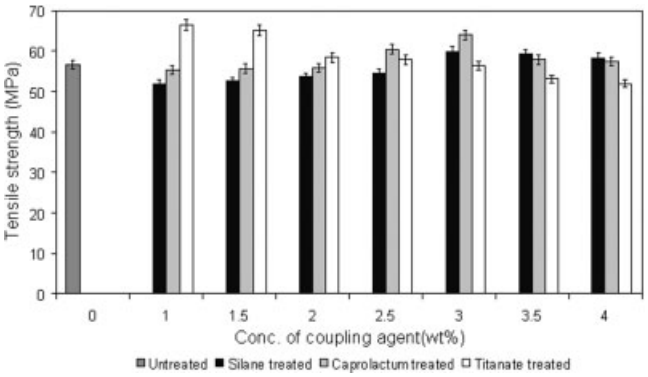

Figure 5 Variations in tensile strength for the composites with mica (25 wt %) treated with the different coupling agents.

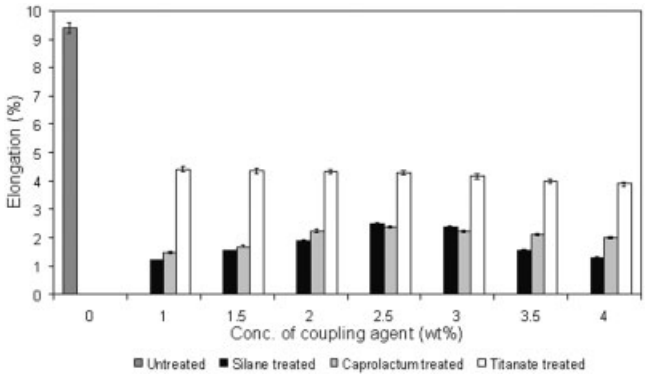

Figure 6 Variations in elongation at break for the composites with mica (25 wt %) treated with the different coupling agents.

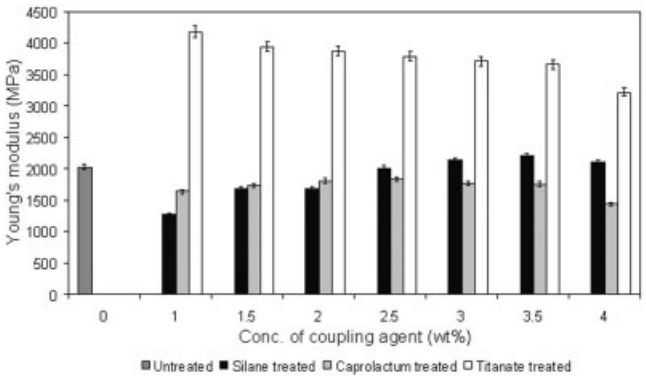

Figure 7 Variations in Young's modulus for the composites with mica (25 wt %) treated with the different coupling agents.

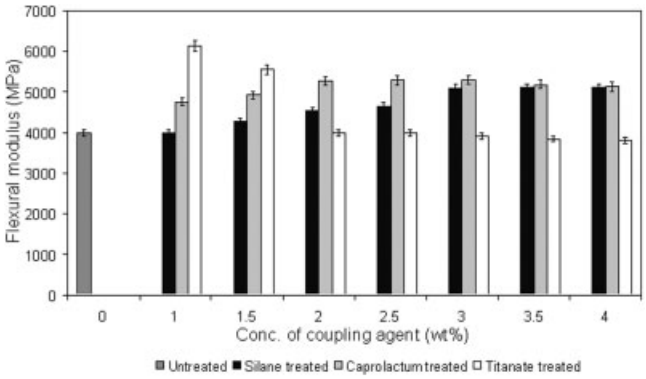

Figure 9 Variations in flexural modulus for the composites with mica (25 wt %) treated with the different coupling agents.

reached maximum at 1 wt % titanate coupling agent, beyond which it decreased marginally. These variations in young's modulus suggest an efficient stress transfer from matrix to the filler having been treated with the titanate coupling agent. It is also evident from the SEM micrographs that titanate coupling agent has an effect to modify the surface characteristics of the filler and improve the interfacial bonding with the matrix. Results of flexural strength and modulus of 75 μm mica (25wt %) /nylon-6 composites can be found in Figures 8 and 9, respectively. The flexural strength values reduced on varying the concentration of titanate coupling agent but in case of flexural modulus, the values attained maxima at 1wt% titanate coupling agent which dramatically reduced on further addition of the coupling agent. The flexural modulus values were significantly improved in case of ε-caprolactum and silane treated mica respectively. The plasticizing effect of titanate coupling agent might have reduced the intermolecular forces in the matrix and consequently increased the flexibility in the composite. The effect of various coupling agents on the impact strength of the composites can be found from Figure 10. It was observed that silane treated mica composites showed significant improvement in the impact strength up to 2 wt % and dramatically reduced on further increasing the concentration of the coupling agent. In the case of titanate coupling agent treated mica the impact strength values attained maxima at 1 wt % and remained almost comparable at higher concentrations of the coupling agent. The results of dielectric strength and heat distortion temperature of 75 μm mica (25 wt %)/nylon-6 composites can be found from Figures 11 and 12, respectively. The dielectric strength values were higher in case of titanate coupling agent treated mica compared with the other coupling agents. But the values of dielectric strength were lower when compared with untreated composites because of leakage of current due to encapsulation of the filler particles by sufficient quantity of the matrix. These variations can also be observed from the SEM micrographs where the untreated composites show some continuity of the filler particles where as for the treated composites the filler particles were

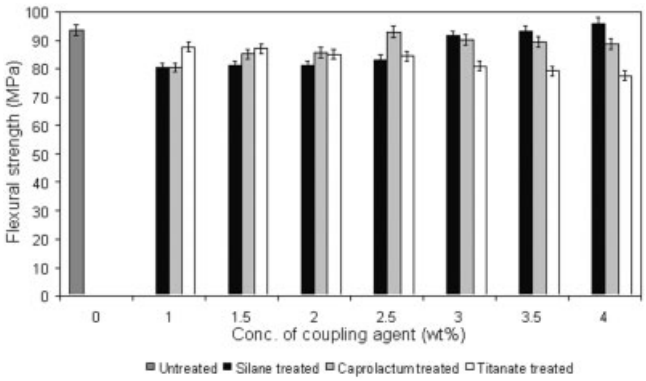

Figure 8 Variations in flexural strength for the composites with mica (25 wt %) treated with the different coupling agents.

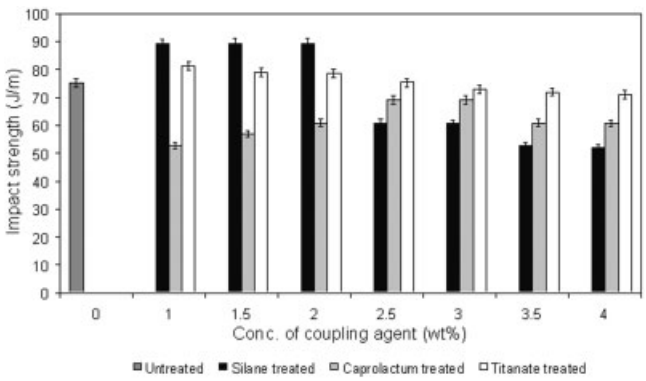

Figure 10 Variations in impact strength for the composites with mica (25 wt %) treated with the different coupling agents.

encapsulated and well dispersed. The heat distortion temperature values increases with increasing concentration of coupling agent, but the values were higher in case of silane compared with ε-caprolactum and titanate coupling agent treated composites.

CONCLUSIONS

Inorganic fillers viz. mica added to the polymer improved its rigidity, strength, and heat resistance, but dramatically decreased the elongation at break. A significant increase in the Young's modulus, flexural modulus, and heat distortion temperature was found with increasing filler loading. It is apparent that the nature of the interlayer between the filler and the polymer matrix introduced by the coupling agents played a significant role in the effectiveness of improving the mechanical properties of composite. It was observed that titanate coupling agent improved the tensile strength and the Young's modulus of the composite most while the impact properties and the heat distortion temperature were enhanced by silane coupling agent and the flexural modulus by ε-caprolactum. It was also observed that elongation at break further reduces on increasing the concentration of coupling agent but this reduction to some extent is controlled by titanate coupling agent. Dielectric strength values were decreased on treating mica with various coupling agents, which was attributed to the leakage of current due to encapsulation of the filler particles by sufficient quantity of the matrix or may be due to fine dispersion. These variations can also be observed from the SEM micrographs. Titanate coupling agent is found to be effective than the other coupling agents used as it has an effect to modify the surface characteristics of filler and improve the interfacial bonding with the matrix as inferred from the morphological studies. Thus the mechanical properties of composite are a function of the particle size, distribution, the dispersion, and the interfacial interaction between the minerals and the polymer matrix.

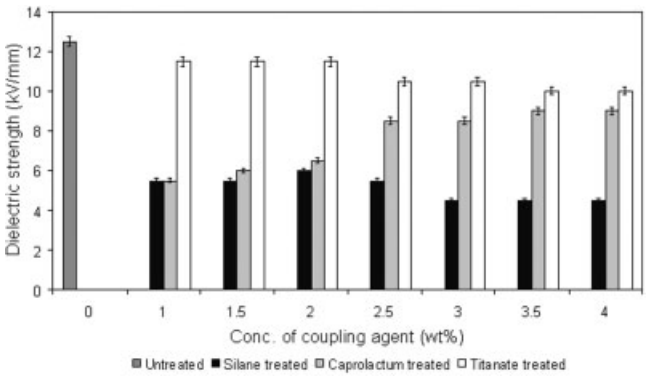

Figure 11 Variations in dielectric strength for the composites with mica (25 wt %) treated with the different coupling agents.

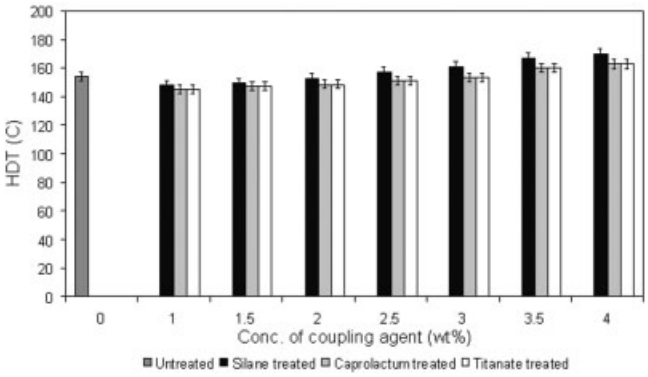

Figure 12 Variations in heat distortion temperature for the composites with mica (25 wt %) treated with the different coupling agents.

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References

1. Maiti, S. N.; Lopez, B. H. J Appl Polym Sci 1992, 44, 353.
2. Kohan, M. I., Ed. Nylon Plastics; Hanser: New York, 1973.
3. Gachter, R.; Muller, H. Plastics Additives Handbook; Hanser: Cincinnati, 1993.
4. Modern Plastics Encyclopedia Handbook; Mc Graw Hill: New York, 1994.
5. Harper, C. A. Handbook of Plastics, Elastomers and Composites; McGraw Hill: New York, 1996.
6. Berins, M. L. SPI Plastics Engineering Handbook; Chapman & Hall: London, 1991.
7. Meddad, A.; Fisa, B. J Appl Polym Sci 1997, 64, 653.
8. Tjong, S. C.; Xu, S. A. J Appl Polym Sci 2001, 81, 3231.
9. Ulrich, M.; Caze, C.; Laroche, P. J Appl Polym Sci 1998, 67, 201.
10. Kyu, T.; Zhou, Z. L.; Zhu, G. C.; Tajuddin, Y.; Qutubiddin, S. J Polym Sci Part A: Polym Phys 1996, 34, 1761.
11. Nielsen, L. E. Mechanical Properties of Polymers and Composite; Marcel Dekker: New York, 1974.
12. Xing, Z. Fuel Energy Abstr 1996, 37, 185.
13. Bose, S.; Mahanwar, P. A. J Appl Polym Sci 2006, 99, 266.
14. Tanaka, H. Polym Eng Sci 1999, 39, 817.
15. Watari, T.; Yamane, T.; Moriyama, S.; Torikai, T.; Imaoka, Y.; Suchiro, K.; Tateyama, H. Mater Res Bull 1997, 32, 719.
16. Cheng, L. P.; Lin, D. J.; Yang, K. C. J Membr Sci 2000, 172, 157.
17. Vaia, R. A.; Price, G.; Ruth, P. N.; Nguyen, H. T.; Lichtenhan, J. J Appl Clay Sci 1999, 15, 67.
18. Bose, S.; Mahanwar, P. A. J Mater Sci 2005, 40, 6423.
19. Hess, K. M. Kunststoffe 1993, 73, 282.
20. Wilbrink, M. W. L.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 2001, 42, 10155.
21. Tjong, S. C.; Meng, Y. Z. Polymer 2001, 40, 1109.
22. Taesler, R.; Wittich, H.; Schulte, K.; Kricheltorf, H. R. J Appl Polym Sci 1996, 61, 783.
23. Avella, M.; Martuscelli, E.; Raimo, M.; Partch, R.; Gangolli, S. G.; Pascuci, B. J Mater Sci 1997, 32, 2411.

24. Katz, H. S.; Milewski, J. V., Eds. Handbook of Fillers and Reinforcement for Plastics; Van Nostrand Reinhold: New York, 1978.
25. Qian, Z. M.; Zhu, C. H. Plast Sci Technol 1983, 4, 10.
26. Chen, H. G.; Xiang, S. Y.; Lv, B. L. Plast Sci Technol 1996, 1, 15.
27. Yao, Z. Y. Plast Ind 1991, 6, 13.
28. Monte, S. J.; Sugerman, G. Polym Eng Sci 1984, 24, 1269.
29. Fuad, M. Y. A.; Ismail, Z.; Ishak, A. M.; Omar, A. K. M. Eur Polym J 1995, 31, 885.
30. Woodhams, R. T.; Xanthos, M. In Handbook of Fillers and Reinforcement for Plastics, Katz, H. S., Milewski, J. V., Eds.; Van Nostrand Reinhold: New York, 1978.
31. Daoji, G.; Lu, S.; Caisheng, S.; Zhijian, W. Eur Polym J 2001, 37, 1359.
32. Maged, A. O.; Ayman, A.; Martin, M.; Ulrich, W. S. Polymer 2001, 42, 6545.
33. Ruofei, Z.; Jin, H.; Bin, S.; Gance, D. J Appl Polym Sci 2001, 82, 2719.
34. Shepherd, P. D.; Golemba, F. J.; Maine, F. W. In Handbook of Fillers and Reinforcements for Plastics; Katz, H. S., Milewski, J. V., Eds.; Van Nostrand Reinhold: New York, 1978.
35. Gupta, V. B.; Brahatheeswaran, C. J Appl Polym Sci 1994, 52, 107.
36. Grace, W. R. Br Patent 1,136,350 (1968).
37. Xanthos, M. Plastic Compound; July 19, 1989.
38. Pastorini, M. T.; Nunes, R. C. R. J Appl Polym Sci 1999, 74, 1361.
39. Okuno, K.; Woodhams, R. T. J Appl Polym Sci 1975, 15, 308.
40. Susan, E. T.; Charles, E. C. J Appl Polym Sci 1982, 27, 4493.
41. Newman, S.; Meyer, F. J. Polym Compos 1980, 1, 37.
42. Verbeek, C. J. R. Mater Lett 2003, 57, 1919.
43. Schrieber, H. P.; Tewari, Y. B.; Wertheimer, M. R. J Appl Polym Sci 1976, 20, 2663.
44. Collins, W. T.; Kludt, J. L. Proceedings of the 30th Annual Technical Conference, Reinforced Plastics/Composites Institute/SPI, Sec 7D, 1975.
45. Pushpa, B.; Jha, N. K.; Anand, K. J Appl Polym Sci 1995, 56, 1339.
46. Bose, S.; Mahanwar, P. A. Polym Eng Sci 2005, 45, 1479.
47. Ying Li; Jian Yu; Zhao, X. G. J Appl Polym Sci 2002, 84, 827.
48. Maiti, S. N.; Mahapatro, P. K. J Appl Polym Sci 1991, 42, 3101.