Indian Journal of Pure & Applied Physics
Vol. 56, October 2018, pp. 787-791

Preparation and properties of nanocomposites based on polyetherimide (PEI)/silicone rubber reinforced with halloysite nanotubes

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Received 13 July 2017; accepted 1 June 2018

This paper presents the results of investigating the effect of halloysite on the thermal, mechanical and morphological properties of PEI/silicone rubber blend based nanocomposites. Novel PEI/silicone rubber filled with halloysite nanotubes nanocomposites have been prepared for various HNTs loadings with the aid of co-rotating twin screw extruder. The results obtained depict that the tensile strength, tensile modulus, elongation at break, hardness and impact strength have significantly increased with increase of HNTs loading. The thermal stability of nanocomposites has been enhanced and found to be maximum at 3 phr HNTs loading. Morphology of the tensile fractured surfaces of nanocomposites has been studied by Scanning electron microscope (SEM). The morphological studies have demonstrated an appreciable reduction in domain size of silicone rubber at 3 phr loading of HNTs and it clearly indicates the reinforcing ability of the HNTs. The interfacial and inter-tubular interactions between HNTs and polymer matrices, and formation of HNTs zig-zag structures are the main reasons for the improvement of various properties.

Keywords- Silicone rubber, PEI, Tensile, TGA, SEM

1 Introduction

In recent years polymer research is by and large devoted on the development of polymer composites with various nanoparticles, which have attracted attention and interest of the scientists globally in a big way[1-6]. During the last few decades, clay-based polymer nanocomposites have attracted considerable attention owing to their excellent improved mechanical and thermal properties, even at low clay loadings[7-15]. Incorporation of such fillers strongly influences the properties of the composites at very low volume fraction because of much smaller inter-particle distances and the conversion of a large fraction of the polymers matrix near their surfaces into an interface of synergistically improved properties. As a result, the desired properties are usually reached at low filler volume fraction, which allows the nanocomposites to retain the microscopic homogeneity and low density of the polymers. There has been very few research report published in recent years related to polymer nanocomposites based on polyetherimide and silicone rubber [9].

Halloysite nanotubes (HNTs) with large aspect ratio offer great opportunity for fabricating nanocomposites with promising performance. HNTs with molecular formula $Al_2Si_2O_5$ $(OH)_4$ nH_2O, are multiwall Kaolinite nanotubes. The tubular halloysite is formed by rolling on Kaolinite sheet preferences to tetrahedral rotation to correct misfit of the octahedral and tetrahedral sheets. Incorporation of HNTs into a polymer matrix leads to considerably large surfaces of polymer, filler interactions in relation to the conventional fillers. Hence, it reduces the oscillation of polymer chain segments, bringing about an increase in degradation of polymer filled with halloysite. Recently, HNTs have been used as a new type of filler for polymers to improve the mechanical and thermal properties [16-23].

In the present work, we have incorporated HNTs to improve the mechanical, thermal and morphological properties in polyetherimide and silicone rubber matrices and the resulting nanocomposites have been characterized for various properties by different analytical techniques like scanning electron microscopy (SEM), thermogravimertric analyzer (TGA) etc. Mechanical properties like tensile strength modulus and elongation at break, etc., have been determined by universal testing machine (UTM).

2 Experimental Details

2.1 Materials and procedures

PEI (Ultem 1000) having specific gravity of

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1.27 gm /cm^3 at room temperature and glass transition temperature (Tg~ 216 °C) was supplied by Sabic Innovative Plastic (USA). Silicone rubber: VMQ (Silastic NPC-40) having the specific gravity of 1.11 gm/cm^3 was supplied by Dow Corning (USA). The halloysite nanoclay having chemical formula $H_4Al_2O_9Si_2.2H_2O$ and specific gravity 1.54 gm /cm^3 was supplied by Sigma-Aldrich (U.S.A.). The purity of HNTs is >95 %.

2.2 Nanocomposites preparation

Prior to compounding, the pellet of polyetherimide has been pre-dried under vacuum at 80 °C in electric blast oven for 12 h. After predrying the PEI, silicone rubber has been mixed in different weight ratio as depicted in Table 1. The homogeneous mixture of PEI/silicone rubber is fed into high performance co-rotating intermeshing twin screw extruder (model ZV20, manufactured by Specific Engineering, Vadodara, India) for melt extrusion. The melt temperature has been maintained between 310 °C to 385 °C and the screw speed is kept at 90 rpm.Test specimen for analyzing the mechanical properties are prepared by high performance injection moulding machine (Model - 90#57, manufactured by Electronica Plastic Machine Ltd. Pune, India). The barrel temperature of different zones has been maintained at 320, 360, 380, 390 °C from hopper to nozzle and injection speed of 30 mm/sec. Prior to testing the test specimens are initially conditioned at 23±2 °C and 50± 5%RH for 24 h.

3 Testing and Characterization

3.1 Tensile strength and tensile modulus

Mechanical properties such as tensile strength, tensile modulus and elongation at break of developed nanocomposites have been determined with the help of INSTRON Universal testing machine model 3382 at room temperature with a gauge length of 50 mm and crosshead speed 5 mm/min. Tensile test are evaluated according to standard ASTM D638 using dumb-bell shaped specimens.

Table 1 – Sample codes and compounding formulations of binary and ternary blends system.

Sample codes	PEI (wt %)	Silicone rubber (wt %)	HNT (phr)
PSH0	85	15	0
PSH1	85	15	1
PSH2	85	15	2
PSH3	85	15	3
PSH4	85	15	4

3.2 Flexural strength and flexural modulus

Flexural properties are evaluated according to ASTM D790 using an INSTRON universal testing machine model 3382. The dimensions of the specimen were 127 mm in length, 12.7 mm in width and 3 mm thickness at room temperature.

3.3 Impact strength

Impact properties are evaluated according to ASTM D-256 using an impact tester machine (Tinius Olsen). The dimensions of the specimens are 64×12.7×3.2 mm for Izod at room temperature.

3.4 Thermo gravimetric analysis (TGA)

The thermal stability and degradation behaviour of developed nanocomposites have been studied with the help of Perkin-Elmer Pyres TGA. The TGA measurements have been conducted with a constant heating rate of 10^{o}C/min under nitrogen atmosphere from 50 to 800 °C.

3.5 Phase morphology

The surface morphology of the tensile fractured surface has been carried out through SEM (JEOL JSM 6490LV) with an accelerating voltage of 10 kV. Prior to SEM analysis fracture surfaces of nanocomposites have been gold coated with the help of gold sputtering unit just to avoid the charging effect and to enhance the emission of secondary electrons.

4 Results and Discussion

4.1 Tensile strength and tensile modulus

Tensile properties results are summarized in Table 2. It is obvious from the data that there is significant increase in tensile strength, tensile modulus and elongation at break of developed nanocomposites, but the maximum improvement is observed at 3 phr HNTs loading in polymer matrix as compared to unfilled PEI/silicone rubber blend. Addition of HNTs leads to increase in the tensile strength of developed nanocomposites by about 33%. Similarly there is enhancement of 27% in tensile modulus. This improvement in tensile strength and modulus may be

Table 2 — Mechanical properties; tensile strength, elongation at break and tensile modulus.

Sample codes	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
PSH0	38.50	5.38	730.90
PSH1	47.94	5.56	849.40
PSH2	50.22	6.23	866.40
PSH3	51.25	6.57	925.37
PSH4	40.74	5.54	778.70

Table 3 — Mechanical properties; flexural strength, flexural elongation, flexural modulus and impact strength.

Sample codes	Flexural strength (MPa)	Flexural elongation (%)	Flexural modulus (MPa)	Impact strength (Izod) J/M
PSH0	76.26	4.21	2304.61	65.4716
PSH1	79.71	4.61	2331.53	70.8727
PSH2	84.07	4.96	2366.15	75.2132
PSH3	90.41	4.97	2850.05	120.2583
PSH4	73.24	3.89	2424.57	102.3623

because of stress transfer from polymer matrix to nanofiller. An effective stress transfer between the polymer and nanofiller might be due to interfacial interaction between the polymer and nanofiller[24]. The reason may be attributed to appreciable dispersion of the nanofiller over the entire polymer matrix. In case of 3 phr loading of HNTs, nanofiller reduces the slippage in polymer- filler interface (under tensile strain) that might be the reason for the enhancement of tensile properties of developed nanocomposites this loadings of HNTs.

4.2 Flexural strength and flexural modulus

To further predict the reinforcing efficiency of HNTs, flexural properties of halloysite nanotubes filled PEI/silicone rubber nanocomposites have also been studied. It appears that incorporation of HNTs (3 phr) leads to an improvement in the flexural modulus and strength of developed nanocomposites. From Table 3, it is clear that there is 24% increase in flexural modulus, whereas, 19% increase in flexural strength as compared to virgin PEI/silicone rubber blend. Decrease in flexural properties at higher loading (4 phr) is due to the over loadings of HNTs that leads to agglomeration of nanotubes (micron size aggregates acting as weak point and failure initiation sites)[25].

4.3 Impact strength

The effect of loadings on the impact strength of developed nanocomposites is summarized in Table 3. It can be seen that the impact strength of developed nanocomposites increases with increase in nanotubes content. Maximum increase in impact strength at 3 phr loading is 84% compared to unfilled PEI/silicone rubber blend. The decrease in impact strength at higher HNTs loading (4 phr) is due to the fact that the increase in nanotubes content leads to the formation of aggregations, which act as a stress concentrator that gives rise to brittle failure. Increase in impact strength may be attributed to the intrinsic toughening properties of HNTs [26]. A better interfacial interaction may also be another reason for the improvement of the impact strength with high absorption energy during impact deformation. Also, high impact energy for developed nanocomposites is due to the fairly good dispersion and proper distribution of nanotubes in matrix. In addition, large aspect ratio of nanotubes may generate the complex matrix-filler interaction during nanotubes bridging, breaking and pull-out that might promote local plastics deformation of matrix[27]. The impact properties of nanocomposites also increase with increase of HNTs content in polymer matrix because of the formation of strong and tough material in the presence of HNTs.

Table 4 — Thermo-gravimetric analyzer results developed nanocomposites

Sample codes	Onset degree temperature (^{0}C)	Loss of weight (%)
PSH0	509.54	98.563
PSH1	510.27	97.434
PSH2	518.30	97.155
PSH3	532.64	96.374
PSH4	523.25	97.994

4.4 Thermal properties

To investigate the influence of HNTs and the thermal properties of PEI/silicone rubber blend systems have been analyzed by TGA and results are given in Table 4 and Fig. 1. All the nanocomposites reveal higher thermal stability as compared to the blend system without filler. The onset degradation temperature of PEI/silicone rubber blend has been found to be 509.54 °C which increases to 532.64 °C with the incorporation of 3 phr HNTs. The incorporation of HNTs reduces the chain mobility of the polymer matrix by imposing large number of restrictions sites which reduce the thermal vibration of C-C bond[28]. Thus, the hypothesis can be postulated by stating that the nanocomposites are in acute need of more thermal energy for the degradation of the polymer matrix which in turn enhances the thermal stability of the nanocomposites.

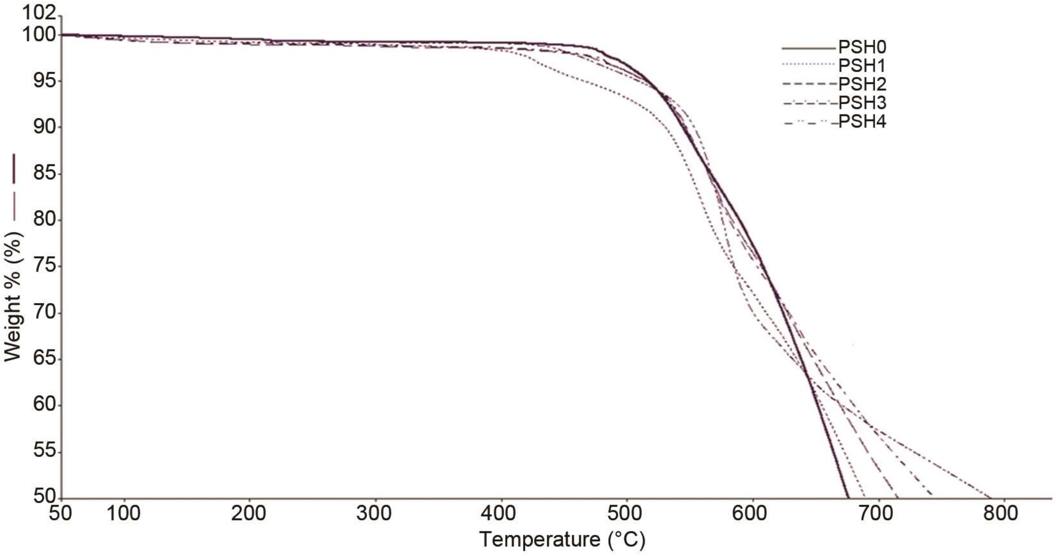

Fig. 1 — TGA thermogram of PEI/silicone rubber blends with different content of halloysite nanotubes.

4.5 Phase morphology

The properties of multiphase polymer system strongly depend upon the phase morphology. In the case of filled polymers, the loading content, dispersion state and interfacial characteristics of the filler particles with the surrounding matrix materials are the most effective factors controlling the ultimate properties of the modified materials. The SEM micrographs of pure HNTs Fig. 2(a) demonstrate cylindrical tubes of 40-50 nm diameter and length of 0.5-3.0 micrometer. HNTs are rather poly dispersed in length. It is known that the dispersion of inorganic filler in a polymeric matrix is a challenge for researchers. This problem is even more severe when nanoparticles are used as filler since nanoparticles have strong tendency to agglomerate. Therefore, uniform and homogeneous dispersion of nanofiller in the polymeric matrices is a difficult process[29].

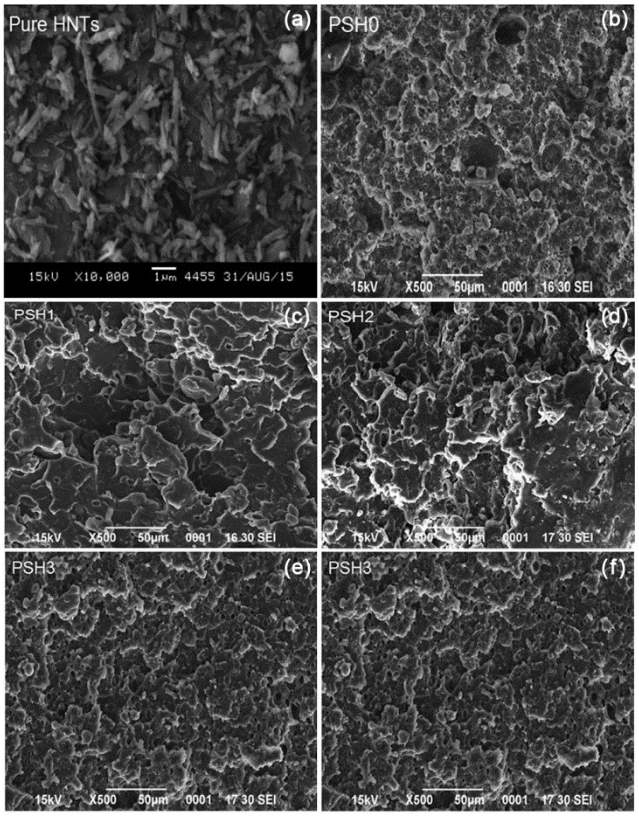

Fig. 2 — (a) SEM micrograph of pure HNTs, (b) SEM micrograph of 0 phr HNTs, (c) SEM micrograph of 1 phr HNTs, (d) SEM micrograph of 2 phr HNTs, (e) SEM micrograph of 3 phr HNTs and (f) SEM micrograph of 4 phr HNTs.

SEM micrographs Fig. 2(a-f) demonstrate the phase morphology and hallow domains which indicate the pulled out silicone rubber phase. The difference between five samples is the average domain size of silicone rubber among the blend systems. PSH3 samples are having the smallest domain size. The reduction in the domain size can be attributed to compatibilizing ability of the HNTs. No sign of de-bonding and/or interfacial voiding is visible for nanocomposites containing 3 phr HNTs. It is believed that this satisfactory interfacial strength is responsible for adequate stress transfer from the matrix to the dispersed structure which; in-turn increases the tensile strength of the developed nanocomposites. Truly speaking the interfacial interaction between the dispersed HNTs and the surrounding matrix is adequate enough. This is because besides the tensile modulus, the ultimate strength of the nanocomposite systems investigated in this work also improves with HNTs content in the polymer matrix. Although a fall in tensile strength has been observed for system with 4 phr HNTs.

5 Conclusions

PEI/silicone rubber nanocomposite with various amounts of HNTs has been prepared by melt mixing process by co-rotating twin screw extruder. It has been seen that the nanocomposites having 3 phr loading of HNTs in polymer matrix provides highest mechanical and thermal properties as compared to unfilled blend system. Reduction in the number average particle size of the dispersed phase has been observed in the presence of HNTs loaded nanocomposites. For 3 phr loaded HNTs nanocomposites, the domain size of silicone rubber is appreciably decreased which indicate that HNTs improved the interfacial interaction between the matrix phase and dispersed phase, giving rise to the improvement in various properties. Thus, it can be concluded that HNTs act as an efficient reinforcing agent for the developed nanocomposites.

Acknowledgement

Authors gratefully acknowledge ER-IPR, DRDO New Delhi for financial support.

References

1 Pal P, Kundu M K, Asish M & Das C K, *J Appl Polym Sci*, 131 (2014) 39587.
2 Liu M, Jia Z, Liu F, Jia D & Gue B, *J Colloid Interface Sci*, 350 (2010) 186.
3 Du M, Gua B & Jia D, *J Eur Polym*, 42 (2006) 1362.
4 Liu M, Gue B, Du J, Chen M F & Jia D, *Polymer*, 50 (2009) 3022.
5 Cassagnau P, *Polymer*, 49 (2008) 2183.
6 Sadhu S & Bhowmick A K, *J Polym Sci Part B: Polym Phys*, 42 (2004) 1572.
7 Ahamad A, Pandey K N, Verma V & Mishra R M, *IJSART*, 2 (2016) 63.
8 Gupta G K, Pandey K N & Upadhyaya P, *IJSART*, 2 (2016) 65.
9 Mishra R M & Rai J S P, *Int J Sci Technol Res*, 5 (2016) 176.
10 Giannelis E P, *Adv Mater*, 8 (1996) 29.
11 Biswas M & Sinha R S, *Adv Polym Sci,* 155 (2001) 176.
12 Das C K, Maitra A, Pal P & Kalra S, *Int J Eng Sci Res Tech*, 8 (2014) 44.
13 Pal P, Kundu M K, Malas A & Das C K, *Polym Compos*, 36 (2015) 955.
14 Verge P, Benali S, Bonnaud L, Mineria A, Mainil M, Lazzaroni R, & Dubois P, *Eur Polym J*, 48 (2012) 677.
15 Singh R.P, Pandey K N, Verma V, Ahamad A & Mishra R M, *J Basic Appl Eng Res*, 2 (2015) 1263.
16 Ye Y, Chen H, Wu J & Ye L, *Polymer*, 48 (2007) 6426.
17 Ning N, Yin Q, Luo F, Zhang Q, Du R & Fu Q, *Polymer*, *48* (2007) 7374.
18 Poh B T & Ng C C, *J Eur Polym*, 34 (1998) 975.
19 Ismail H, Pasbakhsh M N, Ahmad F & Abubakar A, *Polym Test*, 27 (2008) 841.
20 Pasbakhsh P, Ismail H, Ahmad M N & Abubakar A, *Polym Test*, 28 (2009) 548.
21 Guo B, Lei Y, Chen F, Liu X, Du M & Jia D, *Appl Surf Sci*, 255 (2008) 2715.
22 Rybinski P, Janowska G, Jozwiak M & Pajak A, *J Therm Anal Calorim*, 107 (2002) 1243.
23 Rybinski P & Janowska G, *Thermochim Acta*, 549 **(**2012) 6.
24 Sahoo N G, Rana S, Cho J W, Li L & Chan S H, *Prog Polym Sci*, 35 (2010) 837.
25 Selvakumar V, Palanikumar K & Palanivelu K, *J Min Mat Charac Eng*, 9 (2010) 671.
26 Deng S, Zhang J, Ye L & Wu J, *Polymer*, 49 (2008) 5119.
27 Ajayan P M, Schadlen L S, Giamnaris C & Rubia A, *J Polym Res*, 15 (2008) 205.
28 Lozaho K & Barrera E V, *J Appl Polym Sci*, 79 (2001) 125.
29 Momem O, Mazidi M M & Jahagiri N, *Polym Bull***,** 721 (2005) 2757.