

Polyetherimide (PEI) / Silicone Rubber Composite Reinforced With Nanosilica Particles

R. M. Mishra, J.S.P. Rai

Abstract: The present investigation is aimed to prepare polyetherimide (PEI)/silicone rubber nanocomposites reinforced with various amounts of loading (phr) of modified nanosilica using melt mixing process with the help of co-rotating twin screw extruder. Microstructures of the developed nanocomposites have been studied by XRD and SEM. Thermal properties of the developed nanocomposites have been analyzed by TGA. Developed nanocomposites have shown remarkable improvement in mechanical, thermal and morphological properties due to better interfacial adhesion between nanosilica and polymer matrix at 3 phr loading of nanofillers. The addition of nanosilica in polymer matrix has enhanced the thermal stability appreciably at 3 phr loading. This might be attributed to excellent interfacial adhesion and interaction between the nanosilica particles and polymer matrix. SEM micrographs reveal that the entire surface of developed nanocomposites is smooth and has no voids and cavities. It is also evident from SEM images that there is excellent dispersion of nanosilica throughout the entire polymer matrix. Mechanical properties results demonstrate that there is significant in modulus, strength, hardness, impact etc. due to its uniform and homogeneous dispersion of nanosilica in polymer matrix.

Keywords: PEI, Silicone rubber, TGA, Morphology, Mechanical Properties.

1 INTRODUCTION

Nanosilica has an edge over commercial micro silica as a reinforcing agent owing to its better dispersion capability in polymer matrix. The fact is that they are addicted of forming agglomerate because of their high surface energy and they are liberal enough to form inter particle hydrogen bonding via hydroxyl group present on the surface [1, 2]. This may cause in strong filler-filler interactions which are not favorable for effective reinforcement. This problem can be rectified with the help of surface modification of silica particles. The most appropriate surface modifier is silane coupling agents [3-5]. In this way, the compatibility of silica particles with polymer matrix can be increased and it can also play a major role in enhancing the degree of dispersion resulting in significant improvement in thermal and mechanical properties. Polyetherimide (PEI) is a high performance thermoplastic with excellent high strength, modulus and thermal stability. It is extremely useful in aerospace, electronics and various other applications under very adverse conditions [6]. A multifunctional composite materials (MCM) can be prepared by addition of high performance silicone rubber to achieve appreciable mechanical, thermal and morphological properties and also cheaper composite materials. Silicone rubber has excellent strength and temperature resistance -60°C to +360°C. It helps to provide crushing thermal resistance and mechanical properties, load bearing and protective shock absorption qualities to automotive interiors [7-9]. The use of polymer blends is emerging in a big way in satisfying the needs of specific sector in polymer industries [10, 11].

Blending of polymers provides an important route to combine properties of blend components and this gives rise to new material with an optimized performance [12, 13]. Polymer blends properties are greatly influenced by the number, shape and morphology of the dispersed phase particles [14-17]. PEI/silicone rubber nanocomposites properties have attracted a great deal of attention in recent years [18-22]. Polymer blends reinforced with various kinds of nanofillers have been globally accepted for various applications. These polymer blend nanocomposites have synergistic properties of polymer blends and nanofiller. They are controlled by the properties of constituent, morphology and polymer-filler interactions. The incorporation of nanofiller in polymer matrix enhances the various basic and functional properties many times as compared to the virgin polymer or conventional polymer nanocomposites. In the present investigation, a binary blend of polyetherimide /silicone rubber has been prepared by melt blending process using twin screw extruder. An attempt has been made to develop nanocomposites based on PEI/silicone rubber reinforced with modified nanosilica at various loadings. The effect of nanosilica loadings on the performance of developed nanocomposites have been characterize by using various sophisticated analytical technique v, z, TGA, XRD, SEM etc.

2 EXPERIMENTAL

2.1 Materials

PEI (Uitem 1000) having specific gravity of 1.27 gm./cm³ at 250C and glass transition temperature (T_g~216°C) was supplied by Sabic Innovative Plastic (USA). Silicone rubber: VMQ (Silastic NPC-40) having the specific gravity of 1.11 gm/cm³ was supplied by Dow Corning (USA). The organo modified CAB-O-SIL® TS-720 was supplied by Cabot (USA).

2.2 Nanocomposites Preparation

Prior to compounding, the pellet of polyetherimide has been dried under vacuum at 800C in electric blast oven for 12 hours. After predrying the PEI, silicone rubber has been mixed in different weight ratio as depicted in Table 1. The uniform 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

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between 3200C to 3900C and the screw speed is kept at 75 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 330,370,380,3900C from hopper to nozzle and injection speed of 35 mm/sec. The test specimen are initially conditioned at $23\pm 20^{\circ}\text{C}$ and $50\pm 5\% \text{RH}$ for 24 hrs prior to testing.

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

| Sample Codes | PEI (Wt. %) | Silicone rubber (wt. %) | Nanosilica (phr) |
|--------------|-------------|-------------------------|------------------|
| PSN0 | 85 | 15 | - |
| PSN1 | 85 | 15 | 1 |
| PSN2 | 85 | 15 | 2 |
| PSN3 | 85 | 15 | 3 |
| PSN4 | 85 | 15 | 4 |

3. TESTING & CHARECTERIZATION

3.1 Mechanical Properties

Mechanical properties such as tensile strength, tensile modulus, elongation at break and flexural strength of developed nanocomposites have been determined with the help of INSTRON Universal testing machine model 3382 at room temperature with a gauge length of 35 mm and crosshead speed 5 mm/min. Tensile test are evaluated according to standard ASTM D638 using dumb-bell shaped samples. Impact properties are evaluated according to ASTM D-256 using an Impact tester machine (Tinius Olsen). The dimensions of the specimen are 64 x 12.7 x 3.2 mm for Izod at room temperature and Rockwell hardness (M-Scale) of developed nanocomposites has been determined according to ASTM D-785.

3.2 Thermo-gravimetric Analysis (TGA)

The thermal stability and degradation behavior 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 $10^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere from 50 to 700°C .

3.3 X-ray Diffraction (XRD)

The X-ray diffraction (XRD) have been conducted with the help of PW 3050 XPERT-PRO, X-ray diffractometer using copper target ($\text{CuK}\alpha$) having the wavelength of 1.541A0 of continuous scan type operated at 30mA, 45kV.

3.4 Morphological study

The surface morphology of the tensile fractured surface has been carried out through FESEM (Zesis VP SUPRATM 40) with an accelerating voltage of 10 kV. Prior to FESEM 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 Mechanical Properties

Mechanical properties of developed nanocomposites are given in Table 2. There is a remarkable enhancement of both tensile strength, tensile modulus and elongation at break of PEI/silicone rubber blend with the incorporation of nanosilica. But the improvement is more prominent in case of blend having 3 phr content of nanosilica. Incorporation of nanosilica increases the tensile strength of the nanocomposites about 16% when compared to virgin blend. Similarly, there is an enhancement of 23% in tensile modulus. It is worth noting that mechanical properties viz tensile strength, tensile modulus of the nanocomposites are higher than the pure polymer blend. This might be attributed to stress transfer from polymer matrix to the nanofiller. Interfacial interaction between the polymer and nanofiller and dispersion of the nanofiller in the polymer matrix may cause an effective stress transfer between the polymer and nanofiller. It is a bare fact that the slippage of the filler polymer interface, due to large strain, will decrease the stress transfer efficiency [23], which may affect the mechanical properties of the nanocomposites with the strain. Generally, higher the modulus of the nanocomposites, the harder is the nanocomposites and lower the elongation at break. But in our nanocomposites system, this unexpected phenomena of increase in elongation as well as modulus, however, is due to the surfactant role of the compatibilizer ie nanosilica. Simultaneously increase of tensile strength and elongation can be explained by improved interfacial adhesion between the nanosilica and polymer matrices. Modified nanosilica provides better dispersion when compared with unmodified nanosilica, reduces the nanosilica filler slippage at the interface which may be the reason for enhanced mechanical properties of the developed nanocomposites. It is also observable that the hardness increases with the increases of nanosilica content in the blend system. This may due to the cross-linked density. The impact properties of nanocomposites also increase with the increase of nanosilica content in polymer matrix because of the formation of strong and tough material in the presence of nanosilica and also another reason may be due to the bonding between the nanosilica and polymer matrix and the nanosilica becomes as stress transfer medium. Best mechanical properties has been achieved at 3 phr loading of nanosilica in PEI/silicone rubber blend.

Table 2. Mechanical properties results of PEI/silicone rubber nanocomposites.

| Sample code | Tensile Strength (MPa) | Elongation at break (%) | Tensile Modulus (MPa) | Rockwell Hardness (M-scale) | Impact strength (J/m) |
|-------------|------------------------|-------------------------|-----------------------|-----------------------------|-----------------------|
| PSN0 | 38.50 | 8.83 | 730.90 | 84 | 44.6080 |
| PSN1 | 41.07 | 11.16 | 776.86 | 89 | 70.7543 |
| PSN2 | 42.62 | 12.20 | 835.34 | 95 | 77.4172 |
| PSN3 | 44.50 | 13.63 | 898.68 | 104 | 137.367 |
| PSN4 | 39.13 | 10.58 | 760.35 | 96 | 102.602 |

4.2 Thermo-gravimetric Analysis (TGA)

TGA curves of PEI/silicone rubber reinforced with modified with nanosilica are depicted in Fig. 1 and TGA results are summarized in Table 3. From the Table 3 it is evident that the 5% degradation of the nanocomposites containing 3 phr nanosilica occurs around 536 °C which is 11 °C higher than that of pure blend system. But the incorporation of modified nanosilica a vast number of restricted sites for the polymer matrix are created which constraint the chain mobility and reduces the thermal vibrations of carbon-carbon bond [24]. Higher amount of energy will be needed for the degradation of matrix which in turn increases the thermal stability of nanocomposites. Due to better dispersion of nanosilica, the vast number of restricted sites will be more in nanocomposites having 3 phr loading of nanosilica in polymer matrices. TGA results also demonstrate that there is minimum weight loss (39.92 %) at 3 phr loading of nanosilica in polymer matrix. Probably due to this reason, the thermal stability of PEI/silicone rubber reinforced with 3 phr nanosilica is higher than that of virgin polymer blend system.

Table 3. TGA results of PEI/silicone rubber blend with different content of nanosilica.

| Samples Codes | 5 % Weight loss temperature (°C) | 10 % Weight loss temperature (°C) | Loss of weight (%) |
|---------------|----------------------------------|-----------------------------------|--------------------|
| PSN 0 | 525.36 | 568.56 | 43.86 |
| PSN 1 | 521.32 | 553.26 | 42.96 |
| PSN 2 | 530.46 | 569.82 | 40.48 |
| PSN 3 | 536.18 | 575.96 | 39.92 |
| PSN 4 | 522.86 | 552.64 | 41.76 |

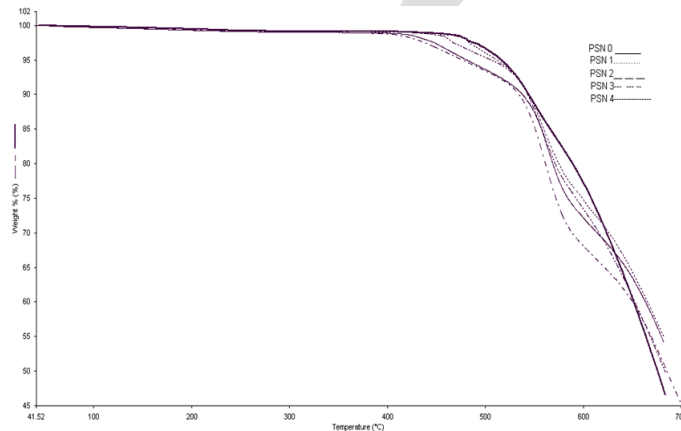


Fig. 1 TGA thermogram of PEI/silicone rubber blend with different content of nanosilica.

3.3 X-ray Diffraction (XRD)

Generally X-ray scans of polymer nanocomposites show a peak reminiscent of the organoclay peak but shifted to lower 2θ or larger d-spacing. Fig. 2 shows the XRD patterns of virgin polymer blend and developed nanocomposites. A shift of diffraction peak toward the lower value reveals an increase of the intergap spacing. Virgin blend system has a diffraction peak around $2\theta=28^\circ$, the corresponding d-spacing is 1.64 \AA whereas the nanocomposites having 3 phr content of modified nanosilica present a peak around 24° , the corresponding d-spacing is 1.89 \AA . These results depict that the gallery of nanosilica have been successfully intercalated and expanded by the organic modified, hence, to improve the

interfacial property between the polymer matrices and inorganic phases.

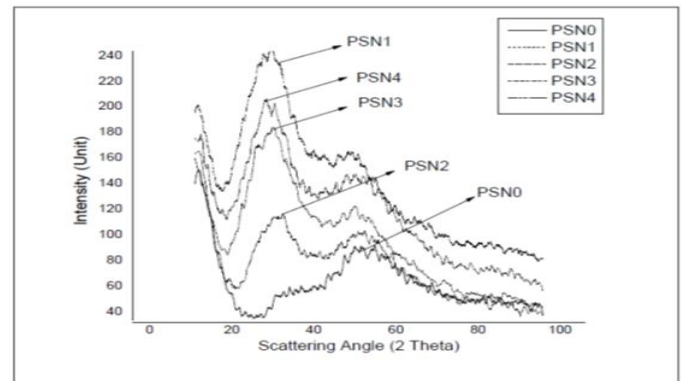


Fig.2 XRD pattern of PEI/silicone rubber blend with different content of nanosilica.

Table 4. XRD results of PEI/silicone rubber blend with different content of nanosilica.

| Sample codes | 2θ Value | d-spacing |
|--------------|-----------------|-----------|
| PSN 0 | 28.0 | 1.64 |
| PSN 1 | 24.0 | 1.89 |
| PSN 2 | 26.0 | 1.76 |
| PSN 3 | 24.0 | 1.89 |
| PSN 4 | 23.3 | 1.95 |

4.4 Morphological Study

The tensile fractured surface of the nanocomposites and the pure blend system are visualized by SEM and the micrographs are depicted in the Fig. 3(a-e). SEM micrographs demonstrate that there is two phase morphology and hollow domain indicates the pulled out silicone rubber phase. The major difference among all the samples is the average domain size. SEM micrographs Fig (3 d) demonstrate that it has smallest average domain size. This reduction in domain size may be because of the compatibilizing efficacy of the modified nanosilica when its concentration is 3 phr in polymer matrix. These results are similar to other earlier studies [25]. It is obvious from SEM micrographs that the nanocomposites having 3 phr content of nanosilica has a better dispersion as compared to other nanocomposites.

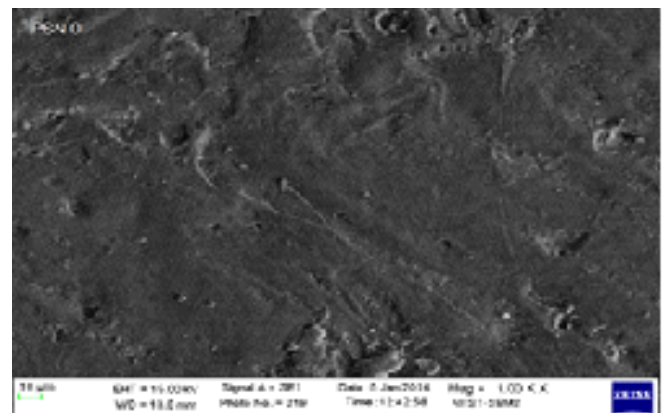


Fig 3 (a) SEM micrographs of PSN 0

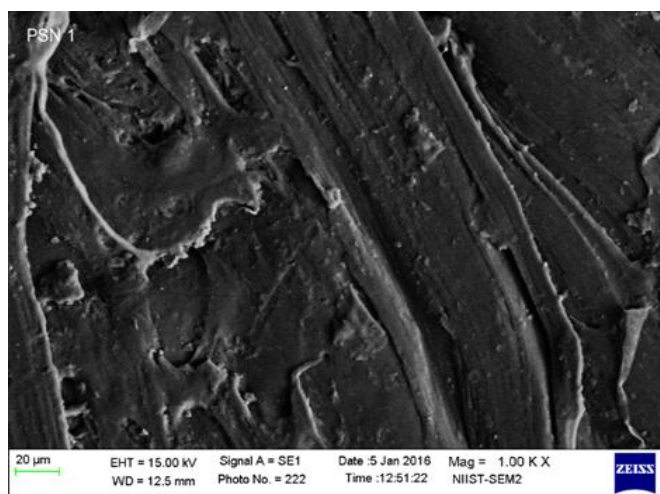


Fig 3 (b) SEM micrographs of PSN 1

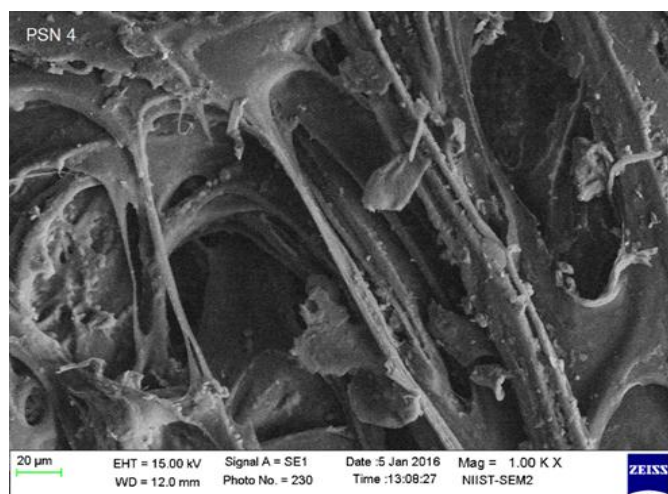


Fig 3 (e) SEM micrographs of PSN 4

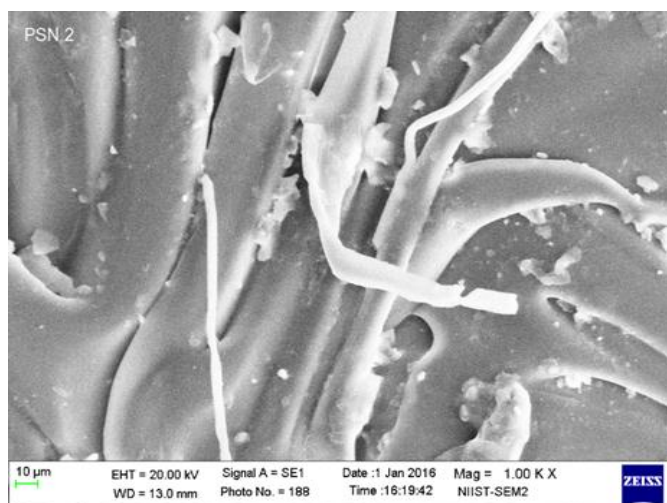


Fig 3 (c) SEM micrographs of PSN 2

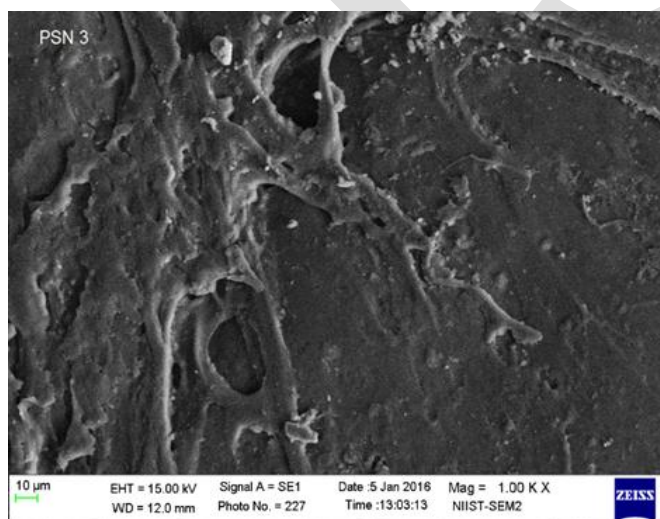


Fig 3 (d) SEM micrographs of PSN 3

5. CONCLUSION

The nanocomposites comprising of PEI/silicone rubber incorporated with various loadings of modified nanosilica have been prepared by melt mixing process through twin screw extruder. Modified nanosilica has a remarkable effect on the performance PEI/silicone rubber nanocomposites because of excellent dispersion of nanosilica over the entire polymer matrices. This has provoked the way for the enhancement of thermal, mechanical and morphological properties of developed nanocomposites as compared to pure blend system.

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