

## Effect of nanosilica on the properties of PEI/silicone rubber blend based nanocomposites

R M Mishra<sup>a</sup>, Abrar Ahamad<sup>a</sup>, K N Pandey<sup>a</sup> & J S P Rai<sup>b</sup>

<sup>a</sup>Central Institute of Plastics Engineering & Technology, Lucknow 226 008, India

<sup>b</sup>Jaypee University of Engineering and Technology, Guna 473 226, India

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The aim of the present study is to prepare nanocomposites based on binary blends of poly ether imide (PEI)/silicone rubber reinforced with varied loadings of modified nanosilica particles. Nanocomposites have been prepared by melt blending process using twin screw extruder. Thermal behaviour of the developed nanocomposites has been studied with the help of TGA and DMA. Morphological properties have been visualized by SEM. Mechanical properties of the nanocomposites have been determined by universal testing machine. It has been observed that almost all the properties have been found to increase upto 25% with the incorporation of modified nanosilica particles in polymer matrices. Enhancement in various properties may be attributed to better interfacial adhesion and fairly good polymer filler interactions.

**Keywords:** PEI, Silicone rubber, Mechanical properties, TGA, SEM

### 1 Introduction

Nanosilica is superior to micro silica as reinforcing agent because of its excellent dispersion attitude in polymer matrix. Truly speaking, they prefer to form aggregates owing to their high surface energy and they are at liberty to form particle hydrogen bonding through hydroxyl group available on the surface<sup>1,2</sup>. This may give rise to strong filler-filler interactions which is undesirable for effective reinforcement. This problem can be overcome with the aid of modification/activation of nanosilica particles. The most favourable surface modifier is silane coupling agent<sup>3-5</sup>. This enhances the compatibility of silica particles with polymer matrix and increases the degree of dispersion, resulting in remarkable improvement in thermal and mechanical properties. PEI is an excellent thermoplastic with extremely good strength, modulus and thermal stability. It has various applications in micro-electronics, aerospace etc. under very undesirable conditions<sup>6</sup>. Silicone rubber is very useful for the development of multifunctional composite materials (MCM) with significant mechanical, thermal and morphological properties. Silicone rubber possesses excellent strength and higher temperature resistance from -60 °C to +360 °C. It is extremely helpful in providing crushing thermal resistance and mechanical properties, load bearing

and protective shock absorption qualities to automotive industries<sup>7-9</sup>.

Now a day's researchers are paying greater attention on the development of polymer nanocomposites for the diversified applications in various sectors<sup>10-18</sup>. Blending is an attractive technique for the development of newer materials with desired set of properties at lower cost and ease of processability. Polymer blends are a mixture of two or more homopolymers with no covalent bonding. Polymer nanocomposites based on blends have synergistic effect of both the partners of blend. The incorporation of nanofiller in polymer blend results in the improvisation of many basic and functional properties as compared to the virgin polymer or conventional polymer composites.

The present studies have been explored to prepare PEI/silicone rubber reinforced with nanosilica at varied loadings by melt blending process using twin screw extruder. The developed nanocomposites have been analyzed with the help of various high-tech analytical instruments, e.g., TGA, DMA, SEM etc.

### 2 Experimental Details

#### 2.1 Materials

PEI (Ultem 1000) having specific gravity of 1.27 gm /cm<sup>3</sup> at 25 °C and glass transition temperature (T<sub>g</sub>~ 216 °C) has been supplied by sabic innovative plastic (USA). Silicone rubber: VMQ (Silastic NPC-40) having the specific gravity of

\*Corresponding author (E-mail: rmmcipet@gmail.com)

1.11 gm/cm<sup>3</sup> has been supplied by dow corning (USA). The organo modified CAB-O-SIL® TS-720 has been supplied by Cabot (USA).

## 2.2 Nanocomposites preparation

Prior to compounding, the pellet of polyetherimide has been 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 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 between 320 °C to 390 °C 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, 380,390 °C from hopper to nozzle and injection speed of 35 mm/sec. The test specimen is initially conditioned prior to testing at 23±2 °C and 50± 5% RH for 24 h.

## 3 Testing and Characterization

### 3.1 Mechanical properties

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 35 mm and crosshead speed 5 mm/min. Tensile test are evaluated according to standard ASTM D638 using

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

Sample Codes	PEI (wt. %)	Silicone rubber (wt. %)	Nanosilica (wt. %)
VB	85	15	-
NCS1	85	15	1
NCS2	85	15	2
NCS3	85	15	3
NCS4	85	15	4

dumb-bell shaped samples. Impact properties are evaluated according to ASTM D256 using an Impact tester machine (Tinius Olsen).The dimensions of the specimen are 64 x 12.7 x 3.2 mm for izod impact strength at room temperature.

### 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 1 TGA. The TGA measurements have been conducted with a constant heating rate of 10 °C/min under nitrogen atmosphere from 50 to 750 °C.

### 3.3 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis of binary blend and nanocomposites are performed by HITACHI, DMA 6100 in single cantilever bending mode. The storage modulus, loss modulus and tanδ have been determined at 1 Hz frequency from room temperature to 300 °C under a controlled heating rate of 5 °C/min in nitrogen atmosphere.

### 3.4 Morphological study

The surface morphology of the tensile fractured surface have been studied out through SEM (JEOL JSM 6490LV) with an accelerating voltage of 10 kV. Prior to SEM analysis fractured 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

The mechanical properties are shown in Table 2. It is obvious from Table 2 that there is remarkable improvization in tensile strength, tensile modulus and elongation at break with the reinforcement of modified nanosilica particles in blend matrix. The improvization is more distinct in case of blend having 3 wt % of nanosilica. Addition of nanosilica increases the tensile strength of the nanocomposites about 16% as compared to virgin blend. Similarly, 23% enhancement in tensile modulus has been

Table 2 – Mechanical properties of PEI/silicone rubber blend with varied loadings of nanosilica.

Sample code	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)	Impact strength (J/m)
VB	38.50	8.83	730.90	44.61
NCS1	41.07	11.16	776.86	70.75
NCS2	42.62	12.20	835.34	77.42
NCS3	44.50	13.63	898.68	137.37
NCS4	39.13	10.58	760.35	102.60

noticed. This increase in tensile strength and modulus of the developed nanocomposites may be because of stress transfer from the polymer matrix to the nanofiller. It is a bare fact that the effective stress transfer between the polymer matrix and nanofiller entirely depends upon the interfacial interaction between the polymer and nanofiller as well as on the dispersion of nanofiller over the entire polymer matrix. The bridging effect of modified nanosilica at the blend interface may also be responsible for enhancement in tensile properties. Increase in elongation at break of nanocomposites may be attributed to increase in ductility. It is evident from Table 2 that the impact properties of the developed nanocomposites also increase with the increase of nanosilica loading in polymer matrix. This may be attributed to the formation of strong and tough material in the presence of nanosilica. Maximum mechanical properties have been achieved at 3 wt % loading of nanosilica in PEI/silicone rubber blend.

#### 4.2 Thermo-gravimetric analysis (TGA)

TGA thermo-gram for the pure blend system and nanocomposites are shown in Fig. 1. TGA plots clearly show that all the nanocomposites possess higher thermal stability as compared to the virgin PEI/silicone rubber blend system. TGA results are summarized in Table 3. Table 3 shows that NCS3 has

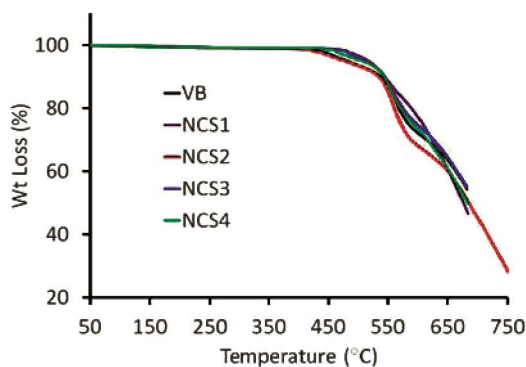


Fig. 1 – TGA thermogram of PEI/silicone rubber blend with varied loadings of nanosilica.

Table 3 – TGA results of PEI/silicone rubber blend with varied loadings of nanosilica.

Samples codes	5 % weight loss temperature (°C)	10 % weight loss temperature (°C)	Loss of weight (%)
VB	480	537	43.8
NCS1	476	524	42.9
NCS2	506	537	40.4
NCS3	511	544	39.8
NCS4	505	543	41.7

highest thermal stability as compared to VB in the entire temperature range of analysis. Table 3 shows that the 5% degradation of NCS3 occurs at 511°C and is 31°C higher than that of VB (480°C). The incorporation of modified nanosilica provides a path in reducing the chain flexibility and interchain slippage of the polymer matrix by imposing large numbers of restricted sites which results in reducing the thermal vibration of C-C bond<sup>19</sup>. Thus, we can conclude by stating that nanocomposites need much higher thermal energy for the degradation of polymer chains that enhances their thermal stability.

In other words we can say that excellent interaction between the blend and modified nanosilica may be responsible for the significant improvement in thermal stability of the polymer nanocomposites. Table 3 also reveals that there is least weight loss 39.8 % at 3 wt % loading of modified nanosilica. It can be concluded by addressing that the nanocomposites comprising of 3 wt % loading of modified nanosilica has the highest thermal stability because this particular nanocomposite has minimum weight loss.

#### 4.3 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) results are depicted in Table 4 and Fig. 2(a and b). Figure 2(a) demonstrates the variation of storage modulus with temperature for PEI/silicone rubber blend and its composition with modified nanosilica. The storage modulus thermo-plot reveals that the enhancement in stiffness of nanosilica nanocomposites with the induction of nanosilica into PEI/silicone rubber blend, both below and above glass transition temperature (around 215 °C). It has been observed that the storage modulus for PEI/silicone rubber blend is the lowest compared to others. The enhancement in storage modulus into higher side for the modified nanosilica incorporated nanocomposites may be attributed to the decrease in polymer chain mobility. It can also be stated that modified nanosilica works as a crosslinking site in between the silicone rubber chain and PEI polymer matrix which results in the enhancement of stiffness of the nanocomposites.

The  $\tan \delta$  thermo-plot for the PEI/silicone rubber blend and nanocomposites is demonstrated in Fig. 2(b). It is evident from the thermo-plot that the glass transition temperature ( $T_g$ ) moves to the higher value with the incorporation of modified nanosilica. The virgin blend system addresses a  $T_g$  at 210 °C which increases to 215 °C for the nanocomposites having

Table 4 – DMA results of PEI/silicone rubber blend with varied loadings of nanosilica.

Sample codes	Storage modulus (MPa)				Glass transition temperature (°C)
	50 (°C)	100 (°C)	150 (°C)	200 (°C)	
VB	3530	4370	4810	1240	DMA 210
NCS1	4600	4350	4980	853	211
NCS2	6380	5530	5190	391	212
NCS3	7420	6455	6080	426	215
NCS4	6830	6000	5210	1130	209

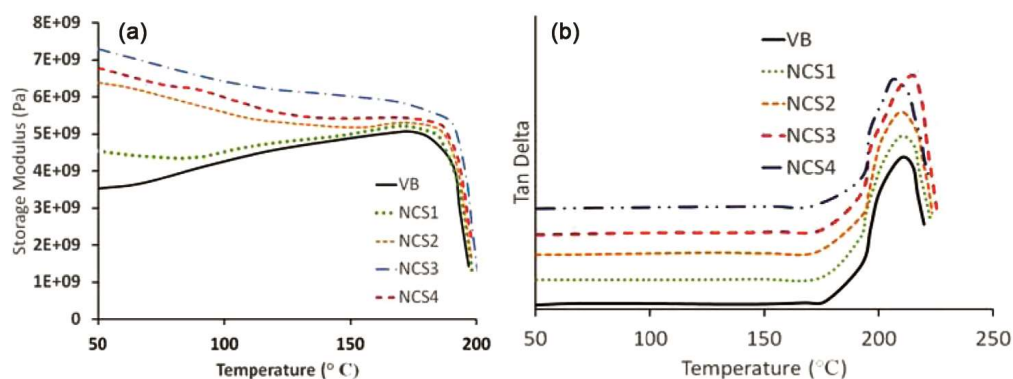


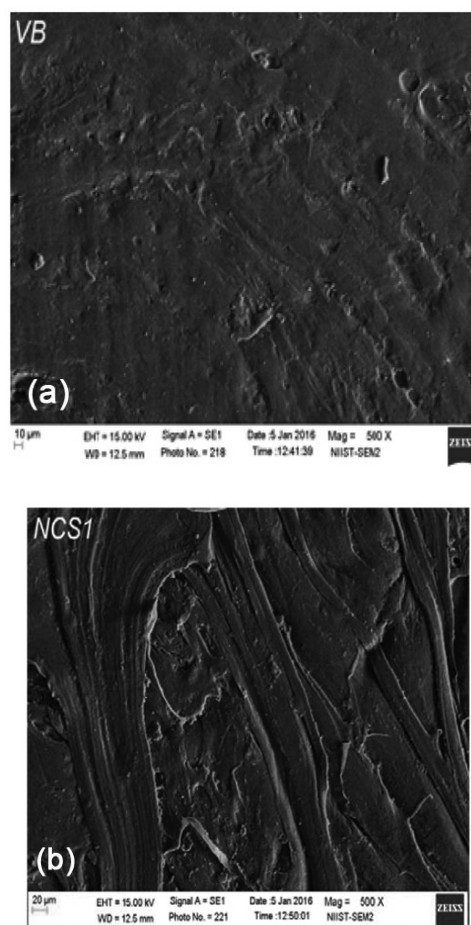
Fig. 2 – (a) Storage modulus vs temperature of PEI/silicone rubber blend with varied loadings of nanosilica, (b) Tan  $\delta$  vs temperature of PEI/silicone rubber blend with varied loadings of nanosilica

3 wt % modified nanosilica in polymer matrix. The enhancement in glass transition temperature can be attributed to the immobilize effect of nanosilica at higher temperature. According to another school of thought, enhancement in Tg value may be because of the restricted movement of the polymer chains by the nanosilica.

#### 4.4 Morphological study

Surface morphology of the blend and nanocomposites has been visualized by scanning electron microscopy and the respective micrographs are shown in Fig. 3(a-e). From the first SEM picture in Fig. 3(a), it is evident that the blend partners PEI and silicone rubber are immiscible in nature and has two phase morphology and hallow domains indicate pulled out silicone rubber phase. The vast difference among all the samples is the average domain size. Figure 3(d) demonstrates that NCS3 has smallest average domain size. This reduction in domain size may be attributed to the compatibilizing efficacy of the modified nanosilica when its concentration is 3 wt. % in polymer matrix. These results are in good agreement to the earlier investigation<sup>20</sup>.

It is concluded from SEM micrograph that the nanocomposites having 3 wt % content of nanosilica has a better dispersion as compared to the other nanocomposites. Modified nanosilica manifests



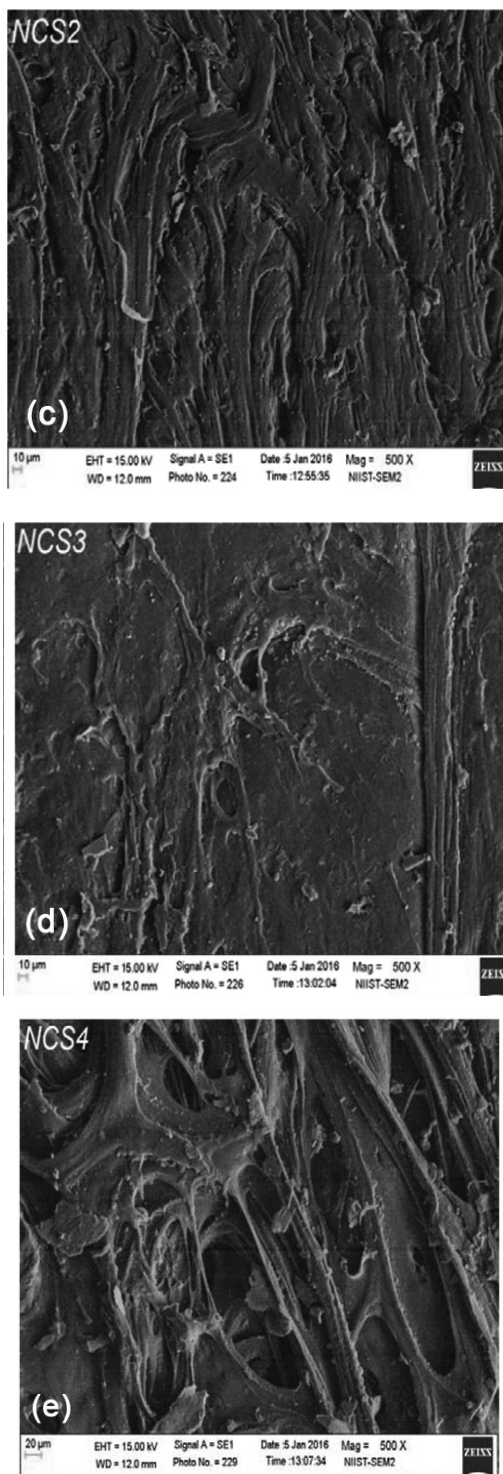


Fig. 3 – (a) SEM micrograph of pure blend, (b) SEM micrograph of 1 wt % nanosilica, (c) SEM micrograph of 2 wt % nanosilica, (d) SEM micrograph of 3 wt % nanosilica, (e) SEM micrograph of 4 wt % nanosilica.

in the reduction/elimination of Van der Waals forces. Modification imparts filler-polymer interaction to a

greater extent which results in excellent dispersion of nanosilica over the entire polymer matrix.

## 5 Conclusions

PEI/silicone rubber/modified nanosilica nanocomposites have been prepared by melt blending process with the help of co-rotating twin screw extruder. Modified nanosilica shows a very good dispersion in the PEI/silicone rubber blend. Therefore, the interfacial adhesion and the ability to transfer the stress between the nanofiller and the polymer matrix are enhanced. It can be concluded that the addition of modified nanosilica in PEI/silicone rubber is capable of enhancing the various properties of developed nanocomposites with respect to mechanical, thermal and morphological aspects.

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## References

- 1 Ansarifara A, Azharb A, Ibrahima N, Shiaha S F & Lawtone J M D, *Int J Adhesion Adhesives*, 25 (2005) 77.
- 2 Bassett D R, Boucher E A & Zettlemoyer A C, *J Coil Interf Sci*, 27 (1968) 649.
- 3 Zau H, Wu S & Shen J, *Chem Rev*, 108 (2008) 3893.
- 4 Hui R, Yixin Q U & Suhe Z, *Chemises J Chem Eng*, 14 (2006) 93.
- 5 Agosino A, Errico M E, Malinconico M, Rosa M D, Avella M & Schiraldi C, *J Master Sci Master Med*, 22 (2011) 481.
- 6 Keating M, *Thermo Him Acta*, 319 (1998) 201.
- 7 Salinier A, Dagreou S, Leonardi F, Derail C & Navascues N, *Composite Structures*, 102 (2013) 81.
- 8 Keller et al, *Adv Function Mater*, 17 (2007) 2399.
- 9 Nayak G C, Rajasekar R & Das C K, *Composite Part A*, 41 (2010) 1662.
- 10 Paul D R & N S, Eds, *Polymer blends*, Vol. 1 & 2 1978 Academic press: New York.
- 11 Utteaki LA, Hansen Publications: Munish, (1989).
- 12 Setua D K, Pandey K N, Saxena A K & Mathur G N, *J Appl Polym Sci*, 74 (1999) 480.
- 13 Lewis C, Buanpa R & Kiatlkamjornwong S, *J Appl Sci*, 90 (2003) 3059.
- 14 Nakason C, Kaesaman A, Somah Z, Homsin S & Kiatlkamjornwong S, *Polymer Test*, 21 (2002) 449.
- 15 Pomposo A, Calahorra E, Eguiazabal I & Cortazar M, *Macromolecule*, 26 (1993) 2104.
- 16 Ismail H & Leong H C, *Polymer Test*, 20 (2001) 509.
- 17 Pandey K N, Setua D K & Mathur G N, *Polym Eng Sci*, 5 (2005) 1265.
- 18 Harrats C, Thomas S & Groeninckx G, CRC Press Talor & Francis Group: Raton, FL, (2006).
- 19 Mehta A & Isayev A I, *Polym Eng Sci*, 31 (1991) 971.
- 20 Botterbruch L & Anders S, Engineering thermoplastics polycarbonate, Polyacetals. Polyesters cellulose Estins, Hanser Verlag Munich (1996).