

Dispersion of SiC Coated MWCNTs in PEI/Silicone Rubber Blend and Its Effect on the Thermal and Mechanical Properties

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ABSTRACT: Multi-walled carbon nanotubes (MWCNTs) are modified by polycarbosilane derived SiC to improve the dispersion of MWCNTs in the polymer matrix. Unmodified and modified MWCNTs are dispersed in PEI/hydroxyl terminated PDMS(HTSR) blend by melt mixing. TEM and FESEM images shows better dispersion of SiC coated MWCNTs in the blend matrix when compared with pure MWCNTs. Thermal stability of the SiC coated MWCNTs added nanocomposite improved drastically than that of the pure MWCNTs.

Compared with pure PEI/HTSR binary blend and unmodified MWCNTs/PEI/HTSR ternary blend, the storage modulus, tensile modulus, and tensile strength of SiC coated MWCNTs/PEI/HTSR blend increased, due to the better dispersion of the modified MWCNTs in polymer matrix. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3574–3581, 2011

Key words: polyetherimide; hydroxyl terminated silicone rubber; blend; SiC coated MWCNTs; dispersion

INTRODUCTION

Carbon nanotubes (CNTs) are the most exciting nanofillers used in recent years for the production of nanocomposites due to their impressive electrical, thermal, and mechanical properties.^{1–5} The mechanical property of CNTs includes exceptionally high axial strength and Young's modulus in the order of TPa.^{6–8} However the uniform dispersion of these nanofillers in the polymer matrix presents the major challenge for the fabrication of high performance nanocomposites. To improve the dispersion of CNTs in the polymer matrix various methods have been adopted like functionalization of CNTs,^{9–12} *in situ* polymerization^{13–16} and optimum physical blending.¹⁷ But functionalization of CNTs introduces defective sites in the nanotubes which deteriorate its properties as reinforcing filler in the nanocomposites. The driving force for the CNTs agglomeration is the Strong van der Waals force of attraction between the nanotubes. Coating of CNTs with ceramics can reduce the van der waals force of attraction between the nanotubes, which can improve its dispersion. Bose et al. found that the dispersion of SiC coated MWCNTs improved, compared with pure MWCNTs, in the ABS/liquid crys-

talline polymer (LCP) blend as a result of which, the thermal and mechanical properties are also higher for SiC coated MWCNTs added system.¹⁸ Yuen et al. studied the effect of TiO₂ coated MWCNTs on the epoxy resin and reported an improvement in the dispersion as well as mechanical properties of the modified TiO₂ coated MWCNTs added nanocomposites compared with pure MWCNTs added system.¹⁹

Polymer blends have been intensively studied since polymers were first synthesized for the improvement of either a specific property or providing materials with a full set of required properties at the low price, improving processability and offering the means for industrial plastic waste recycling.²⁰ Due to the superior properties of the engineering thermoplastics, they are the best polymer to be used in rigorous applications like electrical, electronics, automotive, medicine, optics, athletics, and construction¹³ but the processing of these polymers are very difficult. So these polymers are often blended with other polymers of lower viscosity (like LCP) to improve their processability.

In the present work, a binary blend of poly (ether imide) (PEI) and hydroxyl terminated polydimethylsiloxane (HTSR) has been prepared by melt blending. Multi-walled carbon nanotubes (MWCNTs) are coated with polycarbosilane derived SiC. Both unmodified and modified MWCNTs are dispersed in the PEI/HTSR binary blend in an internal mixture. The effect of the SiC coated MWCNTs on the thermal, mechanical and morphological properties of the binary blend has been studied and compared

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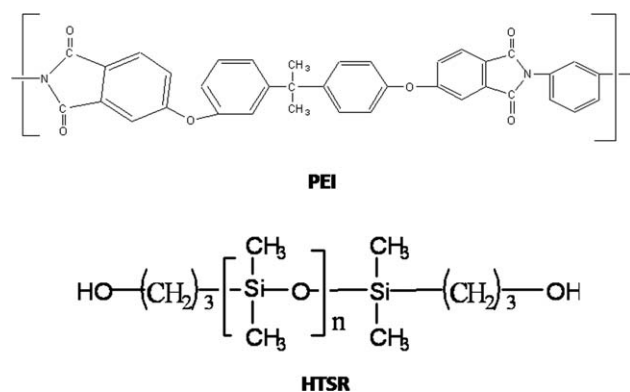


Figure 1 Chemical Structure of PEI and HTSR.

with that of the pure MWCNTs added nanocomposites.

EXPERIMENTAL

Materials and procedure

PEI (Ultem 1010) was supplied by GE. Hydroxyl terminated silicone rubber (HTSR) was developed in our laboratory. (The chemical structures were given in Fig. 1). The MWCNTs (MWCNTs-1000) were obtained from Iljini Nanotechnology, Korea. These MWCNTs are having a diameter of 10–20 nm, length 20 μm , and aspect ratio of ~ 1000 .

The SiC coated MWCNTs were prepared by a method that has already reported in the literature.¹⁸ Briefly, polycarbosilane (PCS) are dispersed ultrasonically in 50 mL of *n*-hexane using a horn-type ultrasonicator for 15 min. Then MWCNTs are added to this solution and ultrasonicated for 30 min at 60°C to disperse the MWCNTs. The solvent is allowed to evaporate in a draft chamber at 25°C. Then the MWCNTs and PCS mixture is cured at 240°C for 90 min and then at 1150°C for 60 min in a quartz crucible.

Preparation of nanocomposites

Prior to mixing, PEI and HTSR were dried under vacuum at 80°C and MWCNTs (both unmodified and modified) at 300°C for 12 h. A sigma high temperature internal mixture equipped with two sigma type counter rotating rotors was used for the preparation of PEI/HTSR/MWCNTs composites, at a temperature of 360°C with a rotor speed of 100 rpm. The formulations of the composites were given in Table I. The composites were compression molded at 360°C and under a constant pressure of 15 MPa for 10 min and allowed to cool to room temperature under the same pressure.

CHARACTERIZATION

X-ray photoelectron spectroscopy study

The SiC coated MWCNTs are analyzed by X-ray photoelectron spectroscopy (XPS) with a PHI ESCA spectrometer (Perkin–Elmer 5400), using Mg Ka radiation (1253.6 eV) to reveal the change in surface characteristics of MWCNTs.

Morphological study

A Carl Zeiss-SUPRATM 40 FESEM with an accelerating voltage of 5 kV and SEM (Tescan//Vega LSU) was employed to observe the morphology of the tensile fractured composites. A thin layer of gold was sputtered on the fracture surface of the specimens for electrical conductivity.

High resolution transmission electron microscopy

The nanocomposites with both unmodified and modified MWCNTs are analyzed by high resolution transmission electron microscopy (HR-TEM, JEOL 2100), to check the dispersion of the nanofillers in the polymer matrix. The samples are microtomed at room temperature and analyzed at an accelerating voltage of 120 kV.

Fourier transform infrared spectroscopy

FTIR of nanocomposites was done using a NEXUS 870 FTIR (Thermo Nicolet) to investigate the possible interaction between PEI and HTSR.

Rheology

Rheology study is carried out in a capillary rheometer (Smart RHEO 1000, CEAST) at 360°C, at different shear rates, to investigate the effect of MWCNTs on viscosity of PEI/HTSR blend.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) curves were recorded with a Dupont 2100 thermogravimetric analyzer. The TGA measurements were conducted with a heating rate of 10°C/min under an air atmosphere from 50 to 650°C.

TABLE I
Sample codes and formulation of binary and ternary blends

Sample codes	PEI (wt %)	HTSR (wt %)	Pure MWCNT (wt %)	SiC coated MWCNT (wt %)
PS	70	30	–	–
PSC	70	30	1	–
PSS	70	30	–	1

Dynamic mechanical thermal analysis

Dynamic mechanical analysis of binary and ternary blends are done by a TA instrument (DMA 2980 model) in single cantilever bending mode. The storage modulus (E'), loss modulus (E'') and $\tan \delta$ were measured at a frequency of 1 Hz from ambient to 250°C and a heating rate of 5°C/min.

Mechanical properties

The tensile tests were carried out on dumb-bell shaped samples using a Hounsfield HS 10 KS (universal testing machine) at room temperature with a gauge length of 35 mm and crosshead speed of 5 mm/min. Tensile values reported here were an average of the results for tests run on at least four specimens.

RESULTS AND DISCUSSION

X-ray photoelectron spectroscopy study

Figure 2(a,b) shows the XPS spectra in the Si 2p and C 1s region. The two broad peaks in the Si 2p spectra were resolved into three peaks that corresponds to the binding energy of 100.4, 101.0, and 102.6 eV. The first two peaks correspond to the Si doublet and the third peak corresponds to the Si-C.²¹ In case of C 1s the spectrum was resolved into two peaks centered around 283.6 and 284.5 eV. These peaks corresponds to C-Si (283.6 eV) and C-C (284.5eV). The presence of Si-C and C-Si bonds in the spectrum of Si 2P and C 1s, respectively, confirms the formation of SiC particles on the CNTs.²²

Morphological study

The cryofractured surface of the nanocomposites and pure blend systems are analyzed by SEM and the images are given in the Figure 3(a-c). All the samples show dual phase morphology and the hollow domain indicates the pulled out HTSR phase. The difference between the three samples is the average domain size of HTSR. Among the three blend systems PSS is having the smallest average domain size followed by PSC and PS. This reduction in the domain size can be attributed to the compatibilizing ability of the unmodified and modified CNTs. Hong et al. also published similar type of results where the clay was acting as a compatibilizer between the PE/PBT blend and results in the reduction in the domain size.²³ The marked section of Figure 3(b) has been magnified and presented in Figure 3(d) which shows the agglomeration of pure MWCNTs in the PSC blend system. To further examine the dispersion state of unmodified and modified MWCNTs in the blend matrix, samples were analyzed by FESEM

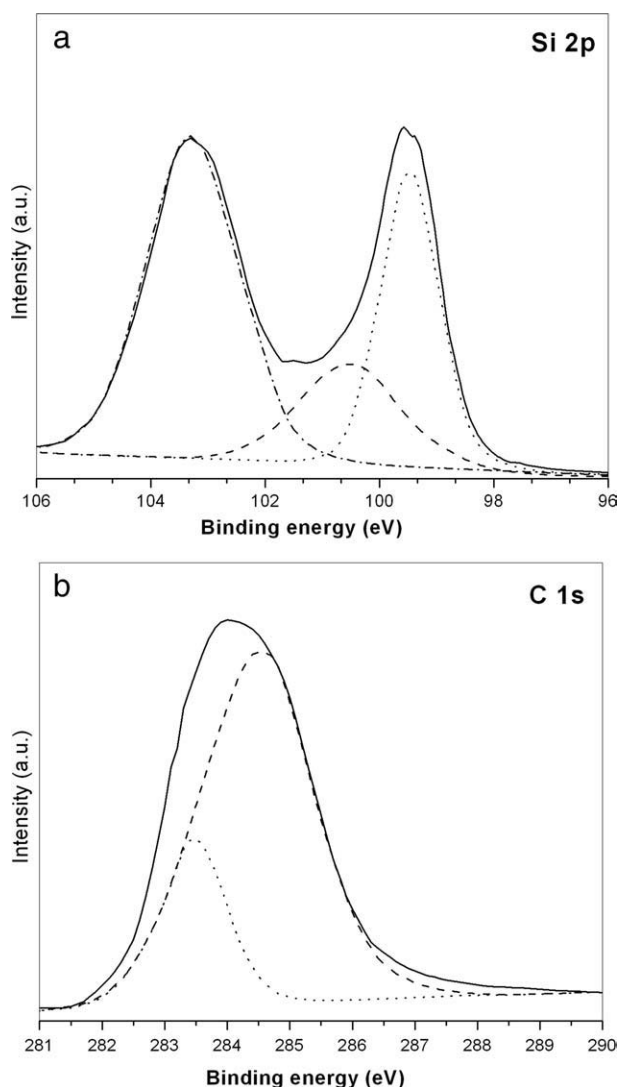


Figure 2 (a) XPS spectrum of Si 2p region of SiC coated MWCNTs. (b) XPS spectrum of C 1s region of SiC coated MWCNTs.

at higher magnification and the images were shown in Figure 3(e,f). Agglomerations of pure MWCNTs can be seen in the PSC sample where as PSS shows a better dispersion of SiC coated MWCNTs. To further confirm the improvement of dispersion of SiC coated MWCNTs in the blend matrix, HR-TEM analysis was done and the results were discussed in the following section.

High resolution transmission electron microscopy study

TEM images of the nanocomposites are given in Figure 4(a,b). From the TEM images, it is clear that the dispersion of SiC coated MWCNTs are much better than the pure MWCNTs in the blend matrix. Due to the Van der waals interaction between the nanotubes, pure MWCNTs are very difficult to disperse uniformly in the polymer matrix which results in

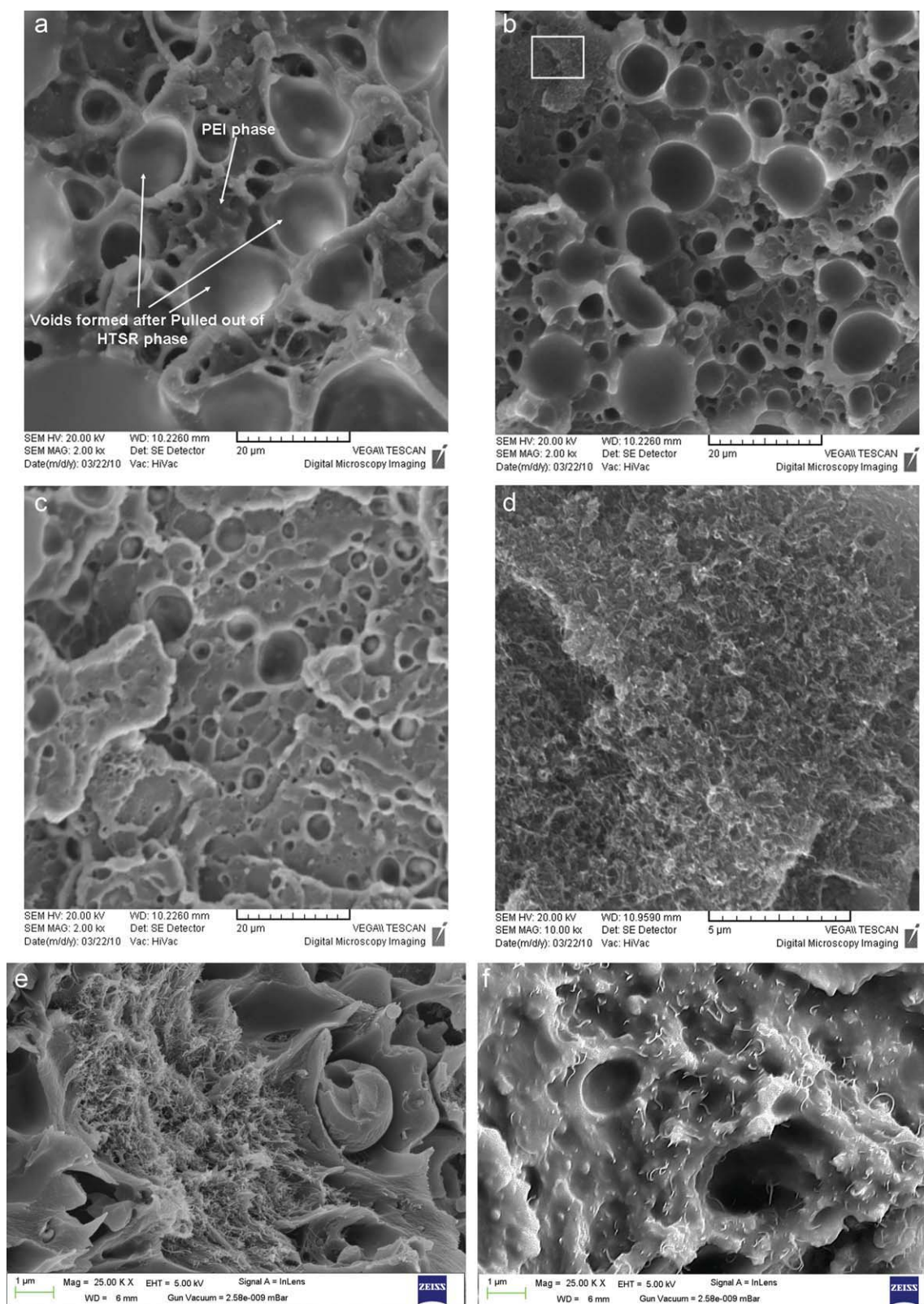


Figure 3 (a) SEM image of fractured surface of PS. (b) SEM image of fractured surface of PSC. (c) SEM image of fractured surface of PSS. (d) Magnified SEM image of marked section of PSC. (e) FESEM image of fractured surface of PSC. (f) FESEM image of fractured surface of PSS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

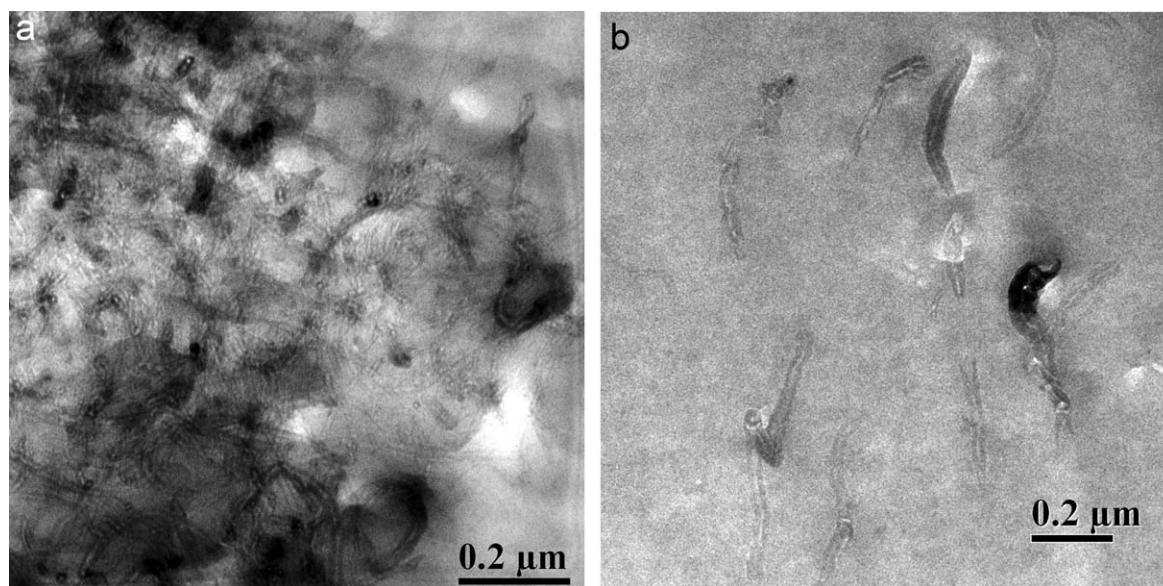


Figure 4 (a) TEM image of PSC. (b) TEM image of PSS.

the formation of agglomeration. Better dispersion can be achieved if this interaction can be eliminated or minimized. It is believed that SiC coating reduces the van der Waals interaction between the MWCNTs which leads to the better dispersion of SiC coated MWCNTs in the blend matrix.

Fourier transform infrared spectroscopy

FTIR spectra for the pure PEI and HTSR and their blend are given in Figure 5. HTSR is having a peak around 3665 cm^{-1} which corresponds to the free OH groups. The intensity of this peak has decreased in the PS blend while a new peak has appeared at 3484 cm^{-1} . This new peak corresponds to the hydrogen bonded OH. The C=O peak of imide at 1726 cm^{-1}

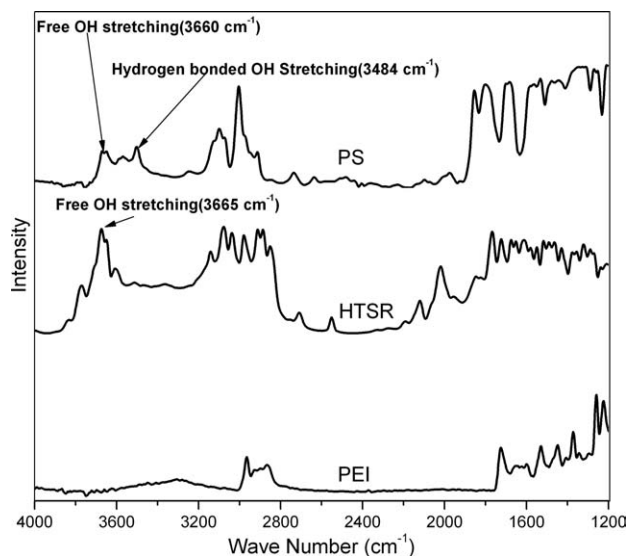


Figure 5 FTIR spectrum of PS, PEI, and HTSR.

(for pure PEI) has also shifted to the higher value in the PS blend. This suggests that there is an interaction between the OH of HTSR and C=O of PEI.

Rheology

The flow behaviors of PS, PSC, and PSS along with pure PEI are shown in Figure 6. With the increase in the shear rate the viscosity of the pure PEI decreases, this corresponds to the shear thinning effect. Blending with silicone rubber reduces the viscosity of the PEI considerably, which corresponds to the improvement of processability of PEI upon blending with silicone rubber. Incorporation of pure MWCNTs increases the viscosity of PSC when compared with PS but it is lower than the pure PEI. The

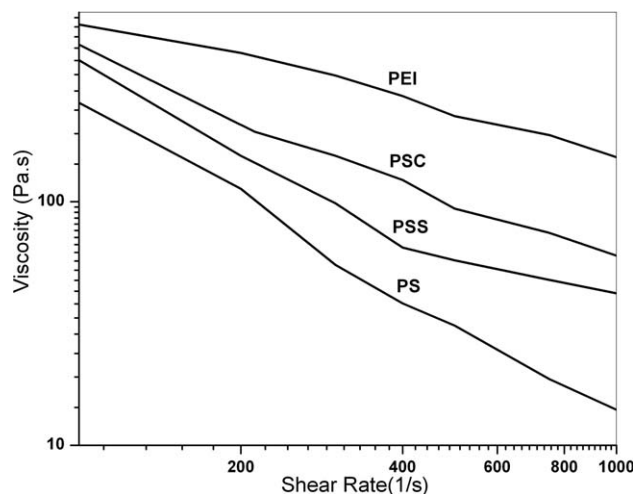


Figure 6 Viscosity versus shear rate plots for pure PEI, PS, PSC, and PSS.

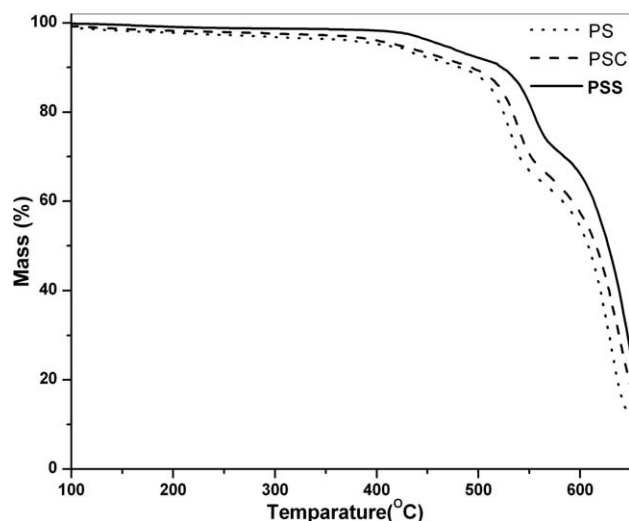


Figure 7 TGA plots of PS, PSC, and PSS.

viscosity of PSS is lower than the PSC. This suggests that at higher temperature SiC coated MWCNTs may acting as a lubricating agent.

Thermogravimetric analysis

Thermal stability of the nanocomposites along with the pure blend has been analyzed by TGA and the resulted plots are given in Figure 7. It is evident from the plots that PSS is having the highest thermal stability over PS and PSC in the whole temperature range of analysis. Results of the TGA analysis are summarized in Table II. From the Table it is clear that, the 5% degradation of the PSC occurs at around 425°C which is 13°C higher than that of PS (412°C). But the incorporation of SiC coated MWCNTs improves the thermal stability of the PSS drastically to 469°C (for 5% weight loss), which is 57°C higher than that of the pure blend system. With the incorporation of MWCNTs a vast number of the restricted sites for the polymer matrix are generated which constrained the chain mobility and reduces the thermal vibration of C—C bond.¹² So for the degradation of the matrix higher amount of energy will be required, which in turn increases the thermal stability of the nanocomposites. Due to the better dispersion of SiC coated MWCNTs, the no of restricted sites (for the polymer chain mobility) will be more in PSS compared with agglomerated pure

TABLE II
Thermal Stability of binary and ternary blends

Sample codes	5% weight loss temperature	10% weight loss temperature
PS	412	481
PSC	425	492
PSS	469	522

MWCNTs in PSC. Probably due to this reason thermal stability of PSS is higher than PSC.

Dynamic mechanical thermal analysis

Storage modulus of binary and ternary blends as a function of temperature are given in Figure 8(a). From the plots, it is clear that incorporation of MWCNTs increase the storage modulus of the ternary blends when compared with the binary blends. This improvement in storage modulus is ascribed to the effective stress transfer from the matrix to the nanofillers. The storage modulus of the nanocomposites at different temperatures is summarized in Table III. At 50°C, PSC shows 19% improvement in storage modulus when compared with PS, which is 31% for PSS. Similarly at 100, 150, and 200°C the enhancement in storage modulus of SiC coated MWCNTs added system is higher than the raw MWCNTs added system. It has been reported that

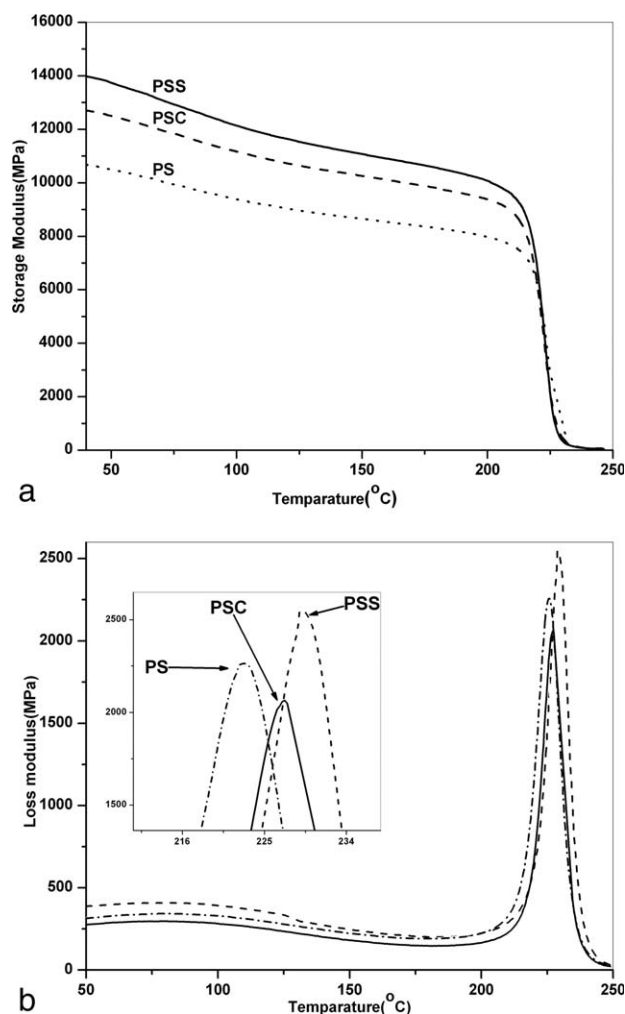


Figure 8 (a) Storage modulus versus temperature of PS, PSC, and PSS. (b) Tan δ versus temperature of PS, PSC, and PSS.

TABLE III
DMTA analysis results of binary and ternary blends

Sample Code	Storage modulus (MPa)				T_g (°C)	
	At 50°C	At 100°C	At 150°C	At 200°C	From DMTA	From DSC
PS	10497	9373	8670	7984	223.4	222.4
PSC	12496	11158	10244	9374	227.9	226.6
PSS	13752	12159	11086	10057	229.9	228.2

decreased alignment and well dispersed nanotubes decreased the bundle-bundle interaction and increase the filler reinforcement.²⁴ Due to the better dispersion of SiC coated MWCNTs, the reinforcement efficiency of these fillers are more than that of the agglomerated pure MWCNTs which increase the stiffness of the PSS over PSC.

Figure 8(b) shows the $\tan \delta$ versus temperature plots of the nanocomposites. As can be seen the T_g of the nanocomposites are higher when compared with the binary blend. The increase in $\tan \delta$ temperature can be ascribed to the restricted movement of the polymer chains by the nanofillers. Owing to the better dispersion of SiC coated MWCNTs than raw MWCNTs in the matrix, T_g of PSS is more than PSC.

The T_g of the nanocomposites along with pure blend are also determined by DSC and the trend is similar to the DMTA analysis. The T_g values are given in Table II. The difference in the T_g obtained from DSC and DMTA is due to the principle of the instruments on which they are working. DMTA gives the T_g under dynamic condition where as DSC gives under static condition.

Mechanical properties

The tensile properties are summarized in the Table IV. There is a notable increase of both tensile strength and tensile modulus of PEI/HO-PDMS blend with the incorporation of MWCNTs. But the improvement is more prominent in case of PSS when compared with PSC. Incorporation of MWCNTs increases the tensile strength of the PSC about 20% when compared with PS, which is increase upto 35% for PSS. Similarly there is an enhancement of 23 and 34% of tensile modulus for the PSC and PSS respectively. Mechanical properties of the composites are higher than the pure polymer

TABLE IV
Tensile properties of binary and ternary blends

Sample codes	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
PS	38.5 ± 1.4	1056 ± 6	6.11 ± 0.5
PSC	46.43 ± 1.5	1298 ± 8	5.14 ± 0.4
PSS	51.92 ± 1.2	1416 ± 5	2.82 ± 0.3

due to the stress transfer from the polymer matrix to the fillers. Effective stress transfer between the polymer and fillers depends on the interfacial interaction between the polymer and fillers and dispersion of the fillers in the polymer matrix. The slippage at the filler-polymer interface, due to large strain, will decrease the stress transfer efficiency,²⁵ which will affect the mechanical property of the composites under strain. The rough surface of SiC coated MWCNTs, due to the SiC coating, combined with better dispersion, when compared with raw MWCNTs, reduces the filler-polymer slippage at the interface (under tensile strain) which may be the reason for the enhanced tensile properties of PSS over PSC.

CONCLUSION

SiC coated MWCNTs is prepared successfully via sol-gel process. Unmodified MWCNTs and SiC coated MWCNTs are dispersed in the PEI/HTSR blend matrix by melt blending in an internal mixture. The dispersion of the SiC coated MWCNTs in the blend matrix found to be better than that of the pure MWCNTs. Better dispersion of SiC coated MWCNTs results in the enhancement of thermal and mechanical properties of the nanocomposites when compared with both pure blend and raw MWCNTs added composite.

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