

# Effect of Montmorillonite Clay on Polyetherimide/Silicone Rubber Blend based Nanocomposites

Abrar Ahamad<sup>1</sup>, K. N. Pandey<sup>2</sup>, Vishal Verma<sup>3</sup>, R. M. Mishra<sup>4</sup>

<sup>1, 2, 3, 4</sup> Central Institute of Plastics Engineering and Technology, Lucknow-226008, India

**Abstract-** The present study investigates the preparation of polyetherimide (PEI)/silicone rubber nanocomposites reinforced with various loadings (phr) of MMT nanoclay using melt mixing process with the aid of co-rotating twin screw extruder. The results obtained for various properties indicate that PEI/silicone rubber nanocomposites have shown significant improvement in mechanical, thermal and morphological properties enhancement due to better interfacial adhesion between MMT and polymer matrix at 2 phr loading of nanofiller. Thermo-gravimetric analyzer (TGA) has been used to predict the thermal stability of the developed nanocomposites. The thermal stability of developed nanocomposites has shown an appreciable enhancement because of better interfacial adhesion between the MMT and polymer matrix. SEM micrographs demonstrate that the entire surface of developed nanocomposite is smooth and has no voids and cavities. It is also evident from SEM micrographs that there is excellent dispersion of nanofiller throughout the entire PEI/silicone rubber matrix.

**Keywords-** PEI, SEM, TGA, Silicone rubber, Mechanical properties.

## I. INTRODUCTION

Now a day's montmorillonite (MMT) is the most exciting nanofillers used for the production of nanocomposites because of its good thermal and mechanical properties [1-3]. The essential nanoclay raw material is montmorillonite layered smectite clay mineral with a platey structure. Individual platelet thicknesses are just one nanometer, but surface dimensions are generally 300 to more than 600 nanometers, resulting in an unusually high aspect ratio [4-7]. Unmodified nanoclay disperses in polymers with great difficulty because polymers are generally organophilic. Montmorillonite can be made organophilic or organomodified through clay surface modification, MMT is compatible with conventional organic polymers. Compatibilized nanoclay disperses readily in polymers [8-11].

Polymer blends have been extensively studied since polymer were first synthesised for the improvement of either a specific property or providing materials with full set of required properties at low price including processability and offering the means for the industrial plastics waste recycling

[12]. Engineering thermoplastics are the best polymer to be used in various applications like electrical, electronics, automotive, medicine, optics, athletics and constructions owing to their excellent properties [13]. The processing of these polymers are very difficult so these polymers are often blended with other polymers having lower viscosity to improve their processability [14,15]. Polyetherimide (PEI) is a high performance amorphous engineering thermoplastic material with a high glass transition temperature ( $T_g \sim 216^\circ\text{C}$ ). It shows various properties like easy processability, a good chemical, hydraulic resistance and also excellent mechanical, thermal properties. PEI has diversified applications ranging from microelectronics to aerospace [16]. A multifunctional composites materials (MCM) can be prepared by addition of high performance silicone rubber material, to achieve the good mechanical, thermal and morphological properties and also cheaper composites materials. Silicone rubber has excellent strength and temperature resistance ( $-60^\circ\text{C}$  to  $+360^\circ\text{C}$ ). It helps to provide crushing thermal resistance and mechanical properties, load bearing and protective shock absorption qualities to automotive interiors [17-19].

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 MMT at various loadings. The effect of MMT loadings on the performance of developed nanocomposites have been characterized by using various sophisticated analytical technique v.z. TGA, FTIR, XRD, SEM etc.

## II. EXPERIMENTAL

### 2.1 Materials

PEI(Ultem 1000) having specific gravity of 1.27 gm/cm<sup>3</sup> at 25<sup>0</sup> C and glass transition temperature ( $T_g \sim 216^\circ\text{C}$ ) was supplied by Sabic Innovative Plastic (USA). Silicone rubber: VMQ (Silastic NPC-40) having the specific gravity of 1.11 gm/cm<sup>3</sup> was supplied by Dow Corning (USA). The organomodified montmorillonite (OMMT) clay: Nanomer® 1.31 PS, was supplied by Sigma Aldrich (USA).

## 2.2 Nanocomposite Preparation

Prior to compounding, the pellet of polyetherimide were dried under vacuum at 80°C in electric blast oven for 12 hours. After predrying the PEI, silicone rubber were mixed in different weight ratio as depicted in Table 1. The uniform mixture of PEI/silicone rubber was fed into high performance co-rotating inter-meshing twin screw extruder (model ZV20, manufactured by Specific Engineering, Vadodara, India) for melt extrusion. The melt temperature was maintained between 320°C-390°C and the screw speed was 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 was maintained 320, 360, 380, 395°C from hopper to nozzle and injection speed of 35 mm/sec. The test specimen are initially conditioned at 23±2°C and 50± 5%RH for 24 hr. prior to testing.

Table 1: Sample codes and compounding formulation of binary and ternary blends

Sample codes	PEI (Wt. %)	Silicone rubber (Wt. %)	MMT (Phr)
A	70	30	-
B	70	30	1
C	70	30	2
D	70	30	3

## III. TESTING & CHARACTERIZATION

### 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. Flexural properties are evaluated according to ASTM D790 the dimensions of the specimen were 127 mm in length, 12.7mm in width and 3mm thickness 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 TGA. The TGA measurement were

conducted with a constant heating rate of 10°C/min under nitrogen atmosphere from 50 to 650°C.

### 3.3 Fourier transform infrared spectroscopy (FTIR)

FTIR studies were carried out with the help of using a Perkin Elmer Spectrum in a humidity free atmosphere at room temperature from 4000-450 cm<sup>-1</sup> to investigate the possible interaction between PEI and silicone rubber.

### 3.4 X-ray diffraction (XRD)

The X-ray diffraction (XRD) had been conducted with the help of PW 3050 XPERT-PRO, X-ray diffractometer using copper target (CuK $\alpha$ ) having the wavelength of 1.541Å<sup>0</sup> of continuous scan type operated at 30mA, 45kV to get an explicit idea of the relative crystallinity of the composites at room temperature.

### 3.5 Morphological study

The surface morphology of the tensile fractured surface were carried out through FESEM (Zesis VP SUPRA<sup>TM</sup> 40) with an accelerating voltage of 10 kV. Prior to FESEM analysis fracture surfaces of nanocomposites were gold coated with the help of gold sputtering unit just to avoid the charging effect and to enhance the emission of secondary electron.

## IV. RESULTS AND DISCUSSION

### 4.1 Mechanical properties

The tensile properties are summarized in the Table 2. There is remarkable increase of tensile strength, tensile modulus and flexural strength of PEI/silicone rubber blend with the incorporation of MMT. But the improvement is more prominent in case of 2 phr MMT loading in polymer matrix as compared to virgin PEI/silicone rubber blend. MMT increases the tensile strength of PEI/silicone rubber about 27 MPa, when compared with virgin polymer blend system. Mechanical properties of developed nanocomposites are higher than the pure polymer matrix due to 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 fillers-polymer interface, due to large strain will decrease the stress transfer efficiency [20]. In case of 2 phr loading of MMT nanofillers reduce the slippage in polymer-fillers interface (under tensile strain) which might be the reason for the enhancement of mechanical properties of developed nanocomposites at 2 phr loading of MMT nanofillers.

Table 2: Mechanical properties (Tensile and Flexural) of PEI/Silicone rubber nanocomposites

Sample codes	Tensile strength (MPa)	Tensile Modulus (MPa)	Elongation at break (%)	Flexural Strength (MPa)
A	42.7	956	6.36	103.19
B	50.06	1149	5.58	112.85
C	69.6	1365	3.41	120.66
D	45.08	1045	5.06	109.45

#### 4.2 Thermo gravimetric analysis

Polymers are often exposed to high temperature during processing or use. Thus, thermal stability is among the most important properties of polymers for a wide range of applications. The thermal stability of polymers and polymer materials are usually defined as the temperature beginning of decomposition of the samples at a programmed heating rate. Thermal stability is among the most valuable properties of polymer for a wide range of applications. The thermal stability of polymer and polymeric material is defined by the specific temperature or temperature-time limit in which the material can be used without excessive mass loss. [21, 22].

The TGA curves of PEI/silicone rubber reinforced with modified MMT are depicted in Fig. 1 and TGA results are summarized in Table 3. From the Table 3 it is obvious that the 5 % degradation of the nanocomposites containing 2 phr MMT occurred around 512°C which is 33 °C higher than that of pure blend system, with the incorporation of MMT a large number of the restricted sites for the polymer matrix are generated which constrain the chain mobility and reduces the thermal stability of C-C bond [23]. 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 MMT, the large number of restricted sites (for the polymer chain mobility) will be more in nanocomposites having 2 phr loading of MMT in polymer matrix. TGA results also demonstrate that there is minimum weight loss (40.1 %) at 2 phr loading of MMT in polymer matrix. Probably due to this reason the thermal stability of PEI/silicone rubber reinforced with 2 phr MMT is higher than virgin polymer blend system.

Table 3. Thermal stability of binary and ternary blends system.

Sample Codes	5 % Weight loss Temperature (°c)	10 % Weight loss Temperature (°c)	Loss of weight (Percentage)
A	479.34	538.04	45.715
B	485.18	544.12	45.292
C	512.26	570.34	40.099
D	464.12	518.20	48.251

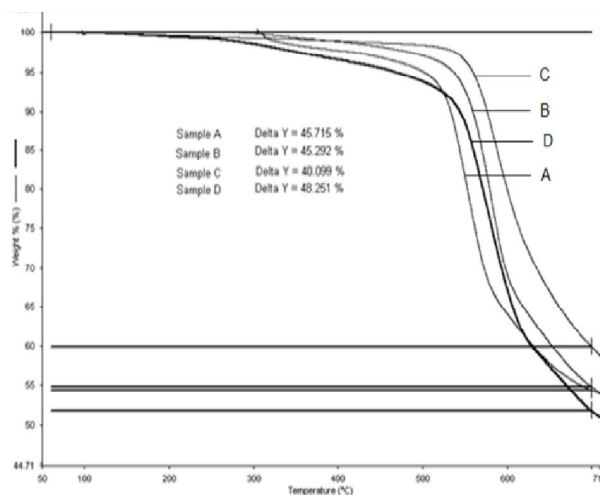


Figure 1: TGA thermograph for various loadings of modified MMT in PEI/silicone rubber matrix.

#### 4.3 Fourier transform infrared spectroscopy

FTIR spectra for the pure PEI, silicone rubber and binary blend of PEI/silicone rubber are given in Fig.2. The spectra reveals that there is a peak at 1721  $\text{cm}^{-1}$  (for pure PEI) which corresponds to C=O peak of imide group. This peak has shifted to the higher value at (1775  $\text{cm}^{-1}$ ) in the PEI/silicone rubber blend, suggesting that there is a possible interaction between the OH of silicone rubber and C=O imide group of PEI. Silicone rubber is having a peak around 3400  $\text{cm}^{-1}$  which corresponds to the free OH group, while a new peak appeared at 3426  $\text{cm}^{-1}$  in the blend of PEI and silicone rubber, this new peak corresponds to hydrogen bonded OH.

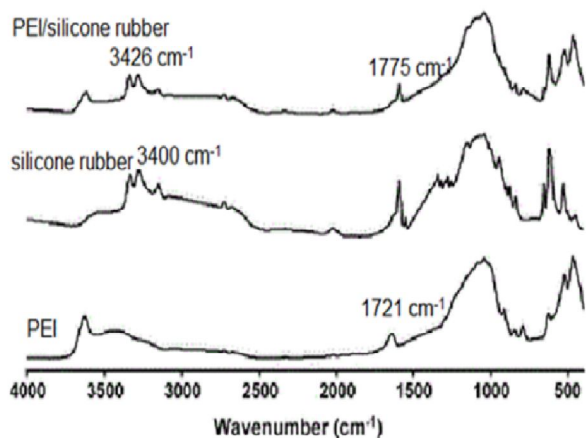


Figure 2: FTIR spectra of PEI, silicone rubber and blend of PEI/silicone rubber.

#### 4.4 X-ray Diffraction (XRD)

X-ray diffraction (XRD) pattern of PEI/silicone rubber blends with various loading of MMT nanoclay are depicted in Fig.3 and corresponding data are summarized in Table 4. It is observed that pure PEI/silicone rubber exhibits the peak at  $2\theta=41.86$  in sample A, this peak shifted to slightly higher side  $2\theta=42.03$  in sample B, and this can be attributed to higher packing density of polyetherimide molecule in the developed nanocomposites. From Table 4, it is also evident that sample 'C' has highest  $2\theta$  value, which is indicative of the fact that this composition of nanocomposites has highest packing density. It is also clear from Table 4 maximum peak height is produced in the 2 phr loadings of MMT blend as compared to PEI/silicone rubber blend system highlighting that the heat build-up is minimized which favours the improved damping properties and also allows better stress transfer from dispersed silicone rubber phase to matrix phase, permitting only a small part of it to strain the interface. Hence, the strong interfaces are characterized by less energy dissipation. Moreover, interplanar distance reduced with the incorporation of 2 phr loading of MMT, this attributes to the compactness of the structure in developed nanocomposites. Therefore, it is concluded that sample 'C' shows more compactness structure as compared to other samples.

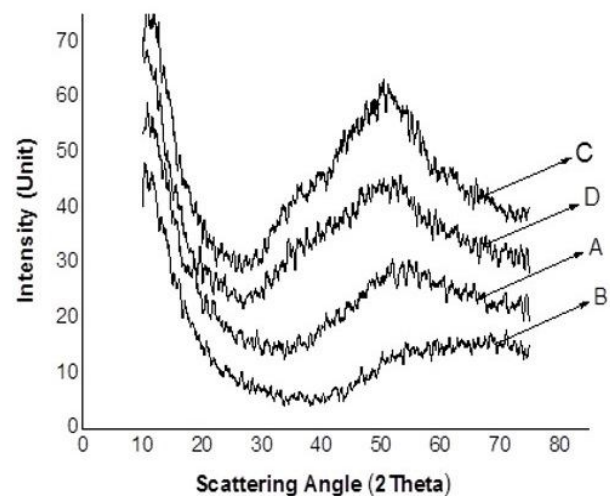


Figure 3: XRD pattern of pure PEI/silicone rubber nanocomposites at different content of MMT.

Table 4. XRD analysis results of binary and ternary blend system.

Sample codes	$2\theta$	$\text{Sin}\theta$	Peak Height	Basal spacing/d-spacing
A	41.86	0.3572	7.46	2.156
B	42.03	0.3599	6.08	2.147
C	60.24	0.5022	5.19	1.534
D	41.80	0.3567	10.91	2.153

#### 4.5 Morphological study

The cryofractured surface of the nanocomposites and pure blend systems have been studied by SEM and the images are given in the Fig.4. All the samples show two phase morphology and the hollow domains which indicate the pulled out silicone rubber phase. The difference between the four samples is the average domain size of silicone rubber. Among these blend systems sample 'C' is having the smallest average domain size followed by A, B and D. This reduction in the domain size can be attributed to the compatibilizing ability of the modified nanoclay. 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. To further examine the dispersion state of modified MMT in the polymer blend matrix, samples have been analysed at higher magnification and the images are shown in Fig 4. Agglomerations of pure MMT can be seen in the B and D sample, whereas, sample 'C' shows a better dispersion of modified MMT and less agglomeration is seen.



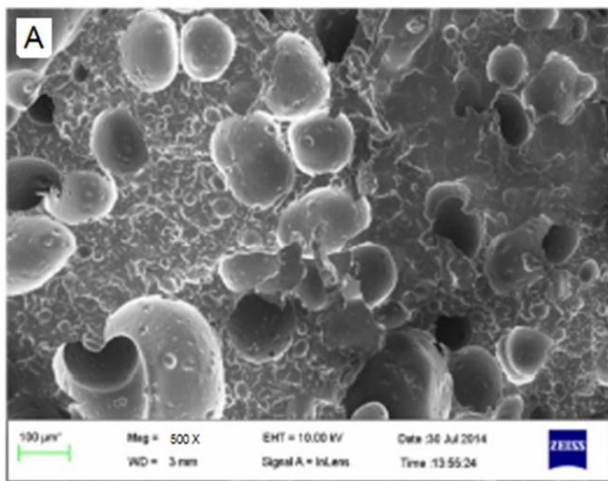


Figure 4 (a) SEM micrographs at 0 phr

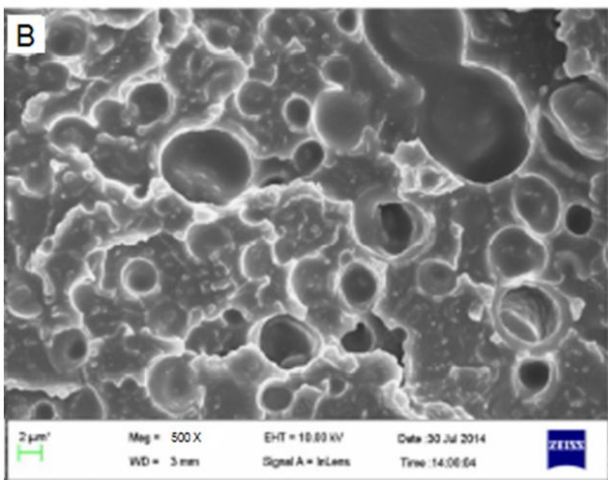


Figure 4 (b) SEM micrographs at 1 phr

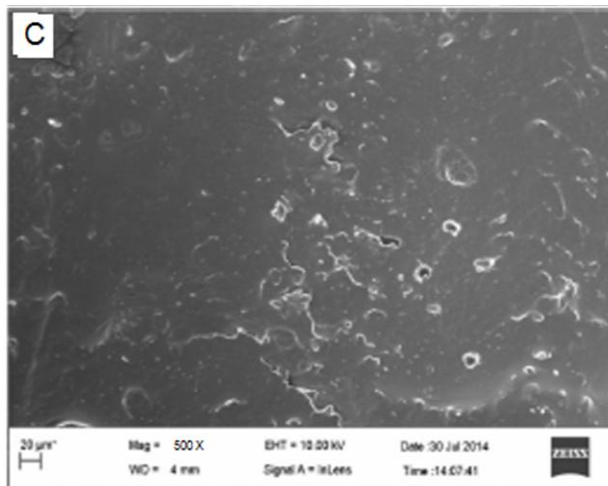


Figure 4 (c) SEM micrographs at 2 phr

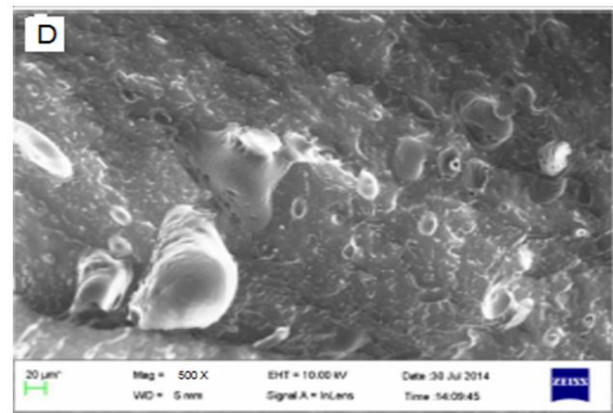


Figure 4 (d) SEM micrographs at 3 phr

## V. CONCLUSION

The nanocomposites based on PEI/silicone rubber filled with various loadings of modified MMT have been prepared in twin screw extruder by melt mixing process. It has been found that modified MMT in the polymer matrix shows the prominent effect on the performance of polymer nanocomposites, due to better dispersion of nanoclay. Better dispersion of modified MMT results in the enhancement of thermal, mechanical and morphological properties of nanocomposites when compared with pure blend system.

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