Nanotitanium Dioxide Reinforced High Performance PEI/Silicone Rubber Composites: Mechanical, Thermal and Morphological Characteristics

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ABSTRACT

The present investigation is targeted to prepare nanocomposites based on binary blends of polyetherimide (PEI)-silicone rubber incorporated with varied loadings of nanotitanium dioxide particles. Nanocomposites have been prepared by melt blending process using twin screw extruder. Thermal properties of the developed nanocomposites have been investigated with the help of thermogravimetric analyzer (TGA) and dynamic mechanical analyzer (DMA). Scanning electron microscopy (SEM) is used to analyze the morphological properties of the nanocomposites. Mechanical properties (tensile strength, tensile modulus, elongation at break, impact strength) of the nanocomposites have been evaluated by universal testing machine (UTM). Mechanical testing results reveal that there is 35% increase in tensile strength, 3% increase in tensile modulus and 41% increase in impact strength at 1 phr loading of nanotitanium into blend polymer matrix. The nanocomposite having 1 phr nano-titanium has got the highest thermal stability than the others. DMA results indicate that at 50°C nanocomposites having 1 phr nano-titanium reveals 69% increase in storage modulus as compared to pure blend system. SEM micrographs clearly indicate that the nanocomposite with 1 phr loading of nano titanium has the smallest domain size as compared to other nanocomposites .This may be due to uniform and homogeneous dispersion of 1 phr nanotitanium in polymer matrix followed by fairly good polymer filler interaction.

KEYWORDS : *PEI, Silicone rubber, DMA, SEM, Tensile properties.*

INTRODUCTION

Nowadays, a big window of opportunities has open for polymer nanocomposites just to overcome the limitations of conventional composites. The research and development of nanoscale filled polymer has been skyrocketed in recent years. The polymer nanocomposite has been exponentially growing field of research are developing the composite in last few decades and especially aiming to enhance the various properties for diversified applications both in defense and civil sectors. In the present scenario polymeric materials and their blends are extensively utilized as the matrix for the development of nanocomposites[1-8]. The industrial importance of polymer has increased exponentially in the form of nanocomposites. Nanocomposites have attracted greater attention in the past decade owing to their wide spectrum of vital applications in many areas, ranging from nano-electronics to bio-medical sciences. Nanocomposites exhibit remarkable enhancement in properties such as tensile strength, tensile modulus, impact strength, and thermal stability, glass transition temperature etc. as compared to virgin polymer or conventional composites[9-12]. Apart from this, nanocomposites are also capable to investigate the structure and dynamics of a polymer in confined environment through unique model system [13-15].

The processing of engineering polymers is very difficult so these polymers are often blended with other polymers having lower viscosity to improve their processability[16-17]. Polyetherimide (PEI) is a high performance amorphous engineering thermoplastics material with a high glass transition temperature (Tg~216 °C). It shows various properties like easy processability, a good chemical, hydraulic resistance and also excellent mechanical and thermal properties. PEI has diversified applications ranging from micro-electronics to aerospace[18]. 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 material. Silicone rubber has excellent strength and temperature resistance (-60 to 360°C). It helps to provide crushing thermal resistance and mechanical properties. It has load bearing and protective shock absorption qualities to automotive interiors[19-21]. There has been very few research report published in recent years related to polymer nanocomposites based on polyetherimide and silicone rubber [22-25]. These results indicate that impact strength and elongation at break have been highly improved in PEI/ silicon rubber blend as compare to virgin PEI but the value of other mechanical properties like tensile strength and tensile modulus have been reduced. These tensile properties have been improved by the reinforcement of nanofillers like HNT, modified, nanosilica.

Now the researchers are paying a great interest in developing nanocomposites reinforced with nanotitanium-di-oxide, since this nano-filler has many potential applications. Nanotitanium incorporated composite material has many significant applications such as pharmaceuticals, cosmetics or paints[26-27], drug delivery system with controlled release[28-30], solar cell[31-34], chemical sensing[35-37], luminescent materials, and photo-catalyst for water purification [38].

It is very difficult to have a uniform dispersion of nanotitanium oxide in polymer matrices. This is because of poor polymer- filler interaction. Therefore, it is essential to modify the inorganic phase i.e. titanium-di-oxide modification can be performed by various methods. A better way is to modify the inorganic phase by sol-gel-process. This process provides the design crystal structure[39].

In the present investigation, a binary blend of polyether imide/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 nanotitanium-di-oxide at various loadings. The effect of nano-titanium oxide loadings on the performance of developed nanocomposites have been characterized by using various sophisticated analytical techniques viz. TGA, DMA, SEM etc.

EXPERIMENTAL

Materials

PEI (Ultem 1000) having density of 1.27 g /cm^3 at 25°C and glass transition temperature (Tg~ 216°C) has been supplied by Sabic Innovative Plastic (USA). Silicone rubber, VMQ (Silastic NPC-40) having the density of 1.11 g /cm^3 has been supplied by Dow Corning (USA). The nanoparticle of TiO$_2$ for the research work has been purchased from IREL Pvt. Ltd, Mumbai, India, having molecular weight 79.865 g/mol, density 4.24 g/cm^3 and particle size is ~50 nm.

Nanocomposites Preparation

Prior to compounding, the pellet of polyetherimide has been dried under vacuum at 80°C in electric blast oven for 12 hours. After pre drying the PEI, silicone rubber has been mixed in 85:15 wt. % (sample code PST 0) and nanotitanium also mixed in 0.5 (PST 1), 1 (PST 2) and 2 (PST 3) phr. The uniform mixture of PEI/Silicone rubber/nanotitanium 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 analysing the mechanical properties are prepared by high performance injection moulding machine (Model - 9057, 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 specimens are initially conditioned prior to testing at 23±20°C and 50± 5% RH for 24 hrs.

TESTING AND CHARACTERIZATION

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 tests are evaluated according to standard ASTM D638 using 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 at room temperature.

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°C/min under nitrogen atmosphere from 50 to 750°C.

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 tan δ 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.

Morphological Study

The surface morphology of the tensile fractured surface has been studied 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.

RESULTS AND DISCUSSION

Morphological Analysis

Morphological study is aimed to study the tensile fractured surface of the nanocomposites and the virgin blend system with the help of SEM. SEM micrographs are demonstrated in the Figure 1(a-d). It is obvious from the Figure 1(a) that pure blend system shows the two phase morphology since PEI and silicone rubber are immiscible in nature. Average domain size is larger in the pure blend system as compared to nano titanium filled PEI/silicon rubber blend system. Figure 1(b-d) reveals that there is reduction in average domain size of nano-composites due to reinforcement nano titanium dioxide (nanofiller). Maximum reduction in average domain size has been achieved at 1 phr loading of nano titanium in polymer matrices. This may be attributed to good
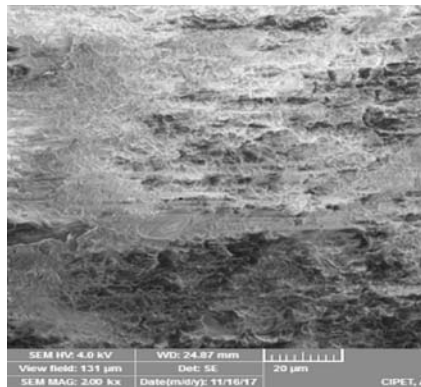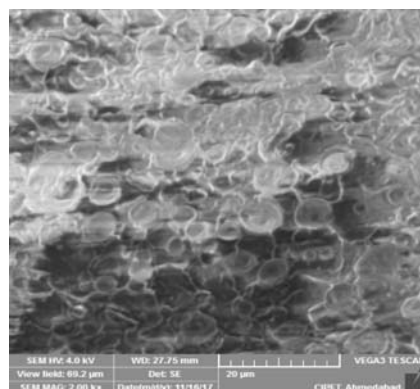

(a) SEM of PST 0
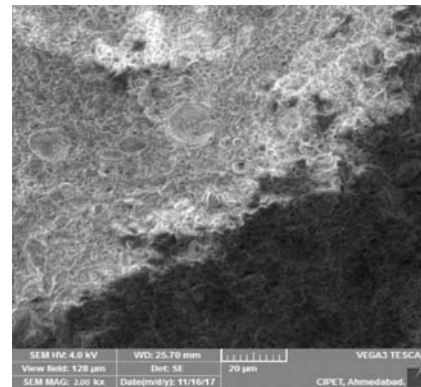
(b) SEM of PST 1
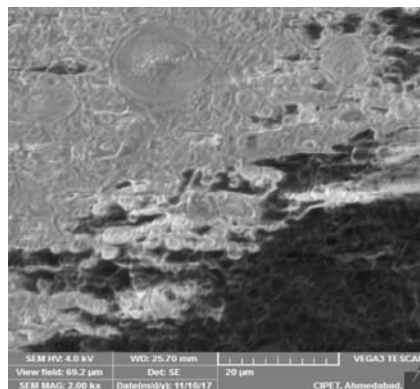
(c) SEM of PST 2

(d) SEM of PST 3

Fig.1. SEM micrographs of PEI/silicone rubber blend with varied loadings of nanotitanium dioxide

interfacial adhesion and superior polymer- filler interaction. In other words, we can say that the nanocomposites having 1 phr content of nano titanium has a finer dispersion as compared to other nanocomposites.

Thermo Gravimetric Analysis

Thermal stability of the nanocomposites has been studied with the help of TGA. Thermograms of PEI/ Silicon rubber blend with varied loadings of nanotitanium are shown in Figure 2. The results are given in Table 1. All the nanocomposites demonstrate higher thermal stability as compared to virgin blend system. It is obvious from the thermogram that onset degradation temperature of pure blend system is 410°C which increases to 542°C with the incorporation of 1 phr nanotitanium. This increase in degradation temperature at 1 phr can be explained by saying that it reduces the chain mobility of polymer matrix by imposing large number of restricted site which minimize the thermal vibration of C-C bond [25]. Thus, we can say that nanocomposites are in grave need of more thermal energy for the degradation of the polymer matrix which is responsible for the enhancement of thermal stability of nanocomposites.

TABLE 1. TGA results of PEI/silicone rubber blend with varied loadings of nanotitanium dioxide

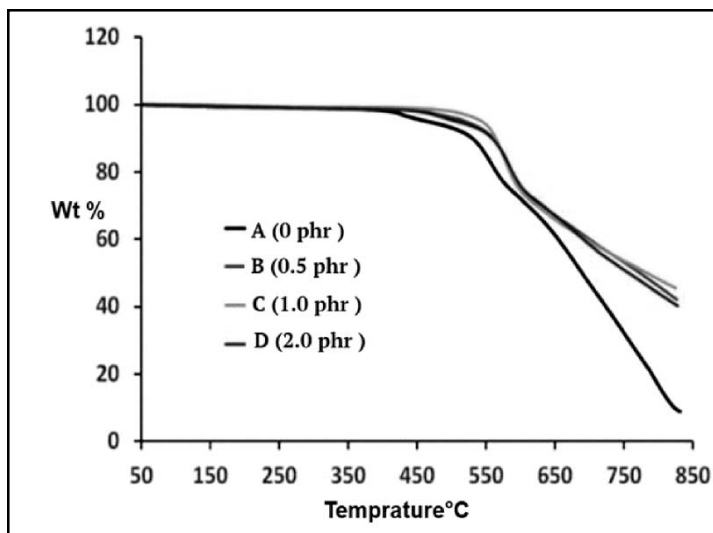| Sample Codes	Onset Degradation Temperature (°C)	Loss of Wt. (%)
PST 0	410°C	99%
PST 1	465°C	98.5%
PST 2	542°C	98%
PST 3	510°C	98.2%

Fig. 2. TGA thermogram of PEI/ Silicon Rubber blend with varied loadings of nanotitanium dioxide

Mechanical Properties

Tensile strength and tensile modulus

Tensile properties are given in Table 2. Mechanical properties results clearly indicate that there is remarkable increase in tensile strength and modulus and elongation at break of developed nanocomposites shown in Figure 3.

TABLE 2. Mechanical properties of PEI/silicone rubber blend with varied loadings of nanotitaniumdioxide.

Sample Codes	Tensile Strength (MPa)	Elongation at break (%)	Tensile Modulus (MPa)	Impact strength (Izod) J/M
PST 0	38.50	5.38	730.90	65.4716
PST 1	56.82	9.57	740.97	103.3556
PST 2	59.27	9.60	751.0	110.3912
PST 3	49.45	9.41	698.55	107.8067

The maximum improvement is obtained at 1 phr nanotitanium loading in polymer matrix as compared to unfilled PEI/Silicone rubber. Incorporation of nanotitanium gives rise to increase in the tensile strength of developed nanocomposite by about 35%. Similarly there is increase in tensile modulus by about 3%. This enhancement in tensile strength and modulus may be because of stress transfer from polymer matrix to nanofiller. The degree of dispersion of nano titanium over the entire surface of polymer matrices provides fairly good interaction between nanofiller and polymer matrix. This is the reason that the adequate effective stress transfer between the nanofiller and polymer matrix is possible. It is an established fact that the slippage of the filler polymer interface will decrease the stress transfer efficiency due to large strain, which may affect the mechanical properties of the nanocomposites with the strain. In case of 1 phr loading of nano titanium, nanofiller reduce the slippage in the polymer filler interface (under tensile strain) that might be the reason for the enhancement of tensile properties of the developed nanocomposites.

Nanocomposites incorporated with nanotitanium dioxide have not been shown remarkable change in the value of elongation at break because of the rigid thermoplastic nature of polyether imide (PEI) in the blends. The effect of varied loadings on the impact strength of the developed nanocomposites has been depicted in Table 2 and Figure 3. It can be observed that the impact strength of the developed nanocomposites increases with increase in nano titanium content. Maximum increase in impact strength at 1 phr loading is 41%. The decrease in impact strength at higher nano titanium loading (2 phr) is due to the fact that the increase in nano titanium content leads to the formation of aggregates, which act as a stress concentration that gives rise to brittle failure. Increase in impact strength may be ascribed to the intrinsic toughening properties of nanotitanium. An excellent interfacial interaction between the polymer matrix and nanofiller may also be another reason for the improvement of impact strength with high absorption energy during impact deformation. Maximum mechanical properties have been achieved at 1 phr loading of nanotitanium in developed nanocomposites.
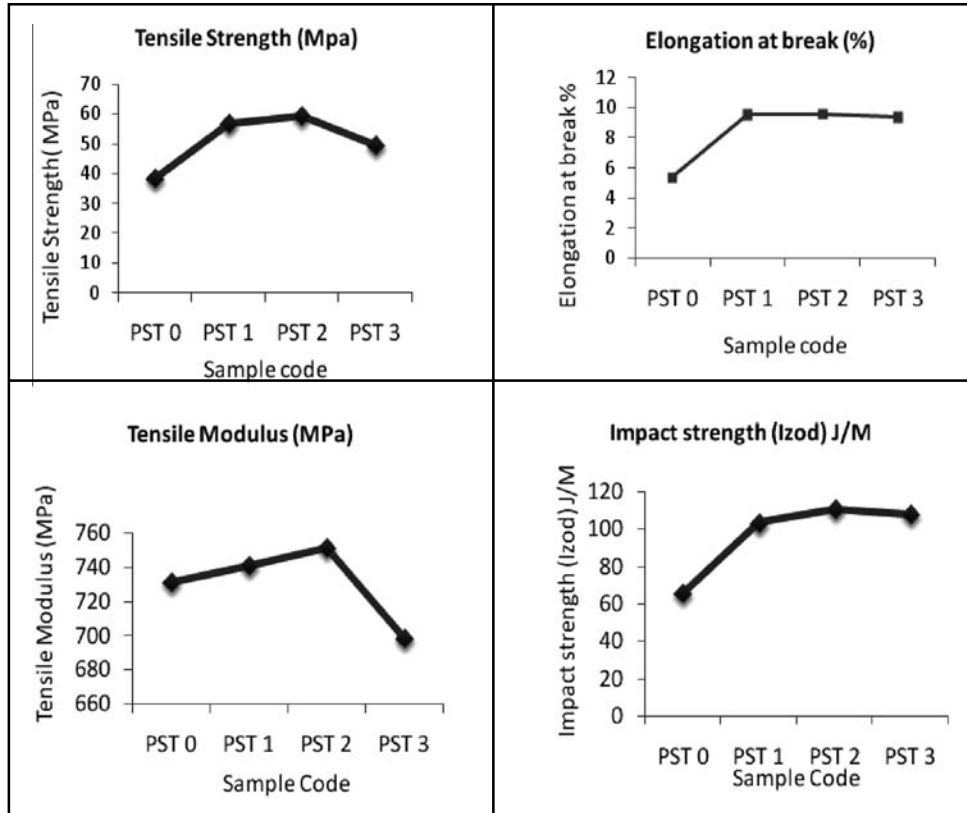
Fig. 3. Mechanical Properties of PEI/ Silicon Rubber blend with varied loadings of nanotitanium dioxide

Dynamic Mechanical Analysis (DMA)

Storage Modulus of blend and nanocomposites as a function of temperature is demonstrated in Figure 4(a). It is evident from the thermograms that there is significant improvement in storage modulus of the nanocomposites due to induction of nanotitanium as compared to the blend system. The increasing storage modulus may be attributed to the effective stress transfer from the polymer matrix to the nanofiller. The

Table 3. DMA analysis results of PEI/silicone rubber blend with varied loadings of nanotitanium

Sample code	Storage modulus (MPa)				Glass Transition Temperature (°C)
	50 (°C)	100 (°C)	150 (°C)	200 (°C)	DMA
PST 0	3550	4864	4870	4862	211.5
PST 1	5991	5452	5458	5269	209.3
PST 2	6910	6612	6130	5782	214.2
PST 3	6909	6202	5785	5462	210.5

storage modulus of nanocomposites at various temperatures is given in Table 3.

At 50 °C PST 1 reveals 69% increase in storage modulus as compared to PST 0 whereas, PST 2 shows 97% at 200 °C. The increase in storage modulus is higher than the pure blend system. It has been observed that the storage modulus for the pure blend system is lowest compared to nanocomposites. The enhancement in storage modulus into higher side for the nano titanium incorporated nanocomposites may be attributed to the decreasing polymer chain mobility. It can also be stated that nanotitanium acts as crosslinking site in between the silicone rubber chains and PEI matrix which felicitate in the enhancement of stiffness of the

nanocomposite. Figure 4(b) demonstrates the thermogram of Tan δ vs. temperature for the developed nanocomposites. It is evident from the thermogram that glass transition temperature (Tg) moves to the higher value with the incorporation of nanotitanium. The virgin blend system shows glass transition temperature at 211.5°C which increases to 214.2 °C for a nanocomposites having 1phr nanotitanium in polymer matrix. The improvement in glass transition temperature can be attributed to the immobilized effect of nano titanium at high temperature. In other words, we can say that enhancement in Tg value may be due to the restricted movement of the polymer chains by the nano titanium.
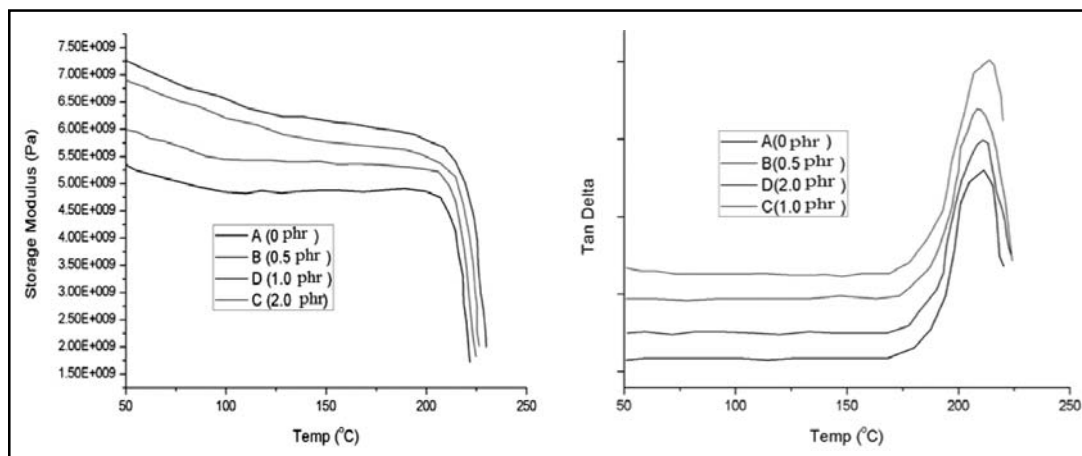

Fig. 4. (a) Storage modulus vs temperature of PEI/ silicone rubber blend with varied loadings of nanotitanium dioxide

Fig. 4. (b) Tan δ vs temperature of PEI/silicone rubber blend with varied loadings of nanotitanium dioxide

CONCLUSION

Nanocomposites comprising of PEI/ silicon rubber blend system incorporated with nanotitanium have been fabricated with the help of melt blending process using twin screw extruder. Mechanical properties of the developed nanocomposites have been evaluated by universal testing machine (UTM). It is evident that due to incorporation of nanotitanium, enhancement in tensile strength

and modulus have been found to be 35% and 3% respectively. TGA results show that the nanocomposites having 1 phr nanotitanium has got the highest thermal stability that the others. Morphological properties of the nanocomposites has been visualized through SEM. SEM micrographs clearly indicate that the nanocomposite with 1 phr loading of nano titanium has the smallest domain size compare to other nanocomposites. This infers that nanotitanium has got strong efficacy at 1 phr loading.

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