

Effect of Nano Fillers on Polyphosphazene Elastomer under the influence of Temperature and Radiation: A Comparative Study

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Abstract:

A selected thermoplastic polyphosphazene elastomer containing two substituents: trifluoroethoxy group and allylphenoxy group had been both heat and radiation treated in presence of nano-silica and nano sized titanium dioxide (TiO₂). Characterization of the heat treated materials were performed by Fourier Transform Infrared Spectroscopy, Field Emission Scanning Electron Microscopy, Dynamic Mechanical Thermal Analysis, and Thermogravimetric Analysis, to obtain information about the possible interactions and dispersion of nano sized fillers on the thermoplastic polyphosphazene matrix. The results were then compared with those obtained from the characterizations of radiation influenced samples. A weak interaction between the nano-fillers and the thermoplastic elastomeric matrix was observed by the FTIR analysis of the samples. FESEM analysis indicated the dispersion morphology of the nano-fillers in the polyphosphazene matrix. Radiation treated samples showed superior storage moduli compared to the storage moduli of the heat treated counterparts. Filled polyphosphazene nano-composites showed increased thermal stability compared to the virgin elastomer.

Keywords: Polyphosphazene; thermoplastic; nano-silica; titanium dioxide; nano-composites; radiation.

1. Introduction:

Polyphosphazenes are one of the most diverse types of polymers containing a long backbone chain of alternating nitrogen and phosphorus atoms including two inorganic, organic or organo-metallic side groups attached to each of the phosphorus atoms. The chain flexibility is mainly provided by the alternating nitrogen-phosphorus backbone while the substituted side groups contributes in tailoring special properties for specific applications like high performance elastomers, biomedical materials, flame retardants, ionic conductors, electronic materials and optical applications. The

side groups also contribute in determining the flexibility of the overall chain as well as chemical and thermal stability. Among the versatile side groups, if only one type of fluoroalkoxy side group is present then the polymer is a non-burning, hydrophobic, nano-crystalline, film and fiber forming material. But if two or more fluoroalkoxy side groups are

present along the same polymer chain, the material becomes a low-glass transition, hydrophobic, solvent, oil, and hydraulic fluid-resistant elastomer. Similarly, mixed-substituent aryloxy derivatives are used commercially as non-burning, low-smoke-forming elastomers for thermal and electrical insulation. These types of elastomeric polymers are synthesized mainly through three different techniques like the ring-opening polymerization followed by macromolecular substitution approach, the cyclic trimer substitution followed by ring-opening polymerization approach and the condensation technique [1-4].

Crosslinking of an elastomeric polymer renders improved thermal, mechanical, physico-chemical properties and hence enhances the polymer's utilization in particular applications. The crosslinking technique engages some parameters such as radiation, temperature, external reactants, etc. through which the reactivity and reaction rate of the specific side groups can be controlled towards the network formation of the sought after product. To obtain a desired material directly, either a very high molecular weight polymer or a cross-linkable oligomer has to be used to accomplish the required properties. If the desired performances are not reached then a further step to post crosslinking would be required [5]. According to knowledge the elementary chemical agents employed for crosslinking are peroxides for saturated systems and sulphur for unsaturated structures, followed by post-mixing thermal treatment. Huang et al. implemented peroxide agents for crosslinking of the specific group containing polyphosphazene elastomer through free radical methodology [6, 7]. Guo et al. discussed on the features of sulfonated and cross-linked

membranes of polyphosphazene [8] where as Song et al. construed the properties of sulfonated polyphosphazene by introduction of self cross-linkable group [9]. Allcock et al. focused on synthesizing of photo cross-linkable chalconebearing polyphosphazenes [10].

The conventional method for crosslinking of elastomers is incorporating various types of fillers, plasticizers, accelerators, stabilizers, etc., and finally the crosslinking agents to upgrade the desired properties of the raw polymer [11]. The effects of fillers on the curing kinetics, network structure, thermal and mechanical properties of elastomers are of great interest because fillers can be used very efficiently to enhance the physico-chemical properties and concurrently the production cost can also be minimized profoundly [12, 13]. Among the assorted types of fillers, the contributions of nano sized silica, nano sized titanium dioxide (TiO_2) and their modified versions towards the intensification of high level technical, mechanical and usage properties for respective elastomeric polymers apart from the crosslinking agents, has been the area of investigation by various researchers. Donnet carried out a comparative study on the reinforcing properties of carbon black and nano-silica for elastomeric compounds [14]. Jarnthong et al. discussed on the properties of modified nano silica reinforced epoxidized natural rubber [15]. Chen et al. investigated the properties of silica nano-particles in association with a curing agent by direct inclusion into the elastomer matrix [16]. The properties of the nano-silica filled latex compound were studied by Meleth et al. for the manufacture of surgical gloves [17]. Besides the nano-silica a variety of nonblack fillers are used in the rubber industry to improve and modify the physical properties of elastomeric materials. Fillers like titanium dioxide (TiO_2) are used to impart preferred physical properties as well as appearance of the concerned compound. The mechanical and thermo physical properties of TiO_2 -filled chlorobutyl rubber composites along with the vulcanizing agents were investigated by Saritha et al. [18]. According to Lin et al. apart from the environmental aspects the nano sized TiO_2 have better photo-activity than the micro sized TiO_2 powders [19]. Elastomer compounding is related to a fixed composition i.e., a type of mixing with specific formulation. After the compounding process, the final step is subjecting the prepared material to proper initiation, propagation and termination of crosslinking reaction under certain techniques such as temperature, radiation, etc.

Compared to the prevalent method of elastomer curing which engages post-compounding thermal treatment the radiation process does not necessarily needs to compound crosslinking additives. Hence, the processing of the materials can be done

at favourable temperatures and also the compounding cost of materials for the irradiation process is cheaper than those of the chemical methods which need expensive crosslinking agents [20]. In the past few years, the technique of radiation crosslinking of thermoplastic elastomer (TPE) sector had emerged with various interesting new products and the speculations are that this area will be growing significantly. However, the inorganic backbone chains of polyphosphazene elastomers are stable towards the irradiation of Gamma-rays, X-rays, and also transparent to visible and near UV light. The use of radiation for crosslinking of the polyphosphazenes is also advantageous as the degree of crosslinking can be controlled within fine limits of the radiation dose. The polymer does not bear chemically reactive side groups before crosslinking and can thus be handled without special precautions. Moreover, there are no impurities other than hydrogen gas (formed by hydrogen radical combination), which may be introduced into the system and this is important when the crosslinked system forms part of a conductive material [21, 22]. Furthermore, compared to the polymers containing rigid chain which requires high temperature for crosslinking, the flexible chain containing polymers like polyphosphazene in our study can easily be influenced by radiation to the reactive radical recombination and hence satisfy crosslinking of the thermoplastic elastomeric matrix. Subsequently, we tried to study the properties of thermoplastic polyphosphazene in presence of nano sized silica and nano sized titanium dioxide, and subjecting the blends to the influence of both temperature and radiation.

2. Experimental:

2.1. Materials Preparation

Thermoplastic polyphosphazene for our study was synthesized in DMSRDE-Kanpur, INDIA. AEROSIL 130, a nano-silica with particle size of around 12 nm was supplied by EVONIK INDUSTRIES, GERMANY. Rutile TiO_2 nano-particles with average particle size of around 14 nm were procured from Reinste Nano Ventures Pvt. Ltd., INDIA. Two materials with different unsaturations (3% and 5%) were prepared. One of the thermoplastic elastomers contains 97% trifluoroethoxy (OCH_2CF_3) groups along with 3% allylphenoxy ($\text{OC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$) groups and the other contains 95% trifluoroethoxy along with 5% allylphenoxy groups. The empirical structure of the thermoplastic polyphosphazene is shown in Figure 1.

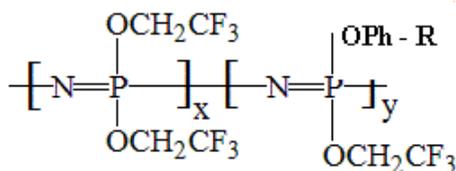


Figure 1: Empirical Structure of Thermoplastic Polyphosphazene (R = allyl vinyl group).

2.2. Materials compounding

The thermoplastic polyphosphazene was compounded with nano-silica and nano sized titanium dioxide in an open two roll mill at room temperature. The speed ratio of front rotor to back rotor was 1:1.4. The formulations of the prepared composites are shown in Table 1. The heat treated polyphosphazene having an unsaturation of 3% by molecular weight and containing 10% nano-silica by weight have been coded as TM-3PZ-10Ns and its radiation treated part is coded as TM-3PZ-10Ns-XL. Similarly, the heat treated matrix material of 5% unsaturation by molecular weight and containing 8% by weight of nano-silica as well as nano sized titanium dioxide have been coded as TM-5PZ-8Ns and TM-5PZ-8Ti respectively. The radiation treated part of the 5% unsaturated systems are coded as TM-5PZ-8Ns-XL and TM-5PZ-8Ti-XL respectively. The weight percentage for addition of the above fillers was calculated on the total weight of the raw sample which was compounded. Based on the observed results, the nano sized TiO₂ was incorporated in the thermoplastic polyphosphazene containing only 5% of unsaturation.

The samples for heat treatment were compression moulded at a temperature of 125 degree Celsius. The samples for radiation influence having an average thickness of 2 mm were prepared by adjusting the nip gap of the open two roll mill. The electron beam cross-linked samples were treated with a dose of 200 kilogray (1kGy = 1kilorads [23]) in 5 steps (40 kGy per step) for TM-3PZ-10Ns-XL and 160 kilogray in 4 steps (40 kGy per step) for both TM-5PZ-8Ns-XL as well as TM-5PZ-8Ti-XL.

Sample Code	Nano-silica (Weight %)	NanoTitanium Dioxide (Weight %)
TM-3PZ-10Ns	10%	--
TM-3PZ-10Ns-XL	10%	--
TM-5PZ-8Ns	8%	--
TM-5PZ-8Ns-XL	8%	--
TM-5PZ-8Ti	--	8%
TM-5PZ-8Ti-XL	--	8%

Table 1: Formulations of the prepared nano-composites of Thermoplastic Polyphosphazene.

3. Results and Discussions:

3.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis of the nano-composites was done by using a NEXUS 870 FTIR (Thermo Nicolet) to investigate the possible interaction between the nano sized fillers and the thermoplastic polyphosphazene.

FTIR spectrums of the samples at absorbance mode are shown in Figure 2. The characteristic peaks at 1287 cm⁻¹ and 1609 cm⁻¹ are attributed to the stretching of C—F in alkyl halide groups and stretching of C=C in allyl groups of the thermoplastic polyphosphazene respectively. Moreover, the characteristic peaks at 1494 cm⁻¹ and 2965 cm⁻¹ represent the C—H bending and stretching of alkanes respectively. The peaks at 3450 cm⁻¹ and 1650 cm⁻¹ are due to the stretching vibration of the O—H group and molecular H₂O respectively. The peak at 3450 cm⁻¹ is attributed to the O—H stretching vibration of Si—OH while the peak at around 1100 cm⁻¹ is assigned to the Si—O stretching vibration in Figure 2(a). The peak at 3450 cm⁻¹ (O—H stretching) slightly shifted towards lower frequency side for both the heat treated and radiation cross-linked nano-composites which may be due to weak interaction between —OH groups of the nanofiller and —F groups of the matrix. In Figure 2(b), Ti—O—Ti bonds appeared in the range of 400–600 cm⁻¹ and the peak at 552 cm⁻¹ substantiates the presence of the rutile nano filler in the composites based upon thermoplastic polyphosphazene.

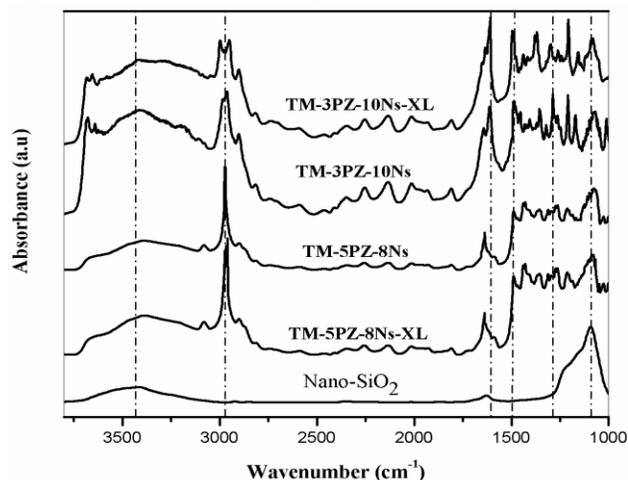


Figure 2(a): Fourier Transform Infrared Spectroscopy of Polyphosphazene with nano-silica.

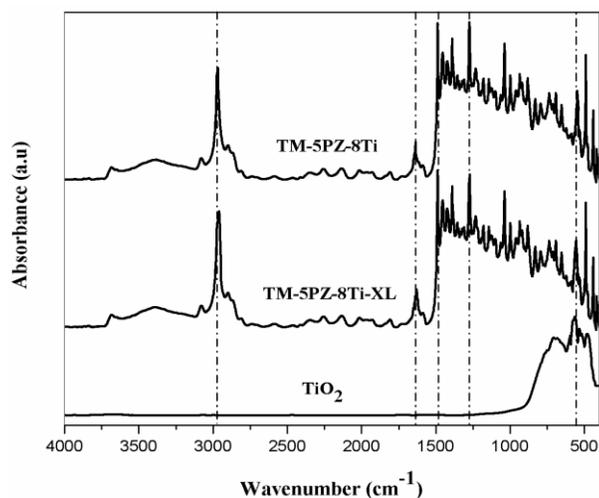


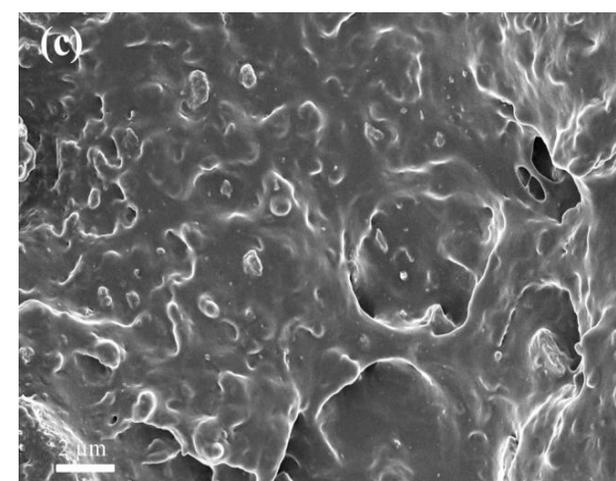
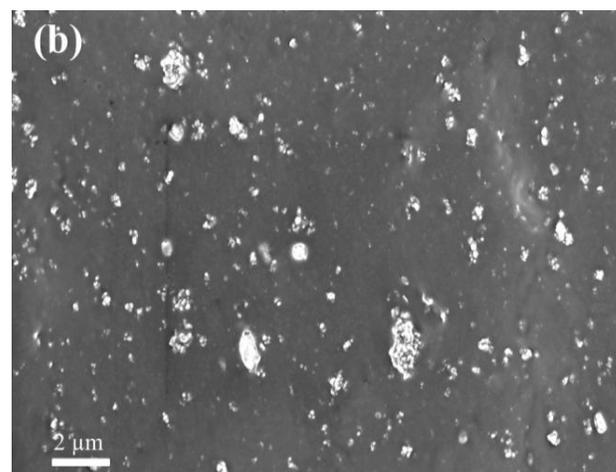
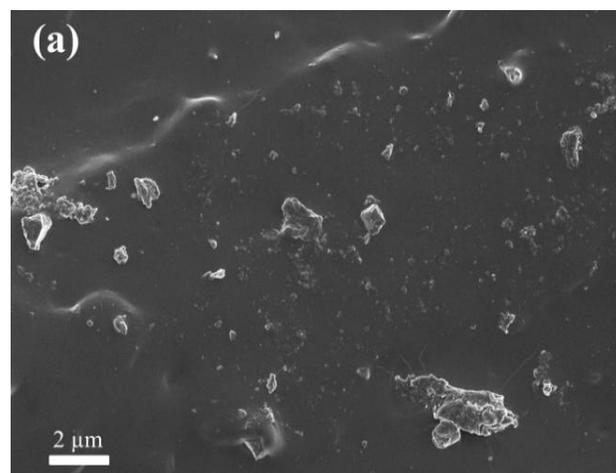
Figure 2(b): Fourier Transform Infrared Spectroscopy of Polyphosphazene with nano-TiO₂.

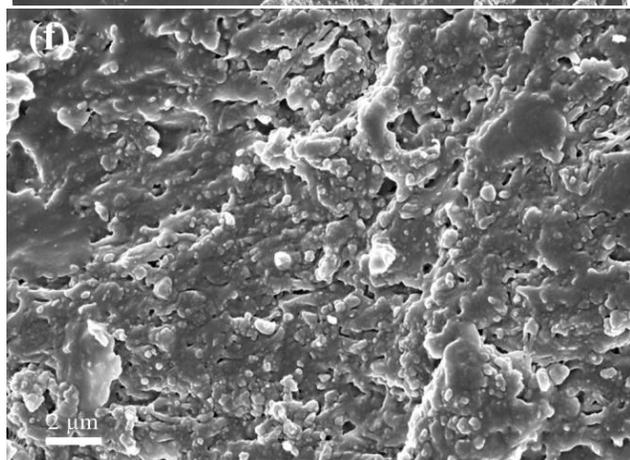
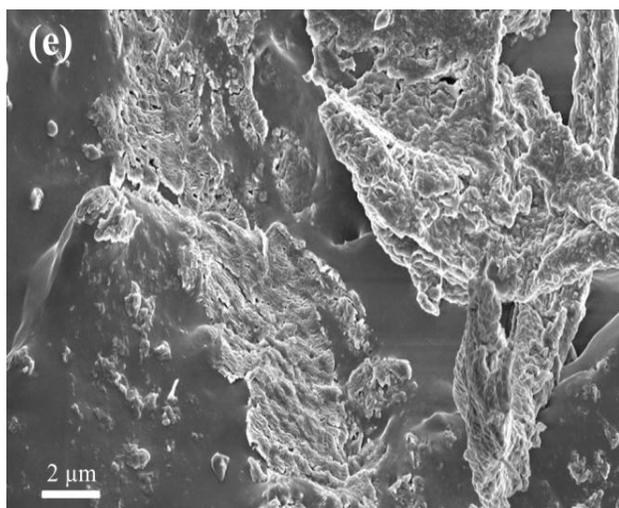
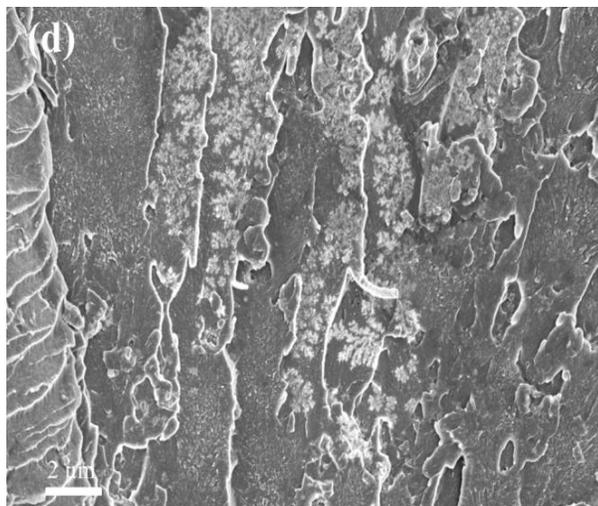
3.2. Field Emission Scanning Electron Microscopy (FESEM)

A Carl Zeiss-SUPRA™ 40 FESEM with an accelerating voltage of 5 kV was employed to observe the morphology of the cryogenically fractured nano-composites. A thin layer of gold was sputtered on the fractured surface of the specimens for electrical conductivity.

The surface morphology of the cryogenically fractured thermoplastic polyphosphazene nano-composites are shown in Figure 3. The dispersion of nano-silica in the polyphosphazene with 3% unsaturation is less than those of the 5% unsaturated samples. As shown in Figure 3(a), the nano-silica formed agglomerated structure in the matrix (TM-3PZ-10Ns). Figure 3(b) shows better dispersion of nano-silica for TM-3PZ-10Ns-XL as compared to the heat treated part of same composition. A rough surface can be observed for TM-5PZ-10Ns accompanied with a good dispersion of nano-silica as shown in Figure 3(c). The cryogenically fractured surface of TM-5PZ-10Ns-XL (Figure 3d) shows change in the crack propagation depending on the orientation of nano-silica in the matrix. Here, the fillers are highly dispersed and the dense roughness can be attributed to better crosslinking of the nano-composite. Figure 3(e) shows the morphology of heat treated nano-TiO₂ filled composite based upon thermoplastic polyphosphazene (TM-5PZ-8Ti). Here, the dispersion of nano sized TiO₂ is better than the polyphosphazene with 10 weight % nano-silica and the surface roughness is prominent. Figure 3(f) shows the morphology of TM-5PZ-10Ti-XL composite. The radiation crosslinked TM-5PZ-10Ti-XL composite exhibits more rough and tortuous surface than the heat treated composite of the same composition. Here, the change in crack

propagation is irregular depending on the orientation of the nano sized filler as compared to TM-5PZ-10Ns-XL composite.





Energy Dispersive X-Ray Spectroscopy (EDS) of both the heat treated and the radiation influenced thermoplastic Polyphosphazene samples are represented by Figure 4. EDS is one of the techniques by which the constituent elements of a compound can be identified. The presence of nano sized fillers in the polyphosphazene matrix is confirmed by the EDS images and they are ordered according to the nomenclature of Table 1.

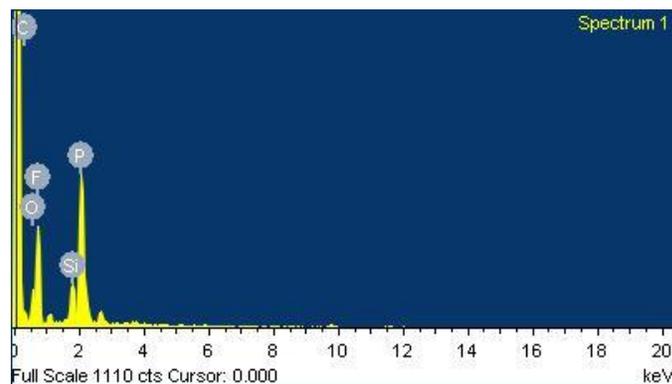
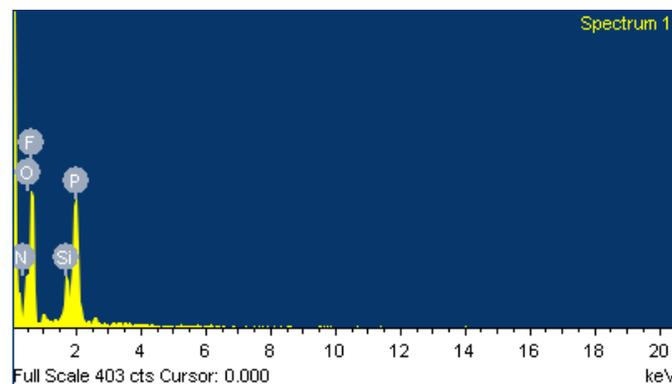
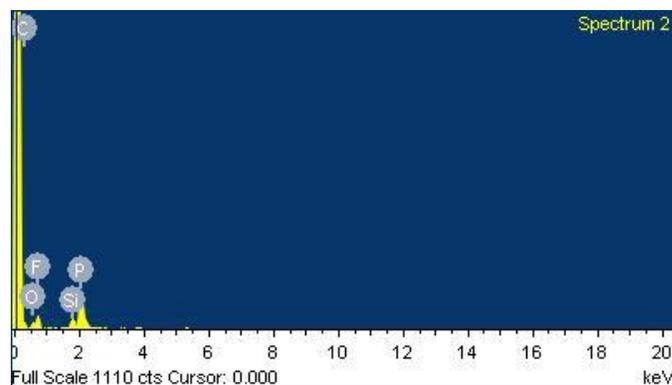


Figure 3: FESEM images of the Thermoplastic Polyphosphazene nano-composites.

EDS Study

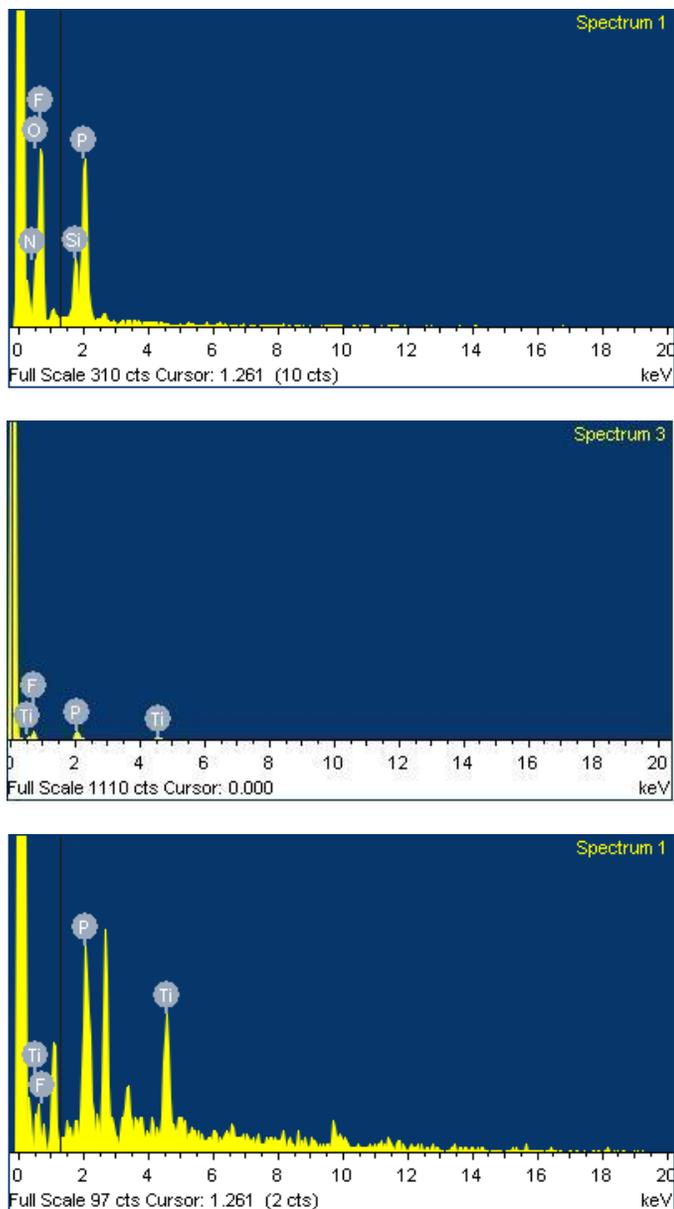


Figure 4: Energy Dispersive X-Ray Spectroscopy of the Thermoplastic Polyphosphazene nano-composites.

3.3. Dynamic Mechanical Thermal Analysis (DMTA)

The viscoelastic behavior of polymeric materials can be studied and characterized by the technique of Dynamic Mechanical Thermal Analysis. The storage modulus (E') of the prepared samples were measured by using TA Instrument's DMA 2980 model in single cantilever mode at constant frequency of 1 Hz and a strain of 0.1%. The temperature ranges from -75°C to 75°C and the heating rate was of $3^{\circ}\text{C}/\text{min}$.

The temperature dependent dynamic storage modulus (E') is represented by the Figure 5(a). The storage moduli of both the samples containing 8% nano-silica are higher than the samples containing 10% nano-silica. With the increased loading of nano-silica some agglomeration may have formed in the matrix and hence, due to poor dispersion of fillers, the storage moduli of the respective samples are lowered. Radiation cross-linked unsaturated (3%) polyphosphazene based composite containing 10% nano-silica (TM-3PZ-10Ns-XL) shows 40% increase in storage modulus than its heat treated part (TM-3PZ-10Ns), which may be due to better crosslinking by the radiation technique. The radiation cross-linked unsaturated (5%) thermoplastic polyphosphazene along with 8% nano silica (TM-5PZ-8Ns-XL) exhibits an increase of 72% in the storage modulus than the heat treated sample of same composition (TM-5PZ-8Ns) which may be due to the same reason as explained earlier. The samples containing 8% nano- TiO_2 shows lower storage modulus than its analogous composition with nano-silica. This may be due to less interaction between the nano sized TiO_2 with polyphosphazene compared to nano-silica with the matrix. Among all the samples the storage modulus of TM-5PZ-8Ns-XL is highest at 4001 MPa. The corresponding storage moduli of the nano-composites are tabulated in Table 2.

Loss $\tan \delta$ curves of the polyphosphazene nano-composites as a function of temperature can be obtained from the DMTA measurements. Figure 5(b) depicts the $\tan \delta$ curves of both the heat treated and radiation influenced samples of filled polyphosphazene. The glass transition (T_g) temperature obtained from the $\tan \delta$ peak is an useful criterion for the mobility of the elastomeric polymer chains. It is the temperature prior to segmental motion of the molecular chain of a polymer. The less the mobility of the elastomer chains, the higher the T_g . The crosslinking of the gum restricts the mobility of the chain and simultaneously the T_g become higher [24]. From the figure it was observed that the radiation crosslinked thermoplastic polyphosphazene matrix containing 8% nano-silica and TiO_2 by weight got a T_g of -33°C and -35°C respectively and the heat treated counterparts of the 5% unsaturated polyphosphazene samples showed a T_g of -36°C and -42°C respectively. This may be due to better dispersion of the nano sized fillers and increased cross linking density for the radiation influenced samples. Consequently, the heat treated and radiation influenced samples of 3% unsaturation showed a T_g of -44°C and -45°C respectively. This may be attributed to poor dispersion and agglomeration of the nano-fillers in the elastomeric matrix.

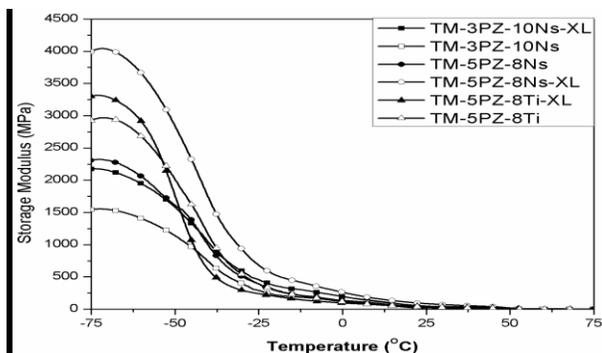


Figure 5(a): Storage Modulus curves of the Polyphosphazene nano-composites.

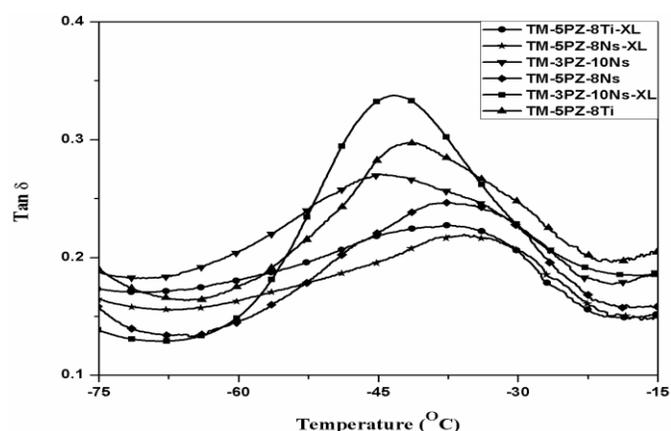


Figure 5(b): Loss tan δ curves of the Polyphosphazene nano-composites.

Sample Code	Storage Modulus (MPa)
TM-3PZ-10Ns	1551
TM-3PZ-10Ns-XL	2173
TM-5PZ-8Ns	2316
TM-5PZ-8Ns-XL	4001
TM-5PZ-8Ti	2929
TM-5PZ-8Ti-XL	3302

Table 2: Storage Modulus of the corresponding Polyphosphazene nano-composites.

3.4. Thermo-gravimetric Analysis (TGA)

Thermo-gravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. The thermo-gravimetric analysis of the nano-composites were done by using DuPont TGA 2100 thermal analyzer in the temperature

range from 100°C to 600°C with a heating rate of 10°C/min under nitrogen atmosphere.

The TGA of the thermoplastic elastomers of different compositions are represented in Figure 6. The degradation temperature of the samples at 10 and 80 weight % losses are shown in Table 3. The thermal stability of the polyphosphazene composites containing both nano-silica and nano-TiO₂ have improved compared to the pure thermoplastic elastomer (TM-PZ). The onset degradation temperatures for the composites are higher than that of pure polyphosphazene. This phenomenon may be attributed to the heat shielding effect of both nano-silica and nano sized TiO₂. The thermal stability of TM-3PZ-10Ns is lower than the radiation cross-linked part of same composition (TM-3PZ-10Ns-XL) which may be due to agglomeration of the fillers in the matrix. At 80% degradation the pure polyphosphazene shows better thermal stability than the heat treated composite (TM-3PZ-10Ns). This may be due to poor cross-linking in the heat treated sample and increased loading of the filler. The composites of unsaturated (5%) polyphosphazene containing nano-silica and nano-TiO₂ show better thermal stability. Here, the fillers are well dispersed but may be due to low density of crosslinking the heat treated samples show lower thermal stability than their radiation cross linked counterpart. Among the other samples the radiation cross linked TM-5PZ-8Ns-XL nano-composite shows the highest onset and maximum (80%) degradation temperature.

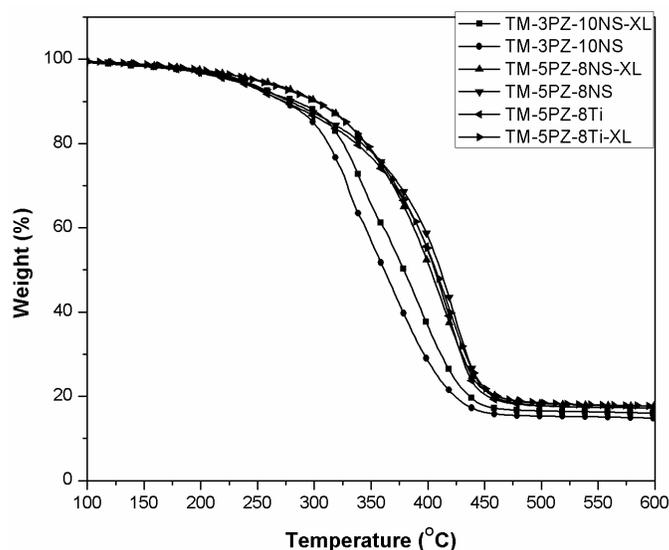


Figure 6: Thermo-gravimetric Analysis of the Thermoplastic Polyphosphazene composites.

Sample Code	Onset Degradation Temperature at 10 Weight %	Degradation Temperature at 80 Weight %
TM-3PZ-10Ns	272	424
TM-3PZ-10Ns-XL	283	436
TM-5PZ-8Ns	278	457
TM-5PZ-8Ns-XL	301	462
TM-5PZ-8Ti	273	452
TM-5PZ-8Ti-XL	299	460
TM-PZ	262	431

Table 3: Degradation temperatures of the Polyphosphazene nano-composites.

4. Conclusion:

The effect of nano fillers on the properties of thermoplastic polyphosphazene has been summarized. The FTIR study and the EDS images clearly depict the presence of nano-silica and nano-TiO₂ in the thermoplastic polyphosphazene based nano-composites. The morphology of the nano-composites observed from the FESEM images demonstrates a better dispersion of nano sized fillers in the radiation influenced samples than the heat treated ones. The Tan δ curves depicted a considerable increase in the glass transition temperature of the radiation influenced samples than their heat treated counterpart. The temperature dependent storage modulus and the thermal stability of the radiation influenced samples are increased compared to the heat treated nano-composites.

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