Particles sizes effect on the Rheological properties of Nickel doped Barium Titanate of Nano particle in IPN-polymer matrix

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Abstract

In this article,we have synthesizedcomposite material by dispersing variable amount of nanoparticles of nickel-doped $BaTiO_3$ nanoparticulate in IPN-polymer matrix.The chemical composition of the selected specimen is represented by general formula $Ba(Ti_{1-z}X_z)O_3$,where X is Ni and z=0.2 and it was prepared by sol-gel technique. For the preparation of the polymer-matrix composite materials, Polyurethane (PU) as soft phase and PEMA as hard phase were selected as matrix materials.The polymer-based composite was fabricated from casting method by dispersing the nanoparticles in the IPN matrix along with coupling agent (vinyl triethoxysilane). The results from the X-ray diffractogram show that the diameter of the particles which are doped with nickel in the specimen lie in the range of 20-60nm. SEM analysis was used to investigate the morphology of the doped $BaTiO_3$ as well as polymer composite. From the SEM observation, the nanoparticles of doped $BaTiO_3$ were found to be homogeneously dispersed in the polymer matrix. The ratio of soft/hard phase actually modifies the crosslinking density of the respective polymer in the matrix and also shows the better impact on the rheological properties. In this paper, the effect of particle size of fine doped $BaTiO_3$ powder on rheological properties of doped $BaTiO_3$/IPN-polymer composite are discussed along with the role of soft/hard phase matrix. Tensile strength, elongation at a fracture of IPN composite, and UTS strength were evaluated by Instran testing machine at room temperature at a crosshead speed of 5mm/min. Better dispersion and strong crossliking showed better hardness and tensile strength

Key Words: IPN-polymer, Nanoparticle, Rheology, Crosslinking, Polymer Composite

Introduction

Owing to its extremely high dielectric constant associated with a series of ferroelectric phase transitions, $BaTiO_3$ is commercially used in multilayer ceramic capacitors (MLCCs).In ferroelectric materials, the direction of spontaneous polarization (Ps) can be reoriented between two or more equilibrium symmetrical states by the application of an appropriate electric field. [1]. Spontaneous polarization in a ferroelectric material arises from non-centrosymmetric arrangement of ions in its unit cell. An electric dipole moment is produced by the shift of positive ions in a direction opposite to that of negative ions. A ferroelectric crystal generally has certain regions which exhibit uniform alignment of electric dipoles and the spontaneous polarization in such regions may be different from one another. Such regions with uniform polarization are called ferroelectric domains. The formation of ferroelectric domains is defined by a balance of electrostatic and strain energies with domain-wall energy. As the poling induces ferroelectric-domain switching and increases polarization, it is expected to increase average ferroelectric-domain size, which in turn should increase the residual strain in grains. Hence, BaTiO3 is used in different applications such as dynamic random-access memory, piezoelectric transducer, thermistor, and actuator.

In 2008, approximately 90% (by volume) of the capacitor market was dominated by the ceramic capacitors [2]. In contrast, various types of polymer film capacitors are predominantly used in applications requiring low dielectric absorption and loss factors over a wide temperature range [3]. An interesting result was found in various types of interpenetrating polymer network. An interpenetrating polymer network (IPN) can be defined as a mix of polymers in network form without any substantial quantities of crosslink, graft or block junctions among the several polymer chains, where at least one polymer is polymerized and/or cross linked in the immediate presence of the others [4-6]. Compared with simple mixed polymers, block polymers, and inarched polymers, IPN is characterized with interspace topology structure. The IPN technique can be a very effective method to improve the properties of existing polymer materials and to synthesize new ones with special properties. The compatibility of the two component polymers in an IPN is an important criterion in determining its physical properties. Nano-composite of the IPN polymer matrix is a special class of the materials formed by dispersing one or more kind of the particles at an almost molecular level into the matrix. The size of the dispersed phase particle in the polymer varies from the conventional level to the nanolevel. Organic-inorganic hybrid as a new class of the composite provides many outstanding mechanical, thermal, optical, electromagnetic,

and biological properties. Interpenetrating networks are formed by swelling or polymerization of cross linked polymer with a monomer and crosslinking with the latter to produce interlocked networks. Therefore, IPN shares some of the advantages of both the polymer blends and network polymers. Epoxy resins (ERs) are widely used as matrices of high-performance composite materials because of their stiffness, chemical resistance and high temperature stability. However, they are inherently brittle [7]. Polyurethanes (PUs) are composed of flexible soft segments and rigid hard segments. The variations in the compositions of the soft and hard segments impart PUs a wide range of physical properties [8-10]. The blending of different sorts of materials produces composite structures which combine different material properties, or may reveal novel properties not existing in the constituent phases [11-13]. For example, oxidicperovskite materials have been employed as ceramic filler in various polymers and the dielectric, piezoelectric and pyroelectric properties of the composites have been investigated in relation to the filling factor and the dielectric properties of the inclusions[14].

In this research article, Ni^{+2} ions doped $BaTiO_3$ nanoparticles was fabricated by sol-gel route. Polyvinyl alcohol (PVA) was used to encapsulate the ferroelectric crystallites within its network. These were interspersed by using the spin-on technique in the IPN which was formed by two different PU prepolymer and 2-hydroxymethyl methacrylate. A series of IPNs were synthesized in a way having –NCO and –OH ratios in 1.2:1.0 in PU network. Alternation of the cross linking density of the PU network was achieved by varying the equivalent ratio of a tri-olto di-ol.

2. Experimental

2.1 Preparation of Ni-doped $BaTiO_3$ by sol-gel methods

The compositions of the specimens can be represented by a general formula$(BaTi_{1-z}X_z)O_3$, where X represents the various substituted group, but in this case X is only Ni with z=0.3. The specimens of the dielectric materials were prepared by sol-gel technique. The polymer template in Ba^{+2} and Ni in doped Ti^{+4} cations was arranged by using PVA molecules and it was obtained by mixing barium acetate, titanium isopropoxide (TTIP, 97 %, supplied by Aldrich Chemical), 15cc Isopropanol (99 %, supplied by Merck) and $Ni(NO)_3$ was added drop by drop into the prepared PVA solution. The required amount of ethyl alcohol and acetic acid in the volume ratio of 75:25 were prepared and the weighed amount of titanium isopropoxide, with Isopropanol was hydrolyzed with proper stirring for 2 hours. Aqueous solution of barium acetate was poured into the mixture and the resulting solution was stirred again for two hours. The solution was clear and transparent. In this mixture, aqueous solution of Nickel nitrate was added drop by drop. In addition, PVA (3g/l) was added to this solution drop-wise in 5:2 ratios. It was observed that at room temperature, several processes like hydrolysis and condensation occurred in the resulting solution which eventually converted into gel. The gel was dried (in oven at 70^oC for 24hr) and then calcined at 750^oC to obtain the $BaTiO_3$ phase.

2.2 Material and methods for the preparation of polymer network

All the raw material used in the preparation of the IPN network is commercially available in the market. The crossed linked polyurethane components PUR, consisted of 1, 1', 3, 3'-tetramethylxylene di-isocyanate (TMXDI), ether type polyols(PPG1000 and PTMG 1000), 1,1,1- trimethyol propane (TMP), was stirred and degassed in a flask at 70^oC under reduced pressure for 16 hours. Two major tasks involved in the preparation of the IPN network are as follows (1) Preparation of HPU pre-polymer and (2) Crosslinking with HUP with PU in 1:1 ratio. The purified chemical along with 1, 1, 1 - trimethyl propane and 1, 4-butanediol was poured into 4-necked reaction vessels and stirred where the reaction was carried out at room temperature. During the mixing the mixture was flashed with nitrogen to remove the dissolve oxygen inside the mixture. It was again left for 24 hrs at 70^oC for further reaction and vaporization of the excess solvent from the mixture. Figure 1 depicts the synthetic processes for the production of IPN polymer of PU and HPU pre-polymer.

2.3 Preparations of the compositematerials

The ferroelectric material was mixed with reactive polymer chain at 80^oC for 10 min. The mixture was poured into a steel mold where the polymerization reaction took place. To avoid the settlement of the ferroelectric materials inside the mixture, the mold vessels were made to continuously rotate on their axes with slightly vibration. The steel mold was clamped with nitrile rubber of 8mm diameter which was placed in between the steel clamps. The polymerization reaction along with the formation of composite materials occurred in three different temperature which were 65, 85, and 95^oC. The volatile monomer and bubbles in the samples were removed at low temperature. The composite powder samples were then hot pressed at 120◦C for 10 min under a pressure of 130 MPa in a steel die of diameter 12 mm. The die was cooled to room temperature underthe application of pressure.

2.4 Characterizations

Tensile testing requires hardened 'dog-bone' shaped samples created from the mixture which is described above. The biggest challenge in creating the sample was to remove all the solvent and to ensure no air pockets existed in the neck region of the sample. Multiple samples were created for each system. The mechanical properties of ferroelectric material reinforced polymer composites, in the form of 25 mm x 9 mm x 0.7 mm test samples, were measured at room temperature using an electro-mechanical testing machine (INSTRON-1195) incorporating a tension/compression transducer (load cell) operated at constant strain rate.Tensile testing of all the polymer composite was performed by application of stress on the material alongwith .Percentage elongation and reductions in the area were computed.Isothermal testing conditions along with the temperature set up were ensured to also study the temperature induced effects. At least five specimens were tested to obtain the averaged values of the results. In order to evaluate the effect of filler content on the mechanical properties of ceramic filled IPN polymer matrix, mechanical properties were also evaluated from the usual condition.

3. Results and discussion

3.1. Characterization of the Ferroelectric material

$BaTiO_3$ is a basic ferroelectric material and having vast applications in different fields. It has two substituting sites: one being Ba^{+2} sites and other from Ti^{+4} sites.According to the results observed by us, 30% of Ti^{+4} ions are replaced by Ni^{+2} sites. The particles of three different sizes were prepared from sol-gel technique and their sizes were measured using XRD. We have compared the XRD pattern of Ni doped $BaTiO_3$ with standard $BaTiO_3$ sample which was derived by heating the pellets of the samples at 750^oC for two hours in air. The obtained results contained the same peak position of $BaTiO_3$ along with peaks of nickel. The peaks were found to be analogous to the tetragonal structure of the $BaTiO_3$. Fig.2 shows an SEM micrograph of 0.5 mole% Ni^{+2} doped $BaTiO_3$. The polymer PVA easily forms the networking with the reinforcing constituents and also adjusts the sizes of the grains. It serves as a better surfactant to encapsulate the cationic species in the available –OH functional and long chain coiling with hydrogen bond during the reaction.

3.2 Characterization of the Composite materials

Generally, the chemically dissimilar nature of the soft and hard segments in polyurethane tends to produce incompatible structures and thus separate the product into different phases during its formation. The dissimilarity arises from the use of two different reactants and present in the functional group in the reactant molecules. Their compatibility can be improved by varying the equivalent ratio of the isocyanate (-NCO) group to the hydroxyl (-OH) group in polyurethane. Fig.3 shows a representative SEM morphology of the modified PU/PEMA composite with uniform distribution of the ferroelectric materials. A good contrast between two distinguished phases could be obtained. The IPN matrix appears white and ferroelectric materials appear black. It illustrates that a good dispersion of toughening particles is achieved at the time of polymerization and addition of second phase particles. The filler nano particles of ferroelectric materials are distributed in a relatively uniform fashion and the particles are almost spherical in shape with irregular boundaries. The filler particles are seen to be clearly embedded in the polymer matrix. These particles maintain the connectivity of the polymer matrix and reinforce the constituents. The ceramic-polymer composites are made up of an active ceramic phase embedded in a passive polymer phase. The properties of the composite depend on the connectivity of the phases, volume percent of ceramic, and the spatial distribution of the active phase in passive phase.

3.3 Effect of the hard/soft phase of polymer segment ratio on the mechanical testing

Engineering materials such as polymer, rubber and metals which are elevated to high temperatures show plastic deformation when subjected to stress or strain. Such flow is accompanied by the dissipation of energy due to some internal loss mechanism. Bond breakage, bond formation reaction, dislocation and the formation of the substructure in metals account for the internal loss mechanism in the material. Materials of this type are known as visco-elastic in response.

Tensile testing with different ratios of soft and hard phase in IPN matrix was performed to determine the bulk mechanical properties of polymer nano-composites. The main factors such as molecular weight, tacticity, and processing history with different contents of the reinforcing constituents, impact mechanical properties of the polymer nano-composite; pure polymer reference systems were tested to ensure more direct comparison with nano-composites. In order to test the composites mechanically, we had to prepare suitable samples from the bulk composite materials. This kind of measurement requires the samples to be of "dog bone" shape. Hydraulic wedge grips were used to secure both ends of the dog bone. Then the universal testing system (MECH C.S. /UTE) was used to experimentally apply increasing load in order to maintain a rate of stretching of 0.25 inches per minute. The sample was stretched until it reached the fracture point, making this a destructive

measurement. Tensile testing data was plotted *using* stress versus strain curves at different operating temperatures, the examples of which are shown in Figure 2. Elastic modulus is defined as the slope of the linear portion of the stress/strain curve. Fig 2 (a) shows the stress strain diagram of the polymer matrix of different soft to hard phase ratio at room temperature. In the polymer matrix from 80:20 to 20:80 the soft phase of the polymer decreases while the hard phase of the polymer increases. The fracture stress or UTS increases continuously as the amount of hard phase in the matrix increases. The nature of the polymer changes with change in percentage of the hard phase content in the matrix. 20:80 polymers are brittle and 80:20 polymers are ductile.

3.4 Mechanical properties of Nano-Ba(Ti$_{1-z}$X$_z$)O$_3$ doped in polymers alloys at the different temperatures.

The polymer matrix provides many advantages such as easy processing, low cost and resistance to corrosion. In many circumstances, the polymeric matrix has been the major constituent contributing to degradation or changes in durability of PMCS. In applications when the matrix material on exposure to environment results in alteration of the properties of the matrix or mechanical loads that act over long time periods, the visco-elastic nature of the matrix becomes a dominant factor in the composite performance. Fig.4-6 (a-c) shows the stress-strain curves of the polymer nanocomposite at different temperatures. With increase in the percentage of the hard phase in the matrix along with reinforcing constituents, the tensile strength increases with decrease in the size of the reinforcing constituents in the matrix. With increase in temperature, the tensile strength decreases as shown in Fig.7. Fig.8 shows the variation of the stress with strain at room temperature with different sizes of the reinforcing constituents. A smaller size of the reinforcing constituents shows higher tensile strength at the room temperature.

3.5 Impacts of variable amounts of reinforcing constituents in polymers alloys at room temperatures.

Fig. 9 represents the effect of filler (BaTiO3) loading on tensile strength. From this figure, it is observed that the tensile strength decreases continuously with the increase in filler concentration. The decrease in both tensile strength and % E.B. with filler loading are due to non-reinforcing nature of Ni-doped BaTiO$_3$ in IPN matrix. Maximum strength was found when the amount of filler constituents in the IPN matrix was low. During this study, the ratio of hard and soft phase in the IPN matrix was kept constant.

Conclusion

Results suggest that the size of the Ba(Ti$_{1-z}$X$_z$)O$_3$,temperature and ratio of hard phase and soft phase are parameters influencing the rheological properties of the material. The tensile strength of the composite material is proportional to the percentage of hard-phase content and inversely proportional to the size of the reinforcing constituents and temperature. Therefore, the material which has hard phase/soft phase ratio as 90:10 with 48nm sized Ba(Ti$_{1-z}$X$_z$)O$_3$ particles doped in the IPN matrix when maintained at room temperature showed the highest strength.

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Scheme-1

Scheme-2
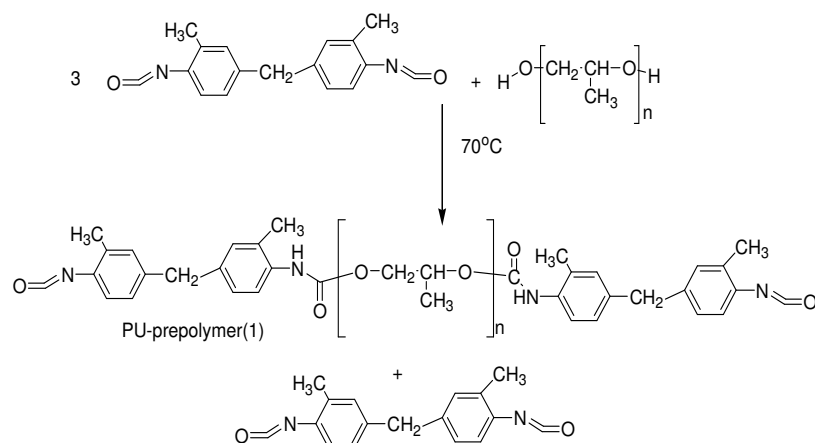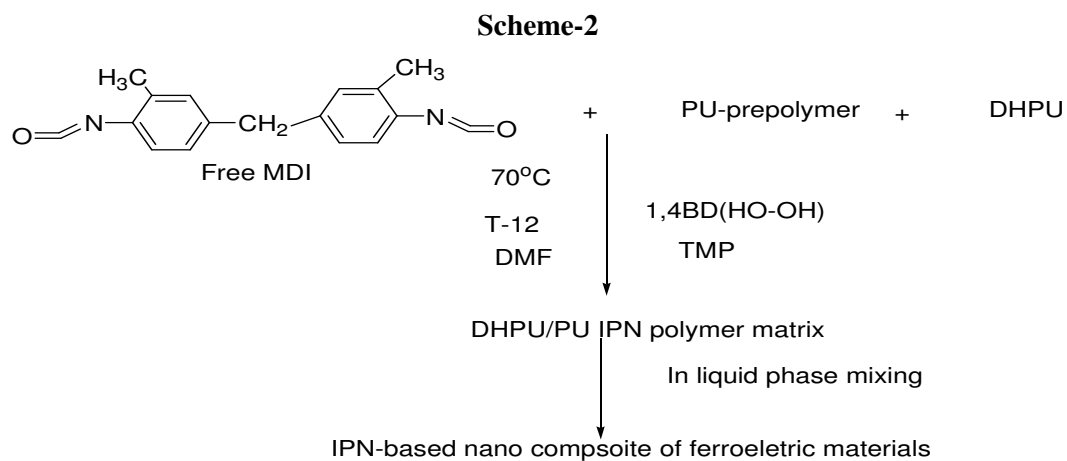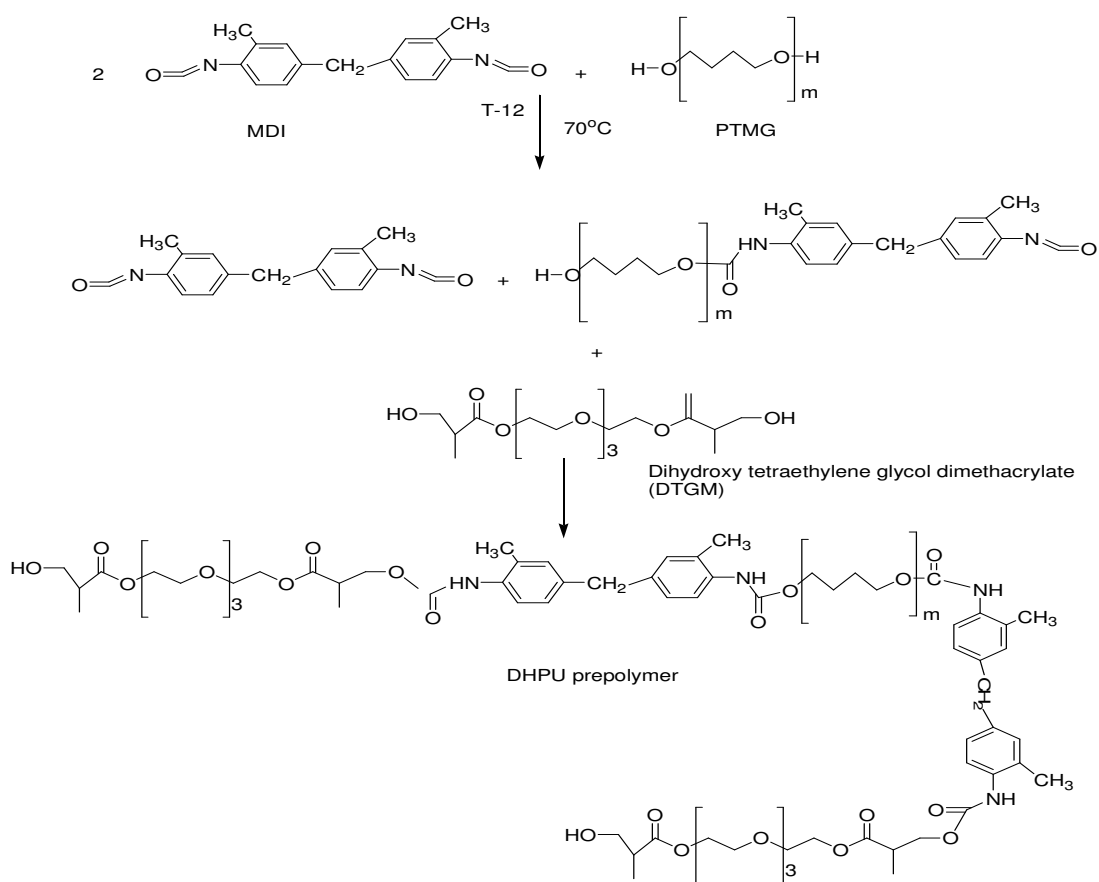
Scheme-3
Figure.1 Synthetic procedure for the preparation of polymer composite along with preparation of the matrix
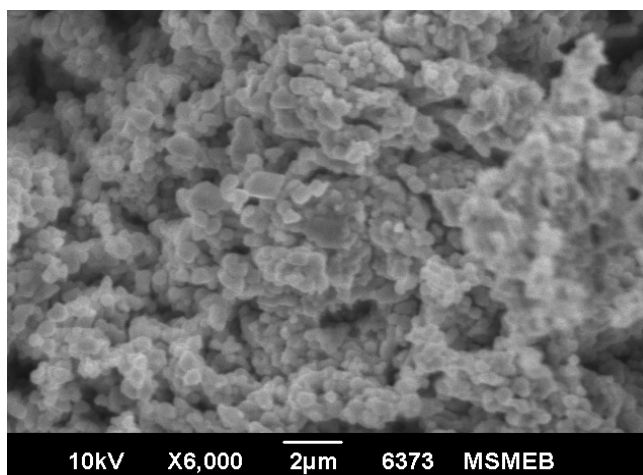
Fig.2 SEM image of Ni^{+2} doped BaTiO$_3$
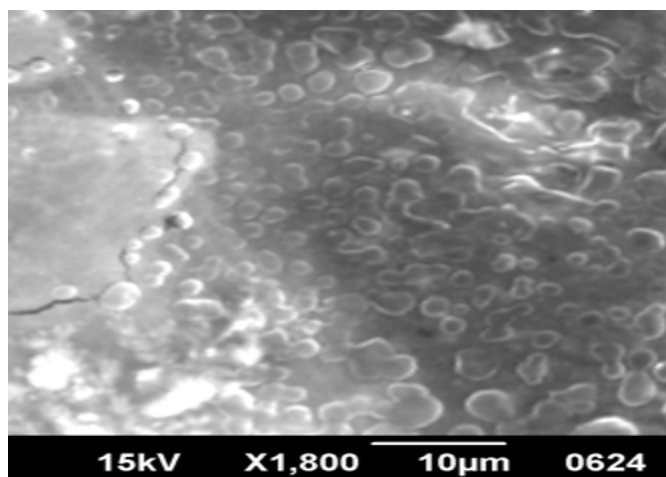
Fig.3 SEM image of Ni^{+2} doped BaTiO$_3$dispersed in IPN polymer matrix
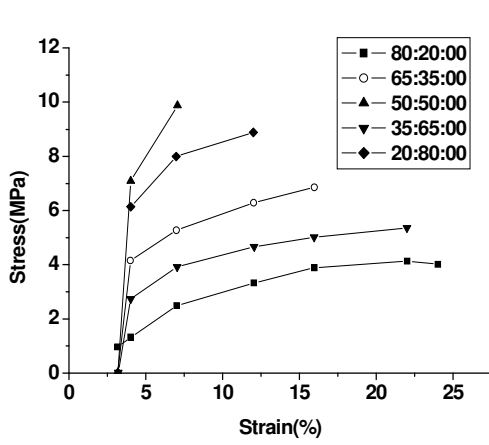
(a)25°C
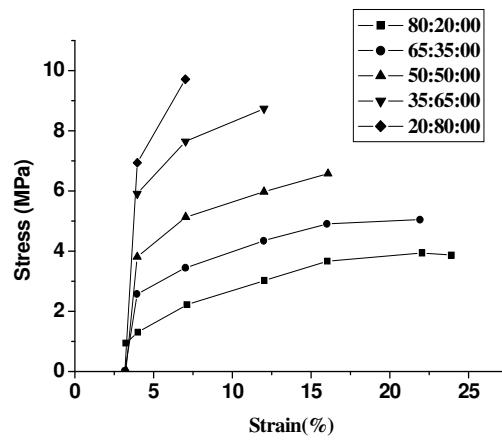
(b) 75°C
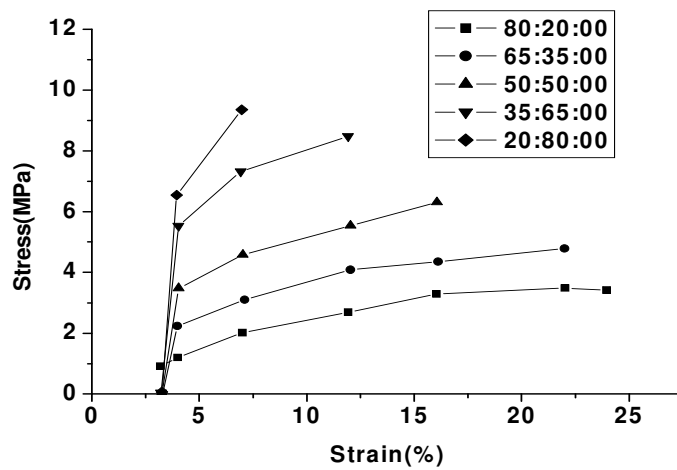
(a) 130°C

Fig.2(a-c) Stress-Strain diagram of different types of IPN matrix at the different temperature
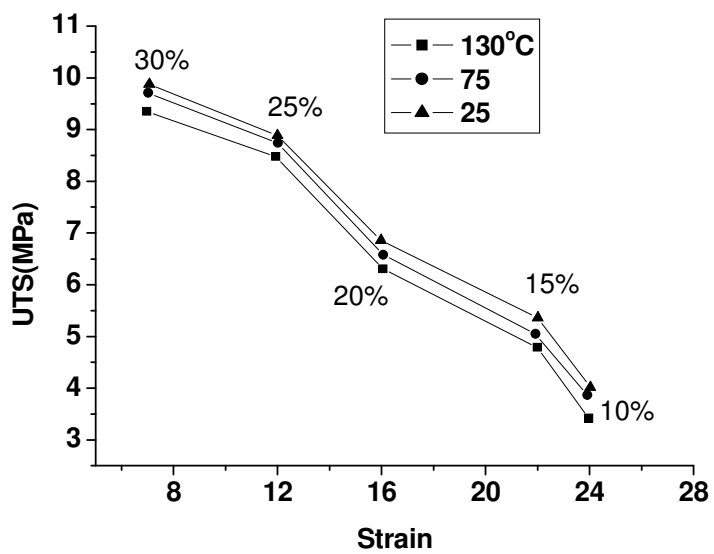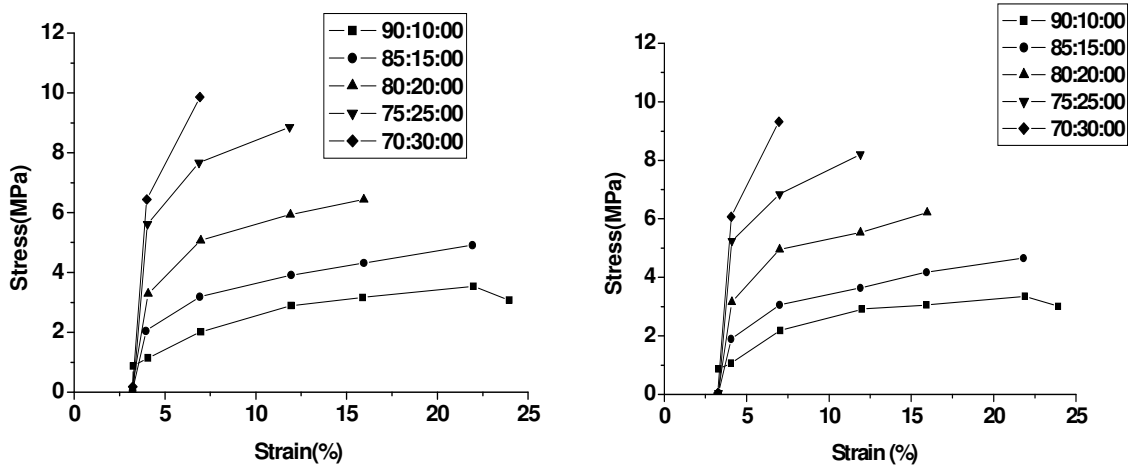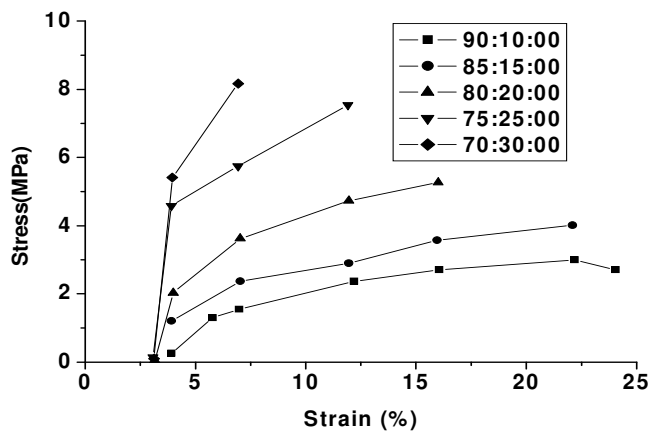
Fig.3 (a-c) Variation of the UTS with strain at the different temperature with the variation of the hard phase

(a)   25°C

(b) 75°C

(C) 130^{0}C

Fig.4 (a-c) Stress-Strain diagram of 95 nm sizes of Ba (Ti$_{1-z}$X$_z$)O$_3$ doped in IPN polymer matrix at different temperatures

(a)25°C

(b) 75°C
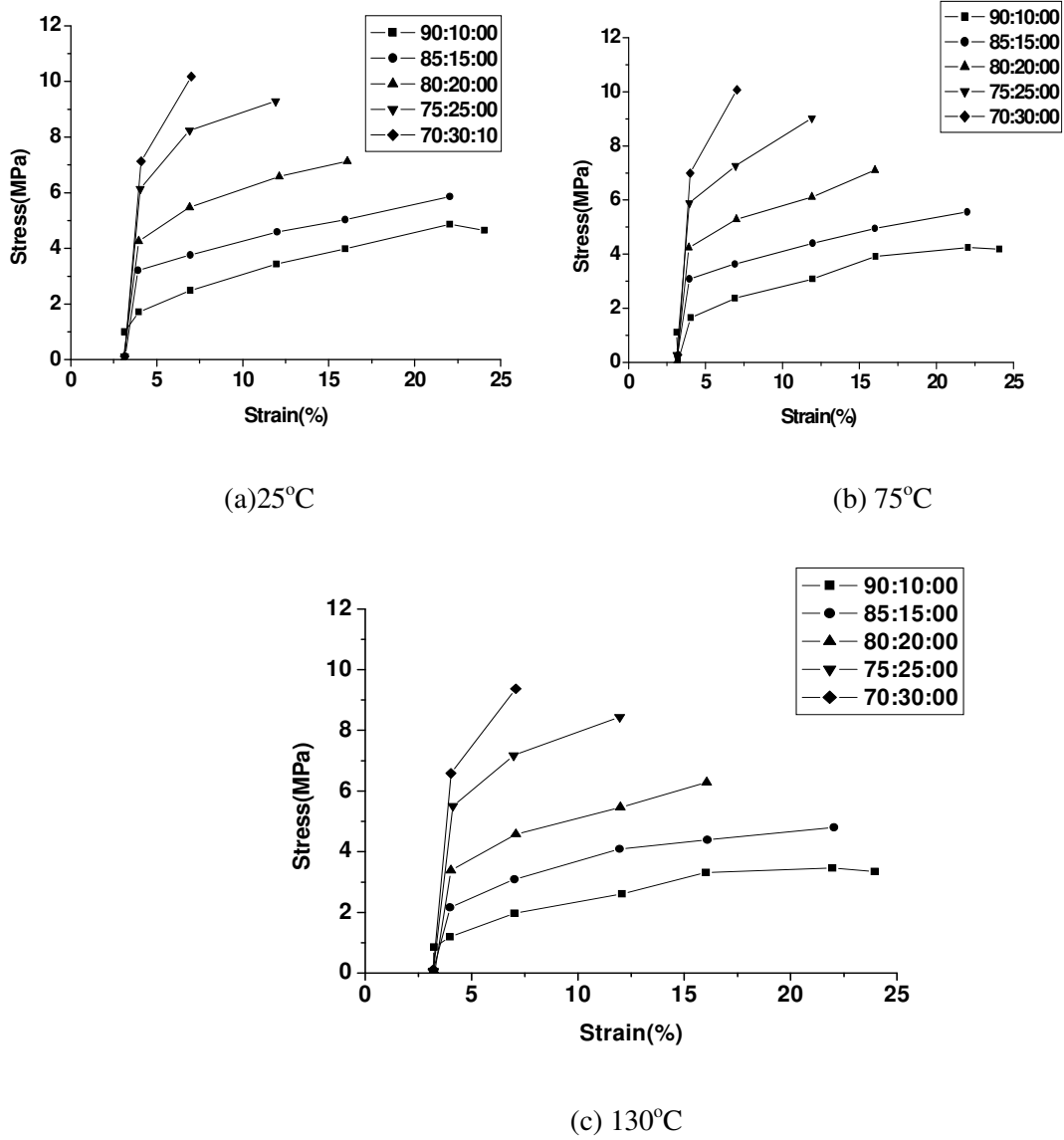
(c) 130°C

Fig.5(a-c) Stress-Strain diagram of 68 nm sizes of Ba(Ti$_{1-z}$X$_z$)O$_3$ doped in IPN polymer

matrix at different temperatures

(a) 25°C

(b) 70°C
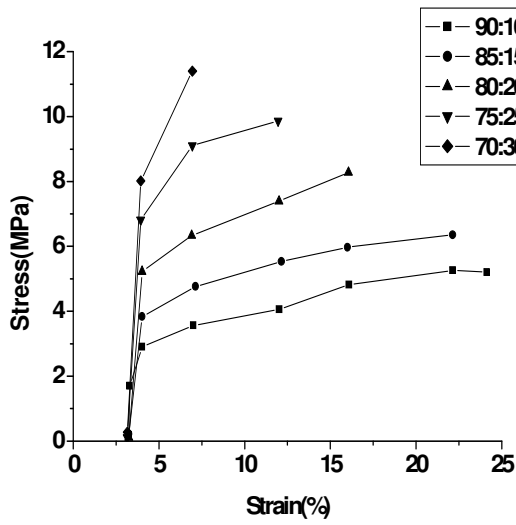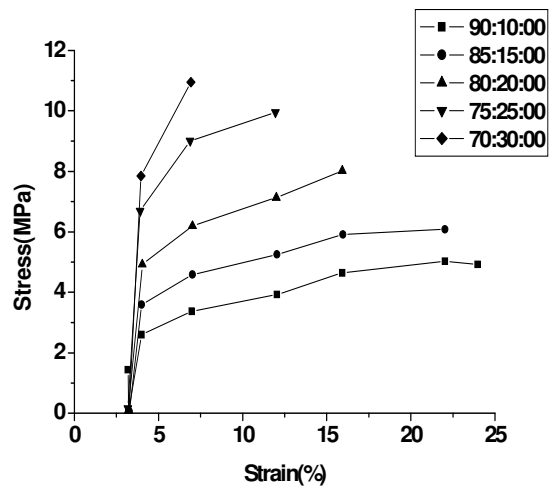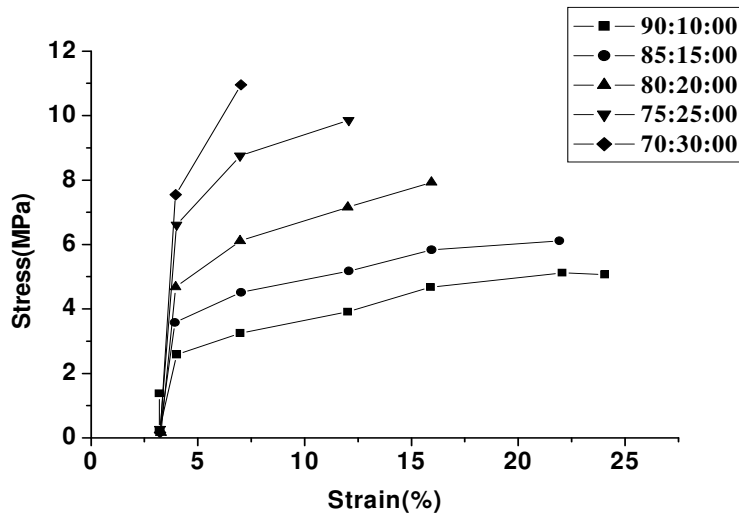
(c)130°C

Fig.6(a-c)Stress-Strain diagram of 48 nm sized Ba(Ti$_{1-z}$X$_z$)O$_3$ particles doped in IPN

polymer matrix at different temperatures
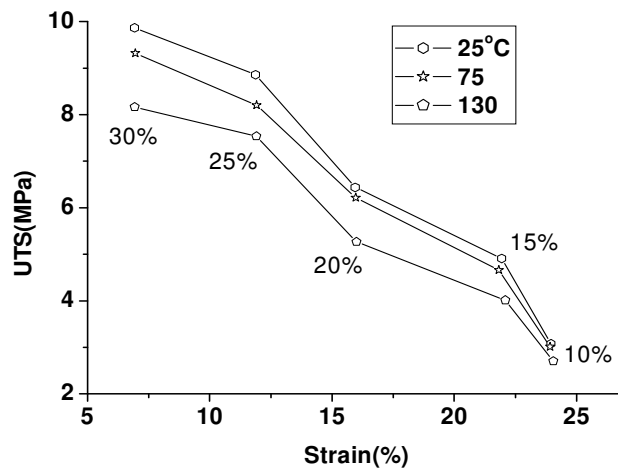
Fig.7 Variation of the UTS with strain of 95 nm sized particles of Ba $(Ti_{1-z}X_z)$ O_3 doped in IPN polymer matrix at different temperatures
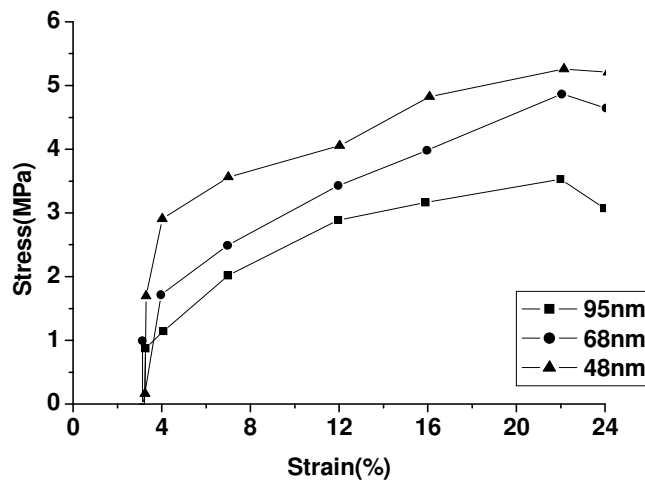

Fig.8 Variation of Stress with strain of different sizes of Ba $(Ti_{1-z}X_z)$ O_3 particles doped in IPN polymer matrix at room temperature
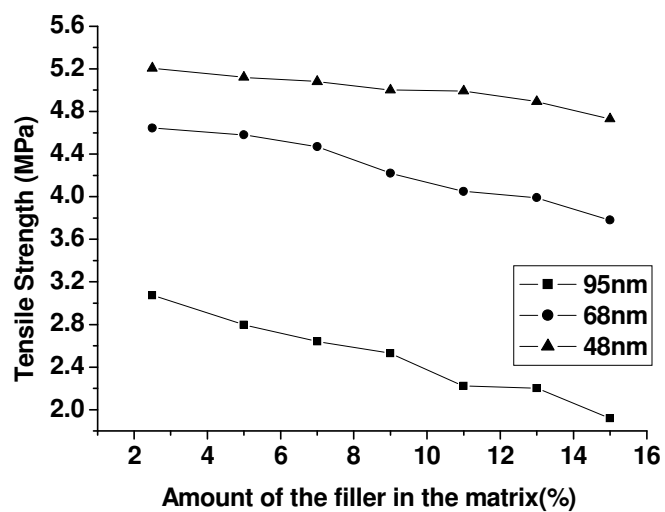
Fig.9 Variation of the Stress with strain of different sizes of $Ba_{1-x}Ni_xTiO_3$doped in IPN's polymer matrix at room temperature

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