Dielectric Properties of $BaTiO_3$/Nylon11/$MgCl_2$/PANI composites

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Abstract— We prepared the composites of $BaTiO_3$/Nylon11/$MgCl_2$/PANI having 0-3 connectivity using hot press method. These samples were poled under different conditions i.e. at different poling temperatures and fields. We characterized these composites for their piezo, pyro and dielectric properties. We are reporting and discussing only the dielectric properties of these composites in this paper.

Keywords: $BaTiO_3$, Nylon11, $MgCl_2$, PANI, composites

I. INTRODUCTION

The piezoelectric materials can be divided in three classes viz. inorganic, organic and composites. In inorganic class there are ceramics and crystals having high dielectric constant, high piezoelectric coefficient, high electromechanical coupling but poor mechanical property and relatively high acoustic impedance restricting their use to only certain applications. In organic class there are polymers, such as Polyvinylidene Fluoride PVDF, having relatively low acoustic impedance, which could provide a good acoustic matching to water or tissues, but its piezoelectric coefficients are also relatively low as compared to ceramics. In composite class mainly there are ceramic:polymer composites having good piezoelectric and dielectric properties as compared to polymer and good mechanical properties as compared to ceramics. These composites have their use in many applications owing to their better and tunable properties.

These composites can be further divided into different classes based on the connectivity scheme of their constituents. Composites of the 0–3 connectivity type comprising ferroelectric ceramic (FC) inclusions in an extended polymer matrix exhibit a variety of useful physical properties [1–4] and are widely used in modern piezoelectric technology, acoustics, and some other fields. Different composites of $BaTiO_3$ with various types of polymers such as PVDF, PVC, PVA and copolymers have been widely studied and reported in literature. However, the composites of $BaTiO_3$ with Nylon have not been reported so far. Nylon has unique physical and chemical properties such as toughness, flexibility, resistance to chemicals, temperature and wear. Therefore the composites of $BaTiO_3$ and Nylon may also have these advantages and may be useful for applications requiring these properties.

In present work we have prepared the piezoelectric composites of $BaTiO_3$ & Nylon 11 as flexible and freestanding films using hot press method having 0-3 connectivity. These films have been prepared with different volume fractions of $BaTiO_3$ and Nylon11. It has been reported in the literature that 0–3 composites cannot be poled fully [5, 6] due to the screen effect of the polymer matrix, so the total properties of the composite are reduced, which limits the practical application of the 0–3 ferroelectric composite. Sakamoto *et al* [7] have found in the PZT/PU composite doped with graphite particles that the poling behavior of the PZT phase was improved and the piezoelectric and pyroelectric properties of the composite were enhanced. Other researchers [8–11] have also found similar experimental phenomena when the electrical conductivity of matrix material was raised. Authors introduced the PANI for the same purpose i.e. to enhance conductivity of the matrix. PANI is a conducting polymer of the semi-flexible rod polymer family having repetitive unit of monomer $(C_6H_4N)_n$. Its inclusion in polymer matrix of 0-3 polymer-ceramic composites have been reported to reduce the resistance of the matrix which results in better poling and enhanced Piezo-pyro properties as suggested by Patil et al. [12]. Similar results have also been reported by Xu Renxin et al. [13]. The polymer seems to be playing the same role as graphite incorporated in matrix of PZT/PU composite.

The $MgCl_2$ was also added to the matrix as, it has been reported by Tawansi et al. that doping PVDF with certain amount of chlorides of Ni, Zn, Al, Cu, Fe, Mn, and Mg [14] increases its crytallinity. So, in the present work we have doped Nylon11 with $MgCl_2$ hoping that it may enhance the crystallinity as crystallinity of Nylon11 is supposed to be responsible for it Piezo-pyro and dielectric properties. In BaTiO3/Nylon11 composites $MgCl_2$ and Polyaniline (PANI) were added as third and fourth phase to enhace crystallinnity and conductivity of thee matrix phase respectively.

II. MATERIALS AND METHODS

a. SAMPLE PREPARATION: The Nylon 11 granules obtained from Sigma-Aldrich were dissolved in DMF by heating and stirring and converted into a mixture of powder and small flakes by grinding. The $BaTiO_3$ powder was prepared in our laboratory using well known mixed oxide route. The PANI for this work was purchased from Sigma-Aldrich. The $MgCl_2$ for the present work was also purchased from Sigma-Aldrich in Magnesium chloride hexahydrate form. The required quantities of $BaTiO_3$, Nylon11, MgCl2 and PANI were mixed and ground using agate mortar for 4 hours. This mixture was then placed in a die for hot pressing. The mixture was first heated upto 184^0C then pressed using pressure of eight tons. The samples were removed from the die after cooling and then electroded using silver paste.

b. POLING: The electroded samples were poled using in-house developed power supply and sample holder in silicon oil bath at different temperature and poling voltages.

c. CHARACTERIZATION: The dielectric properties were measured using Agilent precision LCR meter (4284A) in 100 Hz to 1 MHz range at room temperature.

III. RESULT AND DISCUSSION

Figure 1 shows the frequency dependence of dielectric constant and dielectric loss of the composites. It is evident from the Figure that dielectric constant decreases with increasing frequency, which is obvious. As the frequency increases the different polarization mechanism ceases to happen. The dielectric loss almost remains constant beyond 100 kHz of the frequency. The decrease in dielectric constant is not very significant beyond 100 kHz which is agreeable with the fact that dielectric constant of Barium Titanate changes very little with increasing frequency.

Figure 2 depicts the dependence of dielectric constant and dielectric loss on the volume percentage of Barium Titanate in the composite. It can be seen that dielectric constant increases sharply with the increase of Barium Titanate volume percentage. The dielectric loss also increases with the content except for high frequency. This may because of the reason that an increase in the content of ceramic fillers in the composites increases the interfacial area between the ceramic phase and polymer phase. This increase influences the interfacial polarization which has an effect on the dielectric permittivity and dielectric loss. Thus the relative permittivity increases with ceramic loading. Also the dielectric loss of composites increases with increasing ceramic filler loading. [15]

Figure 3 shows the dependence of dielectric properties on poling field. There is rise in dielectric constant as well as dielectric loss with increasing poling field. But there is a decline in these constant after about 10 kV/mm of the poling field. This suggests that the polarization of the composites saturates at this poling field and slightly decreases if the field is increased beyond this value. This may be because of the leakage due to semiconducting filler beyond this voltage increases. This can also be verified from the fact that the electrical breakdown was observed in samples beyond 14 kV/mm of poling filed.

Figure 4 depicts the temperature dependence of the dielectric properties of the composites poled at optimum value i.e. 10 kV/mm of the poling field. It is clear from the Figure that both dielectric constant and loss increases sharply with increase in temperature. The dielectric loss of composite containing highest percentage of filler increases more sharply beyond about 70^0C in comparison to lower volume contents.

The rise in dielectric constant with ceramic loading may be attributed to two facts; (i) higher ceramic percentage means higher concentration of dipoles and (ii) increased interfacial area.

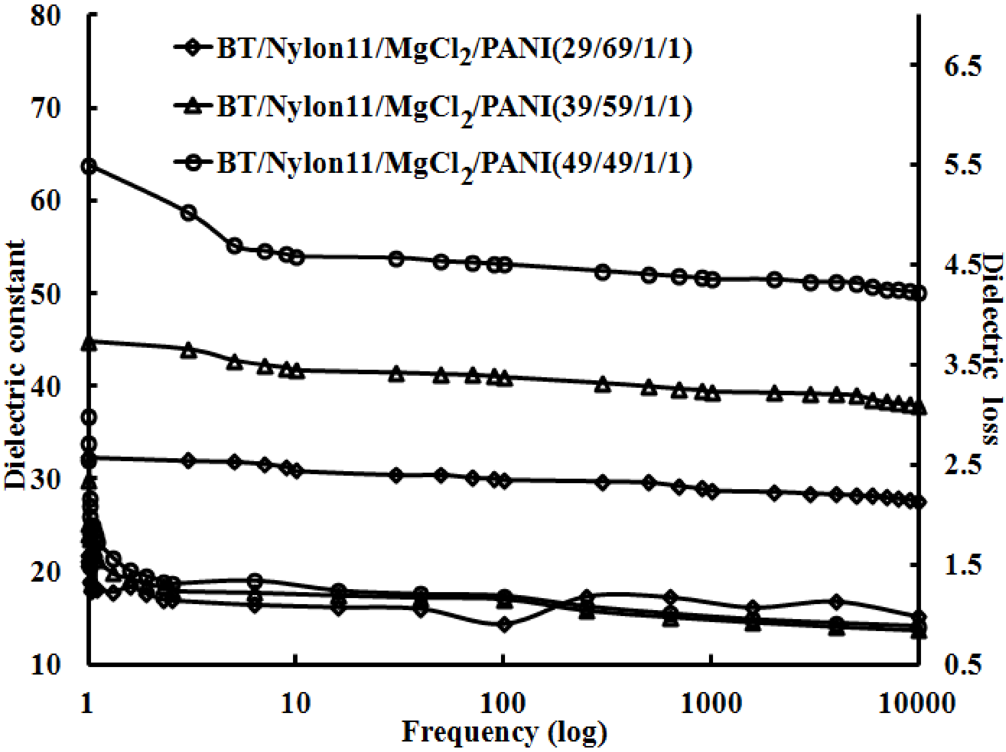

Figure 1: Variation of dielectric constant and loss with frequency for different composites poled at 10 kV/mm

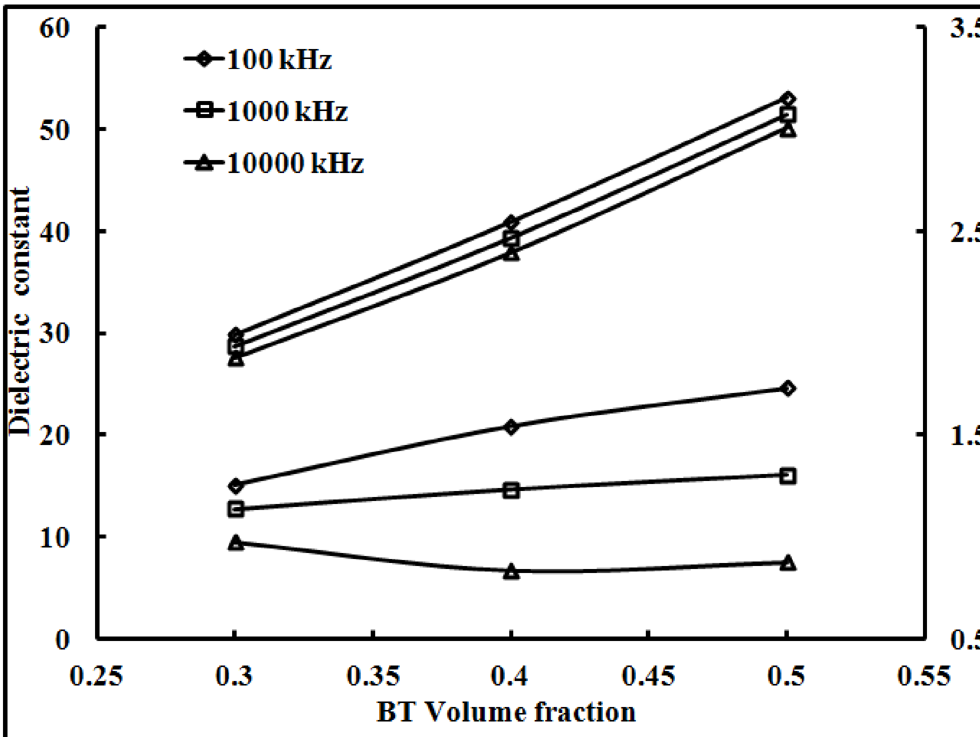

Figure 2: Variation of dielectric constant and loss with BT volume fraction at different frequencies for composites poled at 10 kV/mm

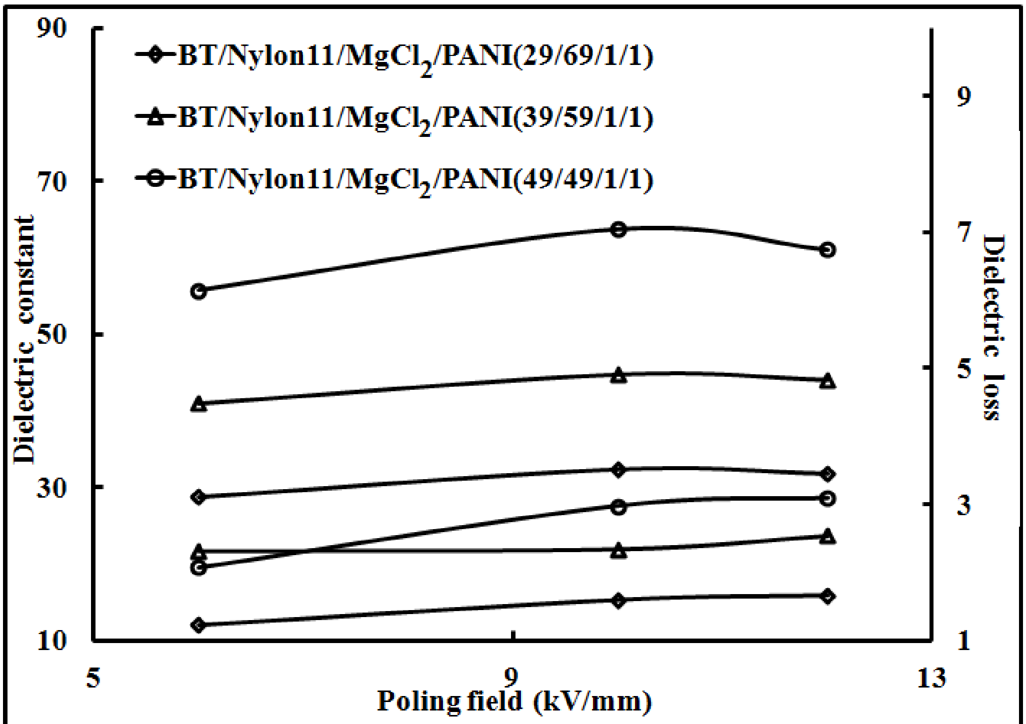

Figure 3: Variation of dielectric constant and dielectric loss with poling field for different composites at 1 kHz

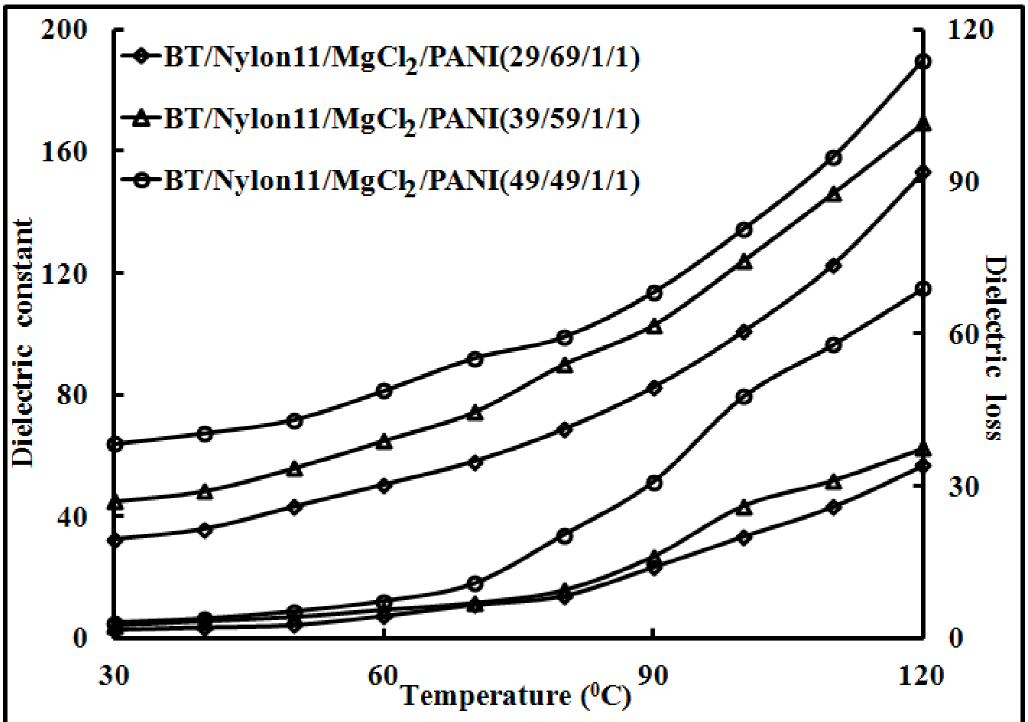

Figure 4: Variation of dielectric constant and dielectric loss with temperature at 1 kHz for different composites poled at 10 kV/mm

IV. CONCLUSIONS

Composites of Nylon 11, BaTiO3, MgCl2 and PANI were prepared by hot press techniques with different concentration of the constituents. The rise in dielectric constant with ceramic loading may be attributed to two facts; (i) higher ceramic percentage means higher concentration of dipoles and (ii) increases interfacial area. The increase of dielectric constant upon addition of PANI can be attributed to the fact that high conductivity in the matrix phase can alter the internal fields in a ferroelectric composite and allows the accumulation and dissipation of free charge at the matrix-inclusion interfaces. [16]

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