Piezoelectric Properties of BaTiO₃/Nylon11/MgCl₂/PANI composites

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Abstract— We prepared the composites of BaTiO₃/Nylon11/MgCl₂/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 piezoelectric and pyroelectric properties of these composites in this paper.

Keywords: BaTiO₃, Nylon11, MgCl₂, PANI, composites, piezoelectric, pyroelectric

I. INTRODUCTION

Polymer/ceramic 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 BaTiO₃ with various types of polymers such as PVDF, PVC, PVA and copolymers have been widely studied and reported in literature. However, the composites of BaTiO₃ 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 BaTiO₃ and Nylon may also have these advantages and may be useful for applications requiring these properties.

In present work we have prepared the composites of BaTiO₃ & 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 BaTiO₃ 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 piezoelectric charge coefficient (d_{33}) was measured using APC d33 meter and piezoelectric voltage coefficient (g_{33}) & FOM (Figure of Merit) were estimated from d_{33}. The hysteresis curve was also plotted for the composite to study its ferroelectric behavior.
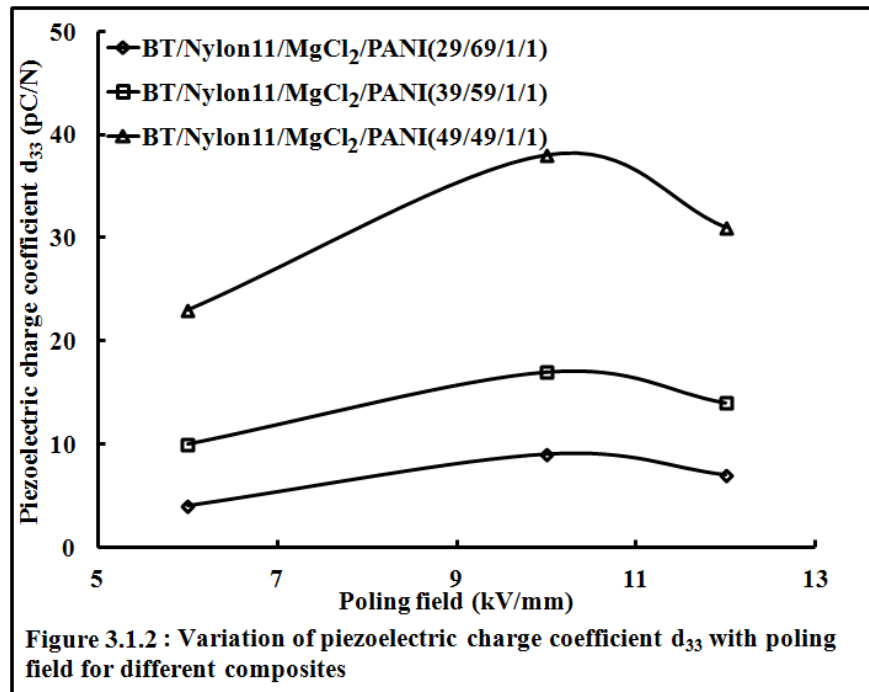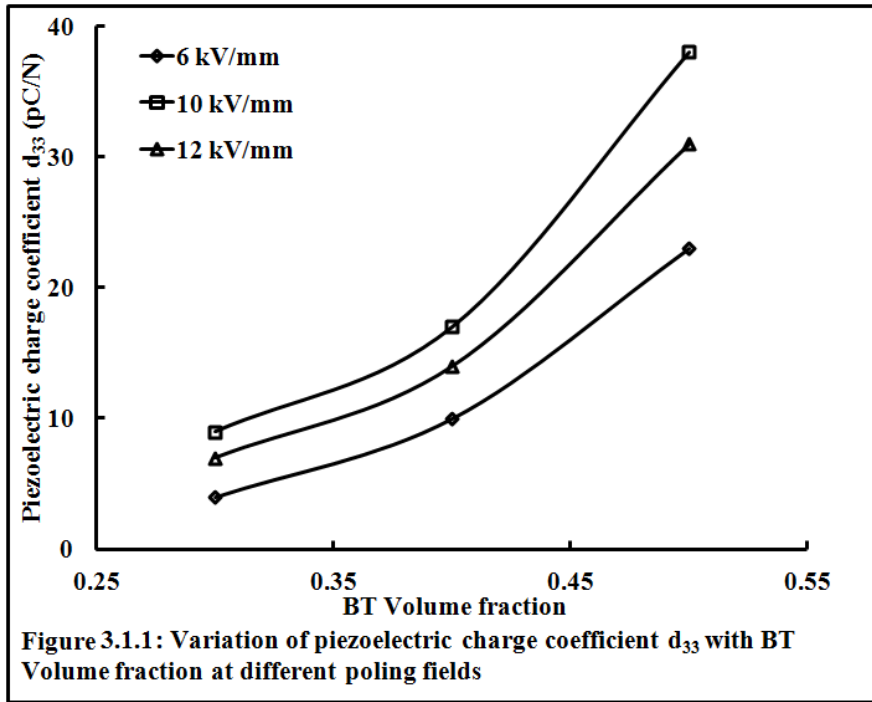
III. RESULT AND DISCUSSION

I.1   PIEZOELECTRIC CHARGE COEFFICIENT (d_{33})

Figure 3.1.1 shows the variation of d_{33} coefficient with volume fraction of Barium Titanate for the BT/Nylon11/$MgCl_2$ composite poled at different poling fields. It can be observed from the Figure that d_{33} increases most steeply with increase in the volume fraction of Barium Titanate (BT) for the composites poled at 10kV/mm of poling field. At this field the d_{33} increases very rapidly beyond 40% BT volume fraction. This can be attributed to higher degree of alignment of the dipoles at higher fields and specially 10 kV/mm of poling field. The d_{33} coefficient of the composite poled at the poling field of 3 kV/mm also shows little increment, which is perhaps due to the fact that the effective poling is more effective in the presence of $MgCl_2$. The value of d_{33} for composite poled at 10kV/mm having 50% volume fraction of BT is almost 38 pC/N, which is greater than reported, though for lower concentration of BT [15].

Figure 3.1.2 shows the variation of the d_{33} coefficient with poling field for composites containing different volume fractions of BT. It is observed from the Figure that d_{33} coefficients of all the composites tends to have a maximum value around 10kV/mm of poling field and slightly decreases beyond this value of poling

field, this suggests that may be the saturation of polarization is reached at 10 kV/mm of the poling filed. If poling field is increased further the value of d_{33} starts decreasing which may due to the leakage of voltage due to increased conductivity of the matrix.
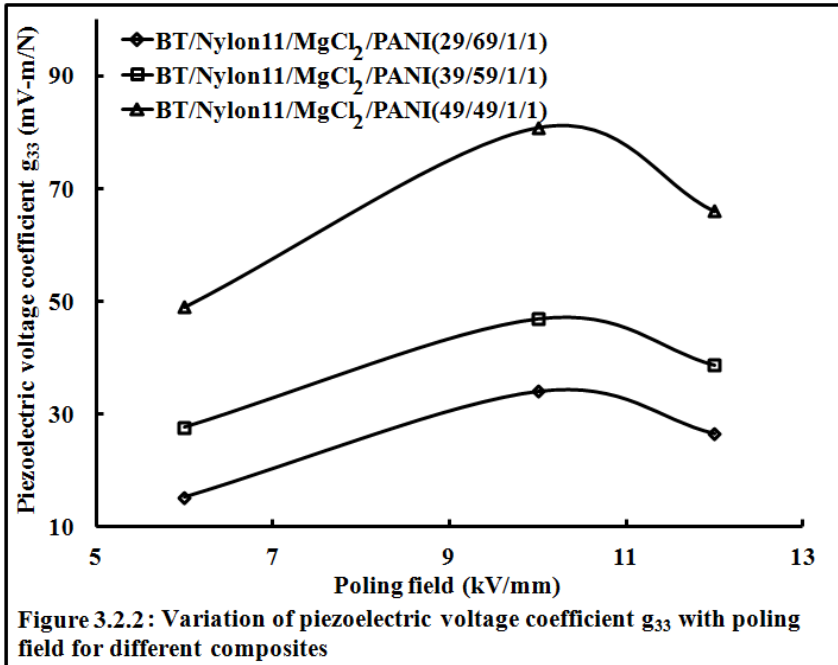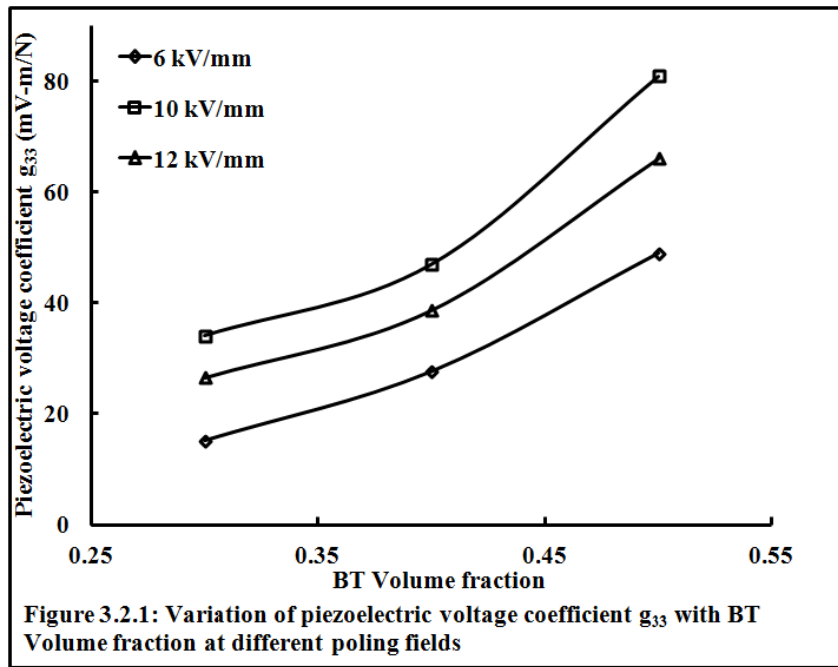

Figure 3.1.1: Variation of piezoelectric charge coefficient d_{33} with BT Volume fraction at different poling fields

Figure 3.1.2 : Variation of piezoelectric charge coefficient d_{33} with poling field for different composites

I.2   PIEZOELECTRIC VOLTAGE COEFFICIENT (g_{33})

Figure 3.2.1 shows the variation of piezoelectric voltage coefficient g_{33} with the volume faction of BT. The g_{33} coefficient tells about the voltage generation ability of composite for a given stress and depends on the
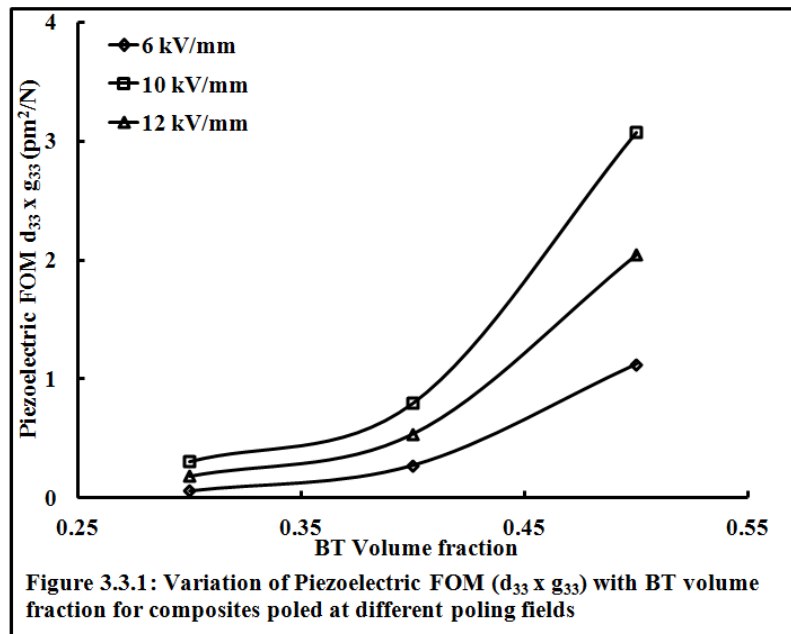
piezoelectric charge coefficient and corresponding dielectric constant. it can be seen from the graphs that the piezoelectric voltage constant increases with increasing BT volume fraction in the composites. The reason for this rise is the rise of piezoelectric charge coefficient with BT volume fraction. The coefficient for all the compositions rises almost linearly with ceramic volume fraction reaching to almost 40, 60 and 80mV-m/N for composites with 30, 40 and 50 volume percent of BT respectively. The shape of these graphs is very much similar to that d_{33} graphs and can be understood by the same reasoning.
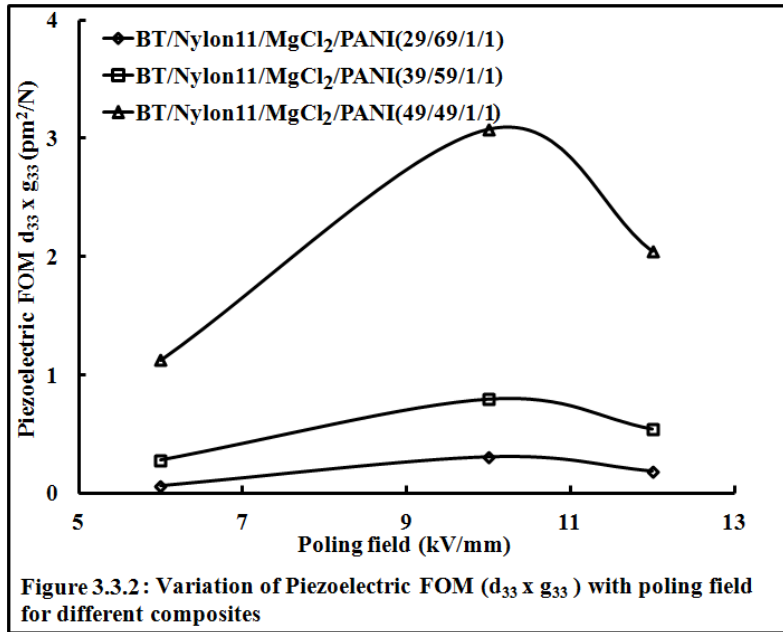
Figure 3.2.2 shows the variation of g_{33} coefficient with poling field. The peak values for all compositions are observed at about 10 kV/mm of poling field, suggesting that composites poled at this field will be most suitable for practical applications.

Figure 3.2.1: Variation of piezoelectric voltage coefficient g_{33} with BT Volume fraction at different poling fields

Figure 3.2.2: Variation of piezoelectric voltage coefficient g_{33} with poling field for different composites

I.3 PIEZOELECTRIC FIGURE OF MERIT (FOM) (d_{33} x g_{33})

The variation of piezoelectric Figure of merit (FOM) as a function of BT volume fraction is shown in Figure 3.3.1. It can be seen that for high poling field the FOM increases with volume fraction of BT significantly. However at low poling field the degree of increase is small in comparison to high poling filed. This may be attributed to the fact that at low poling fields both d_{33} and g_{33} are almost independent of volume fraction of BT due to insufficient field to induce the polarization. But at high poling field the degree of increase in the FOM is high, due to the enhanced polarization and dipole moments which cause increase in both d_{33} and g_{33}. Also it can be seen from the Figure 3.3.2 that FOM increases very sharply for 10kV/mm of poling field for 50 volume percent of BT. This rise can be explained on the basis of a similar rise in d_{33} coefficient and g_{33} coefficient. The rise in FOM is steeper for BT volume fraction rise from 40 to 50 in comparison to rise from 30 to 40 volume fraction in BT. This is due to steeper rise in both the *d_{33}* and *g_{33}* values for similar rise in BT volume fraction. The rise with respect to poling field is maximum for 10kV/mm of poling due to the reason that g33 rises in a similar manner with respect to the poling field.

Figure 3.3.1: Variation of Piezoelectric FOM (d_{33} x g_{33}) with BT volume fraction for composites poled at different poling fields

Figure 3.3.2 : Variation of Piezoelectric FOM (d_{33} x g_{33}) with poling field for different composites

I.4 P-E HYSTERESIS LOOP

Figure 3.4 shows the hysteresis loops for different composites of BT, Nylon11, $MgCl_2$ and PANI. From this Figure it can be observed that both the remnant and saturation polarization increase for composite with BT volume fraction. The coercive field is maximum for composite with 49 percent BT and minimum and almost same for composite with 29 and 39 percent BT. The ratio of remnant to saturation polarization is maximum for 29/69/1/1 composites and minimum for 49/49/1/1 composite. The maximum values of P_r and P_s are 0.83 and 2.0 $\mu C/cm^2$ for composite with highest percentage of ceramic volume but the ratio of remnant to saturation polarization is maximum for composite with minimum volume of BT suggesting that dipoles remain more aligned in this composite when the field is removed.

Figure 3.4 : P-E hysteresis loop for different composites poled at 10 kV/mm
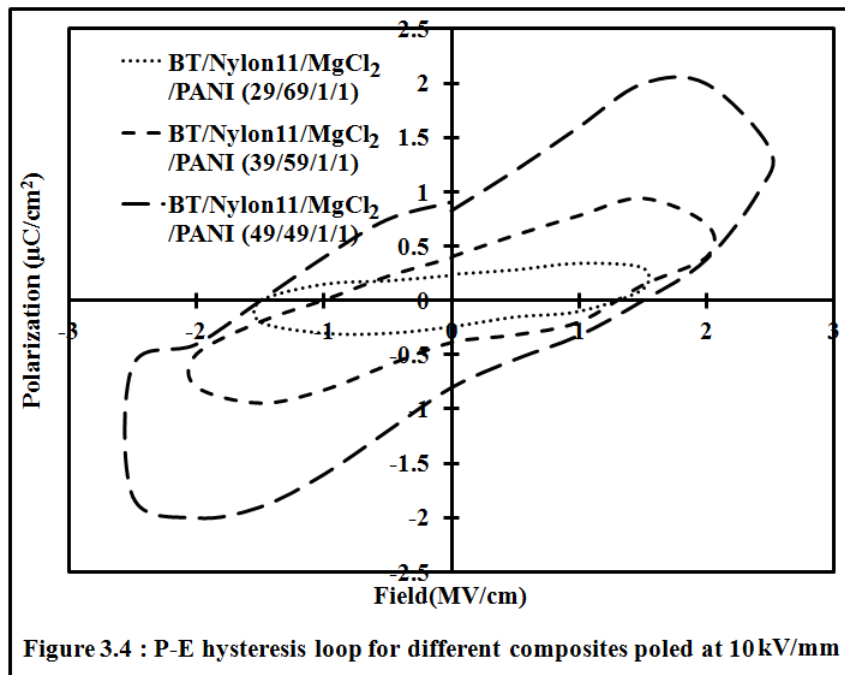
IV CONCLUSIONS

Table 3.5 summarizes the maximum values Piezo-ferroelectric coefficients of BT, Nylon11, $MgCl_2$ and PANI composites. It can be seen from the table that the piezoelectric charge coefficient has a maximum value of 38pC/N. The value of piezoelectric charge coefficient increases with increasing BT content. The value of piezoelectric voltage coefficient is also maximum for composite with 49 volume percent of BT and so is the value of FOM. The value of d_{33}, g_{33} and FOM are significantly higher for composite with highest percent of ceramic in comparison to composites with lower volume of the ceramic.

TABLE 3.5: PIEZOELECTRIC PROPERTIES OF BT/NYLON11/MGCL$_2$/PANI COMPOSITES

Sample	d_{33} (pC/N)	g_{33} (mV-m/N)	FOM (pm^2/N)	P_r ($\mu C/cm^2$)	P_s ($\mu C/cm^2$)	E_c (kV/m m)	P_r/P_s
BT/Nylon11 /MgCl$_2$/PANI (29/69/1/1)	9	34.04	0.3	0.24	0.34	1.22	0.71
BT/Nylon11 /MgCl$_2$/PANI (39/59/1/1)	17	46.94	0.7	0.4	0.94	1.23	0.43
BT/Nylon11 /MgCl$_2$/PANI (49/49/1/1)	38	80.88	3.04	0.83	2.0	1.45	0.42

V ACKNOWLEDGEMENT

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