

Dielectric properties of PVDF-PZT composite films and their thermal dependence

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Abstract

Piezoelectric polymer-ceramic composite materials are promising candidate for transducer application because of their inherent capability of combining the favourable properties of both ceramic and polymer materials. Present work discusses the dielectric properties of such composite films developed from two piezoelectric materials viz. Poly(vinylidene fluoride) (PVDF) as a matrix and Lead Zirconate Titanate (PZT) as filler in PVDF. PVDF-PZT composite films were prepared by solvent casting method followed by hot pressing for better packing and connectivity of ceramic phase in the composite and hence improved piezoelectric properties in the material. The dielectric parameters of these films are evaluated by the measurement of dielectric constants (ϵ' and ϵ''), intrinsic impedance, capacitance and dielectric loss, etc. as function of frequency at room temperature. The temperature dependence of the dielectric properties is studied as well from 40°C to 75°C. It was found that dielectric properties like permittivity and capacitance were quite stable in the frequency range 100 Hz-100 kHz. A variation of 20 to 50% in dielectric properties was observed, for increase in temperature with respect to room temperature, which may be accounted to pyroelectric behaviour of material. Copyright © 2016 VBRI Press.

Keywords: PVDF-PZT composite, piezoelectric, dielectric properties, temperature dependence, sensors.

Introduction

Single-phase piezoelectric materials such as ceramics and polymers have been used and studied extensively for development of sensors and actuators for almost a century. Among piezoelectric materials, piezo ceramic materials (e.g., PZT) are known for their excellent piezoelectric properties, high dielectric constant, and good electromechanical coupling. Ever since their discovery, ceramics like PZT and BaTiO₃, are widely used for sensor and actuator applications despite their toxicity, brittleness, inflexibility, non-conformability, large acoustic impedance and need for matching and backing layers, owing to their high piezoelectric charge coefficients. Polymer piezoelectric materials such as PVDF and its copolymers have their own advantage being flexible, chemically inert and non-toxic despite having low piezoelectric charge coefficient. This issue can be circumvented by using piezopolymer-piezoceramic composite, which derives flexibility from polymeric components and high piezo-properties from piezoceramics. If ferroelectric ceramics are embedded in a ferroelectric polymer, the piezo- and pyroelectric transducer properties can be well

controlled and adjusted in such a way that either the piezo or the pyroelectricity is compensated or enhanced due to the parallel or anti-parallel polarization of the ceramic and the polymer dipoles [1, 2].

Efforts have been made from long back to combine the properties of both ceramic and polymer materials by development of Polymer ceramic composites. In such composites ceramic material is generally dispersed as filler in the polymer matrix. The first attempts to produce such composites could be traced back to Kitayama and Sugawara [3], Pauer [4] and Harrison [5], who used PZT as a filler material and polyurethane as a matrix in (0-3) connectivity. Among the composites studied so far, the simplest types are those with 0-3 connectivity, which consists of a three-dimensionally connected polymer matrix loaded with piezo-electrically active ceramic particles [6-9]. Amongst, the most widely studied composites are those consisting of PVDF or its copolymers and PZT or BaTiO₃ [10-20]. In the past, various other investigators have investigated piezo-composites [21-27]. Different procedures have been used to prepare polymer-ceramic composites, e.g. compression molding [28, 1], solvent casting [29, 30]

and spin coating [31]. Compression molding and solvent casting results in films with thickness ranging from 30 to 500 μm , while spin coating usually leads to relatively thin films of only few μm .

The dielectric properties and the dielectric relaxation behaviour of polymers are directly affected by their molecular structure and morphology. Thus, research related to dielectric properties are frequently used in the study of dielectric behaviour of polymers. Another reason for the use of this technique in studying dipolar polymers is that the dielectric measurement allows the analysis over wider range of frequency (10-4Hz to 1014 Hz) (3×10^6 to 4×10^7) than mechanical measurements [32-35].

In the present study, PVDF-PZT composite films have been developed using solvent cast method followed by hot pressing. Different volume fraction PVDF-PZT composites (10-50 wt%) had been prepared using solvent cast method and reported in our earlier work [36]. It was found that 50 wt% is the optimum PZT content which can be incorporated in the PVDF matrix. Higher content above 50 wt% leads to increased thickness and brittleness in the composite films, which render them unsuitable for the applications. Dielectric properties like permittivity and capacitance were investigated in the frequency range 100 Hz-100 kHz and the variation of these properties have also been studied as a function of temperature. These studies are very important for applications of these materials for supercapacitor applications.

Experimental

Materials and Methods for Development of PVDF-PZT composite films

In the present study, pellets of PVDF have been procured from Pennwalt India Ltd and PZT is obtained from Sparkler Ceramics Pvt Ltd, Pune, India. For preparing the composite film, first PVDF powder is dissolved in Dimethyl Formamide (DMF) with constant stirring using a magnetic stirrer at temperature around 50-60°C. After complete dissolution of PVDF, appropriate amount of PZT powder is mixed in the solution and again put on magnetic stirrer at room temperature for around 6-12 hours. The hence obtained solution is then casted on a glass plate and evaporated in an oven for about 30-45 min. Details of this method have been explained earlier by same author [36]. This method is very easy and simple, but the prepared films sometime have few discrepancies like non-uniformity of filler dispersion in the casted film, curling due to non-uniform thickness and improper connectivity in piezoelectric phase. To avoid this in the present paper, the casted films are hot pressed. The composite films were pressed at pressure of 40-60 MPa and temperature of 170-180°C, for 3 min. While maintaining the same pressure, the films were cooled to room temperature and flexible PVDF-PZT

composite films were obtained. The pressing conditions, time and cooling conditions have been optimized with rigorous trials. In the process adopted here, the films prepared have no porosity and are of uniform thickness (Fig. 1). Using this method, produced PVDF-PZT composite films exhibit higher d_{33} values, while maintaining flexibility.



Fig. 1 PVDF-PZT composite film prepared by solvent casting followed by hot pressing

As stated earlier, that PZT content higher than 50% lead to brittleness in composite films, hence 50 wt% PVDF-PZT composite has been investigated in present work. For comparison purpose lower wt fraction composition i.e. 10 wt% has also been studied. Two compositions of PVDF-PZT composite (10 and 50 wt% PZT) were developed for this study, by the process explained above. These films were then studied for dielectric properties using Novocontrol Alpha-N High Resolution Dielectric Analyzer. Poling of PVDF-PZT film was carried out by subjecting it to high electric field to align the dipole. The poling of PVDF-PZT was done by maintaining the appropriate voltages varying from 7 to 9 kV/mm, temperatures (70-80°C), pin distance (1-2 cm), and poling duration (1 hour) to ensure the maximum alignment of ferroelectrets. The average piezoelectric charge coefficient (d_{33}) for 50 wt% PVDF-PZT composite films is 40 pC/N with tensile modulus of 1.57 GPa. Similar results have been reported earlier [36].

Results and discussion

Dielectric Properties of PVDF-PZT composites films at room temperature

Accurate measurements of dielectric properties can provide scientists and engineers with valuable information to properly incorporate the material into its intended application, for more solid designs or to monitor a manufacturing process for improved quality control. Measurement of dielectric properties of a material can provide critical design parameter information for many electronics applications. For example, the loss of a cable insulator, the impedance

of a substrate or the frequency of a dielectric resonator can be related to its dielectric properties.

The dielectric properties of PVDF-PZT composites with two different weight fractions of PZT in PVDF were studied using Alpha-N High Resolution Dielectric Analyzer.

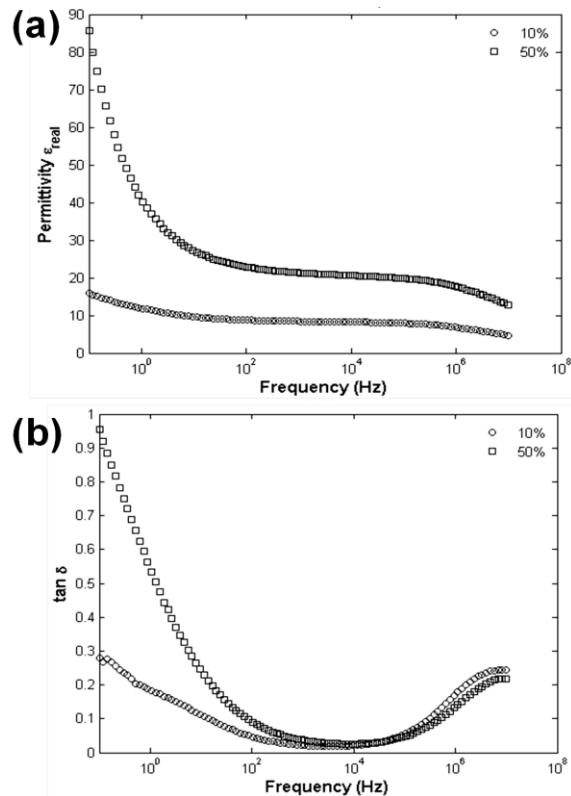


Fig. 2. (a) Relative permittivity, (b) Dielectric loss of PVDF-PZT composite films.

Dielectric constant (k) is equivalent to complex relative permittivity of material (ϵ_r) or the absolute permittivity (ϵ) relative to the permittivity of free space (ϵ_0). The real part of permittivity (ϵ_r') is a measure of how much energy from an external electric field is stored in a material. The imaginary part of permittivity (ϵ_r'') is called the loss factor and is a measure of how dissipative or lossy a material is to an external electric field. The imaginary part of permittivity (ϵ_r'') is always greater than zero and is usually much smaller than (ϵ_r'). The loss factor includes the effects of both dielectric loss and conductivity.

Fig. 2(a) shows relative permittivity (or dielectric constant) of PVDF-PZT composite films. For both compositions of PZT dielectric constant shows good stability in the frequency ranging from 100 Hz-100 kHz and then decreases. The results indicate that the decrease of the relative permittivity of the PVDF-PZT composite films during high frequency range is mainly due to the high frequency dielectric response of the PZT particles. However, the relative dielectric permittivity of the composite films was higher for higher PZT content over the whole frequency range

as indicated in **Fig. 2(a)**. Especially with higher PZT content (50%), the relative permittivity shows high values, which indicate a positive improvement in the composite. The frequency dependence of the dielectric loss ($\tan \delta$) of PVDF-PZT composite with different weight percent of PZT is shown in **Fig. 2(b)**. The dielectric loss shows two relaxations peaks, represented by minima in the curves for 10 and 50 wt% of PVDF-PZT composite; one in the low frequency region (~ 100 Hz) and the other at high frequency (~ 100 kHz). The relaxation beyond 100 kHz is related to the glass transition relaxation and the relaxation that appears at low frequency is attributed to relaxation associated with molecular motion in the crystalline regions [37-39].

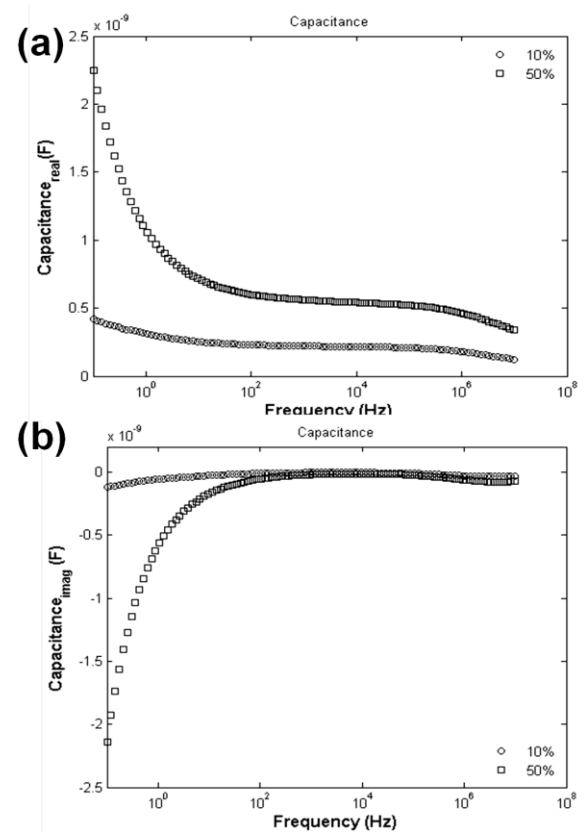


Fig. 3. (a) Real part capacity (b) Imaginary part capacity of PVDF-PZT composite films.

The real and imaginary part capacitance of the PVDF-PZT composite film with different weight fraction of PZT (10 and 50 wt%) is shown in **Fig. 3(a)** and **Fig. 3(b)** respectively. From the **Fig. 3(a)**, it can be seen that the capacitance for 50 wt% composite is higher than that of a 10 wt% composite. The increase in the capacitance using PVDF-PZT composite film is an important step for the practical applications for energy harvesting and storing mechanical energy. Similarly, in case of imaginary part capacitance of PVDF-PZT composite film, higher weight fraction of PZT has higher negative peak value compared to lower weight fraction at a particular frequency as shown in **Fig. 3(b)**.

The electrical conductivity of PVDF-PZT composites with different weight fraction of PZT for 10 and 50 wt% compositions was also determined (Fig. 4(a)). PVDF-PZT composites as dielectric material showed negligible conductivity for all frequencies, except at high frequencies ~1 MHz. The increase in conductivity above certain frequency can be attributed to the release of trapped charge due to the motions of the main polymer chain and to the charge mobility activation [40]. It can be seen from Fig. 4(b), the dielectric modulus value increases at higher frequencies and with increase in PZT weight fraction, modulus reduces. However, the modulus also has almost constant value in the frequency range 100 Hz-100 kHz.

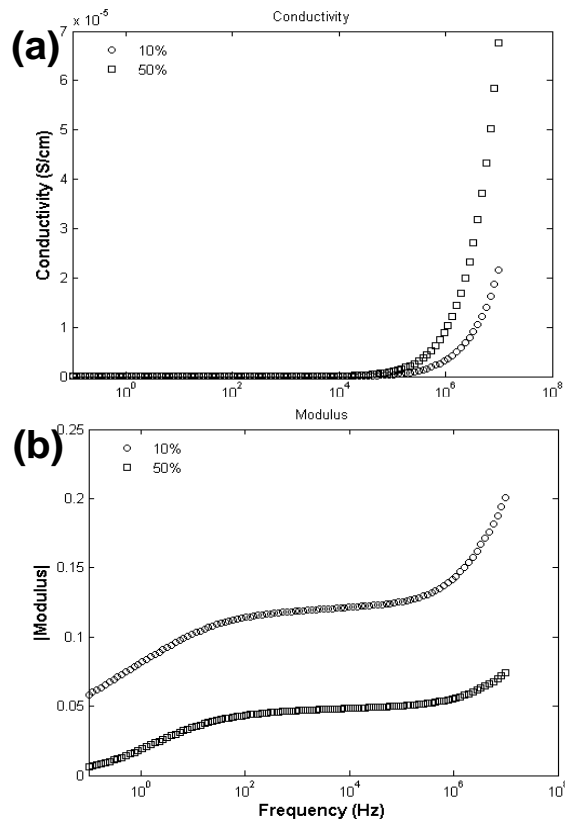


Fig. 4. (a) Conductivity, (b) Modulus of PVDF-PZT composite films

A comparative account of the room temperature dielectric properties of the prepared PVDF-PZT composite films for different wt% is tabulated below. It can be clearly seen that dielectric properties are improved in terms of higher permittivity and capacitance with higher concentration of PZT i.e. 50 wt%. Further temperature dependence studies have been carried out on 50 wt% PVDF-PZT composite sample.

Study of Effect of Temperature on Dielectric properties

For application like sensor and actuators, which are predominant areas for piezoelectric materials, the

sensitivity of device is directly dependent on material properties and the material properties vary with the parameters like temperature, pressure, environment condition etc. Hence, the study of the dependence of material properties (dielectric) with temperature has been carried out for the prepared 50 wt% PVDF-PZT composite films.

Table. 1 Obtained dielectric properties for PVDF-PZT composite films (at 100Hz)

Property	Obtained Value (10%)	Obtained Value (50%)
Relative Permittivity (ϵ_r)	8.74	22.8
Dielectric Loss ($\tan \delta$)	0.046	0.0903
Dielectric Modulus ($ M $)	0.114	0.043
Conductivity ($ \sigma $) (S/cm)	0.443×10^{-9}	1.25×10^{-9}
Capacitance ($ Cp $) (pF)	230	601
Impedance ($ Z $) (M Ω)	6.74	2.57

The study of temperature dependence of dielectric properties was done in following steps:

- Dielectric measurements were done at various temperatures.
- Values obtained at elevated temperatures were normalized with respect to corresponding room temperature values.
- Increment obtained in various dielectric properties as a function of frequency is plotted at various temperatures.

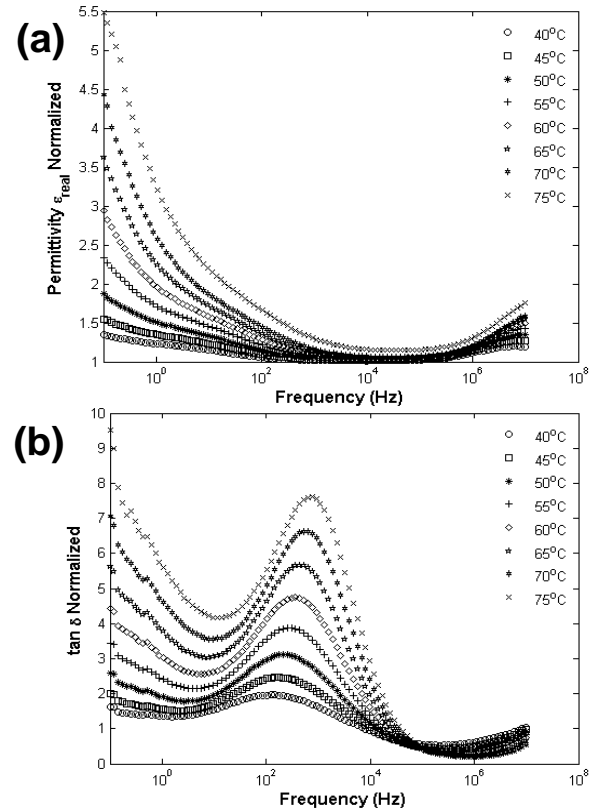


Fig. 5 Variation in (a) Relative permittivity, (b) Dielectric loss at various temperatures for PVDF-PZT composite films Normalized to RT

Fig. 5(a) shows relative permittivity (or dielectric constant) of PVDF-PZT composite films normalized to RT values of the same for 50 wt% PVDF-PZT composite. An increase of about 1.2 to 1.5 times is found in real part permittivity with increase in temperature from 40°C to 75°C in frequency range 100 Hz-100 kHz. The PVDF-PZT composite shows good stability in dielectric constant in the frequency ranging from 100 Hz-100 kHz. However, significant increase in dielectric loss is observed with increase in temperature, even in working frequency range. Losses up to 6-8 times than the RT can be occurring in material at temperature around 70°C and higher. This is due to higher increment in imaginary part permittivity (dielectric loss being ratio of imaginary and real part permittivities), indicating higher losses in material due to temperature (**Fig. 5(b)**).

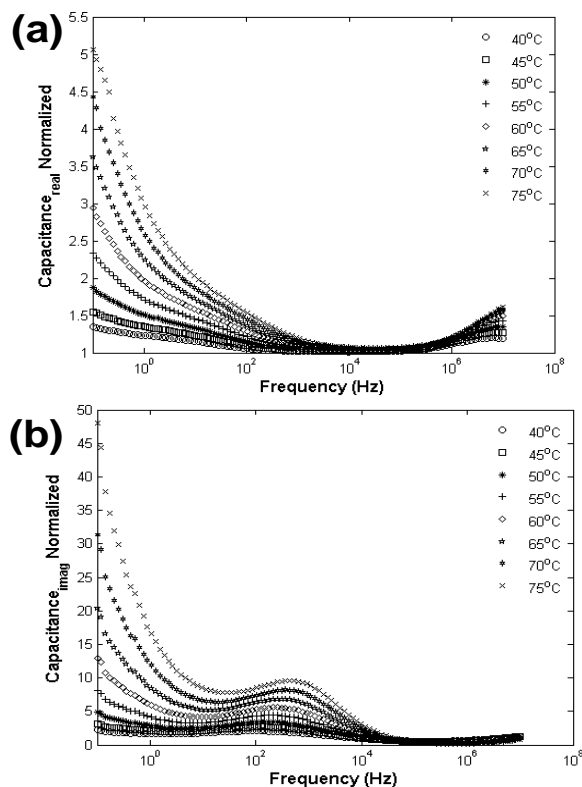


Fig. 6 Variation in (a) Real part capacitance (b) Imaginary part capacitance at various temperatures for PVDF-PZT composite films Normalized to RT

The real and imaginary part capacitance of the PVDF-PZT composite film normalized to RT for 50 wt% at different temperatures is shown in **Fig. 6(a)** and **Fig. 6(b)** respectively. Capacitance being directly related to material permittivity follows same pattern as permittivity. Real part capacitance shows an increase of about 1.2 to 1.5 times with increase in temperature from 40°C to 75°C in frequency range 100 Hz-100 kHz. However, the imaginary part capacitance shows higher increments in the same frequency range. It can cause higher phase difference in current and voltage, which in turn can lead to

higher energy loss, which is seen in dielectric loss as well (**Fig. 5(b)**).

The electrical conductivity of 50 wt% PVDF-PZT composites normalized to RT is shown in **Fig. 7(a)**. With effect of temperature, conductivity is observed to increase, as much as two times in the working frequency range of 100 Hz-100 kHz, and much higher in lower frequency range. This indicates lower impedance of material at lower frequencies and higher temperature, which is deviation from insulator behavior. However, the material conductivity is sufficiently low in the frequency range 100 Hz-100 kHz. The dielectric modulus, on the other hand, is lowered by ~10% near the frequency of 10 kHz with increase in temperature (**Fig. 7(b)**), but is quite low at lower frequencies.

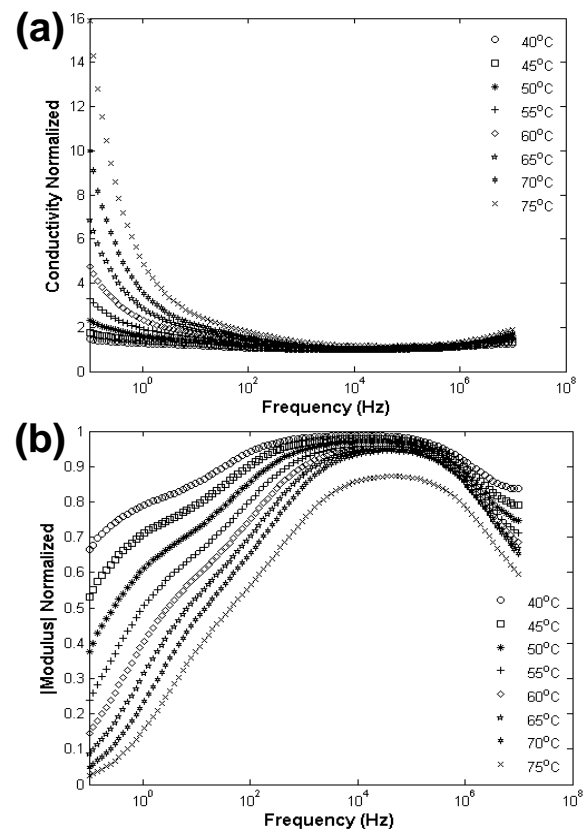


Fig. 7. Variation in (a) Conductivity, (b) Modulus at various temperatures for PVDF-PZT composite films Normalized to RT

Conclusion

To summarize the work, PVDF-PZT composite with two weight fraction of PZT were developed. The preparation method used in the study is combination of solvent casting followed by hot pressing for better packing, connectivity of piezoelectric phase and uniformity of the films. Dielectric behaviour of these films was investigated as a function of frequency (range 10^{-1} to 10^7 Hz) at various temperatures ranging from RT to 75°C. The AC dielectric properties were found to be mostly stable in the frequency range 100 Hz-100 kHz. Typical values of various dielectric

properties obtained for both the compositions have been presented, which shows better properties with higher filler content in the composite. With effect of temperature, increase in dielectric properties values was observed, which may be accounted to pyroelectric behaviour of material. In addition, this increment is quantifiable and stable with frequency in range 100 Hz to 100 kHz. At low frequencies, the deviation from RT characteristics was very significant for different temperatures than at higher frequencies.

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References

1. Beatrix, P.; Bernd, P.; Shin, F. G.; Chan, H. L. W.; Choy, C. L. *Appl. Phys. Lett.* **2000**, *76*, 2776.
2. Chan, H. L. W.; Zhang, Q. Q.; Ng, W. Y.; Choy, C. L. *IEEE Trans. Dielectr. Electr. Insul.* **2000**, *7*, 204.
3. Kitayama, T.; Sugawara, Rept. Prof. Gr. *Inst. Elec. Comm. Eng. Japan*, **1972**, 72.
4. Pauer, L. A. *J. Acoust. Soc. Am.* **1974**, *55*, 444.
5. Harrison, W. B. *Proc. Workshop on Sonar Transducer Mat.* **1976**, *459*, 143.
6. Newnham, R. E.; Skinner, D. P.; Cross, L. E. *Mater. Res. Bull.* **1978**, *13*, 525.
7. Newnham, R. E.; Safari, A.; Giniewicz, J.; Fox, B. M. *Ferroelectrics*. **1984**, *60*, 15.
8. Safari, A.; Lee, Y. H.; Halliyal, A.; Newrtham, R. E. *Am. Ceram. Soc. Bull.* **1987**, *66*, 668.
9. Banno, H. *Ferroelectrics*. **1983**, *50*, 3.
10. Yamada, T.; Ueda, T.; Kitayama, T. *J. Appl. Phys.*, **1982**, *53*, 4328.
11. Muralidhar, C.; Pillai, P. K. C. *IEEE Trans. Electr. Insul.* **1986**, *21*, 501.
12. Sinha, D.; Muralidhar, C.; Pillai, P. K. C. *IEEE Trans. Electr. Insul.* **1986**, *22*, 827.
13. Muralidhar, C.; Pillai, P. K. C. *J. Mater. Sci. Lett.* **1987**, *6*, 346.
14. Sinha, D.; Shroff, N.; Pillai, P. K. C. *Ferroelectrics*. **1990**, *103*, 49.
15. Abdullah, M. J.; Das-Gupta, D. K. *IEEE Trans. Electr. Insul.* **1990**, *25*, 605.
16. Daben, Y. *Ferroelectrics*. **1990**, *101*, 291.
17. Sergeeva, A. E.; Fedosov, S. N.; Pissis, P. *IEEE Dielectric Elect. Insul. Soc.* **1994**, *8*, 748.
18. Sergeeva, A. E.; Fedosov, S. N.; Vanderschueren, J.; Thielen, A. *IEEE*. **1994**, *8*, 742.
19. Wei, B.; Daben, Y. *Ferroelectrics*. **1994**, *157*, 427.
20. Xuexong, H.; Yangz, X.; Jingde, L. *IEEE Dielectric Elect. Insul. Soc.* **1994**, *8*, 760.
21. Venkatragavaraj, E.; Satish, B.; Vinod, P. R.; Vijaya, M. S. *J. Phys. D: Appl. Phys.* **2001**, *34*, 487.
22. Seema, A.; Dayas, K. R.; Varghese, J. M. *J. Appl. Polym. Sci.* **2007**, *106*, 146.
23. Gregorio Jr., R.; Cestari, M.; Bernardino, F. E. *J. Mater. Sci.* **1996**, *31*, 2925.
24. Furukawa, T.; Ishida, K.; Fukada, E. *J. Appl. Phys.*, **1979**, *50*, 4904.
25. Higashihata, Y.; Yagi, T.; Sako, J. *Ferroelectrics*. **1986**, *68*, 63.
26. Wei, B.; Daben, Y. *Ferroelectrics*. **1994**, *157*, 427.
27. Bhimasankaram, T.; Suryanarayana, S. V.; Prasad, G. *Curr. Sci.* **1998**, *74*, 967.
28. Chan, H. L. W.; Chan, W. K.; Zhang, Y.; Choy, C. L. *IEEE Trans. Dielectr. Electr. Insul.* **1998**, *5*, 505.
29. Chan, H. L. W.; Zhang, Q. Q.; Ng, W. Y.; Choy, C. L. *IEEE Trans. Dielectr. Electr. Insul.* **2000**, *7*, 204.
30. Wegener, M.; Arlt, K. *J. Phys. D: Appl. Phys.* **2008**, *41*, 165409.
31. Dietze, M.; Krause, J.; Solterbeck, C. H.; Es-Souni, M. *J. Appl. Phys.* **2007**, *101*, 54113.
32. Fava, R. *Methods of Experimental Physics*; Academic Press: New York, **1980**, pp. 137, 237, 291, 379.
33. Bower, D. I. *An Introduction to Polymer Physics*; Cambridge University Press: United Kingdom, **2002**, pp. 27, 87, 206, 256, 260.
34. Runt, J. P.; Fitzgerald, J. J. *Dielectric Spectroscopy of Polymeric Materials*; American Chemical Society: Washington, DC, **1997**, pp. 67, 81, 227, 307, 380.
35. Jain, A.; Rashmi, P. N.; Jayanth, K. S.; Swaroop, J. C. *Indian Journal of Advances in Chemical Science*, **2014**, 212.
36. Jain, A.; Jayanth Kumar, S.; Ramesh Kumar, M.; Sri Ganesh, A.; Srikanth, S. *Mech. Adv. Mater. Struct.* **2014**, *21*, 181.
37. Gregorio Jr, R.; Cestari M. *J. Poly. Sci. B, Poly. Phys.* **1994**, *32*, 859.
38. Gregorio Jr, R.; Ueno, E. M. *J. Mater. Sci.* **1999**, *34*, 4489.
39. Channal, C. V.; Jog, J. P. *eXPRESS Polym. Lett.* **2008**, *4*, 294.
40. Shash, N. M.; Khoder, H.; Metawe, F.; Negm, A. A. *J. Appl. Polym. Sci.* **2013**, *129*, 2796.