

RESEARCH ARTICLE

Poling Effect and Temperature on Electrical Behaviour of PZT-Polymer Composites with 0-3 Connectivity

P Gowdhaman¹, R Sakthi Sudar Saravanan¹, *V Annamalai¹, Haresh M Pandya¹

¹Department of Physics, Chikkanna Government Arts College, Tiruppur, Tamilnadu, India.

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ABSTRACT

An attempt has been made to prepare PZT-polymer composite using Poly (methyl methacrylate) and a mixed polymer (Polyvinylidene fluoride and Polyvinyl chloride) as polymer phase. Based on the properties of polymer phases, two different preparation techniques have been used for the composite preparation and a hot press method has been adopted for the sample preparation. The inhomogeneity of ceramic phase over the polymer matrix has been revealed from the surface morphological studies. Dielectric constant and dielectric loss of the composite is found to be increased with the increase in temperature irrespective of poled and unpoled samples. Temperature dependence of AC conductivity increases with rise in temperature. The dielectric and pyroelectric performance of PZT-PMMA composite lags behind the PZT-PVDF/PVC composite.

Keywords: PZT-PVDF/PVC, PZT-PMMA, Piezo-composite, AC conductivity, Dielectric constant.

1. INTRODUCTION

The piezoelectric ceramic-polymer composites are one of the versatile materials used for the sensor and accelerometer applications. The presence of piezoelectric behaviour in these composite materials makes them a novel material, which are under study for a broad range of applications [1–4]. Among numerous piezoelectric ceramic materials, a perovskite structured lead based ferroelectric ceramic, Lead Zirconate Titanate (PZT) has been a key material under study due to its excellent dielectric and piezoelectric properties at its Morphotropic Phase Boundary (MPB) [5, 6]. However piezoelectric ceramics have their own limitation which constrains their use as a single phase material for the applications where flexibility is desirable. Piezoelectric polymers are identified to be an alternative material to overcome limitations of raw ceramic phase, but it has low dielectric and piezoelectric properties [1, 4, 7, 8]. Hence ceramic-polymer phases are often combined together to form a biphasic composite material which is reliable for practical applications.

Dispersion of ceramic particles into the polymer matrix have been identified to be a simple and advantageous method for the

preparation of a biphasic solid composite. This type of combination has been represented as 0-3 connectivity which was given by [9].

Composites with different PZT-polymer combinations have been attempted and their dielectric, piezoelectric and pyroelectric properties were mainly focused by many researchers around the globe [2]. Two different composites were prepared in this work by keeping PZT as ceramic phase and varying the polymer phase by fixing 0.5 as the volume fraction of PZT. Poly (methyl methacrylate) (PMMA) and a mixed polymer (Polyvinylidene fluoride (PVDF) and Polyvinyl chloride (PVC)) have been used as a polymer phase for the composite preparation. An attempt has been made to study some of the electrical properties of poled and unpoled piezo-composites and the obtained results were analyzed and reported in this work.

2. EXPERIMENTAL METHODS

2.1. Materials, methods and characterization

The piezoelectric ceramic APC 855 (Navy Type VI) obtained from American piezo-ceramics and piezoelectric polymers

*Corresponding author. Tel.: +919791493045

Email address: annamalai_140795@yahoo.co.in(V.Annamalai)

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PVDF (Sigma-Aldrich Chemicals), PMMA and PVC (Himedia Chemicals) have been used for the composites preparation. For the mixed polymer composite preparation, the ratio of PVDF and PVC has been chosen as 4:1. Cyclohexanone and acetone was used as solvent for mixed polymer and PMMA composite respectively. The mixed polymer composite was made at 160°C whereas PMMA composite was prepared at 120°C. The hot press method has been used to make composite samples in the form of pellet at a uniaxial pressure of 66 Mpa [3, 4]. The pellets were electroded on both sides using conductive silver paste (Sigma-Aldrich Chemicals) and subsequently poling have been done at 25 kV/cm by using poling apparatus.

Surface analysis of the composite samples has been made by using scanning electron microscope (JEOL-model 6390, Oxford Instruments). The capacitance (C) and dielectric loss measurement for the poled and unpoled samples were carried out using an LCR meter (Agilent 4284A) in the temperature range of 40 – 150 °C at 1 kHz frequency.

3. RESULTS AND DISCUSSION

3.1. Surface morphology

The surface morphological spectra of PZT-PVDF/PVC and PZT-PMMA composite has been represented in figure 1. From the figure it is revealed that the ceramic particles are dispersed into the polymer matrix inhomogeneously. On further comparison with both the composites, PZT-PMMA composite has more agglomeration than that of the PZT-PVDF/PVC composite. Since PZT-PMMA composite was prepared using acetone as a solvent at low temperature (say 60°C), the PZT particles get clustered over the polymer matrix. Thus the clustered PZT ceramic particles in the PZT-PMMA composite might have led to the increase of voids in the composite samples. It is also noted that the PZT-PVDF/PVC composite was prepared at 160°C using cyclohexanone as solvent and thereby PZT particles in it is likely to spread over the polymer phase. Therefore, there is a less probability of the formation of voids in the PZT-PVDF/PVC composite samples than that of the PZT-PMMA composite.

3.2. Dielectric properties

3.2.1. Dielectric constant (ϵ_r)

The dielectric constant values were calculated from the measured capacitance values and it is presented in figure A1. For both the composites unpoled samples have greater dielectric constant when compared to the poled one and this might be due to the induced polarization. It is also observed that the PZT-PVDF/PVC composite has better dielectric constant than the PZT-PMMA composite due to the presence of polymer PVDF which has better dielectric properties over PMMA.

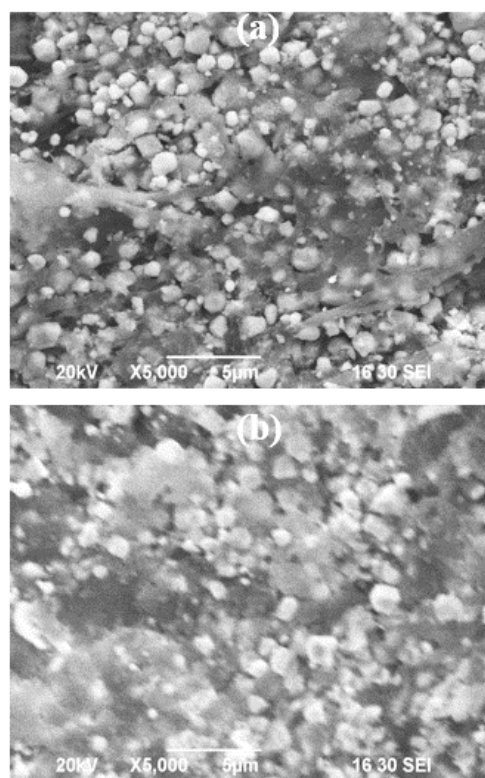


Figure 1. Surface morphology of (a) PZT-PVDF/PVC composite (b) PZT-PMMA composite

The ϵ_r of both poled and unpoled samples increase with increase in temperature. At high temperature region (beyond 100°C) the ϵ_r for unpoled sample has sharply increased with increase in temperature. The steep increase in ϵ_r in this region can be understood in terms of thermally activated transport property and presence of space charges in the prepared composites. The variation in the dielectric constant is mainly attributed due to the relaxation behaviour of polymer (PVDF) phase at higher temperatures [8].

3.2.2. Dielectric loss ($\tan \delta$)

Dielectric loss of poled and unpoled samples of both the composite has been shown in figure A2. From the figure it is clearly shown that the poled sample has more dielectric loss comparing to unpoled sample irrespective of the composite. In both the cases the dielectric loss factor increases with increasing temperature. In the case of PZT-PVDF/PVC composite, above 60°C the value of $\tan \delta$ for both the samples (poled and unpoled) increases monotonically which is related to space charge polarization. However, a steady increase in $\tan \delta$ has been observed in PZT-PMMA composite until 100°C beyond which its start to rise rapidly.

3.3. AC conductivity

The AC conductivity of the prepared composites was calculated by using the formula, $\sigma_{ac} = 2\pi f \epsilon_0 \epsilon_r \tan \delta$, where, ϵ_0 is the permittivity of free space and f is the frequency of the applied field [10].

The conductivity of the poled and unpoled samples at various temperatures has been shown in figure A3. From the figure it shows that the conductivity of poled sample is higher when compared to the unpoled sample due to the orientation of electric dipoles during poling. In the PZT-PVDF/PVC composite, the temperature dependence of the conductivity was found to present a linear behaviour, which indicate the existence of thermally activated transport mechanism. In the case of PZT-PMMA composite when the conductivity becomes low and stable, a steeper increase was observed beyond 110°C due to the higher flexibility of PMMA at higher temperature.

The activation energy of the prepared composites has been found from the slope of the plot between $1000/T$ and $\ln \sigma_{ac}$ (shown in figure A4) by making use of the well-known Arrhenius relation [11]. The calculated values are shown in table 1. From the table it is observed that the poled samples have lower activation energy than that of the unpoled sample irrespective of the composite. The PZT-PVDF/PVC composite has lower activation energy and higher dielectric constant than that of the PZT-PMMA composite which is an essential parameter for the preparation of piezoelectric composites [2, 4, 8].

Table 1. Activation energy of poled and unpoled composites

Composite Type		Activation Energy (eV)
PZT-PVDF/PVC Composite	Unpoled	0.3490
	Poled	0.2809
PZT-PMMA Composite	Unpoled	0.2430
	Poled	0.2267

4. CONCLUSION

The successful fabrication of PZT-PVDF/PVC and PZT-PMMA composite have been done by using the hot press method for a fixed volume fraction of PZT. The dielectric constant and dielectric loss is found to be incremented with the increase in temperature for the poled and unpoled composite samples. The relaxation of polymer matrix at higher temperatures causes the rise in dielectric constant values with increase in temperature. The unpoled sample has greater dielectric constant values when compared to poled sample due to the induced polarization. The conductivity increases with increase in temperature irrespective of poled and unpoled sample because of the thermally activated transportation mechanism. In comparison with both the types of composite, in a nutshell, it can be concluded that the PZT-PVDF/PVC composite have lower activation energy and high dielectric properties with respect to temperature over PZT-PMMA composite. This parameter is an essential one for the preparation of piezoelectric materials.

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REFERENCES

- [1] Anjana Jain, K.J.Prashanth, K.R.Asheesh, Sharma, Arpit Jain and P.N.Rashmi, Dielectric and Piezoelectric Properties of PVDF/PZT Composites: A Review, Polymer Engineering Science, Vol. 55, No. 7, 2015, pp. 1589-1616, <http://dx.doi.org/10.1002/pen.24088>.
- [2] S.Sundaram, P.Sampathkumar, P.Gowdhaman and V.Annamalai,

- Dielectric and Piezoelectric Properties of Various Ferroelectric Ceramic-Polymer Composites, *Journal of Environmental Nanotechnology*, Vol. 3, No. 3, 2014, pp. 27-31, <http://dx.doi.org/10.13074/jent.2014.09.1412088>.
- [3] P.Gowdhaman, H.M.Pandya, P.R.Kumar and V.Annamalai, Influence of Phase Transformation in PVDF-PZT Composites of 0-3 Connectivity, *Journal of Environmental Nanotechnology*, Vol. 4, No. 4, 2015, pp. 28-30, <http://dx.doi.org/10.13074/jent.2015.12.154168>.
- [4] P.Gowdhaman, V.Annamalai and O.P.Thakur, Piezo, Ferro and Dielectric Properties of Ceramic-Polymer Composites of 0-3 Connectivity, *Journal of Ferroelectrics*, Vol. 493, No. 1, 2015, pp. 120-129, <http://dx.doi.org/10.1080/00150193.2016.1134028>.
- [5] P.Gowdhaman, V.Annamalai, H.M.Pandya and P.R.Kumar, Significance of Micro and Nano PZT Particles on Dielectric and Piezoelectric Properties of PZT-PVDF Composites, *International Journal of Scientific Research*, Vol. 2, No. 3, 2016, pp. 64-68, <http://dx.doi.org/10.7439/ijasar.v2i3.3099>.
- [6] V.Tiwari and G.Srivastava, Structural, Dielectric and Piezoelectric Properties of 0–3 PZT/PVDF Composites, *Ceramics International*, Vol. 41, No. 6, 2015, pp. 8008-8013, <http://dx.doi.org/10.1016/j.ceramint.2015.02.148>.
- [7] R.Senthilkumar, K.Sridevi, J.Venkatesan, V.Annamalai and M.S.Vijaya, Investigations on Ferroelectric PZT-PVDF Composites of 0–3 Connectivity, *Journal of Ferroelectrics*, Vol. 325, No. 1, 2011, pp. 121-130, <http://dx.doi.org/10.1080/00150190500328544>.
- [8] P.Gowdhaman, K.Antonyraj and V.Annamalai, An effective approach on physical and dielectric properties of PZT-PVDF composites, *International Journal of Scientific Research*, Vol. 1, No. 8, 2015, pp. 322-328, <http://dx.doi.org/10.7439/ijasar.v1i8.2511>.
- [9] R.E.Newnham, D.P.Skinner and L.E.Cross, Connectivity and Piezoelectric-Pyroelectric Composites, *Materials Research Bulletin*, Vol. 13, No. 5, 1978, pp. 525-536, [http://dx.doi.org/10.1016/0025-5408\(78\)90161-7](http://dx.doi.org/10.1016/0025-5408(78)90161-7).
- [10] M.Meena, C.K.Mahadevan, R.Shakthi Sundar Saravanan and V.N.Praveen, Effect of Added Impurities on the Properties of LAHCL Single Crystals, *International Journal of Macro and Nano Physics*, Vol. 1, No. 1, 2016, pp. 12-18, <http://dx.doi.org/10.18831/djphys.org/2016011002>.
- [11] R.Sakthi Sudar Saravanan, D.Pukazhselva and C.K.Mahadevan, Studies on the Synthesis of Cubic ZnS Quantum Dots, Capping and Optical–Electrical Characteristics, *Journal of Alloys and Compounds*, Vol. 517, 2012, pp. 139-148, <http://dx.doi.org/10.1016/j.jallcom.2011.12.060>.

APPENDIX

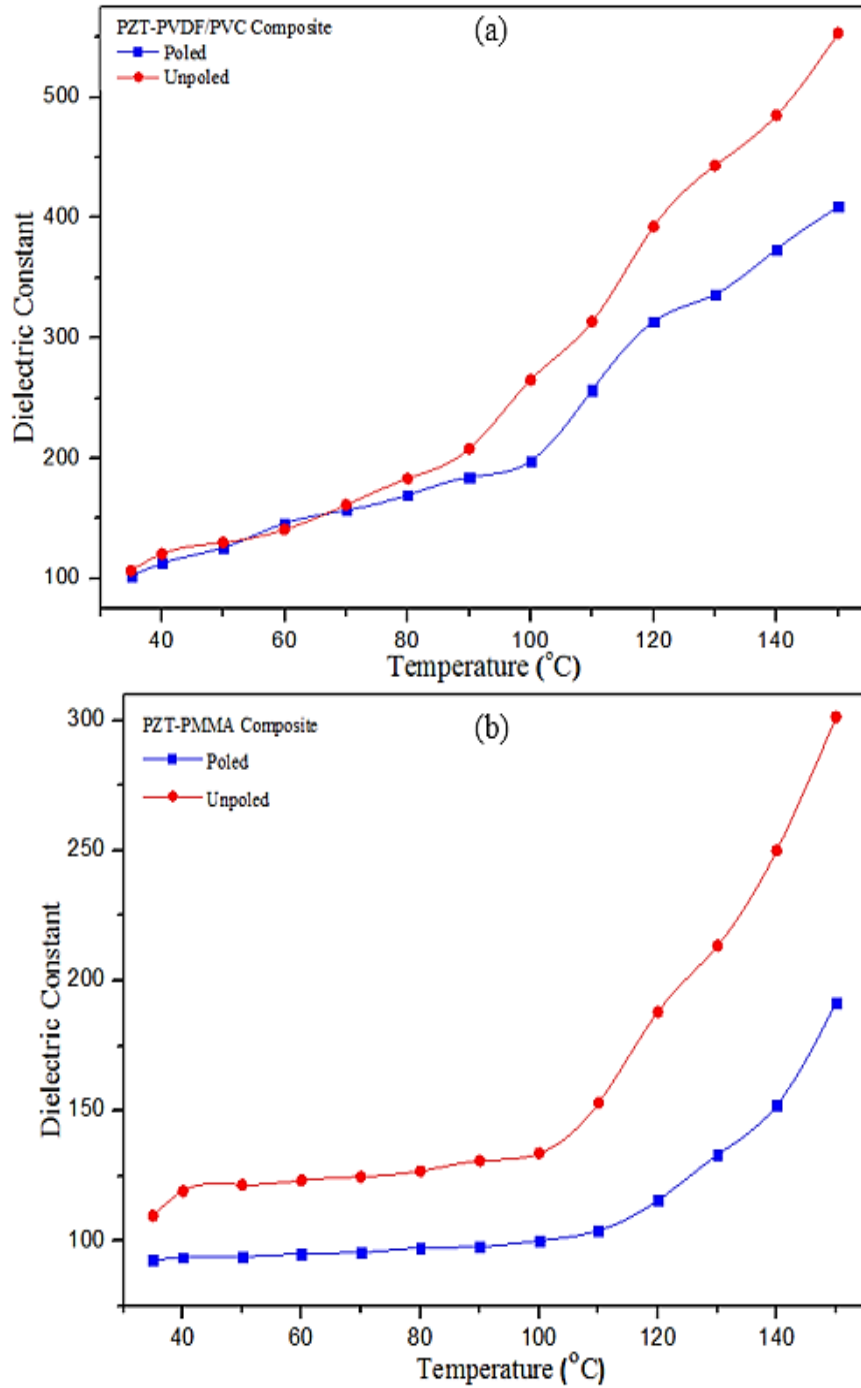


Figure A1. Variation of dielectric constant with temperature for (a) PZT-PVDF/PVC composite (b) PZT-PMMA composite

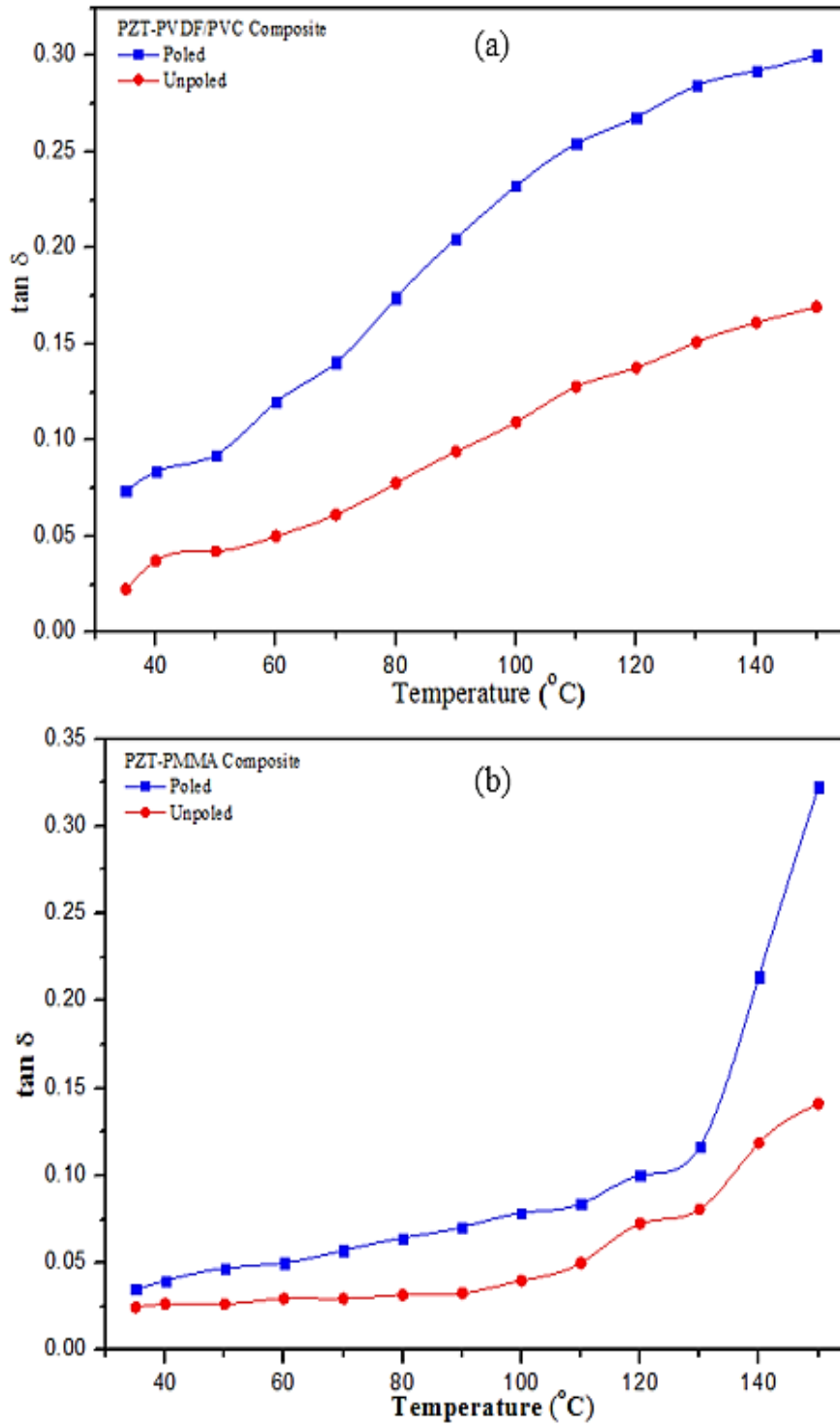


Figure A2. Dielectric loss of poled and unpoled (a) PZT-PVDF/PVC composite (b) PZT-PMMA composite

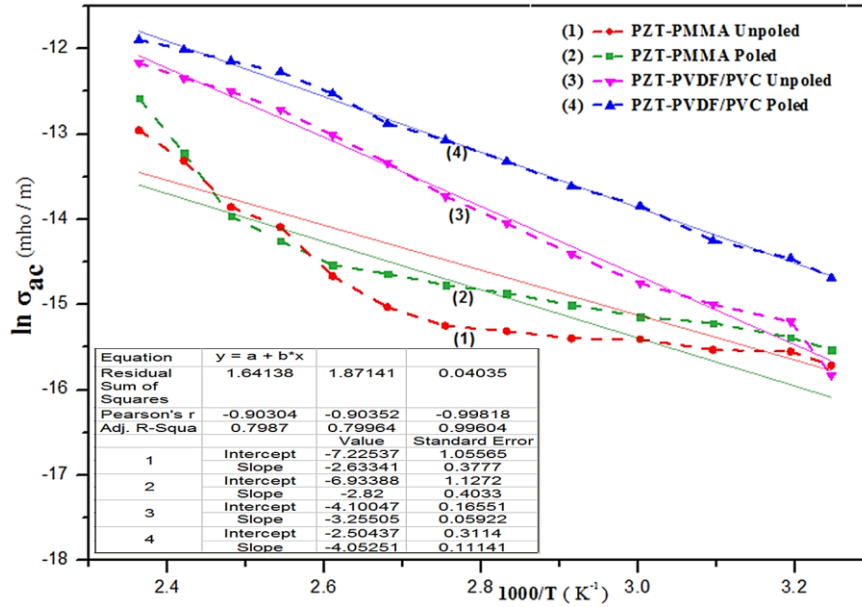


Figure A3. Temperature dependence of AC conductivity for (a) PZT-PVDF/PVC composite (b) PZT-PMMA composite

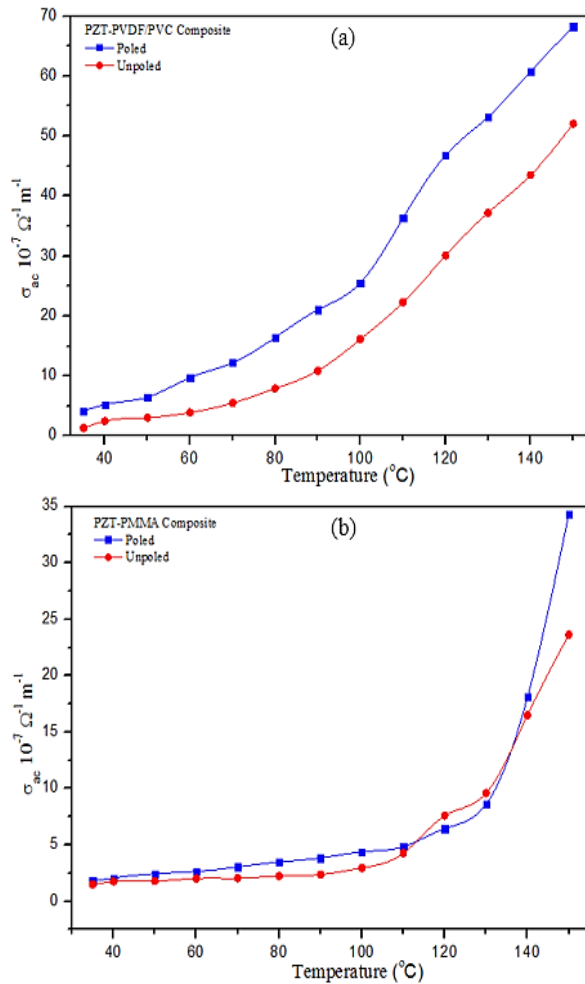


Figure A4. Comparison plot between 1000/T and $\ln \sigma_{ac}$ for poled and unpoled composite