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Electrical properties of a composite of polyurethane and ferroelectric ceramics

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Ferroelectric ceramic particles based on lead titanate zirconate (PZT) were dispersed in a polymer matrix based on castor oil. After the poling process, the pyroelectric activity of this composite was measured using a direct method in which a linear heating rate was applied to the pre-poled samples. The pyroelectric coefficient at 343 K is comparable with that of a PZT–poly(vinylidene fluoride) (PVDF) composite and significantly higher than that of PVDF.

1. Introduction

The composite systems of polymer and ferroelectric lead titanate zirconate (PZT) ceramics reveal pyroelectric properties if they have been subjected to a high direct-current electric field [1, 2]. This process causes the orientation of PZT ceramics in the composites. It is the well-known poling process and, as a result, the composites show an electrical response due to a change in temperature.

The ferroelectric composites have received considerable attention because of some advantages compared with ferroelectric ceramics or ferroelectric polymers [3, 4]. Relative to ceramics, they are flexible and light and combine the mechanical strength of polymeric films with the high pyroelectric responses of ceramics.

The piezo-electric and pyroelectric polymers have been studied since the early work on piezoelectricity in biopolymers realized by Fukada [5, 6]. A great number of papers were published mainly about poly(vinylidene fluoride) (PVDF) [7–9]. These properties in composites were also described by many researchers, using an epoxy-resin-like polymeric matrix and PVDF [10–12].

An excellent review about the piezoelectric and pyroelectric properties of polymer and composite has been given by Furukawa [13] and Das-Gupta [14]. Although piezoelectricity and pyroelectricity in composites have been studied for a long time, the interest in new materials for use in electronic industry has motivated the continuing work on this topic. The present paper shows the pyroelectric activity of a composite of polyurethane (PU) and PZT ceramics and a composite of PU and barium titanate ($BaTiO_3$). The PU is based on castor oil.

2. Experimental procedures

PZT–PU composites were prepared from PZT ceramic powder (EPC 21; European Piezo Ceramics, Ltd) of mean diameter 2 μm, mixed with the PU of vegetable origin, resulting from the reaction of isocyanate and ester of ricinoleic acid. The inclusions of ceramics powder in the polymeric matrix provide a two-phase system in which the piezoelectric crystalline phase is dispersed in a non-piezoelectric amorphous phase.

The composites were obtained in a thin-film form by the spin-coating method in a thickness range 100–300 μm. An aluminium electrode of circular area with 1.5 cm radius was deposited on both sides of the sample film in the Cooke vacuum evaporator system. $BaTiO_3$–PU composites were obtained in a similar way using a $BaTiO_3$ powder from Aldrich Chemical Company, Inc., with a grain size about 3.0 μm.

A Keithley 247 high-voltage supply was used for poling the samples. The pre-poled samples were placed in the thermally stimulate current (TSC) measuring system from Toyo Seiki with a temperature controller. The currents were monitored with a Keithley 610 C electrometer and were then suitably fed to an ECB-102 recorder.

The dielectric data were taken using an HP 4192A LF impedance analyser and microcomputer automatic system which has recently been developed in our laboratory. The pyroelectric currents were measured using a direct method [15, 16] in which a linear heating rate of $1\,\mathrm{K\,min^{-1}}$ was applied to the pre-poled samples. Fig. 1 shows the main part of the TSC measuring system.

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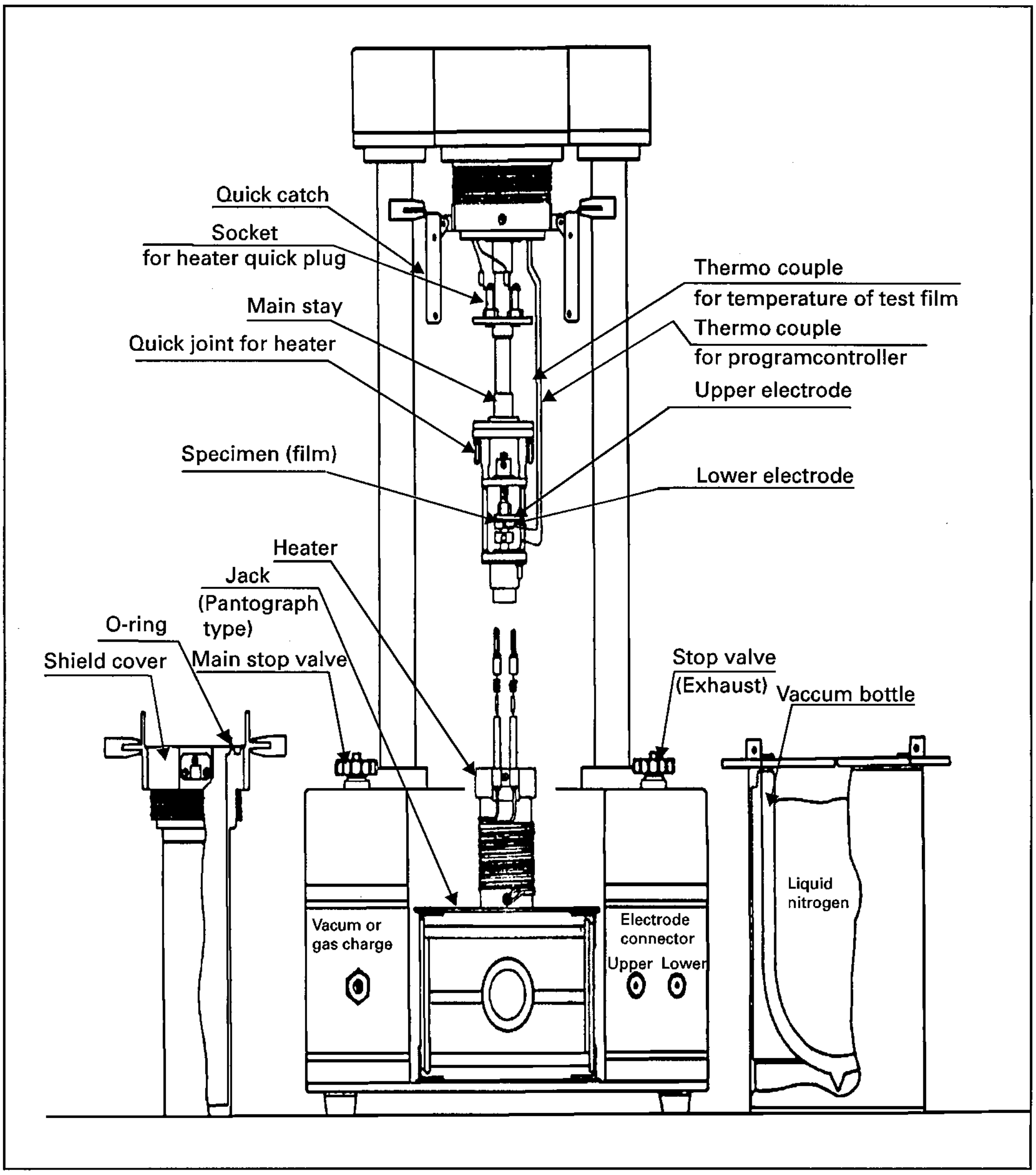

Figure 1 Main part of the TSC measuring system from Toyo Seiki.

3. Results and discussion

Fig. 2a shows the behaviour of the dielectric permittivity of PZT–PU composites as a function of temperature. In all PZT–PU composite compositions (11, 15, 19 and 32 vol% PZT) used in this work, ε' increased with increasing temperature and also with increasing PZT content, Table I. There is a significant difference between the permittivity values for samples with 15 and 19 vol% PZT and a small difference between the samples with 19 and 32 vol% PZT. A higher PZT content than 32 vol% was not used because of the inflexibility of the sample. Fig. 2b shows the variation in ε' as a function of frequency for different temperatures for a sample, 19 vol% PZT–PU. There is no appreciable change in the dielectric permitivity in the frequency range 10–100 kHz in the temperature range 313–333 K.

Fig. 3 shows the behaviour of the dielectric loss, ε'', for 19 vol% PZT–PU at different temperatures. It may be observed that the value of ε'' increases as the temperature is increased. A relaxation peak is observed and it shifts to a higher frequency for increasing temperature. Using the Arrhenius equation, $f_m = f_0 \exp(-\Delta E/kT)$, the activation energy of this process is found to be 1.65 eV which is comparable with that of PU, i.e., 1.47 eV [20]. This suggests that the relaxation process in the PZT–PU composite may be due to α relaxation in the polymer phase. The same behaviours of ε' and ε'' is observed for the $BaTiO_3$–PU composite, as shown in Figs 4 and 5.

To measure the pyroelectric coefficient, the sample is heated at a constant rate with its electrode shorted and the short-circuit current is monitored with an appropriate impedance electrometer. The first run provides an irreversible current owing to the released space charge injected during the poling process. The amplitude of this current is reduced in subsequent

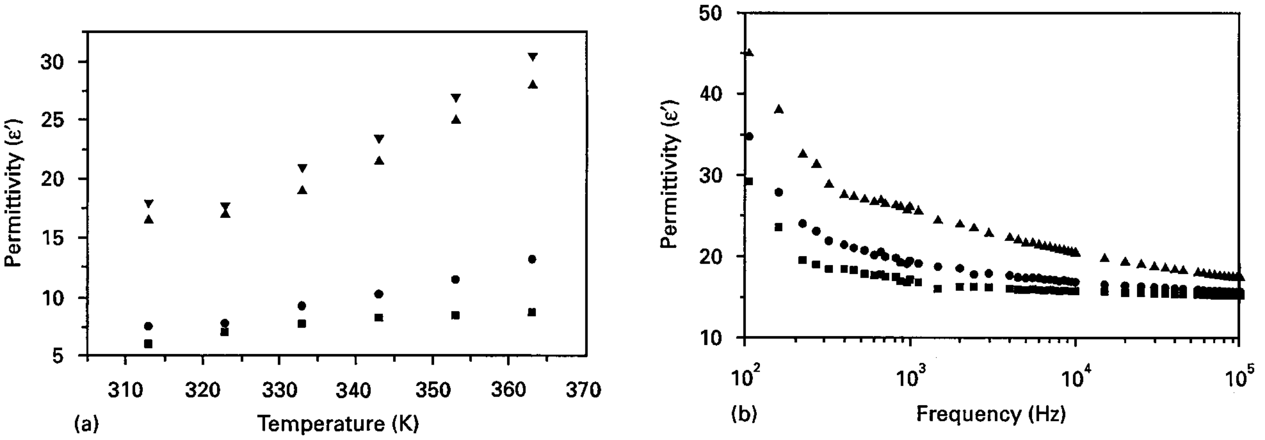

Figure 2 (a) The behaviour of ε' against temperature for PZT–PU at 1 kHz. (■), 11 vol% PZT–89 vol% PU; (●), 15 vol% PZT–85 vol% PU; (▲), 19 vol% PZT–81 vol% PU; (▼), 32 vol% PZT–68 vol% PU. (b) The behaviour of ε' against frequency for 19 vol% PZT–81 vol% PU. (■), $T = 313$ K; (●), $T = 333$ K; (▲), $T = 353$ K.

TABLE I Data for the composites reported in this paper in comparison with the data for composites described in the literature.

Composite (volume)	ρ (10^3 kg m^{-3})	*p* (343 K) (10^{-4} C m^{-2} K^{-1})	*k* 1 KHz (343 K)	FM (10^{-4}) (343 K)	FM FM$_{\mathrm{PZT}}$ (343 K)
PZT/PU:11/89	4.33	3.3×10^{-4}	8.3	0.4	1.0
PZT/PU:15/85	4.96	7.9×10^{-6}	10.3	0.8	2.0
PZT/PU:19/81	5.4	3.3×10^{-5}	21.0	1.6	4.0
PZT/PU:32/68	6.23	5.8×10^{-5}	24.0	2.4	6.0
PZT/PVDF:50/50[14]	—	1.4×10^{-4}	85.0	1.7	4.3
PZT/VDF-TrFE:50/50[14]	—	1.4×10^{-4}	95.0	1.5	3.8
PZT[14]	7.50	5.0×10^{-4}	1200.0	0.4	1.0
PVDF[14]	1.96	9.0×10^{-6}	12.0	0.8	2.0

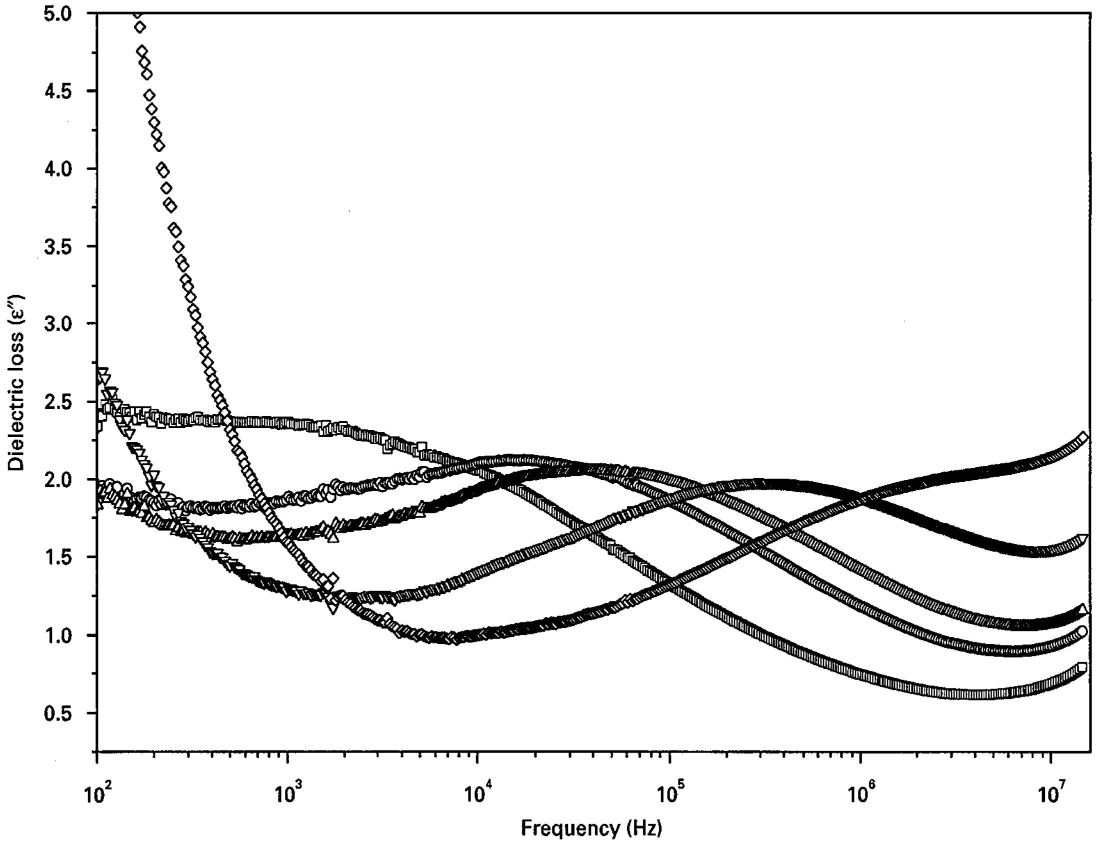

Figure 3 Dielectric loss behaviour against frequency for the 19 vol% PZT–81 vol% PU composite for various temperatures. (□), $T = 364$ K; (○), $T = 381$ K; (△), $T = 387$ K; (▽), $T = 404$ K; (◇), $T = 425$ K.

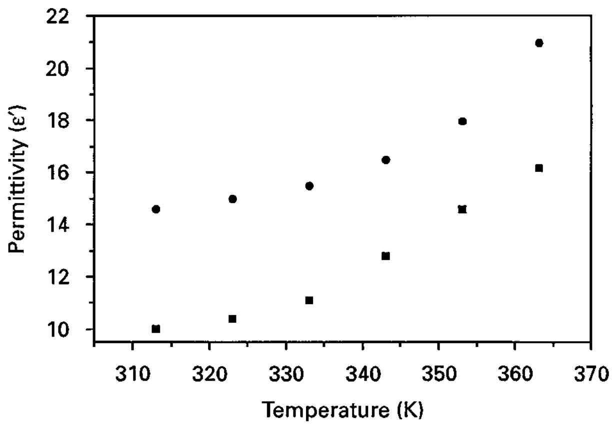

Figure 4 The behaviour of ε' against temperature for $BaTiO_3$–PU at 1kHz. (■), 15 vol% $BaTiO_3$–85 vol% PU; (●), 19 vol% $BaTiO_3$–81 vol% PU.

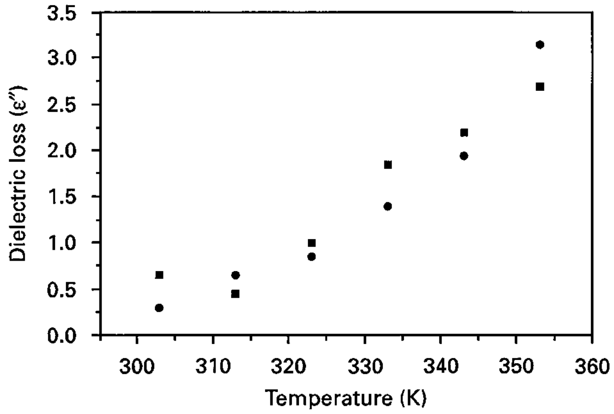

Figure 5 Dielectric loss behaviour against temperature for $BaTiO_3$–PU at 1 kHz. (■), 15 vol% $BaTiO_3$–85 vol% PU; (●), 19 vol% $BaTiO_3$–81 vol% PU.

following runs. When no appreciable current reduction is observed, a reversible pyroelectric current in the sample is established. A typical thermally stimulated discharge current in a 19 vol% PZT–PU composite is shown in Fig. 6 which was obtained with the pre-poled sample at 363 K in an electric field of $10\,\mathrm{KV\,mm^{-1}}$ for 1.0 h and cooled to room temperature in the presence of field. The peak observed in the first run could be attributed to the relaxation of the polymer. This is due to dipolar disorientation of the lateral groups. This peak resulted from the superposition of dipolar groups with a continuum distribution of the relaxation time [20].

The pyroelectric coefficient, $p(T)$, can be evaluated using the relation

$$P(T) = \frac{1}{A}\left[\frac{I_p}{\mathrm{d}T/\mathrm{d}t}\right] \tag{1}$$

where I_p is the short-circuit pyroelectric current, A is the sample area and $\mathrm{d}T/\mathrm{d}t$ is the heating rate ($1\,\mathrm{K\,min^{-1}}$).

Using Equation 1 and the thermally stimulated discharge current we can obtain the pyroelectric coefficient as a function of temperature. Fig. 7 shows the pyroelectric coefficient of PZT–PU composites of various compositions. The pyroelectric activity is very small for the 11 vol% PZT–PU composite in the 320–340 K temperature range, but for the 32 vol% PZT–PU composite the value of the pyroelectric coefficient is comparable with those of other composites described in the literature, as shown in Table II. The values ε'(PZT) = 1250 and ε'(PZT–PU) = 24 at 343 K were used to obtain the PZT and PZT–PU figures of merit (FMs).

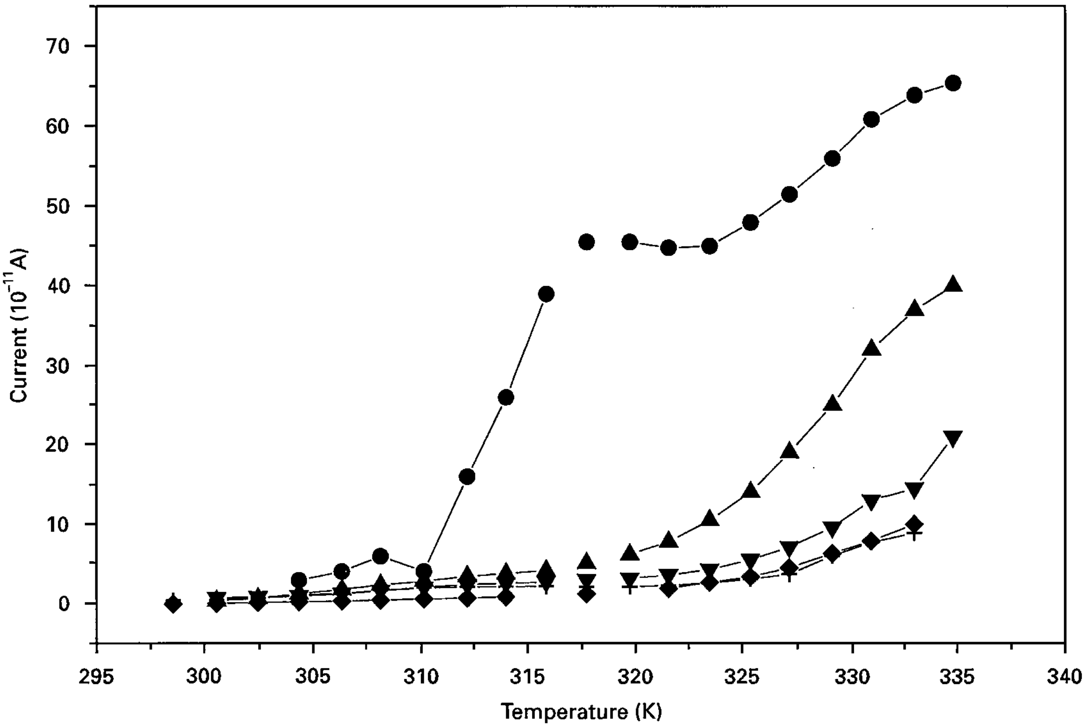

Figure 6 Thermally stimulated discharge current and pyroelectric current for the 19 vol% PZT–81 vol% PU composite (poling, 1 h, 363.15 K; $E = 10\,\mathrm{MV\,m^{-1}}$). (●), first run; (▲), second run; (▼), third run; (◆), fourth run; (+), fifth run.

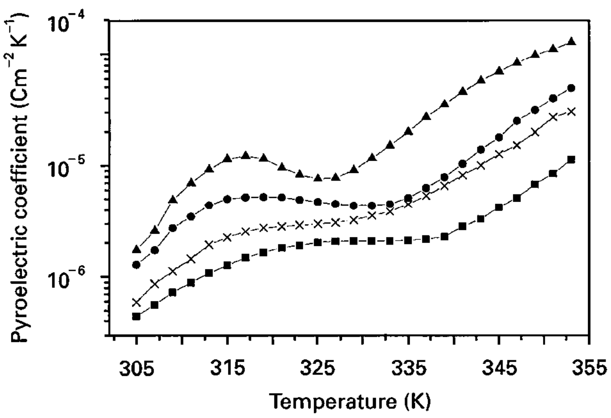

Figure 7 The pyroelectric coefficient as a function of temperature for different ceramic concentrations (poling, 1 h, 363 K; $E = 10\,\mathrm{MV\,m^{-1}}$), (■), 11 vol% PZT–89 vol% PU; (×), 15 vol% PZT–85 vol% PU; (●), 19 vol% PZT–81 vol% PU; (▲), 32 vol% PZT–68 vol% PU.

TABLE II Value of pyroelectric coefficient to some materials.

Material	$p(T)$ (coul m^{-2} K^{-1})	Ref.
PZT	5.0×10^{-4}	[17]
PVDF	1.0×10^{-5}	[18]
PZT/PVDF: 50 vol%.	2.0×10^{-4}	[17]
BaTiO$_3$/rubber: 20 vol%	6.0×10^{-5}	[19]
PZT/PU: 19 vol%.	1.0×10^{-4}	

The calculated value of $p(T)$ at 343 K is about $6.0 \times 10^{-5}\,\mathrm{C\,m^{-2}\,K^{-1}}$ for the 32 vol% PZT–PU composite. This result is comparable with that of 50 vol% PZT–PVDF and significantly higher than that of the well-poled PVDF. Although the $p(T)$ value obtained for this material is lower than that of PZT, its pyroelectric FM, p/ε', is about six times higher. Using the PZT–PU composite, a fire alarm sensor was developed [21].

4. Conclusions

Flexible and mechanically resistant thin films of a composite of PU and PZT with piezoelectric and pyroelectric properties were obtained.

As expected, the dielectric permittivity increases with increasing PZT content. The inclusion of ceramic grains in the polymer matrix enhanced the dielectric permittivity from 5 (for PU) to 24, much smaller than the value of ε' (1250) for PZT ceramic; so the pyroelectric FM of the composite is approximately six times that of PZT at 343 K. Although the $p(T)$ value in this composite is lower than that of PZT, the larger FM is advantageous and makes this composite a very interesting material.

The activation energy of the composite is comparable with that of PU. The small increase may arise because the ceramic grains makes the motion of the lateral group of the polymer chain difficult.

Acknowledgements

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