A Series of 0-3 Composites of Lead Zirconate Titanate and Ferroelectric Nylon77: Preparation and Electrical Properties

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ABSTRACT: A series of 0-3 composites of lead zirconate titanate (PZT) and nylon77 was prepared with PZT volume fractions between 0.1 and 0.6 using the combined method of solvent casting and hot pressing. Depending upon the volume fraction of PZT, the relative permittivities of the composites were found to be in the range of 200–2000 when measured at the highest practically possible temperature of 200°C. As PZT volume fraction increases, both the relative permittivity and the piezoelectric constant d_{33} increase. The best combination of electrical properties and flexibility was obtained in 0.5 PZT volume fraction composites. At this composition, the remanent polarization P_r of composites was up to 1000 mC/m^2 at the applied electric field of 40 MV/m and it increased with an increase in temperature. The highest piezoelectric strain coefficient d_{33} was obtained at 17 pC/N in 0.6 PZT volume fraction composites. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1048–1054, 2009

Key words: nylon77; composite; PZT; ferroelectric properties

INTRODUCTION

Numerous studies have been conducted on piezoelectric ceramic/polymer composites because of their considerable potential for applications such as pyroelectric sensors, ultrasonic transducers, and hydrophones.[1–5] Ceramic/polymer composites possess high piezoelectric properties from the piezoelectric ceramic, whereas flexibility and ease of processing are derived from the polymer. Over the last two decades, a great deal of effort has been devoted to 0-3 composites of ceramics/polymers, where the most studied polymers were polyvinylidene fluoride (PVDF) and poly(vinylidene fluoride-*co*-trifluoroethylene) (P(VDF/TrFE)). In these cases, both the ceramic and the polymer can be piezoelectrically active, providing a good opportunity for the development of high-dielectric constant 0-3 composites.[6,7]

Ferroelectric (odd-numbered) nylons are recently emerging as new materials for high-temperature transducers.[8] They also exhibit many excellent properties, such as high Young's modulus, prominent toughness, high abrasive resistance, and good thermal stability. Their piezoelectricity derives from the strong interaction of hydrogen bonds between amine and carbonyl (—NH— and —CO—) groups among neighboring molecular chains. The all-trans alignment of hydrogen bonding gives rise to a large dipole moment in the unit cell of the crystalline phase. It is known that these macroscopic dipoles are affected by the dipole density. The higher dipole density of the low-ordered nylons, such as nylon5 and nylon7, results in higher remanent polarization which could be comparable with those of PVDF and its copolymers.[9] Consequently, the composites of piezoelectric ceramic with odd or odd–odd nylons have been expected to exhibit superior piezoelectric performance in high-temperature applications, which are outside the safe operating range of those with PVDF and its copolymers.

This work aimed at the preparation and evaluation of electrical properties of lead zirconate titanate (PZT) and nylon77 composites. A series of 0-3 composites of PZT/nylon77 was prepared with various PZT volume fractions. Electrical properties of these composites were measured in terms of relative permittivity ε_r, piezoelectric strain coefficients d_{33}, and polarization. Nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy were used to investigate the chemical structure and morphology of the polymer component.

EXPERIMENTAL

Materials

The starting materials for nylon77 synthesis were 1,7-diaminoheptane (>95 % purity; Fluka, USA) and pimelic acid (synthesis grade; Merck, Darmstadt,

Germany). The as-received solvents used during the experiment were ethanol (99.7–100% purity; VWR International, Singapore), dichloroacetic acid (98.5% purity; Fluka) and 2,2,2-trifluoroethanol (≥98% purity; Fluka). The PZT powder used was "PZT850" (APC International, USA), which possesses a relative permittivity of 1750 at 1 kHz, a piezoelectric strain coefficient d_{33} of 400 pC/N, and a Curie temperature (T_c) of 360°C. The PZT powder was calcined at 880°C for 2 h before use for composite processing. After calcination, the average particle size of the PZT powder was 3.7 μm.

Instrumentation

The chemical structure and morphology of all the nylon obtained were characterized by ^{1}H-NMR and FTIR, respectively. ^{1}H-NMR of nylon77 was recorded with an AVENCE 300 MHz digital nuclear magnetic resonance spectrometer. To enable this characterization, the nylon77 was dissolved in a mixed solvent of 0.5% deuterated dimethylsulfoxide (DMSO-d_6) in trifluoroacetic acid. FTIR spectra were taken directly on a film with a NICOLET 6700 FTIR system. Nylon77 film was cast from trifluoroacetic acid.

The temperature dependence of relative permittivity of the composites was measured using a 4194A Impedance Gain/Phase analyzer (Hewlett Packard, USA) for frequencies from 1 kHz to 1 MHz and the temperature range of –70 to 200°C which was the highest practical temperature of the measurement since nylon77 started to melt beyond this temperature.

The P-E hysteresis characteristics of the composites were examined at room temperature using a RT66A Standardized Ferroelectric Measurement Test System (Radiant Technology, USA). The piezoelectric strain coefficient d_{33} was measured after 24 h of poling using a piezoelectric d_{33} meter (KCF Technologies model PM3001, USA).

Preparation of PZT/nylon77 composites

Nylon77 was synthesized from 1,7-diaminoheptane and pimelic acid by means of salt forming and melt-polycondensation as described elsewhere.[10,11] The PZT/nylon77 composites were prepared by the combined method of solvent casting and hot pressing. Nylon77 was first dissolved in trifluoroethanol. Predetermined amounts of PZT-calcined particles such as 0.1, 0.2, 0.3, 0.5, and 0.6 volume fractions were then added into the nylon77 solution. Each mixture was ultrasonically vibrated to produce uniform dispersion for 10 min, and then the well-dispersed mixture was cast onto a glass slide for evaporation. Each dried composite film was removed from the slide and then hot pressed for several times until a
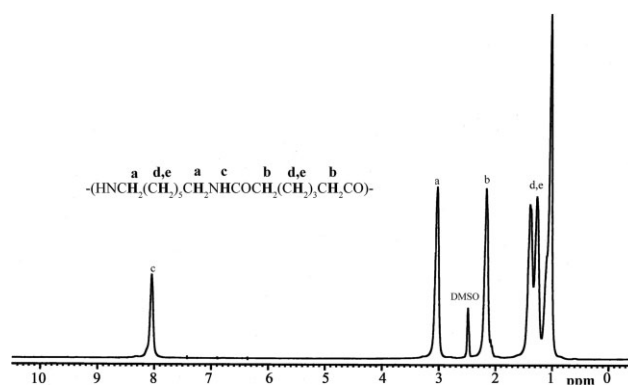

Figure 1 Typical ^{1}H-NMR spectrum of nylon 77.

thin film with a thickness of approximately 100–200 μm was obtained. To investigate the electrical properties, the composite film was gold electroded on both sides and poled at room temperature under an applied electric field of 20–25 MV/m for 20 min.

RESULTS AND DISCUSSION

Characterization and electrical properties of nylon77

Figure 1 shows the typical ^{1}H-NMR spectrum of nylon77. The chemical shift at 3.0 ppm (a) originated from methylene protons on carbon atoms bonded to the amine group (—CH_2NHCO—), whereas the chemical shift at 2.2 ppm (b) arose from the methylene protons on carbon atoms adjacent to the carbonyl group (—$CH_2NHCOCH_2$—). The broad peaks at approximately 1–1.5 ppm (d,e) have been attributed to other methylene protons in the aliphatic chains. The methine proton on the nitrogen atom in —CH_2NHCO— caused the chemical shift at 8.0 ppm (c), whereas d_6-DMSO induced the chemical shift at 2.5 ppm.

FTIR spectroscopy enables the identification of crystal structure and morphology because of its sensitivity to minor variations in polymer structure. Normally, nylons can exhibit several morphologies such as α-, β- and γ-phase depending on the type of nylon and the method of sample preparation.[12,13] Among these three crystal structures, the γ-phase shows much higher ferroelectric properties than the others, i.e., the d_{31} and e_{31} for the γ-phase structure are about twice or three times larger than those of α-phase structure.[14] The possible cause is that the γ-phase has more regular arrangement of dipoles and stronger hydrogen bonding, resulting in high piezoelectricity. Figure 2 shows the comparison of the FTIR spectra of nylon77 and nylon66. Four distinguishing characteristic bands used to identify the existence of α- or γ-phase in nylon are amide V, CH_2 bending, amide II, and N—H stretching. The α-phase of nylon66 [Fig. 2(b)] showed a characteristic band
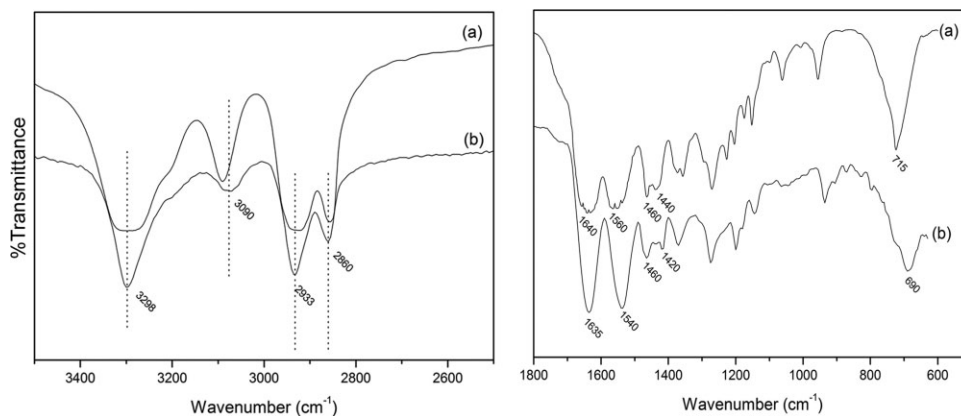
Figure 2 FTIR spectra of nylon77 (a) and nylon66 (b).

for amide V at 690 cm^{-1}, whereas the γ-phase showed a band at 715 cm^{-1}, as shown in nylon77 [Fig. 2(a)]. Four peaks of CH$_2$ bending of α-phase were observed at 1475, 1465, 1440, and 1420 cm^{-1}, whereas only two peaks at 1460 and 1440 cm^{-1} can be found in γ-phase. In agreement with a previous work,[13] the peak corresponding to the amide II was found to be sensitive to its crystalline structure in that the peak for the γ-phase was at 1560 cm^{-1} and this shifted from 1540 cm^{-1} for the α-phase, indicating the possibility of the presence of the γ-phase in nylon77. In addition, the method of polymer films preparation by quenching from melt and annealing at 80°C also supported the existence of γ-phase in nylon77.

In the region of N—H stretching, the broad band at 3298 cm^{-1} wavenumber of nylon77 indicated the various hydrogen-bonding formations between N—H and C=O groups such as in ordered domains, in disordered arrangement, and as "free" carbonyl groups, whereas the sharp peak in nylon 66 at similar wavenumber indicated fewer hydrogen bonds. A similar effect was seen in the C=O stretching region where the C=O stretching band at 1640 cm^{-1} wavenumber of nylon77 was broader than that of nylon66 at a wavenumber of 1635 cm^{-1}. The broadness and shifting of the peaks indicated the different arrangements in the two samples.

Figure 3(a) shows P-E hysteresis characteristics of nylon77 at room temperature under various applied electric fields of 15, 25, and 35 MV/m. At low field ($E = 15$ MV/m), an elliptical hysteresis shape was obtained with a remanent polarization P_r at 19.8 mC/m^2, a saturation polarization P_s at 26.9 mC/m^2, and a coercive field E_c at 6.9 MV/m. An increase in the applied electric field enhanced the P_r, P_s, and E_c values of nylon77. However, at high field ($E = 35$ MV/m), the saturation polarization (P_s) became lower than the remanent polarization (P_r) indicating the occurrence of loss due to the ionic conduction, which became large at high E and caused the saturation of charge amplification.[15] The optimum remanent polarization (P_r) and coercive field (E_c) of

nylon77 were achieved at 50 mC/m^2 and 18 MV/m, respectively. This remanent polarization of nylon77 was comparable with that of P(VDF/TrFE) copolymer, whereas the coercive field was much lower than that of P(VDF/TrFE) ($E_c = 50$ MV/m).[15,16] This indicated that nylon77 required lower energy for dipole orientation. In other words, the poling process of nylon77 was much easier than that of PVDF and its copolymer. The evidence in Figure 3(b) indicated that the polarization of nylon77 was affected by temperature. As the temperature increased, the polarization of nylon77 increased; however, the shape of the hysteresis loop gradually changed from a slim ellipse to a rounded one due to the reason stated earlier. Therefore, the room temperature was considered optimum for the poling condition of nylon77 because an elliptical hysteresis loop was maintained.

Figure 3(c) shows the temperature dependence of relative permittivity and dielectric loss of nylon77 measured at 1, 10, 100 kHz, and 1 MHz. Unlike P(VDF/TrFE) copolymer, nylon77 did not show a dielectric anomaly which indicated a Curie transition, until it melted. The relative permittivity of nylon77 at room temperature was comparable with that of PVDF and its copolymer ($\varepsilon_r = 10$–14).[14] It showed a broad shoulder at about 50–70°C, which centered at 65°C. As the temperature further increased, the relative permittivity of nylon77 showed a steep increase. One of the reasons for a steep increase of relative permittivity beyond the glass transition was the segmental motion of polymer chains, which facilitated dipole orientation resulting in an increase in the relative permittivity. Another reason may be related to ionic response. Dielectric loss of this polymer showed a relaxation at about 50–70°C. Normally, nylon samples exhibit three noticeable relaxation processes, the high-temperature relaxation is commonly designated as α-relaxation, which corresponds to the glass transition temperature.[17] Thus, it is possible that a relaxation at around 50–70°C for the present sample was associated with the glass transition temperature. Unfortunately, it
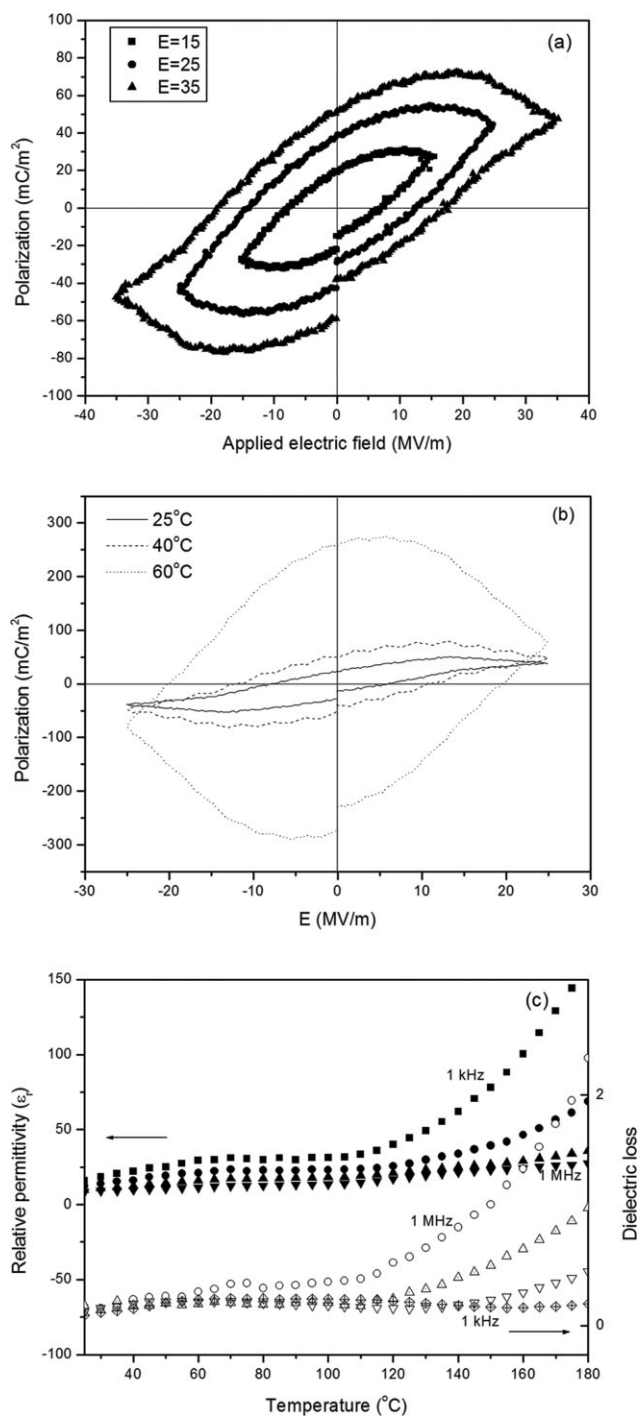
Figure 4 Polarizations (P_r and P_s) as a function of temperature in nylon77.

in Figure 4, in which remanent polarization (P_r) and saturation polarization (P_s) have been plotted versus temperature. According to Takase et al.'s report,[17] a steep increase of properties, d_{31} and e_{31}, was found at around the glass transition temperature. Therefore, it was thought that this steep increase of P_r around 50–70°C for the present sample was associated with glass transition temperature.

Properties of PZT/nylon77 composites

The distribution of ceramic powders in PZT/nylon77 composites of different compositions was observed by SEM before electrical measurements. Figure 5 shows an SEM micrograph of the composite with 0.5 PZT volume fractions (ϕ). No agglomeration could be observed. The PZT particles were well dispersed and embedded in a three-dimensionally continuous

Figure 3 Electrical properties of nylon77: (a) *P-E* hysteresis loops as a function of applied electric field; (b) *P-E* hysteresis loops as a function of measuring temperature; and (c) temperature dependence of relative permittivity.

was not possible to detect T_g of this sample by differential scanning calorimetry (DSC) to confirm this behavior. This may be because the second-order endothermic transition of nylon77 was not sensitive to heat capacity change. However, a steep increase in the properties at around 50–70°C and beyond was observed in the polarization measurement as shown
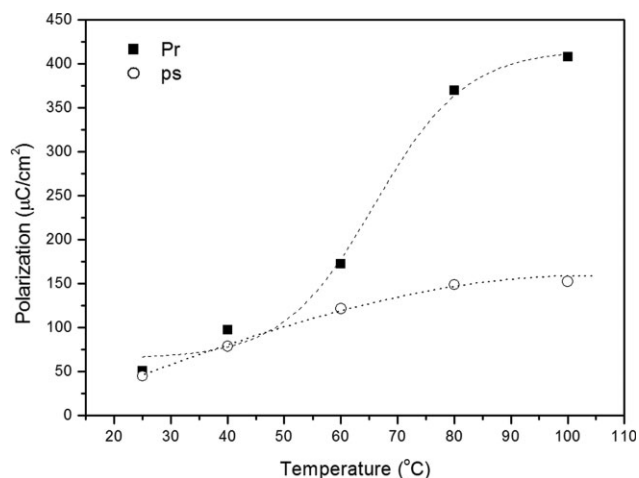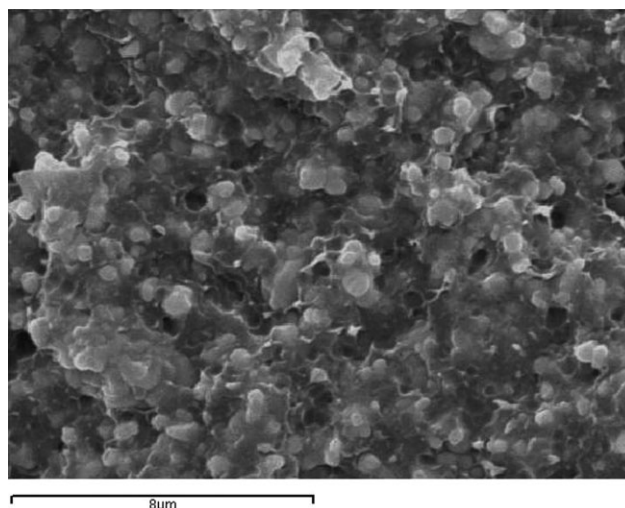

Figure 5 SEM micrograph of PZT/nylon77 composite at 0.5 PZT volume fraction ($\phi = 0.5$).
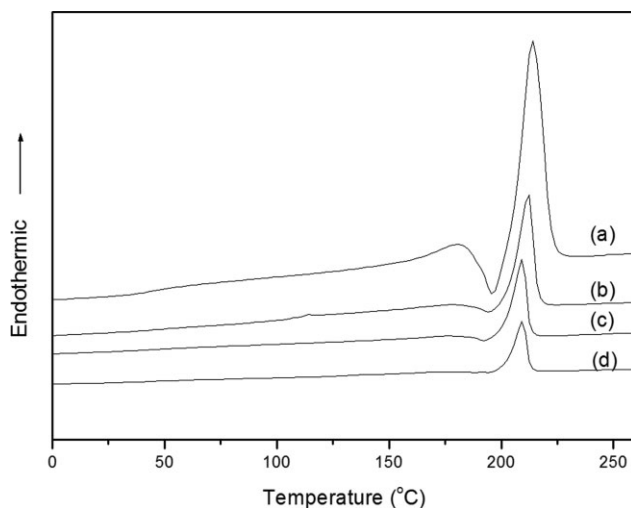
Figure 6 DSC thermograms of PZT/nylon77 composites with various PZT volume fractions when compared with that of pure nylon77: (a) pure nylon77; (b) at $\phi = 0.2$; (c) at $\phi = 0.35$; and (d) at $\phi = 0.5$ composites.

polymer (nylon77). Therefore, the composite had 0-3 connectivity.

Figure 6 illustrates DSC thermograms of PZT/nylon77 composites at various PZT volume fractions when compared with that of pure nylon77. All composites exhibited melting temperature at around 210°C, which is the same temperature as that of pure nylon77. The glass transition temperature of all composites and pure nylon77 was invisible probably because of the insensitivity of second-order transition of nylon77 to the heat capacity change.

Prior to dielectric and piezoelectric measurement, composites were electroded and poled. The optimized poling conditions, applied electric field, and temperature were determined based on two parameters, the difference of X-ray reflections before and after poling and the hysteresis shape under an applied electric field. To identify the X-ray reflections for PZT/nylon77 composites, X-ray diffraction (XRD) measurement was performed on a JEOL diffractometer (JDX-3530) using Cu Kα radiation. Figure 7 illustrates the XRD patterns of the composite films with $\phi = 0.5$ at various poling conditions. The reflections of PZT/nylon77 composites indicating the optimized poling electric field were determined by an analysis of the lines [h00] groups, which were split into triplets, at 2θ values of 44.2°, 44.5°, and 45° associated with the $(002)_T$, $(200)_R$, and $(200)_T$, respectively. Such multiplicity of the XRD profiles was believed to be due to the coexistence of both tetragonal (T) and rhombohedral (R) ferroelectric phases. By using JADE (materials data JADE XRD pattern processing), a deconvolution of the diffraction profile lines was performed. The deconvolution of the profile provides information of the ceramic poling ratio (α_c),
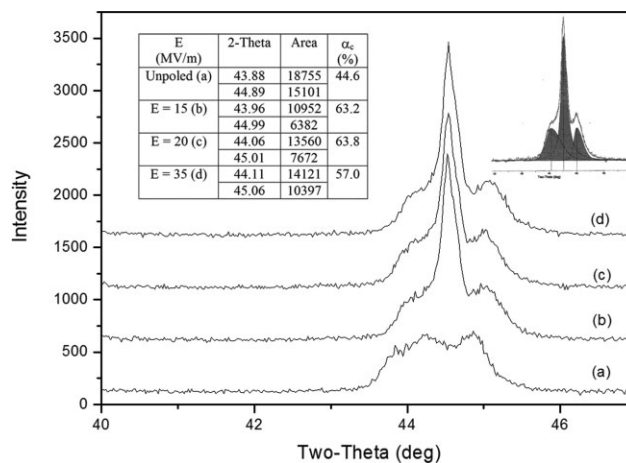

Figure 7 XRD profiles of composites at 0.5 PZT volume fraction ($\phi = 0.5$) at different poling electric fields (E): (a) an unpoled PZT/nylon 77 composite; (b) at $E = 15$ MV/m; (c) at $E = 20$ MV/m; and (d) at $E = 35$ MV/m.

which was calculated from integrated intensity of the $(200)_T$ and $(002)_T$ X-ray reflections using eq. (1). All calculated results were recorded and summarized as shown in Figure 7.

$$\alpha_c = I_{(200)}/[I_{(200)} + I_{(002)}] \tag{1}$$

It was found that as the applied electric field for poling increased, the ceramic poling ratio increased from 44.6% for the unpoled nylon composite to about 63.8% for an applied electric field at 20 MV/m. As the applied electric field for the poling increased to 35 MV/m, the ceramic poling ratio decreased. Therefore, the applied electric field for poling of composites for the next experiments was set at 20–25 MV/m for 20 min.

Figure 8 shows the hysteresis characteristics of PZT/nylon77 composites at the applied electric field
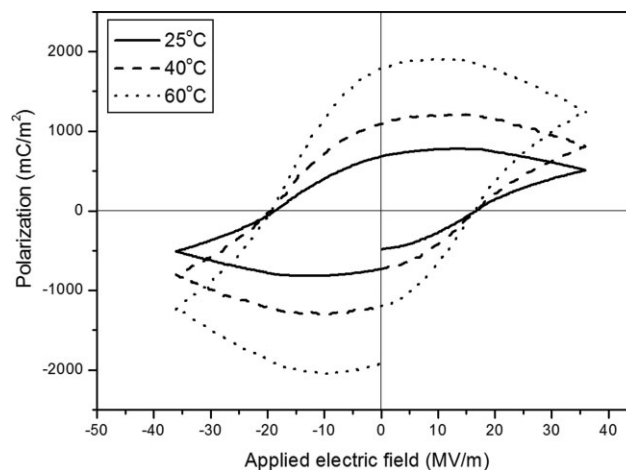

Figure 8 *P-E* hysteresis loops at various temperatures of PZT/nylon77 composite at 0.5 PZT volume fractions and an applied electric field of 25 MV/m.

of 25 MV/m under various temperatures. The remanent polarization P_r of composite increased as the temperature increased. This is because, at higher temperature, as the glass transition temperature of nylon77 ($T_g \sim 60°C$) is approached, the movement of the dipoles is easier resulting in larger polarization. However, as temperature increased higher than 40°C, the hysteresis loop became rounded and P_r became higher than the P_s. The possible cause is that the polarization of nylon77 originated from strong interaction of hydrogen bonds among neighboring molecular chains. As temperature increases, some hydrogen bonding may be broken causing the reduction of spontaneous polarization.[17] The other reason could be related to the ionic conduction at high electric field causing the saturation of charge amplification as occurred during the hysteresis measurement of nylon77. However, the coercive field (E_c) of composites did not vary with temperature, and their average values were approximately 15 MV/m.

As previously mentioned, the optimized poling temperature of the composite was obtained from polarization measurement. It was found that at high temperature, the possibility of the broken hydrogen bond or the overamplification of charge saturation might occur resulting in rounding of the elliptical hysteresis shape. At room temperature, the ellipse-shaped hysteresis behavior was maintained and the electric breakdown did not easily occur. Consequently, the poling of PZT/nylon77 composites was performed at room temperature for the rest of the experiments.

Ferroelectric properties of PZT/nylon77 depended not only on the measurement temperature but also on the applied electric field. Figure 9 presents the
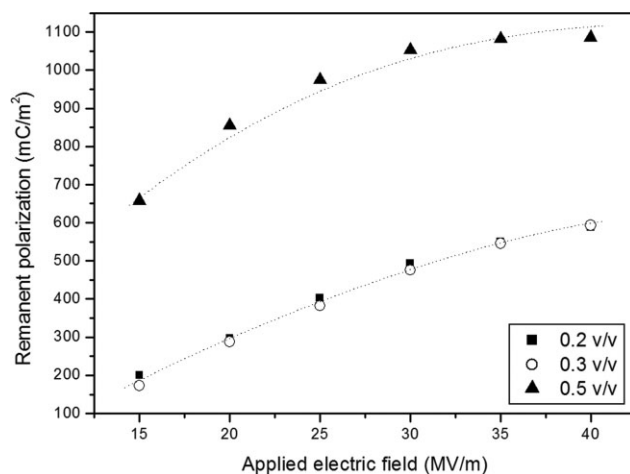
TABLE I
The Polarization of Various PZT/Nylon77 Composites, PZT/PVDF, and PZT/P(VDF/TrFE)Copolymer Composites

Materials	Polarization at $E = 35$ MV/m, 25°C		
	P_s (mC/m^2)	P_r (mC/m^2)	E_c (MV/m)
0.35 PVDF/PZT[18]	124	44	7.5
0.5 P(VDF/TrFE)/PZT[18]	344	215	11.8
Nylon 77	48	52	19.7
0.2 Nylon77/PZT	131	171	20.2
0.35 Nylon77/PZT	204	247	20.5
0.5 Nylon77/PZT	503	669	16.5

different P_r values at 40°C of PZT/nylon77 composites at different ϕ and E. The P_r of composite increased with an increase of E and became saturated at approximately 35 MV/m. The P_r of composite at $\phi = 0.5$ is significantly higher than others. The E_c of all composites were in the range of 8–17 MV/m. Table I shows the comparison between the polarization properties of PZT/nylon77 composites and those of PVDF and P(VDF/TrFE) copolymer composites. It was noted that among these composites of the same PZT volume fraction, the P_s and P_r of PZT/nylon77 composites exhibited the highest values. In addition, nylon itself has a higher T_g and no Curie transition, which are of crucial importance for high-temperature piezoelectric applications.

The piezoelectric strain coefficients d_{33} of ceramic/polymer composites were measured at the frequency of 97 Hz. Prior to the d_{33} measurement, the composites were poled at room temperature by applying an electric field of 25 MV/m for 20 min. The d_{33} values increased as the PZT volume fraction (ϕ) increased (Fig. 10). The d_{33} values of PZT/nylon77 composites were significantly smaller when compared

Figure 9 Remanent polarizations (at 40°C) versus electric field of PZT/nylon77 composite at various PZT volume fractions.
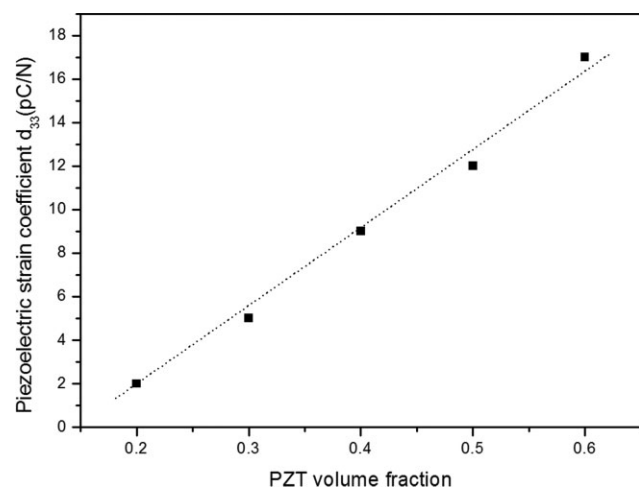

Figure 10 Piezoelectric strain coefficients (d_{33}) of PZT/nylon77 composites at various PZT volume fractions.
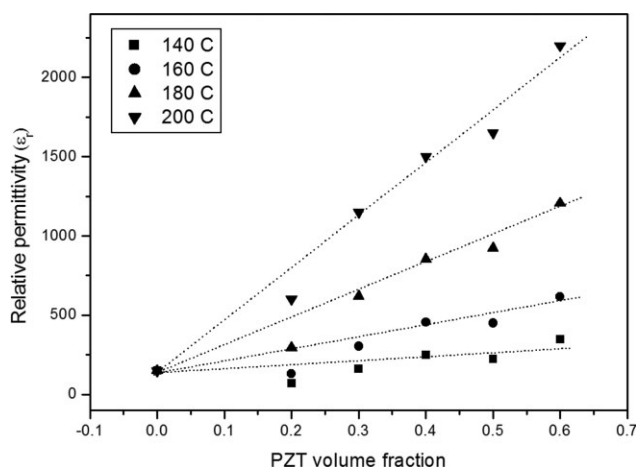
Figure 11 Temperature dependence of relative permitivities of PZT/nylon77 composites at 1 kHz as a function of PZT volume fractions.

with the value of $d_{33} \sim 400$ pC/N) for the PZT alone; however, these numbers were comparable with that of PZT/PVDF composites. For example, the d_{33} of PZT/PVDF composite at $\phi = 0.5$ was 14 pC/N,[7] whereas that of PZT/nylon77 at the same PZT volume fraction was 12 pC/N. Nevertheless, for better comparison, the measurement of d_{33} of PZT/nylon77 should be performed at above its T_g, the same as that of PZT/PVDF. Takase et al.[17] found that nylon11 and nylon7 exhibited higher value of d_{31} and e_{31} when the temperature was beyond T_g. Therefore, to obtain optimum piezoelectric strain coefficient of PZT/nylon77, it is important to conduct experiments above its T_g, which is still under investigation.

For the application of piezoceramic/polymer composites at high temperatures, e.g., in resonance-mode ultrasonic transducers, the measurements of high-temperature dielectric properties are of particular importance. Figure 11 illustrates the relative permittivity of PZT/nylon77 composites as a function of PZT volume fractions at various measuring temperatures. The relative permittivities of these piezocomposites increased with increasing temperature and also PZT volume fraction. At higher temperature, molecules are more mobile and dipoles are more easily oriented causing a steeper increase in relative permittivity. The maximum relative permittivity of approximately 2200 was achieved with 0.6 PZT volume fractions at 200°C.

CONCLUSIONS

The electrical properties of PZT/nylon77 composites with various PZT volume fractions have been investigated. It was found that the electrical properties of composites improved significantly when compared with those for pure nylon polymer. The composite exhibited the highest value of relative permittivity at temperatures between 140 and 200°C. The relative permittivity, piezoelectric constant d_{33}, and polarization increased with the PZT volume fraction. The optimum electrical properties were obtained for the composite with 0.5 PZT volume fractions without sacrifice of the flexibility.

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