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Design Requirements for Amorphous Piezoelectric Polymers

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Institute for Computer Applications in Science and Engineering (ICASE)
Langley Research Center, Hampton, Virginia

J. A. Young
University of Virginia, Charlottesville, Virginia

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Abstract

An overview of the piezoelectric activity in amorphous piezoelectric polymers is presented. The criteria required to render a polymer piezoelectric are discussed. Although piezoelectricity is a coupling between mechanical and electrical properties, most research has concentrated on the electrical properties of potentially piezoelectric polymers. In this work, we present comparative mechanical data as a function of temperature and offer a summary of polarization and electromechanical properties for each of the polymers considered.

Introduction

Kawai's [1] pioneering work almost thirty years ago in the area of piezoelectric polymers has led to the development of strong piezoelectric activity in polyvinylidene fluoride (PVDF) and its copolymers with trifluoroethylene and tetrafluoroethylene. These semicrystalline fluoropolymers represent the state of the art in piezoelectric polymers. Research on the morphology [2-5], piezoelectric and pyroelectric properties [6-10], and applications of polyvinylidene fluoride [11-14] are widespread in the literature. More recently Scheinbeim et al. have demonstrated piezoelectric activity in a series of semicrystalline, odd numbered nylons [15-17]. When examined relative to their glass transition temperature, these nylons exhibit good piezoelectric properties (d_{31} = 17 pC/N for Nylon 7) but have not been used commercially primarily due to the serious problem of moisture uptake. In order to render them piezoelectric, semicrystalline polymers must have a noncentrosymmetric crystalline phase. In the case of PVDF and nylon, these polar crystals cannot be grown from the melt. The polymer must be mechanically oriented to induce noncentrosymmetric crystals which are subsequently polarized by an electric field. In such systems the amorphous phase supports the crystalline orientation and polarization is stable up to the Curie temperature.

Nalwa et al. have also examined piezoelectricity in a series of polythioureas [18-19]. Though not highly crystalline, these thiourea polymers have a very high degree of hydrogen bonding which stabilizes the remanent polarization in such systems after poling.

The literature on amorphous piezoelectric polymers is much more limited than that for semicrystalline systems. This is in part due to the fact that no amorphous piezoelectric polymers have exhibited responses high enough to attract commercial interest. Much of the previous work resides in the area of nitrile substituted polymers including polyacrylonitrile (PAN) [20-22], poly(vinylidenecyanide vinylacetate) (PVDCN/VAc) [23-26], polyphenylethernitrile (PPEN) [27-28], and poly(1-bicyclobutanecarbonitrile) [29]. The most promising of these materials are the vinylidene cyanide copolymers which exhibit large dielectric relaxation strengths and strong piezoelectricity. The carbon-chlorine dipole in polyvinylchloride (PVC) has also been oriented to produce a low level of piezoelectricity [30,31]. Motivated by a need for high temperature piezoelectric sensor materials, NASA has recently begun research in the development of amorphous piezoelectric polymers. In this paper an amorphous, aromatic piezoelectric polyimide developed at NASA [32] is presented along with other amorphous and paracrystalline piezoelectric polymers shown in Table 1. The purpose of this overview is to explain the mechanism and key components required for developing piezoelectricity in amorphous polymers and to present a summary of polarization and electromechanical properties of currently

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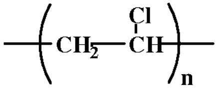
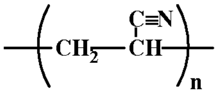
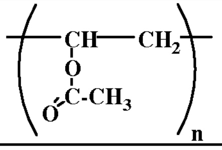
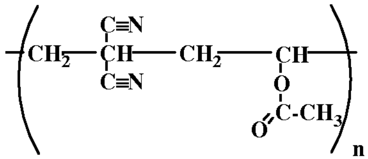
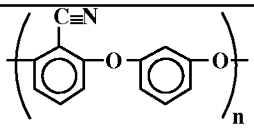
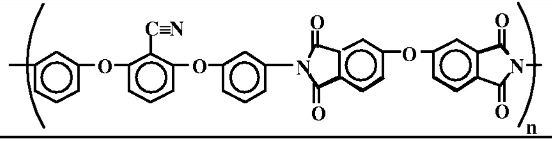
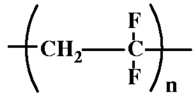
Table 1. Structure, Morphology and T_g for Piezoelectric Polymers.

Polymer	Repeat Unit	Morphology	T_g (°C)
PVC		Amorphous	80
PAN		Paracrystalline	90
PVAc		Amorphous	30
P(VDCN-VAc)		Paracrystalline	170
PPEN		Amorphous	145
(β-CN) APB/ODPA		Amorphous	220
PVDF		Semicrystalline	-35

Background

The piezoelectricity in amorphous polymers differs from that in semi-crystalline polymers and inorganic crystals in that the polarization is not in a state of thermal equilibrium, but rather a quasi-stable state due to the freezing-in of molecular dipoles. As mentioned by Broadhurst and Davis [33], four criteria are essential to make an amorphous polymer exhibit piezoelectric behavior. First, molecular dipoles must be present. As seen in Table 1, these dipoles are typically pendant to the polymer backbone as are the nitrile groups in PAN, PVDCN-VAC, and (β-CN) APB/ODPA. However, the dipoles may also reside within the main chain of the polymer such as the anhydride units in the (β-CN) APB/ODPA polyimide. In addition to a dipole moment μ, the dipole concentration N (number of dipoles per unit researched amorphous systems.

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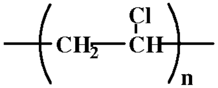
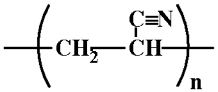
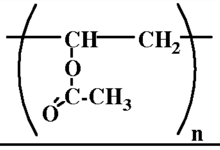
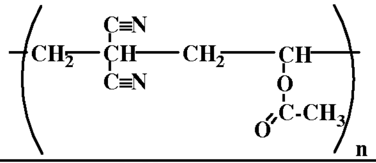
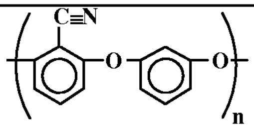
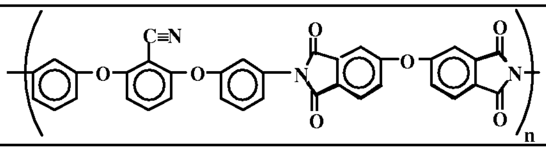
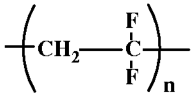
PVC	 $-(CH_2-CHCl)_n-$	Amorphous	80
PAN	 $-(CH_2-CH(C\equiv N))_n-$	Paracrystalline	90
PVAc	 $-(CH(OC(=O)CH_3)-CH_2)_n-$	Amorphous	30
P(VDCN-VAc)	 $-(CH_2-C(C\equiv N)_2-CH_2-CH(OC(=O)CH_3))_n-$	Paracrystalline	170
PPEN		Amorphous	145
(β-CN) APB/ODPA		Amorphous	220
PVDF	 $-(CH_2-CF_2)_n-$	Semicrystalline	-35

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$$P_u = N\mu \tag{1}$$

Equation (1) is for a rigid dipole model and gives a maximum value for the polarization which assumes all dipoles are perfectly aligned with the poling field. Table 2 lists some amorphous piezoelectric polymers along with ultimate polarizations, remanent polarizations, and calculated and measured dielectric relaxation strengths, $\Delta\varepsilon$. The dielectric relaxation strength is defined as the change in dielectric constant as the polymer traverses the glass transition temperature. Semicrystalline PVDF is added for comparison.

Table 2. Polarization Data for some Amorphous Piezoelectric Polymers and PVDF.

Polymer	μ (10^{-30} Cm)	N (10^{28} m^{-3})	P_u[a] (mC/m^2)	$\Delta\varepsilon$[b] calculated	$\Delta\varepsilon$[c] measured	$P_{remanent}$[d] (mC/m^2)	P_r/P_u (%)
PVC	3.7	1.33	50	7.0	10.0	16.0 (E_p = 32 MV/m)	32
PAN	11.5	1.48	170	35.0	38.0	25.0	17
PVAc	6.0	0.83	50	6.6	6.5	5.0	10
PVDCN/VAc	19.0	0.44	84	30.0	125.0	50.0	60
PPEN	14.0	0.37	52	12.0	12 .0	10.0	19
(β-CN) APB/ODPA	29.5	0.14	40	23.0	17.6	14.0	35
PVDF	7.0	18.40	130	-	-	40.0-55.0	30-42

[a] Calculated using equation 1.

[b] $\Delta\varepsilon$ is calculated by equation 2.

[c] $\Delta\varepsilon$ is measured as ($\varepsilon_{\text{above Tg}} - \varepsilon_{\text{below Tg}}$).

[d] P_r is the actual polarization in the polymer, measured by the thermally stimulated current method, or hysteresis measurements in the case of PVDF.

The importance of dipole concentration on ultimate polarization is evident from a comparison of polyacrilonitrile (PAN) and the polyimide (β-CN) APB/ODPA. PAN has a single nitrile dipole per repeat unit (μ = 3.5D) resulting in a dipole concentration of 1.34 x 10^{28} m^{-3}. This translates into an ultimate polarization of 152 mC/m^2 [20]. The (β-CN) APB/ODPA polyimide, on the other hand, has a single nitrile dipole pendant to a phenyl ring (μ = 4.2 D), as well as two anhydride dipoles (μ = 2.34 D) resulting in a total dipole moment per monomer of 8.8 D [34]. However, the dipole concentration of (β-CN) APB/ODPA is only 0.136 x 10^{28} m^{-3}, resulting in an ultimate polarization of 40 mC/m^2, which is less than a fourth of that of PAN.

The second criterion for piezoelectricity is the ability to align the dipoles. Orientation polarization of volume) is also important in determining the ultimate polarization, P_u, of a polymer,

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The second criterion for piezoelectricity is the ability to align the dipoles. Orientation polarization of molecular dipoles is responsible for piezoelectricity in amorphous polymers. It is induced by applying an electric field (E_p) at an elevated temperature ($T_p \geq T_g$) where the molecular chains are sufficiently mobile to allow dipole alignment with the electric field. Partial retention of this orientation is achieved by lowering the temperature below T_g in the presence of E_p as shown in Figure 1. The resulting remanent polarization (P_r) is directly proportional to E_p and the piezoelectric response. The procedure used to prepare a piezoelectric amorphous polymer clearly results in both oriented dipoles and space or real charge injection. The real charges are usually concentrated near the surface of the polymer as schematically shown in Figure 2, and they are introduced due to the presence of the electrodes. However, Broadhurst et.al. [35] have shown that the presence of space charges does not have a significant effect on the piezoelectric behavior. The reason for this is two fold. The magnitude of the space charges is usually not significant with respect to the polarization charges. Secondly, space charges are essentially symmetrical with respect to the thickness of the polymer therefore when the material is strained uniformly their contribution to the piezoelectric effect is negligible. A number of authors have demonstrated this by use of phenomenological models [33,35].

A study of the relationship between relaxation times, poling temperatures and poling fields is crucial to achieve optimal dipole alignment. Theoretically, the higher the electric field, the better the dipole alignment. However, the value of the electric field is limited by the dielectric breakdown of the polymeric material. In practice, 100 MV/m is the maximum field that can be applied to these materials. Poling times need to be of the order of the relaxation time of the polymer at the poling temperature. It is unlikely that a high degree of alignment is achievable in amorphous polymers as evidenced by P_r/P_u data in Table II. Using computational chemistry techniques the orientation polarization of the (β-CN) APB/ODPA polymer has been assessed by monitoring the angle, θ, that the dipoles make with the applied electric field [34]. The unpoled state is found to exhibit random orientation of the dipoles, $\theta = 90°$, as shown in Figure 3a. Upon poling, the nitrile and anhydride dipoles are perturbed by the electric field to form average angles of $\theta = 50^{\circ}$ and $\theta = 63^{\circ}$, respectively, Figure 3b. As shown in Table 2, for most polymers the ratio of measured remanent polarization to the calculated ultimate polarization is 30%.

When local ordering or paracrystallinity is inherent in the polymer or is induced by mechanical stretching, an increase in the value of the remanent polarization is observed. For example, some researchers [23, 36, 37] assert that the large discrepancy between the measured and calculated $\Delta\varepsilon$ for PVDCN-VAc (Table 2) may be attributed to locally ordered regions in the polymer. A number of authors have suggested that PVDCN-VAc also exhibits ferroelectric-like behavior [38] due to switching of the nitrile dipoles under AC-field. Several investigators [20, 33, 39] have proposed that the difficulty of poling PAN in the unstretched state is related to the strong dipole-dipole interaction of nitrile groups of the same molecule which repel each other, thus preventing normal polarization. Upon stretching, the intermolecular dipole interactions facilitate the packing of the individual chains and give rise to ordered zones [39]. Comstock et al. [40] measured the remanent polarization of both unstretched and stretched PAN using the thermally stimulated current method (TSC) and observed a two-fold increase in the remanent polarization (TSC peak at 90ºC) for PAN that was stretched four times its original length.

The third criterion for making an amorphous piezoelectric polymer is the locking-in of dipole alignment and its subsequent stability. As explained earlier, the temperature is lowered to room temperature while the field is still on, to freeze in the dipole alignment. In a semi-crystalline material, however, the locking-in of the polarization is supported by the crystalline structure of the polymer, and is therefore stable above the glass transition temperature of the polymer. It is for that reason that PVDF ($T_g = -35^{\circ}$ C) can be used from room temperature to about 100º C. In semi-crystalline materials, piezoelectricity remains until the Curie temperature is reached. Although there is little data addressing the stability of piezoelectric activity in amorphous polymers, the general effect of time, temperature and pressure has been noted. Broadhurst and Davis [33] state that as temperature decreases the structural molecular dipoles is responsible for piezoelectricity in amorphous polymers. It is induced by applying an electric field (E_p) at an elevated temperature ($T_p \geq T_g$) where the molecular chains are sufficiently mobile to allow dipole alignment with the electric field. Partial retention of this orientation is achieved by lowering the temperature below T_g in the presence of E_p as shown in Figure 1. The resulting remanent polarization (P_r) is directly proportional to E_p and the piezoelectric response. The procedure used to prepare a piezoelectric amorphous polymer clearly results in both oriented dipoles and space or real charge injection. The real charges are usually concentrated near the surface of the polymer as schematically shown in Figure 2, and they are introduced due to the presence of the electrodes. However, Broadhurst et.al. [35] have shown that the presence of space charges does not have a significant effect on the piezoelectric behavior. The reason for this is two fold. The magnitude of the space charges is usually not significant with respect to the polarization charges. Secondly, space charges are essentially symmetrical with respect to the thickness of the polymer therefore when the material is strained uniformly their contribution to the piezoelectric effect is negligible. A number of authors have demonstrated this by use of phenomenological models [33,35].

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The final determining factor for a material's degree of piezoelectric response is the ability of the polymer to strain with applied stress. Since the remanent polarization in amorphous polymers is lost in the vicinity of T_g, the use of these piezoelectric polymers is limited to temperatures well below T_g. This means that the polymers are in their glassy state, and the further away from T_g the use temperature is, the stiffer the polymer. This also means that measurement of the bulk physical properties is crucial both for identifying practical applications and for comparing polymers. The electromechanical coupling coefficient, k_{31}, is a measure of the combination of piezoelectric and mechanical properties of a material (refer to Table 3). It can be calculated using the equation below:

$$k_{31} = d_{31}\sqrt{\frac{Y_{11}}{\varepsilon\varepsilon_0}} \tag{2}$$

where d_{31} is the piezoelectric strain coefficient, Y_{11} is Young's modulus, ε is the dielectric constant of the polymer and ε_0 is the dielectric constant of free space. The piezoelectric amorphous polymer may be used at temperatures near its T_g to optimize the mechanical properties, but not too close so as not to lose the remanent polarization.

Table 3. Piezoelectric and mechanical properties (at 25ºC).

	E_{11}[a] (10^9 Dynes/cm^2)	d_{31} (pC/N)	k_{31}[f]
PVC	0.34	0.7[b]	0.001
PAN	1.70	1.7[c]	0.010
PVDCN-VAc	-	7.0[d]	0.050
(β-CN)APB/ODPA	2.80	0.3[e]	0.002
PVDF	2.60	27.0[e]	0.120

[a] Measured in our laboratories using a Rheovibron.
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Dielectric properties as predictors of piezoelectric behavior

This section addresses the origins of the dielectric contribution to the piezoelectric response of amorphous polymers. The potential energy U of a dipole μ at an angle θ with the applied electric field is $U = \mu E \cos\theta$. Using statistical mechanics and assuming a Boltzman's distribution of the dipole energies, the mean projection of the dipole moment, $<\mu>_E$, in the direction of the applied electric field is obtained.

$$\frac{<\mu_E>}{\mu} = \coth\frac{\mu E_p}{kT} - \frac{kT}{\mu E} \tag{3}$$

This is the Langevin equation which describes the degree of polarization in a sample when an electric field, E, is applied at temperature T. Experimentally, a poling temperature in the vicinity of T_g is used to maximize dipole motion. The maximum electric field which may be applied, typically 100 MV/m, is determined by the dielectric breakdown strength of the polymer. For amorphous polymers $\mu E / kT \ll 1$, which places these systems well within the linear region of the Langevin function. The following linear equation for the remanent polarization results when the Clausius Mossotti equation is used to relate the dielectric constant to the dipole moment [42].

$$P_r = \Delta\varepsilon\ \varepsilon_0 E_p \tag{4}$$

It can be concluded that remanent polarization and hence piezoelectric response of a material is determined by $\Delta\varepsilon$, making it a practical criterion to use when designing piezoelectric amorphous polymers. The dielectric relaxation strength, $\Delta\varepsilon$ may be the result of either free or cooperative dipole motion. Dielectric theory yields a mathematical way of examining the dielectric relaxation due to free rotation of the dipoles, $\Delta\varepsilon$. The equation incorporates Debye's work based on statistical mechanics, the Clausius Mossotti equation, and the Onsager local field and neglects short range interactions [43]

$$\Delta\varepsilon_{calculated} = \frac{N\mu^2}{3kT\varepsilon_0}\left(\frac{n^2+2}{3}\right)^2\left(\frac{3\varepsilon(0)}{2\varepsilon(0)+n^2}\right)^2 \tag{5}$$

N is the number of dipoles per unit volume, k is the Boltzmann constant, $\varepsilon(0)$ is the static dielectric constant and n is the refractive index. If the experimental value of $\Delta\varepsilon$ ($\Delta\varepsilon_{measured}$) agrees with the theoretical value of $\Delta\varepsilon$ ($\Delta\varepsilon_{calculated}$), then the material exhibits free dipolar motion. Table II shows that in polymers such as PAN, VAc, PVC, PPEN, and (β-CN) APB/ODPA the dielectric relaxation strength corresponds to free dipolar motion since $\Delta\varepsilon_{calculated}$ and $\Delta\varepsilon_{measured}$ are in agreement. This table also shows that for the copolymer PVDCN/VAc, $\Delta\varepsilon_{calculated} = 30$ while $\Delta\varepsilon_{measured} = 125$ [25,26]. This large discrepancy in the values of $\Delta\varepsilon$ is indicative of cooperative motion of several CN dipoles within the locally ordered regions of the polymer. Cooperativity means that instead of each dipole acting independently, multiple CN dipoles respond to the applied electric field in a unified manner. When x dipoles act cooperatively, the number density of dipoles decreases by 1/x yet the effective dipole moment increases by x^2 to yield a large dielectric relaxation strength. Intramolecular and/or intermolecular interactions between individual dipoles may be responsible for this particular phenomenon [25]. Such interactions are manifested in the existence of paracrystalline regions within the PVDCN/VAc polymer [27]. The large relaxation strength

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Designing an amorphous polymer with a large dielectric relaxation strength and hence piezoelectric response would require the ability to incorporate highly polar groups at high concentrations and cooperative dipole motion.

Mechanical and electromechanical properties

Mechanical properties are often overlooked when investigating piezoelectric polymers. It is important to note that the piezoelectric response is a result of the coupling between the mechanical and dielectric properties in an amorphous polymer. The piezoelectric coefficient, d, is defined as

$$d = \frac{1}{A}\frac{\partial Q}{\partial T}\bigg|_{E=0,T} \qquad (6)$$

where Q is the charge per unit area displaced through a closed circuit between two electrodes, T is the applied stress, A is the area of the electrodes, and E is the applied field. This equation is used for the direct measurement of the d_{31} piezoelectric coefficient by stressing the polymer in the plane of the film, and measuring the charge that forms on the electrodes under zero field. Figure 4 shows the Young's modulus, Y'_{11} as a function of temperature. A decrease in the modulus of the four amorphous polymers, PVDCN-VAc, unstretched PAN, PVC, and (β-CN) APB/ODPA, occurs in the region of the glass transition. Figure 5 presents d_{31} as a function of temperature for several piezoelectric polymers. As the polymers approach their respective glass transition temperatures, d_{31} increases due to the decrease in the modulus. The trend continues until the thermal energy randomizes the molecular dipoles to yield a decrease in d_{31} as shown for PAN which has a T_g = 90 °C. The effect of the mechanical properties on the piezoelectric response is also evident by comparing two polymers with comparable remanent polarizations, PVC, and (β-CN) APB/ODPA. The lower modulus (higher compressibility) of PVC results in a larger piezoelectric response relative to (β-CN) APB/ODPA. It is important to note that data for identical processing conditions for the various polymers (E_p, t_p and T_p) is not readily available in the literature. This type of data would be very useful for a comparative analysis of the relative effects of mechanical and dielectric properties on the piezoelectric response.

Stretching can also have an effect on the piezoelectric coefficient of a polymer as shown for PAN in Figure 5. The increase in d_{31} with stretching has both mechanical and polarization contributions. Stretching in the 1-direction aligns the chains in the plane of the film, which results in an increase in the exhibited by PVDCN/VAc gives it the largest value of P_r (Table II) and hence d_{31} (Table III) of all the amorphous polymers. Although the existence of cooperative dipole motion clearly increases the piezoelectric response of amorphous polymers, the mechanisms by which cooperativity can be systematically incorporated into the polymer structure remain unclear at this time. Finally, Table II demonstrates the efficiency with which polarization may be imparted into the sample. The polymers which exhibit free dipolar motion show relatively low ratios of P_r / P_u (10-30%) which indicates low dipole orientation, while the ratio of P_r / P_u for PVDCN/VAc polymer is as high as 60%. It is noted that in Table II, P_r is measured using the previously mentioned TSC method. As a result, P_r could include space charge effects as well as dipolar reorientation. However, for all the amorphous polymers of Table II except PVDCN-VAc, P_r measured was seen to vary linearly with E_p, which is an indication that space charge effect is negligible since space charge polarization varies nonlinearly with the poling field. Also for these polymers, P_r measured is of the order of P_r given by equation (4), again indicating a linear relationship.

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Figure 6 stresses the importance of the relative effect of the temperature on the piezoelectric activity. Although from Figure 5, PAN (stretched) looked like it outperforms (β-CN) APB/ODPA, a closer look of Figure 6 shows that at 70°C below T_g, d_{31} of PAN is 1.7 pC/N whereas that of (β-CN) APB/ODPA is 5 pC/N. It is clear that the amorphous piezoelectric polymers have to be used below their T_g as PAN quickly depolarizes as T_g is approached. This is in contrast to PVDF (and other semicrystalline polymers) which are used well above their T_g's.

The coupling between mechanical and dielectric properties is also evident in the hydrostatic piezoelectric coefficient, d_h which is given by [33]:

$$d_h = -\beta \, \Delta\varepsilon \, \varepsilon_0 \varepsilon_\infty \, E_p/3 \qquad (7)$$

As seen in equation 7, both the mechanical properties (through the compressibility, β) and the dielectric properties (represented by Δε) affect the piezoelectric coefficient. Figure 7a presents the mechanical and electrical properties as a function of temperature for (β-CN) APB/ODPA. The compressibility of (β-CN) APB/ODPA increases slightly with temperature until T_g is reached. The remanent polarization is relatively stable until about 50 degrees below the glass transition at which point it decreases due to dipole randomization. Consequently as shown in Figure 7b, d_h increases slightly with temperature prior to the onset of depolarization.

Summary

This review has brought together the dielectric theory and the mechanical properties which define the piezoelectric response in amorphous polymers. The basic requirements for designing an amorphous piezoelectric polymer are the presence and concentration of dipoles, the ability to orient these dipoles and to lock them in this alignment, and the ability to sufficiently strain the polymer. Calculating the ultimate polarization P_u is a good starting point when designing piezoelectric amorphous polymers. A primary weakness of amorphous polymers is poor dipole alignment during poling (low P_r/P_u value). This would be overcome by incorporating cooperativity such as the case of PVDCN-VAc. Until this phenomenon is understood where the polymer structure may be engineered to include cooperativity, incremental steps are being made to improve the response by incorporating large dipoles (primarily CN) at high concentrations.

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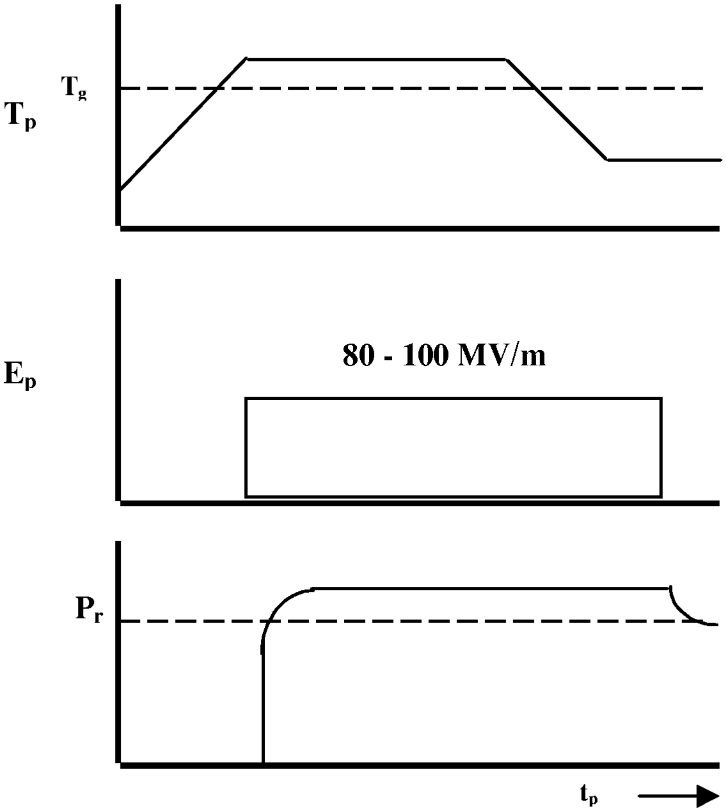

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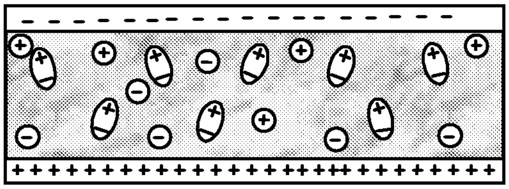
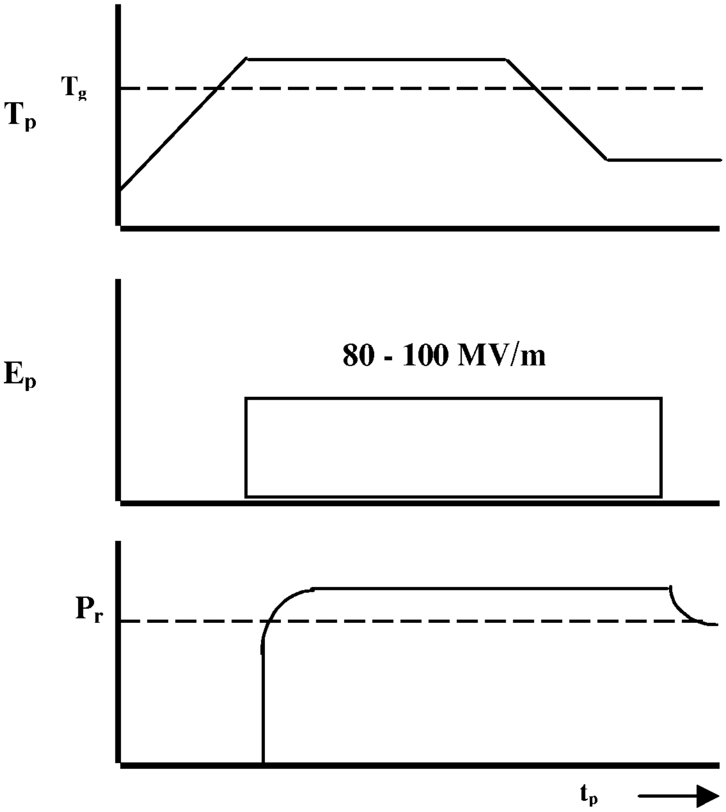


Figure 2. Real charges in an amorphous electret.



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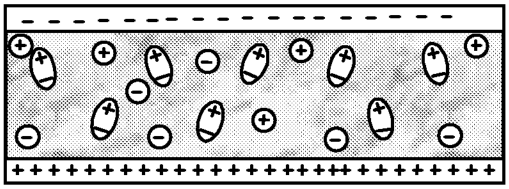

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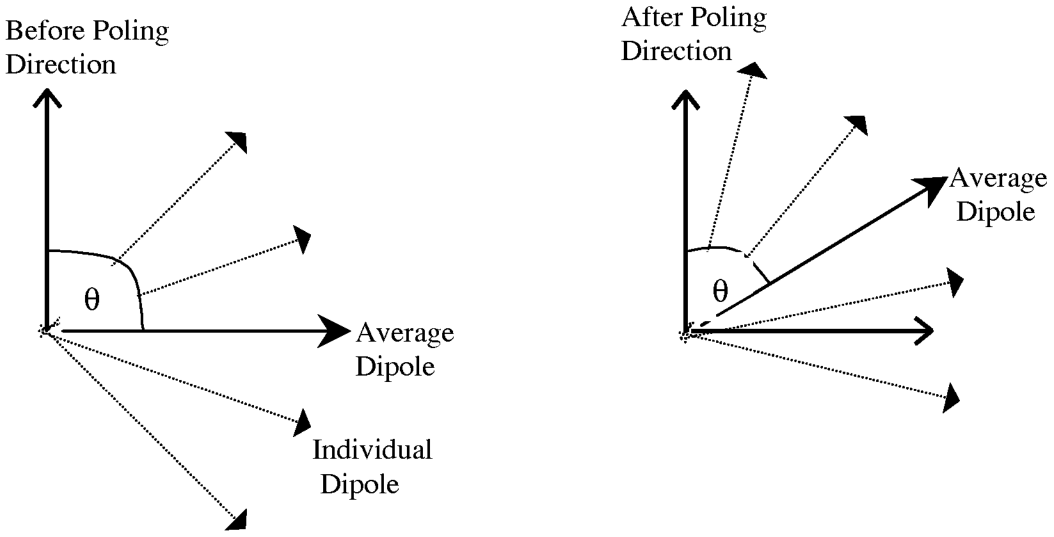
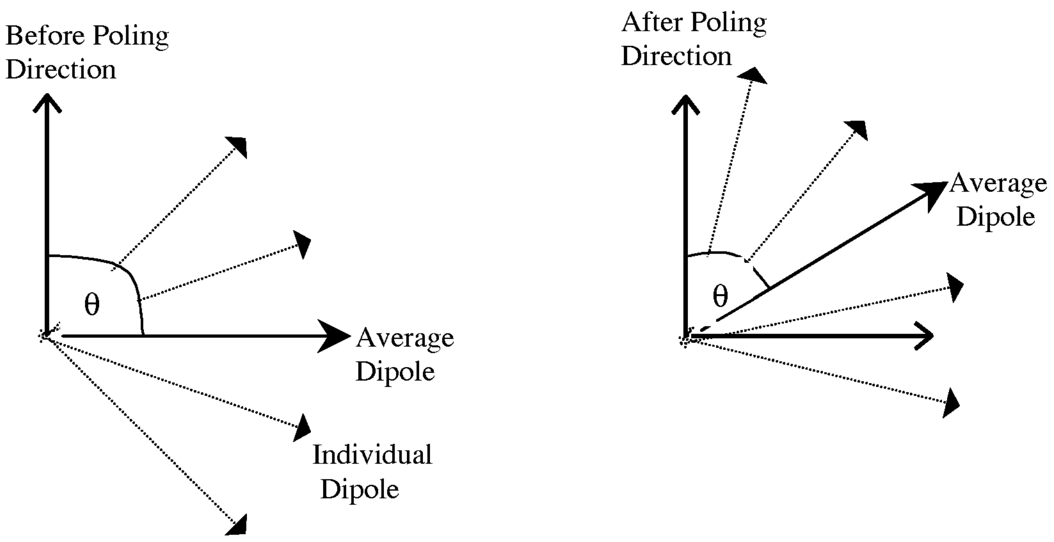


Figure 3. Orientation polarization of the (β-CN) APB/ODPA polymer.



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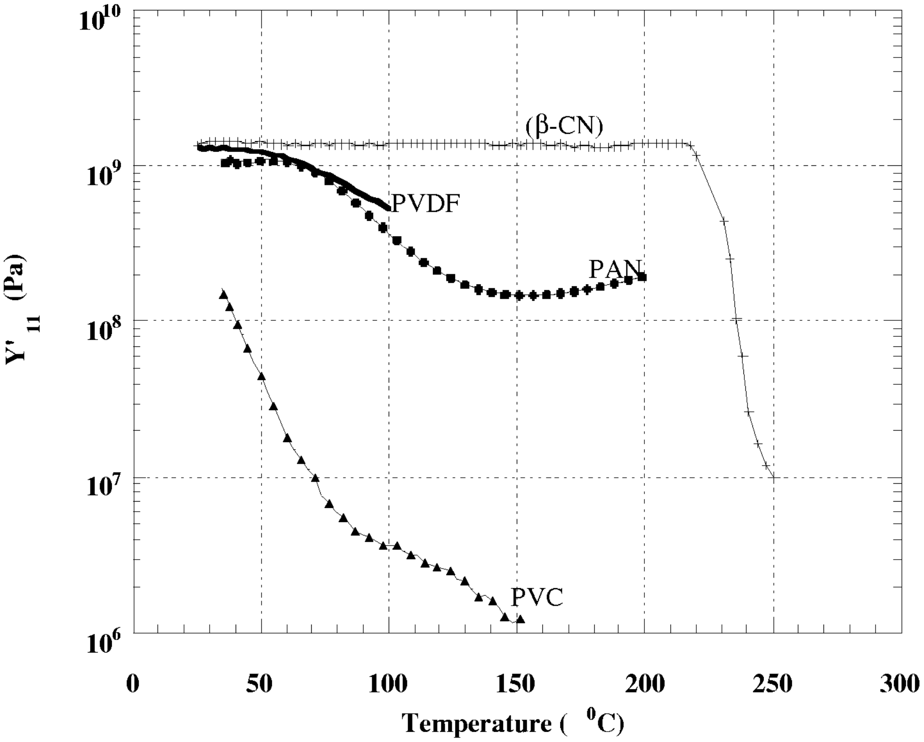
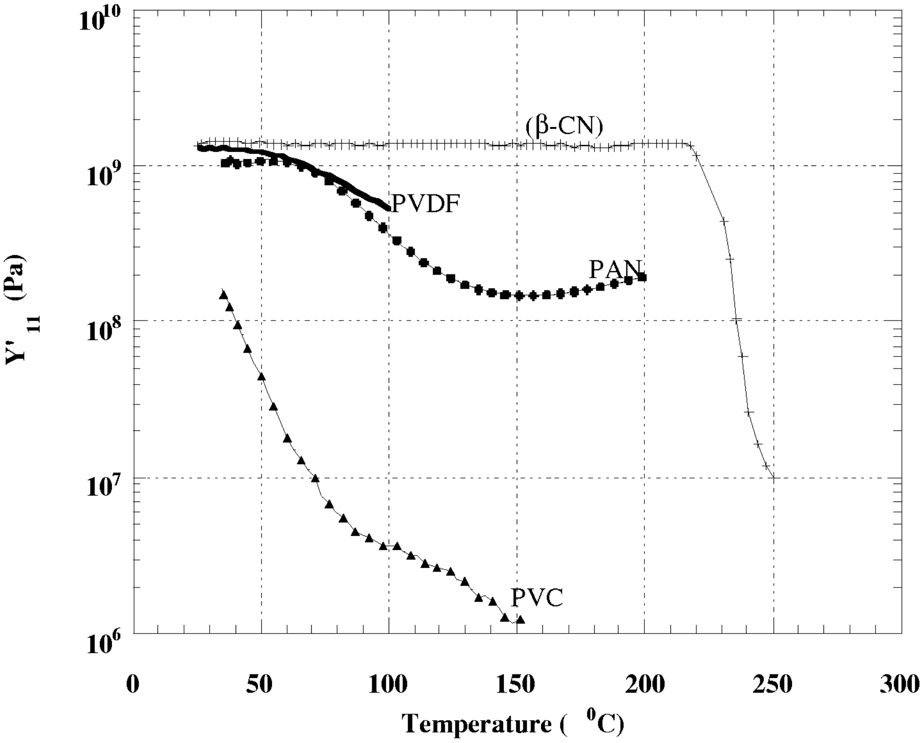


Figure 4. Modulus as a function of temperature.



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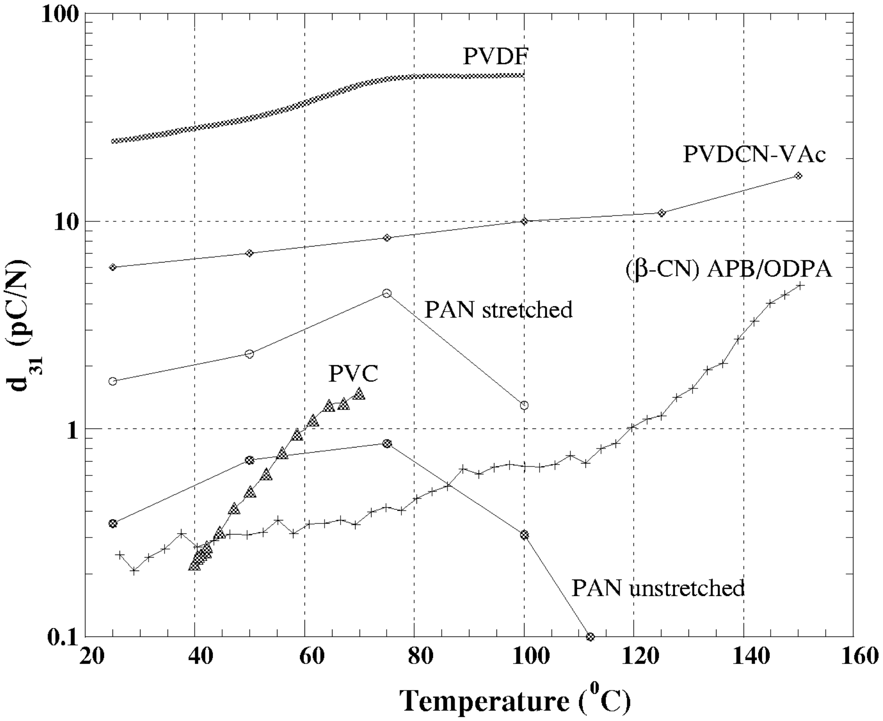
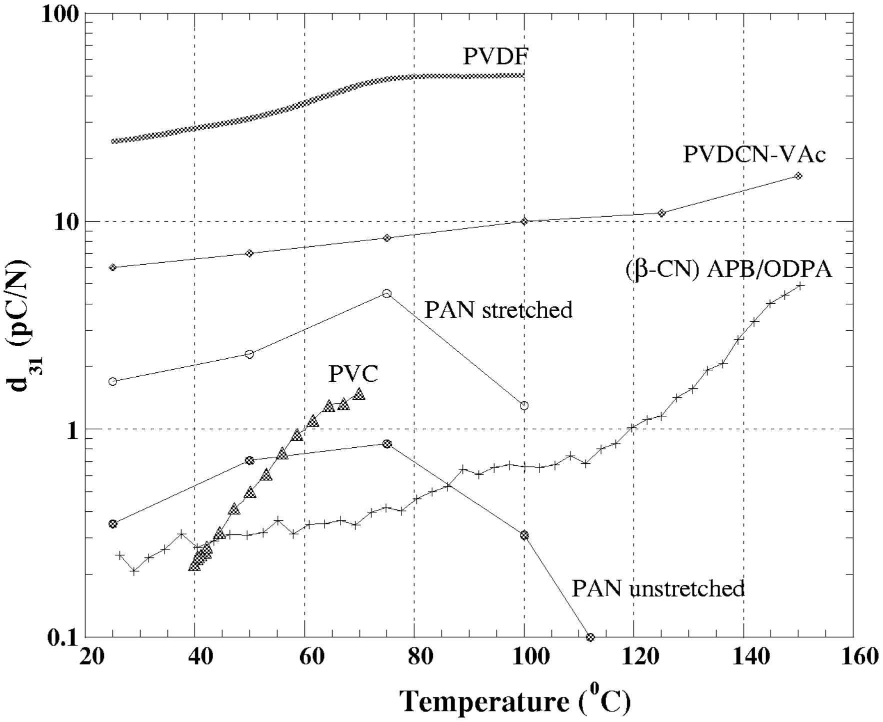


Figure 5. Comparison of the piezoelectric strain coefficient, d_{31}.



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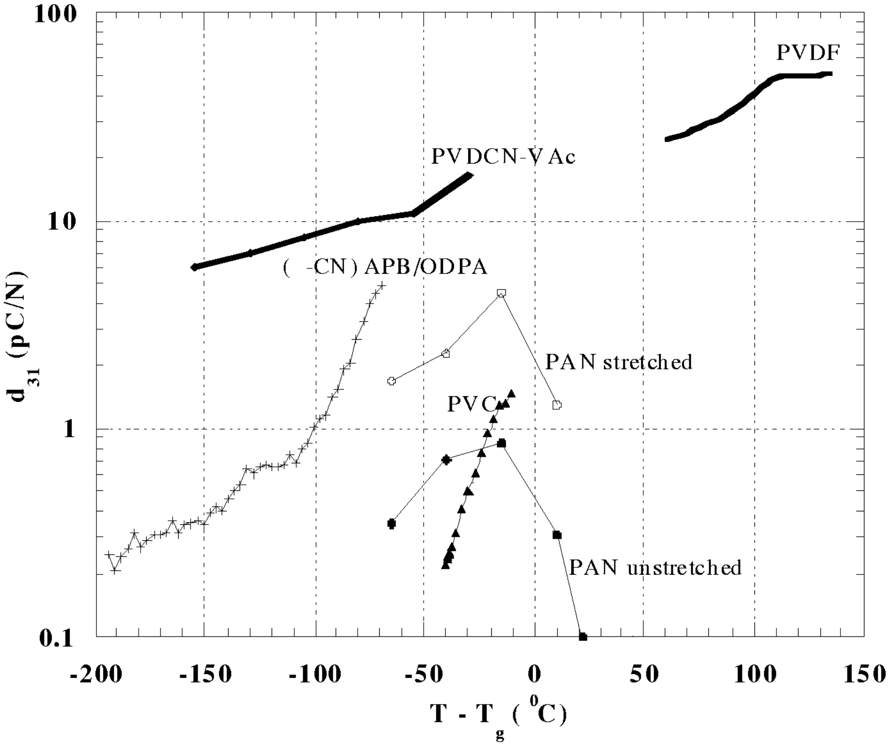
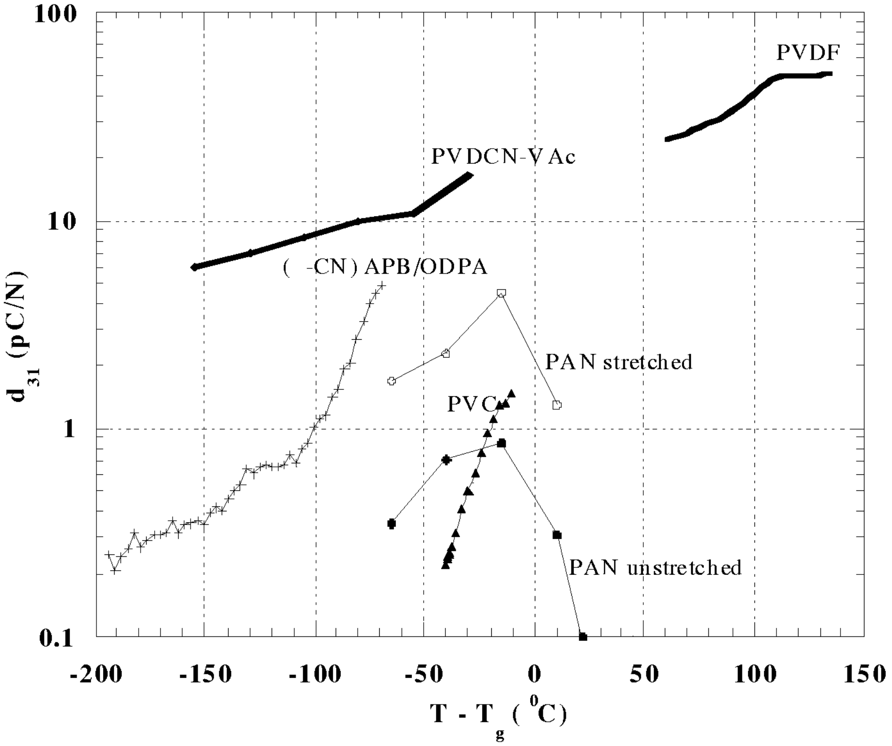


Figure 6. Piezoelectric strain coefficient d_{31} with respect to T_g.



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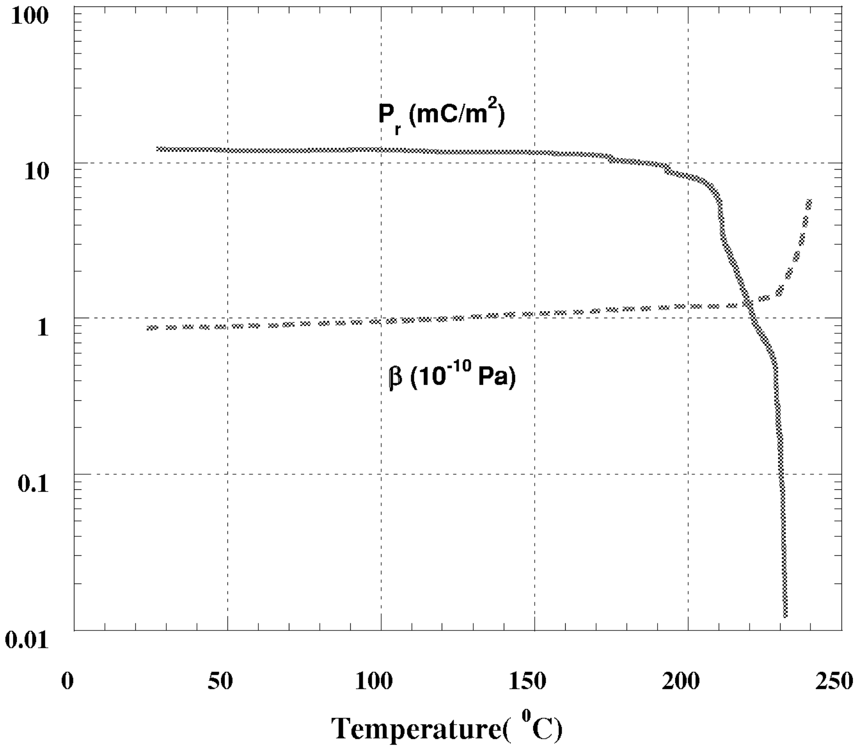
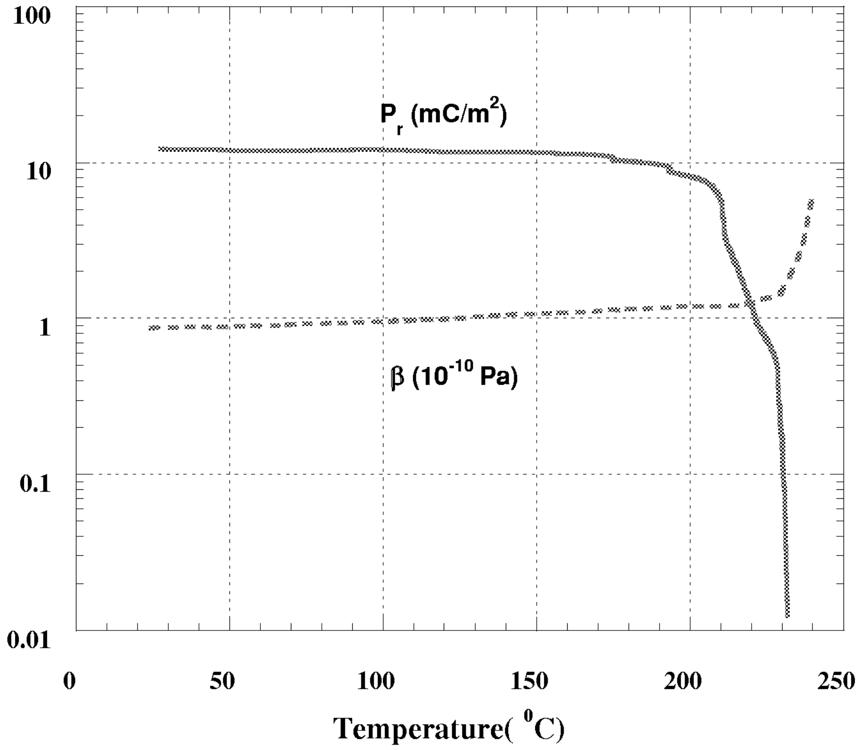


Figure 7a. Mechanical and electrical properties of (β-CN) APB/ODPA as a function of temperature.



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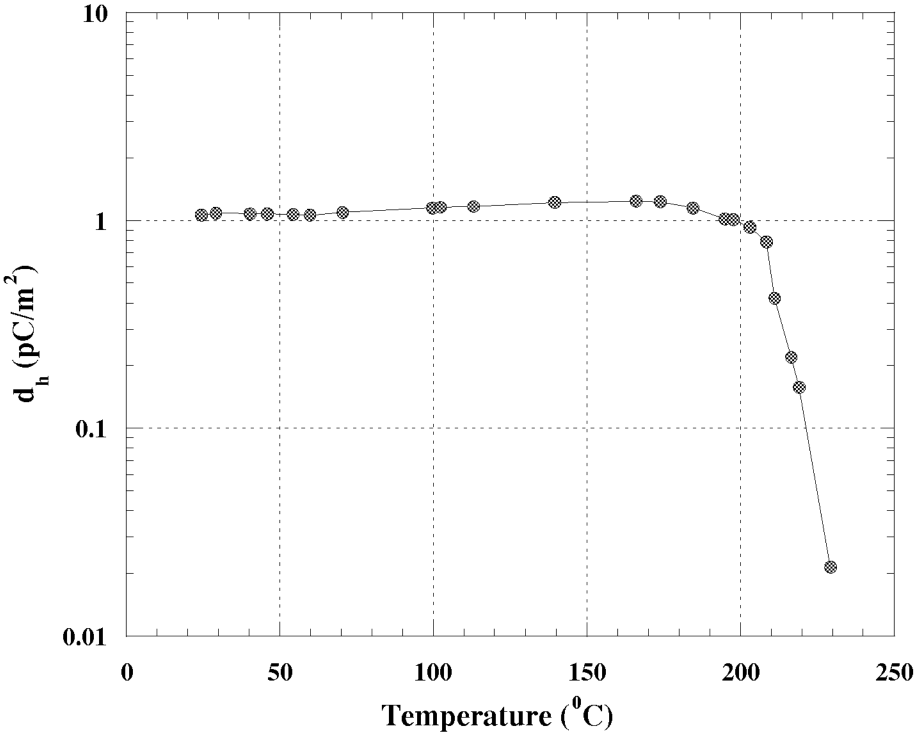

Figure 7b. Hydrostatic piezoelectric coefficient, d_h.

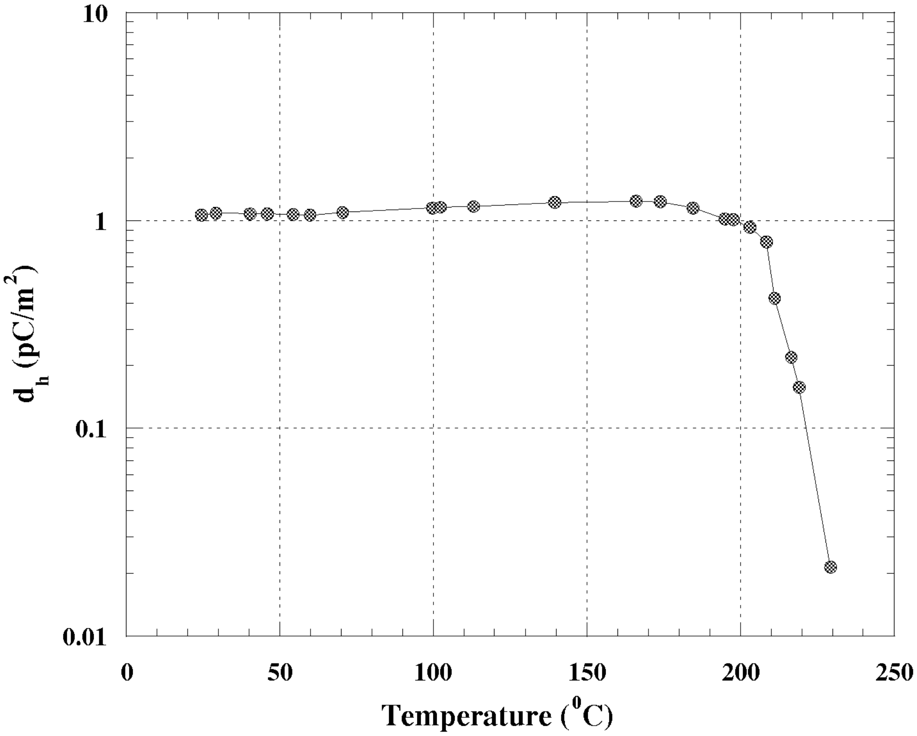

Figure 7b. Hydrostatic piezoelectric coefficient, d_h.

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