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Effects of plasticization on the piezoelectric properties of nylon 11 films

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Nylon 11 films (δ'-form) were plasticized by immersion in 2-ethyl 1,3 hexanediol. Two different kinds of studies were performed. In the first study, poled nylon 11 films were plasticized by immersion in the plasticizer for different lengths of time. The piezoelectric strain constant, d_{31}, initially increased up to a plasticizer content of $\sim 14\%$ (by weight) and then decreased. The values of piezoelectric stress constant, e_{31}, however, decreased with increase in dipping time. In the second study, the films were initially plasticized and then poled. Both d_{31} and e_{31} were higher for plasticized films compared to unplasticized films under identical poling conditions. X-ray diffraction studies showed some conversion of δ'-phase to α'-phase during the process of plasticization.

1. Introduction

Most of the work related to the piezoelectric properties of polymers such as poly(vinylidene fluoride) (PVDF) and nylon 11 has been done on the basis of the response originating from the crystalline regions of these semicrystalline polymers. For the case of PVDF, it is well known that film polarization results from ferroelectric switching of polar crystallites [1, 2] and/or field-induced crystal transitions from nonpolar to polar or polar to more polar structures [3–7]. The importance of the modification of the amorphous regions on the resulting piezoelectric response has now been recognized from recent studies. The first study dealing with the effects of plasticization on the resulting piezoelectric response was reported by Newman *et al.* [8] for the case of PVDF. At about 3% plasticizer (tricresyl phosphate) by weight, the piezoelectric strain constant, d_{31}, was observed to have increased by 20%. Sen *et al.* [9] reported that for PVDF, field-induced crystal transition from phase II to phase I took place at lower poling fields for plasticized (initially unoriented) phase II films as compared to unplasticized films under identical poling conditions. The pyroelectric response also increased with increase in the plasticizer content.

The effect of modification of the amorphous regions on the resulting piezoelectric response has also been observed for the case of odd nylons. In the case of nylon 11, Scheinbeim [10] observed that d_{31} increased rapidly with increasing temperature as the nylon 11 sample was heated through and above the glass transition temperature. The effects of absorbed water on the piezoelectric properties of nylon 11 and nylon 7 have been studied by Kim [11]. Water acts as a plasticizer for nylons and is expected to modify primarily the amorphous regions. The values of d were observed to have increased with increase in the water content of the samples. For the case of slowly crystallized nylon 11 (α'-form) films, which are known to show very low piezoelectric response [12], d_{31} increased rapidly when the films were plasticized and stretched before poling [13].

Recent crystal structure studies for nylon 11 and nylon 7 [11] indicated that the crystal form found in films slowly cooled from the melt may be nonpolar and for the films quenched from the melt, the quenched form (called δ'-form) may not actually have long-range three-dimensional order but may have an amorphous or quasi-amorphous nature. The piezoelectric response has been observed to be larger for samples containing larger amounts of the amorphous phase before poling. The presence of significant crystallinity in nylon 11 before poling actually reduces the piezoelectric response obtained after poling, compared to quenched films with low crystallinity.

Scheinbeim *et al.* [14] recently studied the piezoelectric response from nylon 11 films with very low initial crystallinities, obtained by solution casting from the plasticizer, 2-ethyl 1,3 hexanediol. A high piezoelectric response ($d_{31} = 7.1\,\mathrm{pc\,N^{-1}}$) was observed for the films subjected to the maximum electric field ($E_p = 350\,\mathrm{kV\,cm^{-1}}$) while the sample contained a large fraction of the plasticizer. More recently, Mathur *et al.* [15] studied the draw ratio dependence and poling field dependence of different kinds of nylon 11 films. Using infrared spectra, they showed that the strength of hydrogen bonds in the quenched films was lower, compared to that in the slow crystallized films. The larger piezoelectric response in the quenched films

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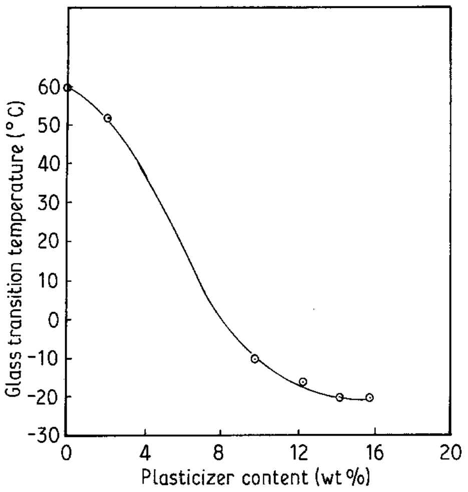

Figure 1 Variation of glass transition temperature with plasticizer content.

resulted from the ease in the rotation of weakly hydrogen-bonded amide groups into the direction of the applied field. Annealing prior to poling resulted in rearrangement of the hydrogen bonds and consequently an increase in the strength of the bonds.

A systematic study of the effects of plasticizer on the piezoelectric properties of different kinds of nylon 11 films (δ' or α' form) in unoriented and oriented states will provide further insight into the effects of modification of both the amorphous and crystalline regions. In the present paper, the initial studies for unoriented nylon 11 δ'-form films are presented. The combined effects of uniaxial stretching and plasticization is reported in a separate paper [16].

2. Experimental procedure

The plasticizer used in this study was 2-ethyl 1,3-hexanediol. Initially, to observe the general effects of plasticization, samples of nylon 11 (δ'-form) films were immersed in the plasticizer at 75° C for different lengths of time. The plasticizer content was estimated from the increase in the weights of the samples. Measurement of the glass transition temperature was performed for these samples using dynamic mechanical measurements in the Piezotron. Two different kinds of experiments were performed.

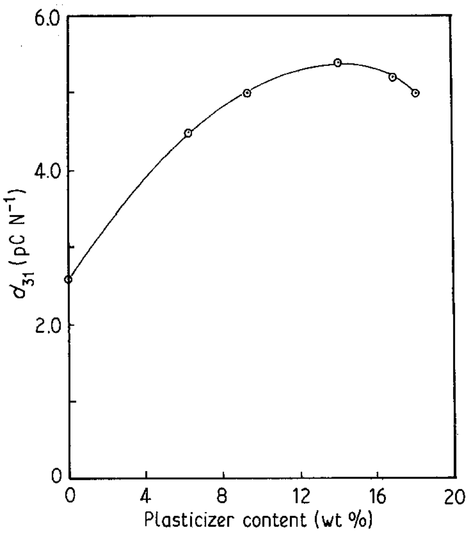

Figure 2 Piezoelectric strain constant, d_{31}, plotted against plasticizer content for films plasticized after poling.

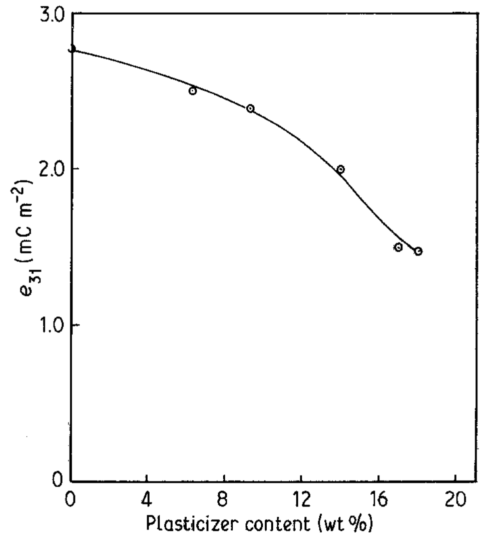

Figure 3 Piezoelectric stress constant, e_{31}, plotted against plasticizer content for films plasticized after poling.

(a) In the first experiment, a nylon 11 δ' sample was poled at 500 kV cm^{-1} for 30 min at 75° C. The values of d_{31}, e_{31}, modulus and dielectric constant were measured in the Piezotron. The sample was then submerged in the plasticizer at 65° C for different lengths of time. After each immersion the plasticizer content was measured by the increase in the weight of the sample and the measurements of d_{31}, e_{31}, modulus and dielectric constant, were performed. The same sample was used for all the measurements.

(b) In the second experiment, the samples were first plasticized by immersion in the plasticizer at 75° C for 30 min. The plasticizer content was found to be 18% (by weight). The samples were then poled at different poling fields at 50° C for 30 min. Excessive dielectric breakdown occurred if poling was attempted above this temperature. The measurements of d_{31}, e_{31}, modulus and dielectric constant were performed as a function of poling field. Unplasticized samples were also poled under identical poling conditions for comparison.

3. Results

Fig. 1 shows the variation of the glass transition temperature with increase in the plasticizer content in the films. The dependence of d_{31} and e_{31} on the plasticizer content for the films plasticized after poling are shown in Figs 2 and 3, respectively. The values of d_{31} and e_{31} for the poled sample before dipping in the plasticizer were 2.6 pC N^{-1} and 2.9 mC m^{-2}, respectively. With increase in the plasticizer content, d_{31} increased to 5.4 pC N^{-1} at a plasticizer content of $\sim 14\%$ (by weight) and then the values decreased as further plasticizer was added by immersing the sample in the plasticizer for longer lengths of time. The piezoelectric stress constant, e_{31}, however, decreased over the whole range as the plasticizer content was increased. Similar behaviour was observed for unoriented phase II PVDF films [8]. Figs 4 and 5 show the measured values of dynamic mechanical modulus and dielectric constant of the same sample with increase in the plasticizer content. The decrease in the modulus is $\sim 80\%$

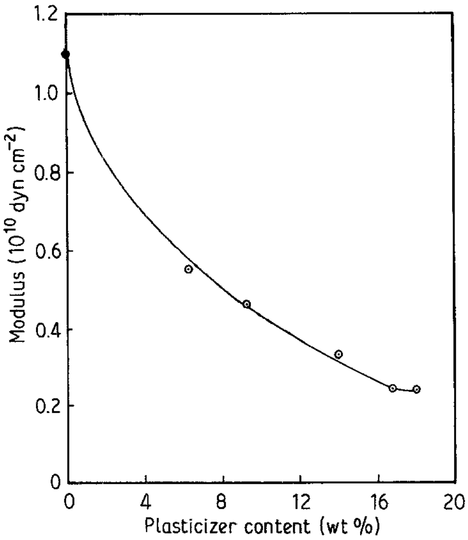

Figure 4 Dynamic mechanical modulus plotted against plasticizer content for films plasticized after poling.

and the increase in dielectric constant is ~200% at the highest plasticizer content.

Figs 6 and 7 compare the values of d_{31} and e_{31}, respectively, between unplasticized and plasticized nylon 11 δ' films as a function of poling field. The latter samples were plasticized before poling. Both d_{31} and e_{31} values are higher for the plasticized films compared to those of the unplasticized films under identical poling conditions. The increase in the values occurs at faster rate with poling field for the plasticized films compared to the unplasticized films. Under identical poling conditions ($400\,\mathrm{kV\,cm^{-1}}$) the value of d_{31} is more than four times higher than the value for the unplasticized film, and that of e_{31} is 1.4 times higher. The values of modulus and dielectric constant remain essentially unchanged with poling fields. The modulus for the plasticized film is ~70% lower than the unplasticized film (modulus $= 1.1 \times 10^{10}\,\mathrm{dyn\,cm^{-2}}$) and dielectric constant is ~3.5 times higher compared to the unplasticized films as shown in Figs 8 and 9, respectively.

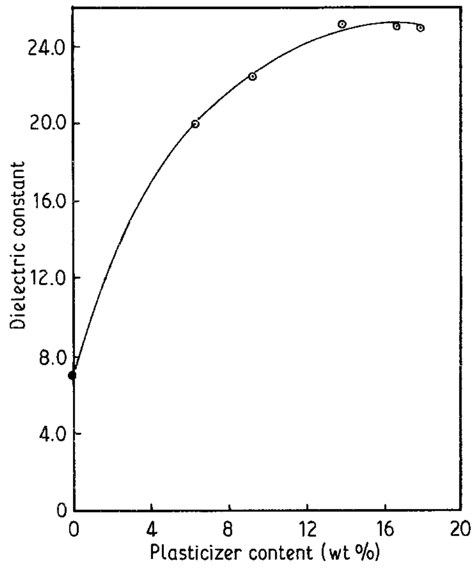

Figure 5 Dielectric constant plotted against plasticizer content for the films plasticized after poling.

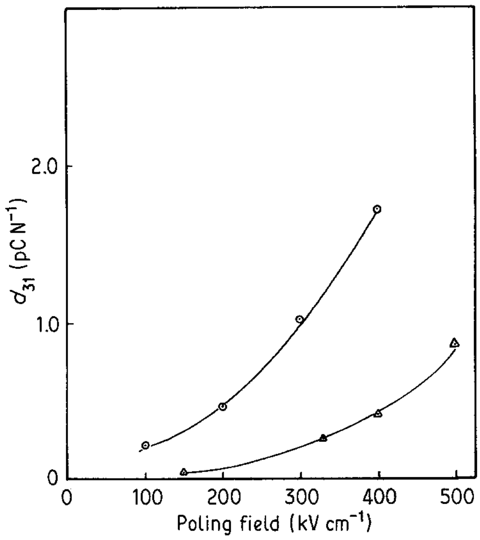

Figure 6 Piezoelectric strain constant, d_{31}, plotted against poling field. (Δ) Unplasticized films, (○) plasticized and poled.

X-ray diffraction studies were performed to find out if any phase transformations were occurring during plasticization. Fig. 10 compares the wide-angle diffraction scans in reflection mode for the plasticized and unplasticized films. These scans indicate that upon plasticization, δ' converts to the α' form. The single peak at $2\theta = 21°$ splits into the two distinct peaks characteristic of the α'-form.

4. Discussion and conclusions

The results for d_{31} and e_{31} for the films plasticized after poling have to be interpreted on the basis of how these constants are related to the rate of change of polarization with either stress or strain. The piezoelectric strain constant is defined as the rate of change of bulk polarization with stress, σ, (applied in the plane of the film) or

$$d_{31} = (dP/d\sigma)$$

while the piezoelectric stress constant is defined as the rate of bulk polarization with strain, s, or

$$e_{31} = (dP/ds)$$

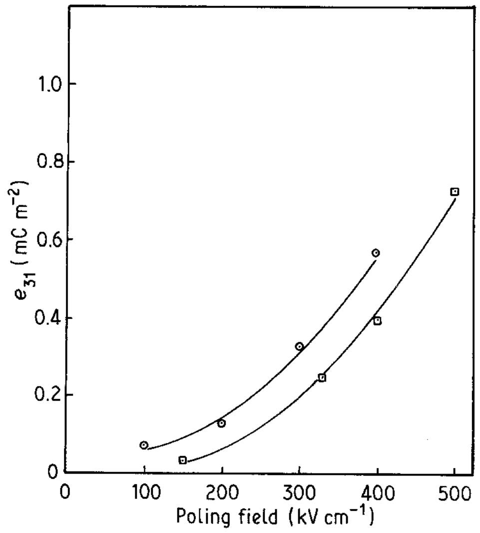

Figure 7 Piezoelectric stress constant, e_{31}, plotted against poling field. (□) Unplasticized films, (○) plasticized and poled.

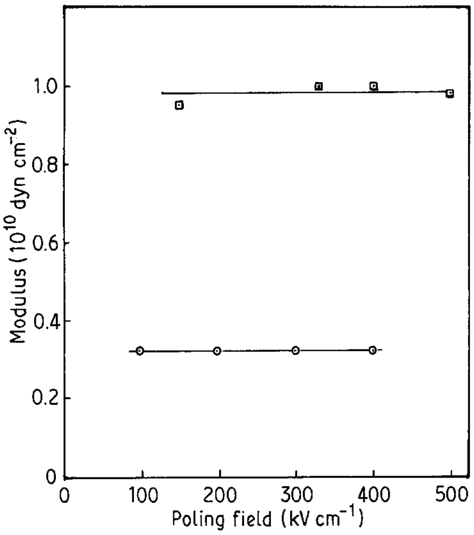

Figure 8 Dynamic mechanical modulus plotted against poling field. (□) Unplasticized films, (○) plasticized and poled.

From the definition, it follows that

$$E =.\ e_{31}/d_{31}$$

where E is the elastic modulus. Because all these constants have been measured, the ratio was checked for all data and found to be within experimental error. The piezoelectric strain constant is related to the rate of change of polarization with application of stress in the plane of the film. The thickness of the film is reduced depending upon the Poisson's ratio with application of the stress in the plane of the film, and results in a consequent change in polarization. In the presence of plasticizer, it is seen from Fig. 4 that the modulus decreases with increasing amounts of plasticizer and, hence, with the same amount of stress one should expect greater strain and therefore a greater reduction in the thickness of the film (assuming Poisson's ratio does not change appreciably with plasticizer content). Under these conditions, d_{31} is expected to increase with increasing plasticizer content. The decrease in the value above about 14% plasticizer content could be due to the possibility of depolarization occurring, as the same poled sample was repeatedly immersed in the plasticizer after each measurement. Above ~14% plasticizer content the decrease in modulus is less significant (as seen from Fig. 4) and, presumably, the depolarization effect predominates resulting in a decrease in the value of d_{31}.

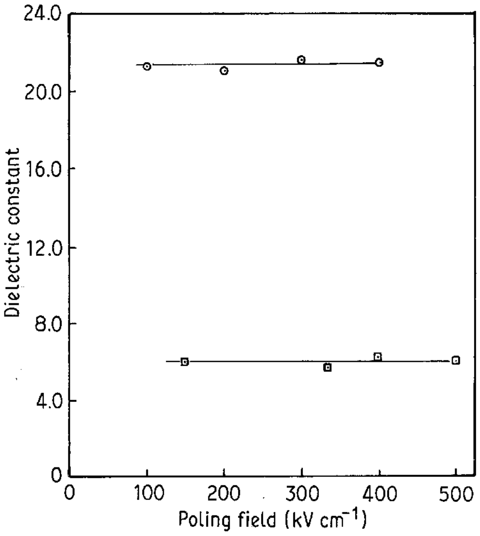

Figure 9 Dielectric constant plotted against poling field. (□) Unplasticized films, (○) plasticized and poled.

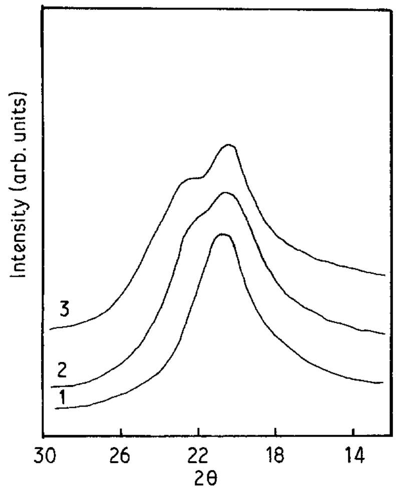

Figure 10 Wide-angle diffraction scans in reflection mode for plasticized and unplasticized films. (1) Unplasticized, (2) plasticized (8.0 wt %), (3) plasticized (18.0 wt %).

For the case of e_{31}, the changes in bulk polarization with respect to increments in strain in the plane of the film are measured. For the same levels of strain in the plane of the film, reductions in the thickness of the film will be the same (independent of modulus) assuming no significant change in Poisson's ratio with increase in plasticizer content. In this case plasticization should not change the values of e_{31}. The observed decrease for films plasticized after poling could be attributed to a decrease in total polarization of the film (depolarization) resulting from the immersion in the plasticizer at the elevated temperatures.

The increase in d_{31} in films plasticized prior to poling can be explained from the reduction in modulus as before, but the increase in the values of e_{31} cannot be explained from the reasoning given before. Here the role of the amorphous component is quite important. Higher mobility in the amorphous regions due to plasticization increases the bulk dielectric constant, and Hayakawa's model [17] predicts an increase in e_{31} with increase in the bulk dielectric constant. The increase in e_{31} can be explained from an increase in bulk polarization resulting from larger fractions of dipoles switching in the field direction due to the increased mobility (or decreased hydrogen bond strength) provided by the presence of plasticizer.

The X-ray diffraction patterns indicate (see Fig. 10) that a conversion of δ' phase to α' phase occurs during plasticization. For unplasticized films the presence of α' phase has been shown to be detrimental to the piezoelectric response [11]. However, here the increase in bulk polarization and reduction in modulus seem to predominate and an increase in response with plasticization is observed, in spite of the increase in α'-form.

In conclusion it can be said that the effects of plasticization of the unoriented δ' nylon 11 films after poling is an increase in the value of piezoelectric strain constant, d_{31}, with increase in the amount of plasticizer. The increase can be explained on the basis of the reduction in modulus, assuming Poisson's ratio does not change appreciably with plasticization. The decrease in the values after ~14% (by weight) plasticizer content is attributed to depolarization. The decrease in the values of e_{31} for the films plasticized after poling also indicate the occurrence of depolarization with repeated immersion of the same sample in the plasticizer.

The presence of plasticizer in the films prior to poling results in an increase in the bulk polarization produced during the poling process. This is indicated by the higher d_{31} and e_{31} values for the plasticized films compared to the unplasticized films under identical poling conditions. This study provides further indication that the amorphous regions play a major role as far as the piezoelectric response from nylon 11 films is concerned. More detailed study involving the combined effects of uniaxial stretching and plasticization will be presented in a separate publication.

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