

FERROELECTRIC AND PIEZOELECTRIC PROPERTIES OF BLENDS OF POLY(VINYLDENE-TRIFLUOROETHYLENE) AND GRAFT ELASTOMER

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ABSTRACT

A piezoelectric polymeric blend system has been developed. The system contains two components: ferroelectric poly(vinylidene-trifluoroethylene) and graft elastomer. The remanent polarization, P_r , and the piezoelectric strain coefficient, d_{31} , of the blends have been studied as a function of relative composition of the two components, temperature and frequency. Both blended copolymer and graft unit in the elastomer contribute to the total crystallinity of the blend-system, and hence to the remanent polarization and piezoelectricity. The piezoelectric strain coefficient, d_{31} , of the blend systems shows dependence on both the remanent polarization and the mechanical stiffness, which in turn are determined by the fraction of the two components in the blends. This mechanism makes it possible for the piezoelectric strain response of the blend to be tailored by adjusting the relative composition. Although P_r of the copolymer is higher than that of the blends, the blend films containing 75 wt.% copolymer exhibit a higher d_{31} at room temperature, possibly due to their lower modulus. The blend films containing 50 wt.% copolymer exhibit a constant value of d_{31} , from room temperature to 70°C.

INTRODUCTION

Ferroelectric and piezoelectric poly(vinylidene-trifluoroethylene) copolymers have been extensively studied in the last two decades due to their electromechanical properties[1-4]. Recently, the electrostrictive properties of high energy electron irradiated poly(vinylidene-trifluoroethylene) copolymers have been reported and the results show promising properties for applications in actuation technologies[5,6]. In the present work, a ferroelectric copolymer-elastomer blend system was developed to improve the toughness of the electromechanical copolymers since the brittleness of the pure copolymers may limit their applications. Both the ferroelectricity and piezoelectricity of the blend-system were investigated. The results show that the piezoelectric strain response and the modulus of the blend films can be tailored by adjusting the ratio of both phases in the system. By careful selection of the composition, an enhanced piezoelectric strain response and a temperature-independent piezoelectric strain response can be obtained.

EXPERIMENT

Film preparation: The blend films were prepared by solution casting. The ferroelectric poly(vinylidene-trifluoroethylene) copolymer (50/50 mol.%) and graft elastomer powders were added to N,N-dimethylformamide. The mixture was heated to 60°C while stirred to make a 5 wt.% polymer solution containing the desired fraction of the two components. The solution was then cooled to room temperature, cast on glass

substrates, and placed in a vacuum chamber. After drying overnight under vacuum, tack-free films were obtained. In order to increase their crystallinity, and possibly their remanent polarization, the blend films were thermally annealed at 140 °C for 10 hours. The thickness of the films was around 20µm. The films were tested using X-ray diffraction (XRD) and differential scanning calorimetry (DSC) in order to assess their composition and degree of crystallinity.

Poling and Measurements: Gold electrodes were sputtered on the opposing surfaces of the films to establish electrical contact. The films were poled using a triangular wave signal with a peak value of 100MV/m at 30 mHz. The modulus, E_{11} , and the piezoelectric strain coefficient, d_{31} , were measured using a modified Rheovibron. The capacitance of the blend films was measured using a HP Analyzer 4192A, and the dielectric constant, ϵ , was calculated from the value of the capacitance. These measurements were performed as a function of the relative composition of the blends (wt.% copolymer content), temperature, and frequency.

RESULTS AND DISCUSSION

Figure 1 shows the crystallinity as a function of copolymer content in the blend. The calculated crystallinity of the blend system is found from

$$X_{\text{total}} = f_{\text{copolymer}}X_{\text{copolymer}} + f_{\text{elastomer}}X_{\text{elastomer}} \quad (1)$$

where f is the fraction of the components and X is the crystallinity. Both the measured and calculated crystallinities increase with increasing copolymer content in the blend, however, the measured crystallinity is lower than the calculated one. This indicates that the presence of both components in the blend may reduce their crystallization as compared to each individual one.

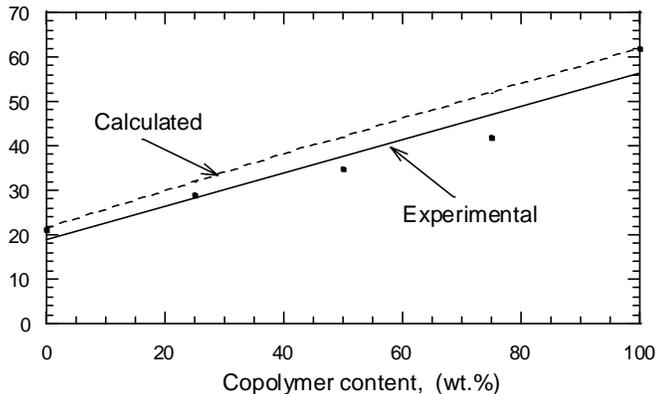


Figure 1. The relationship between the copolymer content and the crystallinity in the blends

To determine the remanent polarization, the measurement of the polarization, P , versus the electric field, E , was carried out. Corrections were made to eliminate the effects of conductivity on the ferroelectric hysteresis loops [7]. The measured remanent polarization, P_r , as a function of the copolymer content in the blends is shown in Figure 2 and compared with the remanent polarization calculated using the following equation:

$$P_{r(\text{total})} = f_{\text{copolymer}} P_{r(\text{copolymer})} + f_{\text{elastomer}} P_{r(\text{elastomer})} \quad (2)$$

where f is the relative fraction of the components, $P_{r(\text{copolymer})}$ is the remanent polarization in the pure copolymer, $P_{r(\text{elastomer})}$ is the remanent polarization in the elastomer, and $P_{r(\text{total})}$ is the resulting remanent polarization of the blend film. As can be seen, both the measured and the calculated remanent polarization increase with increasing copolymer content in the blends. The value of the measured remanent polarization is very close to the calculated one. This is an indication of the linear relationship between P_r and the polar crystallinity in the blends.

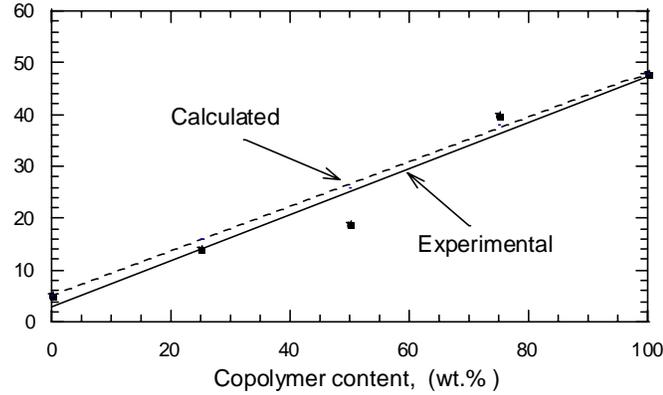


Figure 2. Relationship between the copolymer content in the blend and the remanent polarization.

Figure 3 shows the mechanical modulus, E_{11} , for all the blends as a function of temperature at 1 Hz. As expected, the mechanical modulus of the blends increases with the increase of the copolymer content and the copolymer has the highest modulus. It is also noted that due to the copolymer's brittleness, samples tended to fail at 65°C .

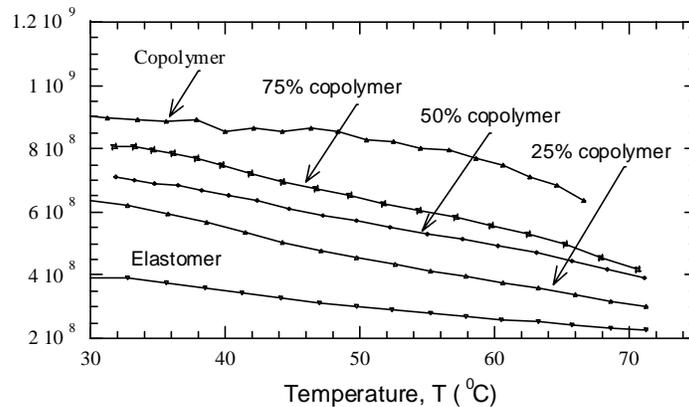


Figure 3. Comparison of the mechanical modulus E_{11} of blend films and homopolymer films.

Figure 4 shows the temperature dependence of the piezoelectric strain coefficient, d_{31} , for blend films with various compositions. The piezoelectric strain coefficient, d_{31} increases with increasing copolymer content. However, the blend film with 75 wt.%

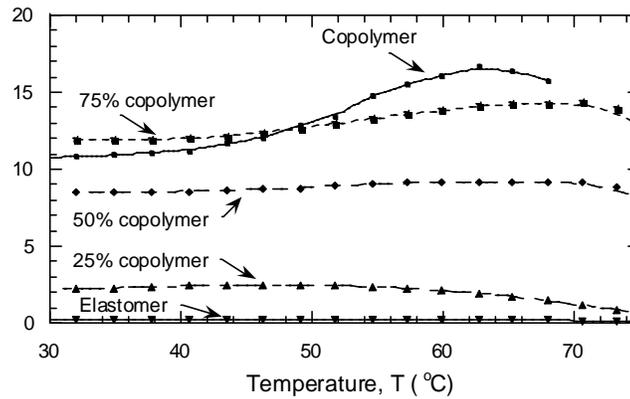


Figure 4. The temperature dependence of the piezoelectric strain coefficient, d_{31} , of the blend films (1 Hz) as a function of the various compositions.

copolymer exhibits the highest d_{31} from room temperature to about 45°C. Additionally, the blend film with 50 wt.% shows an almost constant piezoelectric response from room temperature to 70°C. These results reflect the influence of both the electrical polarization and mechanical modulus of the films on the piezoelectric strain response. As observed in the case of the 75 wt.% copolymer blend, even though it had a lower remanent polarization than the pure copolymer, it showed a higher piezoelectric strain response due to its lower modulus. Improvement in the toughness of the materials is also observed. Under the present experimental conditions, the pure copolymer film breaks at a temperature close to 65°C, while the rest of the blend films maintain their piezoelectric response up to 75°C without mechanical failure. In particular, the piezoelectric strain response of the 75 wt.% copolymer and 50 wt.% copolymer blend films is still significantly high up to 75°C.

When the dependence of the piezoelectric strain coefficient, d_{31} , on the relative composition of the two components in the blend is examined, different trends were observed at 30°C and 65°C (Figure 5). The reason for the non-linear dependence may be

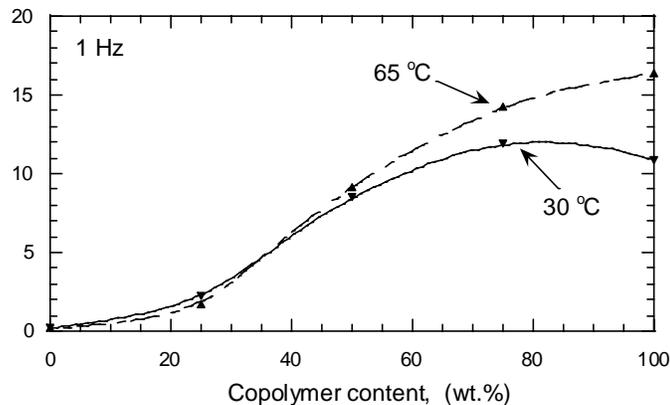


Figure 5. The relative composition dependence of the piezoelectric strain coefficient, d_{31} , at 30°C and 65°C.

attributed to the nature of the piezoelectric strain response of the material. As previously stated, the intrinsic contributions of both the mechanical properties (through the modulus) and the electrical properties (through the polarization) may yield this non-linear behavior.

Figures 6a and 6b show the temperature dependence and composition dependence of the dielectric constant at 10 Hz for the copolymer-elastomer blend films. The temperature dependence of the dielectric constant shown in Figure 6a gives a reasonable

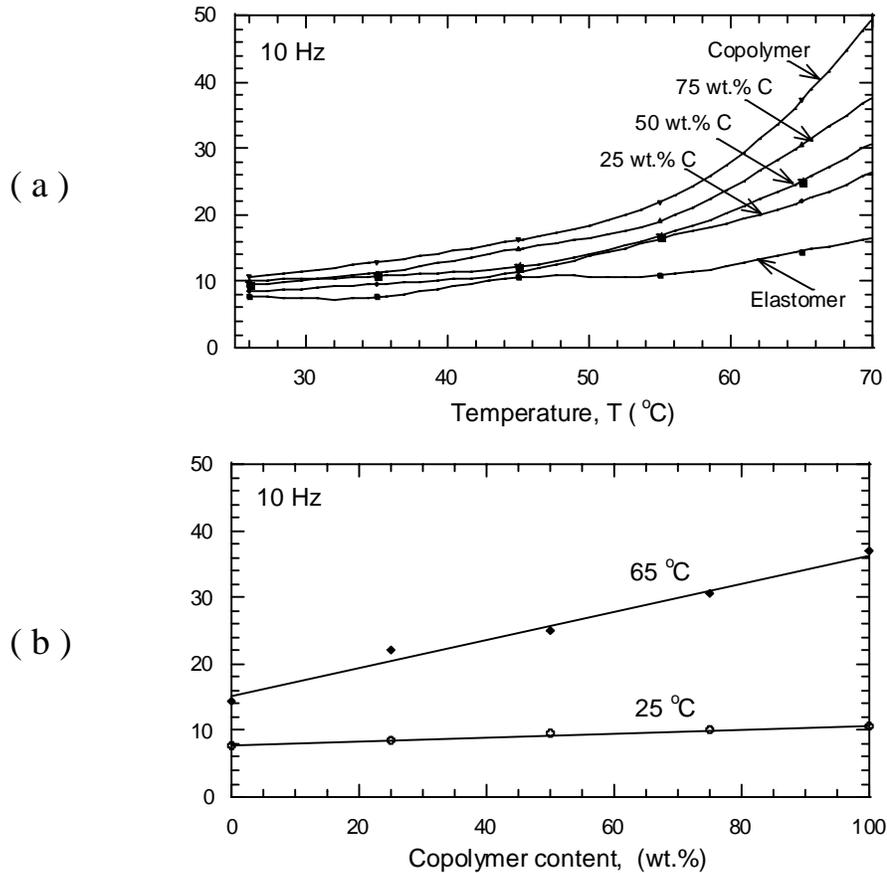


Figure 6. (a) Temperature dependence of the dielectric constant, and (b) Composition dependence of the dielectric constant.

trend for a blend system. The elastomer shows a transitional change in the temperature range from 40°C to 50°C and less temperature dependence than the copolymer in the measured temperature range. The transitional change is the second glass transition of the elastomer due to the molecular motion of the graft crystal cross-linking sites. It is obvious that the addition of the copolymer in the blend decreases the second glass transition of the graft elastomer significantly. This might be attributed to the molecular interaction between the added copolymer and graft unit in the elastomer. This interaction may also be the reason that the measured crystallinity of the blend is lower than the calculated one. The dielectric constant of the copolymer shows an obvious increase above 50°C due to the ferroelectric-paraelectric phase transition [8]. For the blend system, as the copolymer content increases, the transition behavior in the dielectric constant becomes more apparent. Figure 6b shows the inter-relationship between the dielectric constant and the

relative composition of the two components in the blend. Unlike the piezoelectric strain response, the dielectric constant shows a linear dependence to the relative composition at both 25°C and 65°C.

SUMMARY

The ferroelectric copolymer-graft elastomer blend system exhibited a marked improvement in toughness as compared to the pure copolymer. The blends also offer a potential of modifying the relative fraction of the two components in the blend in order to tailor the properties to desired applications. By combining the contributions of both the polarization and the mechanical stiffness, the blend system can give a higher piezoelectric strain response than the pure copolymer. As an example, the blend containing 75 wt.% copolymer exhibits a better piezoelectric strain response from ambient to 45 °C than the pure copolymer. Furthermore, by adjusting the relative fraction of the two components in the blend, the piezoelectric strain response of the blend film (such as in the case of the 50 wt.% copolymer) can become temperature-independent.

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