

Structure and Dielectric Properties of Poly(Vinyl Chloride) Thermoplastic Elastomer Blends

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SYNOPSIS

The structure, development, morphology, and dielectric relaxation have been investigated in poly(vinyl chloride)-thermoplastic elastomer (copolyester-ether) blends having different compositions. The changes in the intensities of dielectric relaxation peaks for the β and γ processes with respect to blend composition have been found to be associated with corresponding changes in crystalline structure and morphology of the elastomeric component. The critical composition for observing such modification of properties is about 50% of poly(vinyl chloride) above which the blend becomes almost amorphous. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Modification of polymers by blending them with other materials such as plasticizers, low-molecular-weight polymers, and rubbery materials in order to increase flexibility, impact, strength, etc. has been extensively used in the past.^{1,2} Poly(vinyl chloride) (PVC) in particular has been subjected to such modification by a variety of materials,³⁻⁶ and its use in electrical applications especially in rubberized form is well known.⁴ With the advent of thermoplastic elastomers one would expect that the conventional materials in PVC-rubber blends would be replaced by new components since these would facilitate easier compounding and processing routes than conventional materials. In this connection, a few reports are available on mechanical properties of PVC-thermoplastic elastomer blends δ , in which semicompatibility was noted⁷⁻¹⁰ depending on composition. It is rather surprising that electrical properties of these blends have not been investigated in the past. Recently, we reported the dielectric properties of co-polyester thermoplastic elastomer films cast under different conditions and brought out the importance of morphology in governing their electrical response.¹¹ In continuation of those studies,

we have modified the morphology of this block copolymer by blending it with PVC, which is expected to be miscible with one of the component blocks,^{7,8} thus giving rise to difference in morphology under the same processing conditions. The effect of these changes on structure and dielectric properties are described in this study.

EXPERIMENTAL

The samples were made by solution blending the thermoplastic elastomer (Hytrell grade 5526) containing 76% hard segments of polybutylene terephthalate (PBT) and polytetramethylene oxide (PTMO) with PVC (ICI, England, Corvic-D65/1) in required proportion using tetrachloroethane as mutual solvent. The solution mixture was cast in flat glass petri dishes held at 40°C and dried over 24 h. Films, which were 100 μ m thick, opaque, white but flexible, were peeled off, cut to size, and studied for crystallinity, morphology, and electrical properties in the same manner as reported earlier.¹²⁻¹⁵

RESULTS AND DISCUSSION

Figure 1 shows the wide-angle X-ray (WAX) diffraction scans for PVC-Hytrell blends having different compositions. Curve A to E correspond to

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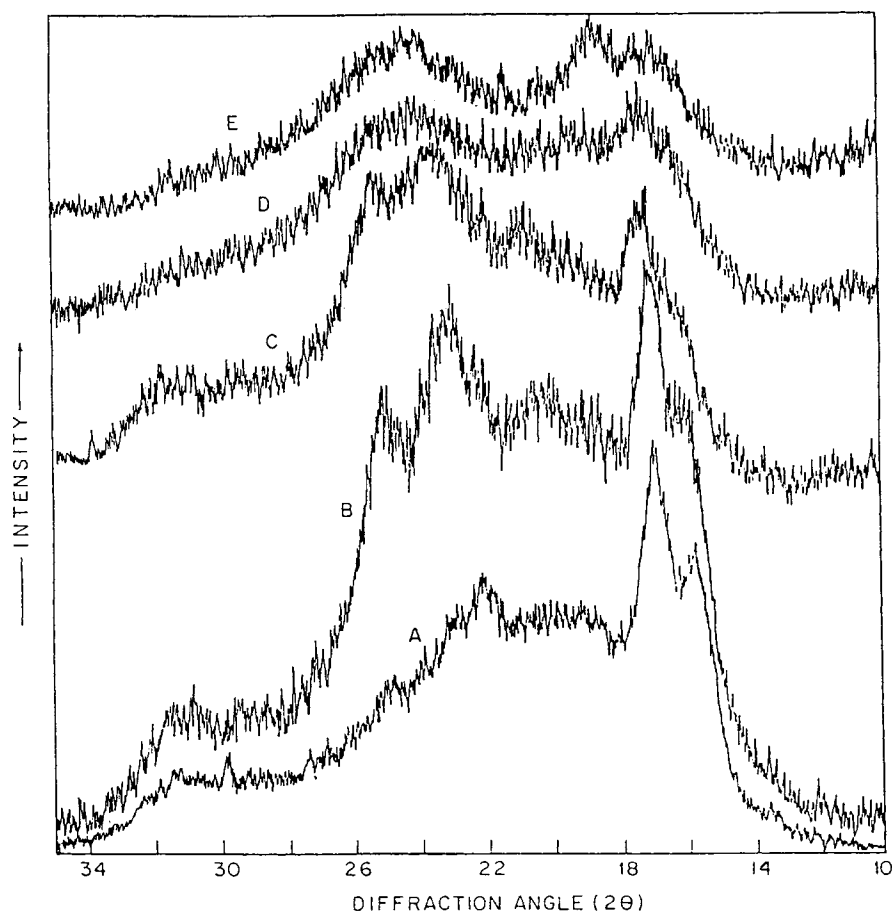
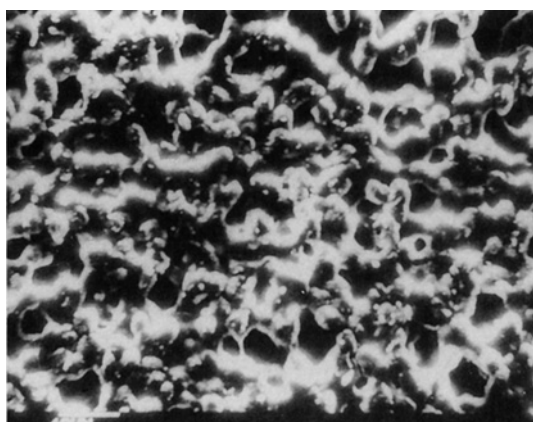


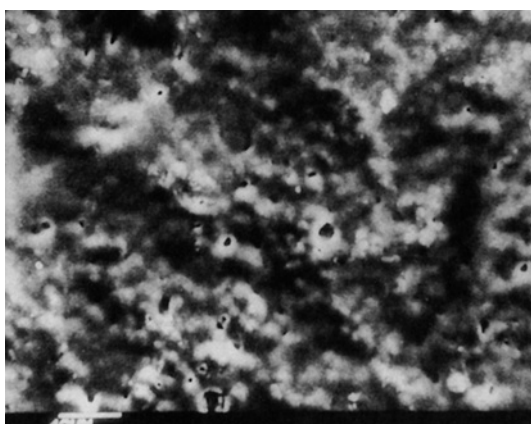
Figure 1 Wide-angle X-ray diffraction for PVC-Hytrel blends having PVC content of (a) 0, (b) 25, (c) 50, (d) 75, and (e) 100%.

Table I WAXS Data for Polyether-co-Ester (Block Copolymer) and Its Blend with PVC

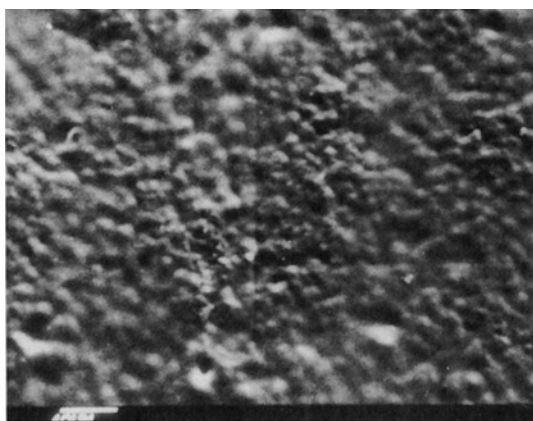
Melt Grown (MFA)		Solution Grown (SF)		PVC (25%) + Hytrel (75%)	
d (Å)	Int. (Rel)	d (Å)	Int. (Rel)	d (Å)	Int. (Rel)
5.61	30.5	5.68	26.5	5.54	77.0
5.16	49.0	5.34	44.6	5.16	100.0
4.33	69.0	4.60	30.0	4.44	80.0
3.85	100.0	4.00	38.0	3.87	94.0
3.58	77.0			3.55	80.0
3.05	27.0			3.04	45.0
2.86	30.0	2.95	35.0	2.88	41.0
2.40	21.0	2.83	23.0		
2.28	22.0	2.47	23.0		
2.14	27.0	2.32	27.0		
2.06	43.5	2.18	71.0		
2.00	27.0	2.09	100.0		
1.94	27.0	1.88	40.0		
1.85	22.0	1.81	54.0		
1.77	27.0				



a



b



c

Figure 2 SEM micrograph of PVC-Hytrel blend films after light etching with tetrahydrofuran vapors. PVC-Hytrel composition (a) 25/75, (b) 50/50, and (c) 75/25. Magnification 2.5K.

PVC content of 0, 25, 50, 75, and 100% by weight, respectively. Curve A corresponds to the same structure as pure Hytrel when cast from solution and contains mainly α form of PBT crystallites, with some PTMO-ordered domains.¹¹ The overall crystallinity is low in this case. On the other hand, addition of small amount of PVC (curve B) leads to increase of crystallinity and modification of structure as evidenced by additional diffraction peaks at 2θ of 23.1° and 25.1° . This is a very surprising result since one would expect much lower ordering when a material such as PVC, having low crystallinity and partial miscibility, is added to the copolymer. On increasing the PVC content above 50% the crystallinity no doubt decreases, but there are few noteworthy changes in the X-ray diffraction patterns. These are (a) the intensity of diffraction peaks increases and then decreases with the increase of PVC content, (b) there are new peaks on higher diffraction angle side, (c) the intensity of these new peaks decreases more gradually than those for low 2θ side with the increase of PVC content. Further, comparison of these scans with those reported for melt-processed and solution-cast copolyester elastomer¹¹ reveals that in the 25/75 blend, the elastomer has the same crystalline structure/morphology as the melt-processed one. Table I gives the comparison of the present X-ray diffraction data with that of melt-processed and solution-cast copolyester elastomer. Thus the addition of PVC induces the conformational changes in one of the components and corresponding changes in the crystalline structure of the thermoplastic elastomer.

The morphology of these blends was investigated by scanning electron microscopy (SEM). The samples were exposed to tetrahydrofuran vapors for 15 min in order to enhance the contrast between the domains by selective etching of the PVC. Figure 2(a), (b), and (c) show the SEM of PVC-Hytrel blends with PVC content of 25, 50, and 75%, respectively. It is clear from these micrographs that in all cases the samples contain two distinct phases, and domain size of one of the phases decreases with the increase of PVC content. Considering the fact that samples become more crystalline with the addition of PVC up to 25% and then progressively amorphous for higher concentrations, the chain configuration of Hytrel (crystallizing component) is altered by the presence of PVC. On the other hand, one cannot consider these blends to be completely miscible since in such cases one expects the crystallinity to decrease quite rapidly with the addition of amorphous component.¹³ In a noninteractive sys-

tem following a simple rule of mixtures, the total crystallinity (C_i) would be given as¹⁶

$$(C_i)_T = m_1(C_i)_1 + m(C_i)_2 \quad (1)$$

where m is the mass fraction and the subscripts refer to the components 1 and 2, respectively. Figure 3 shows the variation of crystallinity as a function of PVC content in the blend together with that expected from Eq. (1) with $(C_i)_1 = 33\%$ and $(C_i)_2 = 5\%$, corresponding to Hytrel and PVC, respectively. The comparison of these curves shows that these blends do not follow a simple rule of mixtures, and despite the fact that they are phase separated, there is some interaction between the components, which influences their morphology. Further, if PVC and thermoplastic elastomers were completely immiscible, there would be large domains of the latter with very little interdomain region in blends with low PVC content, and these would be revealed after selective etching of PVC. However, we have observed considerable extent of continuous phase surrounding the domains [see Fig. 2(a)] suggesting that there may be partial mixing of the two components.

The dc electrical conductivity of these blends is shown in Figure 4 as a function of temperature. It is seen that the temperature dependence of conduc-

tivity has two regions having small and large slopes corresponding to low and high values of activation energy. The individual polymeric components on the other hand (curves A and E) exhibit a continuous rise without break of conductivity with the increase of temperature. The values of activation energy determined from these graphs for different compositions are indicated in Figure 3. The break in the graph of $\log \sigma$ versus $1/T$ and the appearance of the two regions may be attributed to the two-phase morphology of these blends. Since the charge carrier (mostly ionic) transport is easier in the amorphous region than in crystalline one, the conductivity behavior can be understood in terms of the relative contents of each of these phases. It is interesting to note that whereas the activation energy for region I is lowered (see curve E1, Fig. 3) with the addition of PVC, that in the region II remains high even after blending. The latter effect is especially noted when crystallinity increases as in the case of 25/75 blend. These findings clearly suggest that PVC interacts mainly with the amorphous component of Hytrel to form a mixed phase having higher conductivity and lower activation energy than the starting material.

The dielectric relaxation of these blends was investigated in the temperature range of -100 – 150°C and frequency range of 0.1 – 100 kHz. Figure 5 shows

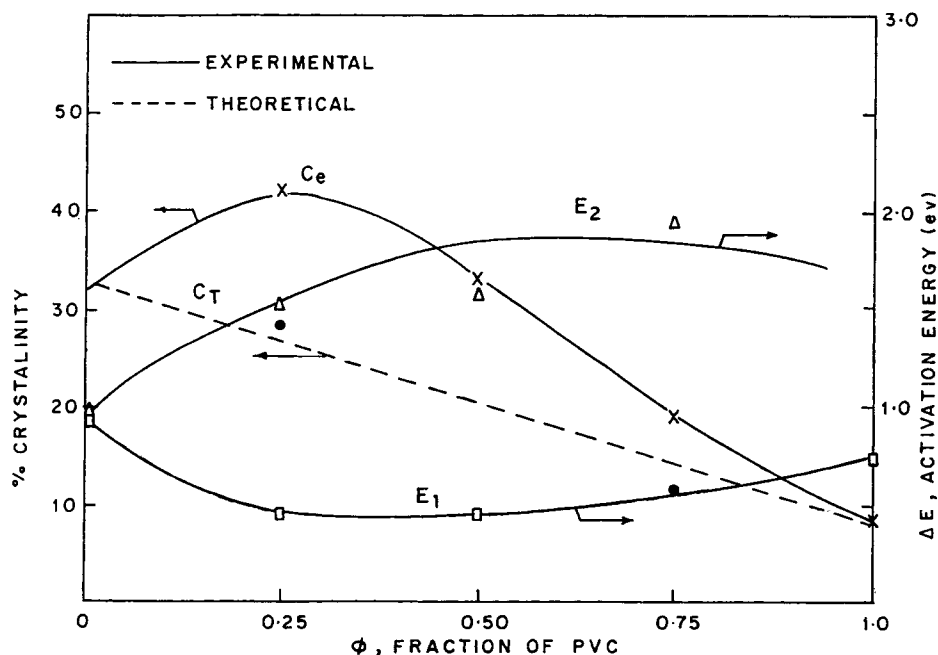


Figure 3 Overall crystallinity of PVC-Hytrel blends as a function of composition. Curve A experimental values, curve B estimated from Eq. (1). Curves C and D show the dependence of activation energy for conductivity in region I and II of Figure 4.

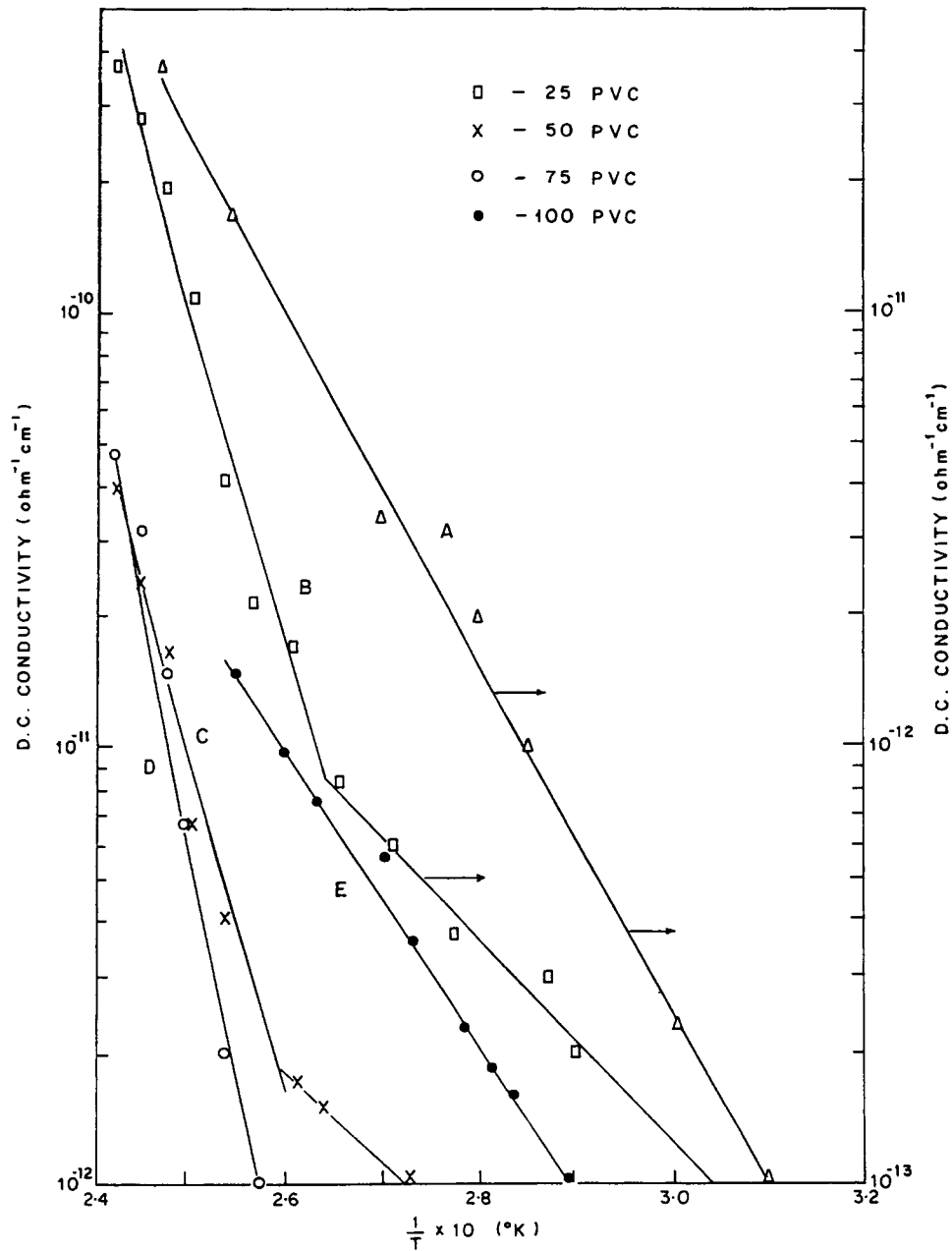


Figure 4 dc conductivity of PVC-Hytrel blends as a function of temperature. Curves (1) to (5) correspond to PVC content of 0, 25, 50, 75, and 100%, respectively. Conductivity of right-side scale for curves 1 and 2.

the dielectric loss factor ($\tan \delta$) at 1 kHz as a function of temperature for these samples containing 0, 25, 50, 75, and 100 wt % PVC. It is seen that in all cases, excepting pure PVC, there are three relaxation peaks occurring in the temperature region studied, viz. -40 to -30°C (γ), 10 to 35°C (β), and 45 to 75°C (β'); the α relaxation lies above 80°C in all

cases (even PVC). The relative intensities of these peaks depends strongly on the composition of the blend. The γ peak, for example, is very pronounced in 25/75 PVC-Hytrel blend while the β peak is intense in the 50/50 blend. It may be noted that although there is some change in the position of the peaks with composition, these can still be clearly

distinguished from one another. On comparing the present data with the dielectric data for the Hytrel polymer reported in detail by us, it appears that the changes observed here are mainly due to morphological changes, which is discussed later in this study.

There are very few studies^{17,18} reported in the past on PVC-Hytrel blend and even among these, there

appears to be some controversy. For example, a few authors^{9,19,20} contend that these blends are fully compatible in as much as they show single glass transition (T_g) as determined from dynamic mechanical analysis (DMA). On the other hand, there are others^{7,8,21,22} who observed phase separation and very little compatibility especially after thermal an-

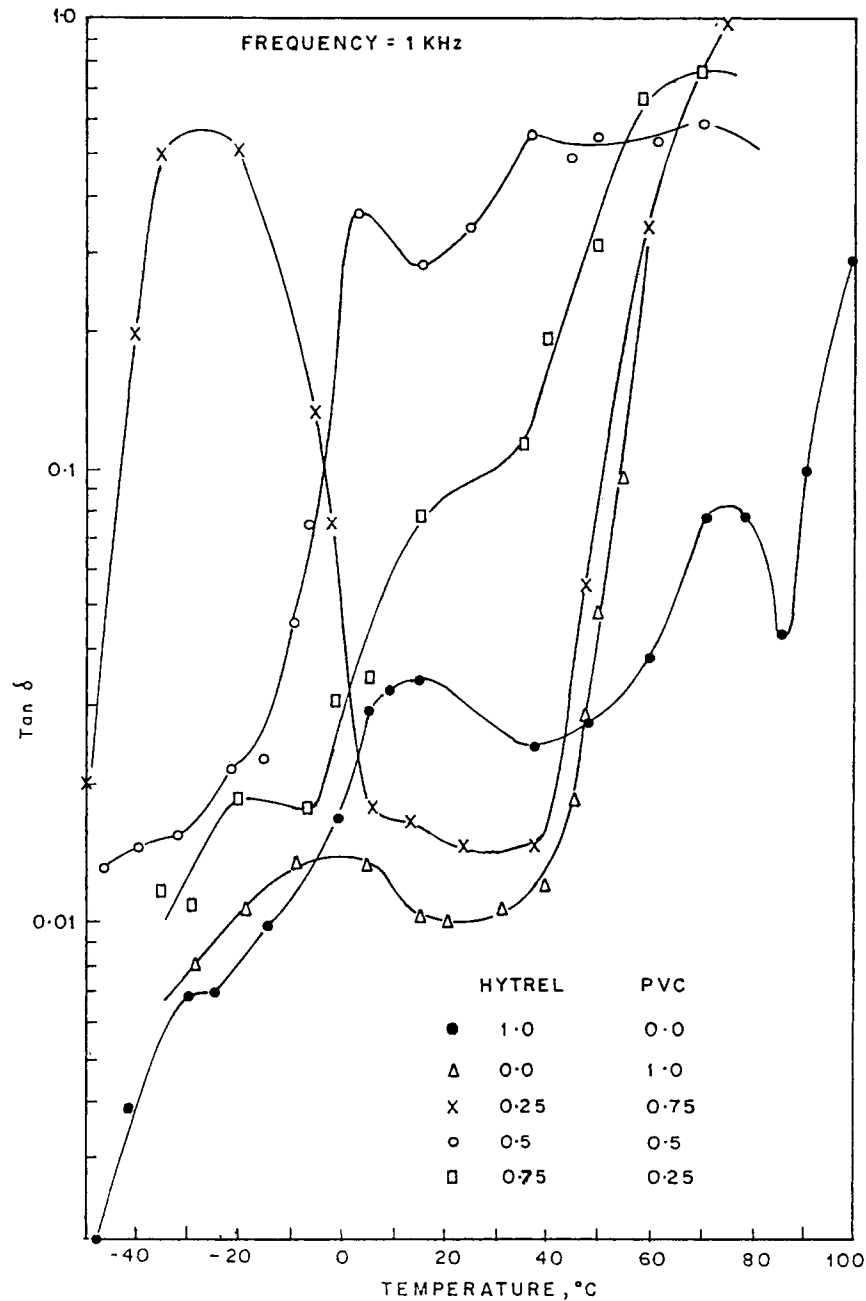


Figure 5 Dielectric loss as a function of temperature at 1 kHz for PVC (Δ) PVC, (\bullet) Hytrel, and PVC-Hytrel blend: (\times) 25/75, (\circ) 50/50, and (\square) 75/25, respectively.

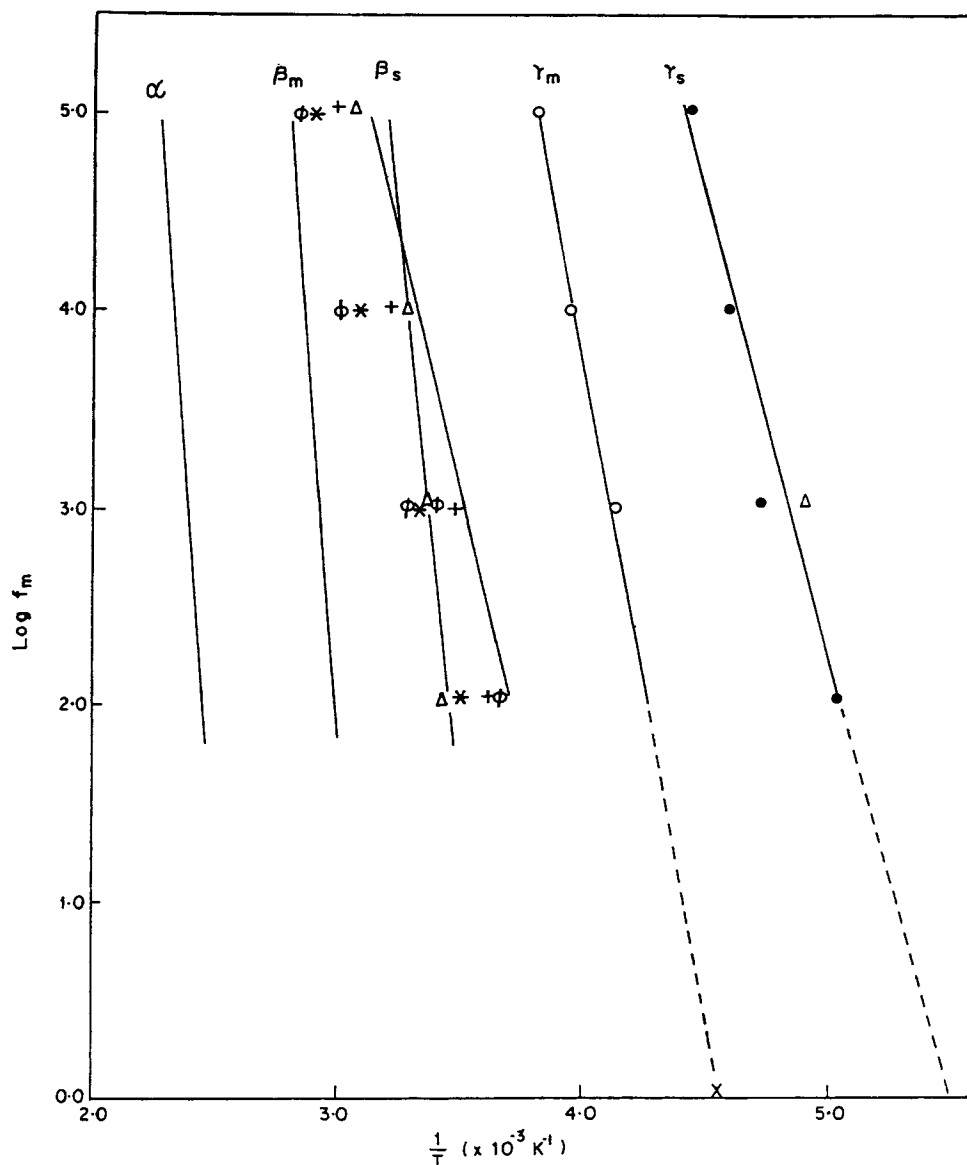


Figure 6 Relaxation map for Hytrel elastomer showing f_{\max} vs $1/T$ for various processes. Points refer to PVC-Hytrel blend: (Δ) 25/75, ($+$) 50/50, and ($*$) 75/25, respectively; (ϕ) PVC.

nealing. Even Hourston and Hughes,¹⁰ who observed continuous decrease of T_g with increase of Hytrel content have remarked that a distinct shoulder is seen on the mechanical loss peak for certain compositions. Such being the case, it is necessary to distinguish the exact origin of the relaxation peaks in these blends before assigning any to the glass transition. This is especially true for dielectric spectroscopy since, being much more sensitive, reveals a larger number of peaks as compared to DMA. As reported earlier by us, the Hytrel elastomer by itself

exhibits three relaxations: α , β , and γ in the temperature range of -100 – 140°C . The β and γ relaxations are very sensitive to sample preparation technique and shift on temperature scale when samples are solvent-cast as compared to melt-cast ones. These changes have been attributed to morphological and chain conformation changes (confirmed by WAX and IR spectroscopy) induced by the preparation techniques. Figure 6 shows the transition map of Hytrel together with the present data for the blends, and it is quite evident that the

relaxation peaks noted in the temperature range of -10 – 80°C correspond to the β -relaxation regime. Thus, the addition of PVC to Hytrel alters only the β relaxation, changing its activation energy. It appears that earlier authors have attributed the β relaxation of Hytrel (T_β) to the T_g process of the blend whereas the α process actually lies at much higher temperature than this. Such an error can arise especially since the relative intensities of the peaks differ markedly with composition and also the α process of PVC overlaps the same. This is brought out clearly in Figure 7, which shows the variation of T_β with composition of the blend together with the T_g values estimated from the well-known Flory-Fox relation,²³ viz.

$$\left(\frac{1}{T_g}\right)_{\text{blend}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (2)$$

where W_1 and W_2 are mass fractions of the individual polymeric components 1 and 2, respectively, which are assumed to be miscible. It is evident from

this figure that in the midrange of composition the variation of T_β (low frequency) is quite similar to that expected for T_g as per Eq. (2). However, large deviations are noted at either end of compositions. A linear increase of T_g with increase of wt % of PVC does not appear for this case. Such differences in behavior of T_g with composition when determined by different techniques has been observed even in polystyrene-polyphenyleneoxide blend, which is conventionally known to be "miscible" or compatible.^{24,25}

In order to confirm the phase separation in these blends, differential scanning calorimetry (DSC) scans were taken on first and second heating cycles. Figure 8 shows the DSC scans of 75 : 25 blend on first heating (A) and the same sample reheated on second run (B). It is evident that there is a large recrystallization peak occurring at 120°C in the first heating, which also shows a melting endotherm at 204°C . A small inflexion is seen to occur at 80°C , which can be attributed to its glass transition. On the other hand, in the second heating scan there are apparently two endotherms: broad and weak one at

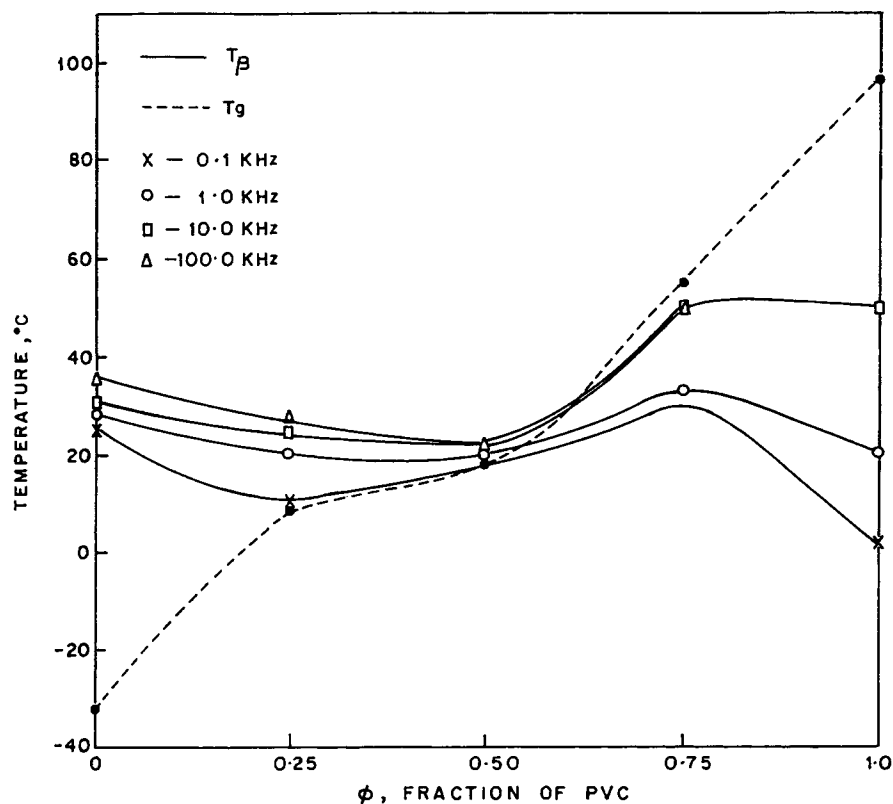


Figure 7 Variation of T_g (---) from Eq. (2) and T_β (experimental) with composition in PVC-Hytrel blends.

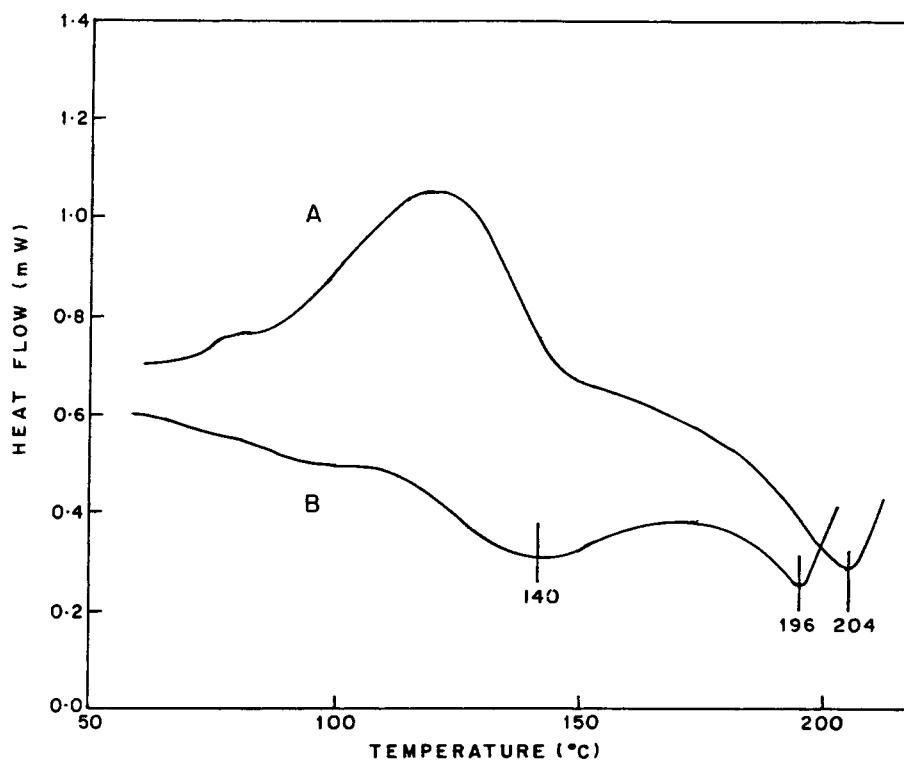


Figure 8 DSC scans of PVC-Hytrel blend 25/75. Curve A first heating and curve B some sample second heating.

140°C while a sharp one at 196°C, thus suggesting that the sample has undergone a phase separation during the first heating cycle. The glass transition also becomes weak but does not shift upon thermal cycling, which suggests that the amorphous regions of the components are miscible.

The above discussions indicate that PVC-Hytrel blends have no doubt two-phase morphology, but these phases are not totally segregated noninteractive ones. There appears to be partial mixing and/or some form of interaction (dipolar or ionic) between the two types of molecules especially in the amorphous regions. This is particularly reflected in various physical properties: (a) change in crystallinity and chain configuration of crystallizing component, (b) increase in conductivity, (c) decrease in activation energy for carrier transport, (d) enhancement in the intensity of secondary relaxation processes, and (e) shift in the β -relaxation peak with composition for these blends.

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