Annealed segmented polyether ester—poly (vinyl chloride) blends

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Hytrel, PVC and blends of these polymers containing, respectively, 75% and 45% by wt of Hytrel were annealed and the dynamic mechanical and sonic velocity behaviour of these annealed samples were compared with the unannealed materials. The annealed Hytrel showed evidence of enhanced segregation of the hard and soft segments, while for PVC there was a shift of the glass transition to a higher temperature. Annealing of the 75% by wt Hytrel blend resulted in increased phase separation of the constituent materials and a very broad tan δ—temperature dispersion. It was also concluded that the 45% by wt Hytrel blend again showed phase separation on annealing, but to a lesser extent.

INTRODUCTION

A number of papers[1–4] have been published on the synthesis and properties of polyether ester thermoplastic elastomers and on various aspects of the behaviour of blends of this polymer with poly(vinyl chloride)[5–7]. Studies by Nishi *et al.*[5] on solution-cast and melt blends of poly(vinyl chloride) and Hytrel, which is a Du Pont-produced polyether ester, have indicated the presence of an upper critical solution temperature. They noted that isothermal annealing of the blends at 130°C resulted in properties typical of two-phase systems. Thus, the existence of an upper critical solution temperature offers a mechanism for controlling the morphology of the blends.

In this annealing study two Hytrel—PVC blends, plus the constituent homopolymers, are investigated. The blends chosen contained 75% and 45% by wt of Hytrel, respectively, and were prepared by solution blending. The samples were annealed at 100°C for 2.5 h. Annealing did not appear to result in any significant degradation of the samples.

EXPERIMENTAL

Polymers

Hytrel (grade 4055) is a segmented polyether ester which was kindly donated by the Du Pont Company. It is a random block copolymer with crystallizable tetramethylene terephthalate (4GT) hard segments and poly(tetramethylene ether) glycol terephthalate soft segments[7]. The unplasticized PVC (Corvic D60/11) was supplied by ICI Ltd. Characterization data for the homopolymers have been published previously[7].

Blend preparation

The Hytrel—PVC blends were prepared by solution blending. The Hytrel in methylene chloride and the PVC in tetrahydrofuran were mixed as 3% solutions and the polymeric blend precipitated by adding an excess of methanol. The precipitated blends were centrifuged and then vacuum dried at about 20°C for 2–3 days prior to hot pressing (170°C) to form sheet. Sheets of the homopolymers were pressed at the same temperature. Samples were annealed under vacuum at 100°C for 2.5 h and were then cooled to room temperature at a rate of about 1°C min^{-1}.

Measurements

The dynamic mechanical measurements were made using a Rheovibron dynamic viscoelastometer (model DDV-II) at a frequency of 110 Hz. The rate of temperature change was 1–2°C ·min^{-1}.

The longitudinal sonic velocity (V_L) measurements were made at a frequency of 15 kHz with a Morgan pulse propagation meter[8] (model PPM-5R) which measures the time elapsed in μsec between transmission and reception of a sound pulse passing through a known distance in a strip of sheet 1 cm wide.

RESULTS AND DISCUSSION

Figure 1 and *Table 1* show the effects of annealing on the tan δ *versus* temperature behaviour of Hytrel. The tempera-

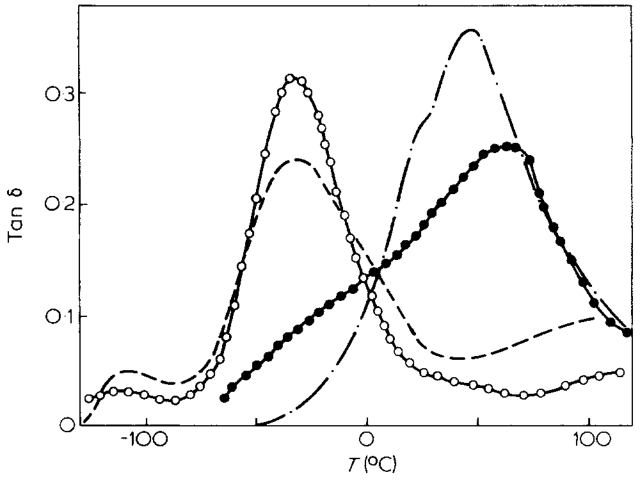

Figure 1 Tan δ *versus* temperature plots of unannealed (— — —) and annealed (○) Hytrel and of the unannealed (— · —) and the annealed (●) blend containing 75% of Hytrel by weight

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Table 1 Certain properties of the homopolymers and blends

Hytrel content (wt %)	T_g (°C)	Tan δ_{max}	Half peak width (°C)	V_L (km/s)
	Unannealed			
100	−32	0.24	68	0.22
75	49	0.36	76	0.55
45	63	0.40	52	0.92
0	97	1.10	29	1.83
	Annealed			
100	−32	0.32	50	0.24
75	65	0.25	107	0.58
45	80	0.42	55	1.15
0	112	0.81	27	2.24

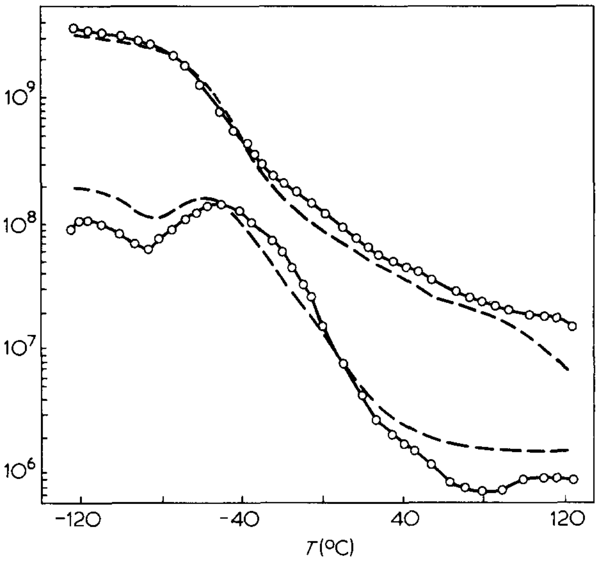

Figure 2 Dynamic storage modulus and dynamic loss modulus *versus* temperature plots for unannealed (— — —) and annealed (○) Hytrel

ture of the soft segment glass transition[9] is seen to be unaltered (−32°C), but the height of the peak (tan δ_{max}) is increased from 0.24 to 0.32. It was previously postulated[7] that annealing at 100°C results in the formation of small, imperfect crystallites which involve, however, virtually all the 4GT segments. Certainly the narrowing of the relaxation time distribution is in keeping with this theory as the enforced mixing of incompatible segments always leads to a broadening of a transition. The extent of the narrowing of this soft segment glass transition can be seen from the half-peak widths given in *Table 1*.

There is also a marked decrease in the magnitude of the low temperature transition which has been assigned to a restricted motion of the soft segments[9,10]. However, in *Figure 2* the dynamic loss modulus curves show this transition to be at least as clearly defined as for the unannealed Hytrel.

At temperatures above about 40°C the effect of annealing is again marked. The higher values of tan δ shown by the unannealed sample probably arise as the result of the 4GT glass transition at around 80°C. A slight shoulder in the tan δ–temperature plot is just evident in the non-heat-treated sample. This conclusion agrees with the belief that nearly all of the hard segments are involved in crystallite formation in the annealed sample.

Figure 2 shows the dynamic storage modulus (E') and the dynamic loss modulus (E'') *versus* temperature plots for the annealed and unannealed Hytrel. Annealing is observed to have little effect on E' prior to the rubbery region where it is evident that heat treatment results in both a slight extension to higher temperatures of the rubbery plateau and a small increase in the rubbery modulus. These effects are commonly shown where the degree of crosslinking in a polymer is increased. It is apparent, therefore, that annealing results in a more thermally stable three-dimensional network possessing a greater number of physical crosslinks. The dynamic loss modulus curves clearly show the reduction in damping ascribed to the crystallization of the majority of the 4GT segments.

Table 1 presents values of longitudinal sonic velocity for Hytrel in both the annealed and unannealed states. It is evident from this Table that annealing results in a somewhat higher value of V_L, possibly arising from the slight increase in the overall crystalline content. In a polymeric composite the sonic velocity is sensitive to both the composition and the overall distribution of the phases[7,8].

Figure 3 shows the tan δ–temperature dispersion for a similarly annealed sample of PVC. Annealing is observed to result in an increase in T_g, but a decrease in the peak height (see *Table 1*). The peak width is, within experimental error, unaltered by such heat treatment. It is believed that annealing results in enhanced crystallization of the PVC, although the degree of crystallinity is not expected to exceed about 15%. The unannealed sample had been cooled rapidly in the hot press, and, consequently, its crystallinity was not well developed. Annealing of thermoplastics above the glass transition temperature is also known[11] to reduce the free volume. The shift of the glass transition to higher temperatures is thought to arise largely from free volume effects, but also there is possibly a contribution from restrictions on motions imposed by the crystallites. The decrease in peak height at the glass transition temperature is expected since there are now fewer amorphous chain segments to relax.

Figure 4 shows the E' and E'' *versus* temperature curves for PVC. Annealing results in a slight increase in E' below the glass transition temperature. The loss modulus spectrum shows a shift to higher temperatures of the glass transition from 93° to 98°C. D.s.c. thermograms also showed an increase in T_g from 82° to 87°C upon annealing. A broad β-transition is observed for both the annealed and unannealed samples[12,13]

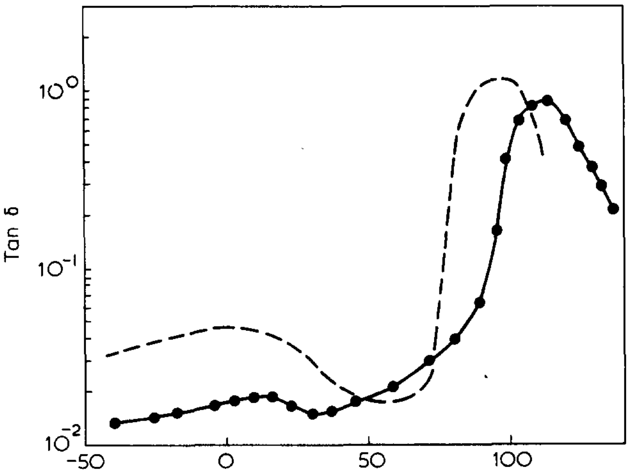

Figure 3 Tan δ *versus* temperature plots of unannealed (— — —) and annealed (●) PVC

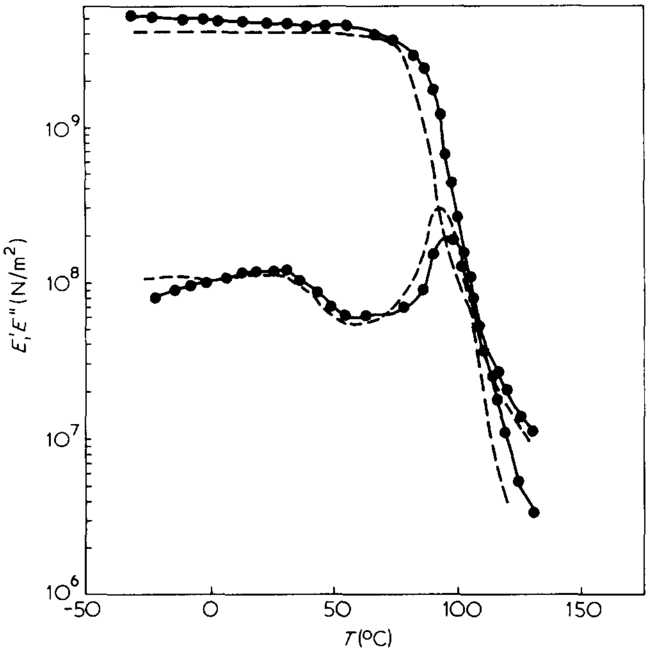

Figure 4 Dynamic storage modulus and dynamic loss modulus *versus* temperature plots for unannealed (— — —) and annealed (●) PVC

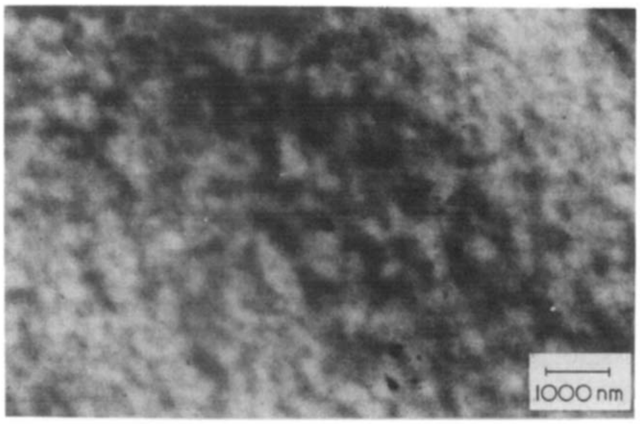

Figure 5 Electron micrograph of the annealed 75% by weight Hytrel blend

The longitudinal sonic velocity of the homopolymer is seen (*Table 1*) to be greatly increased by annealing. As already stated all the polymer sheet used in this work was cooled rapidly from the pressing temperature to around 25°C. This allows annealing of PVC to produce a substantial increase in the degree of crystallinity, and, consequently, in longitudinal sonic velocity.

Figures 5 and *6* show electron micrographs of two samples of the blend containing 75% by wt of Hytrel. Both samples were stained with osmium tetroxide to provide greater contrast. The morphology of the annealed blend is shown in *Figure 5*. The blend shown in *Figure 6* has received no thermal treatment other than hot pressing to form the sheet. It is clear that annealing results in a much coarser two-phase structure. It is not known with certainty which phase is preferentially stained by the OsO_4, but it is thought that the lighter areas are rich in PVC.

Figure 1 shows the tan δ *versus* temperature dispersion for the 75% by wt Hytrel blend. The non-heat-treated sample has previously been reported[7] to be partly phase separated, because of the existence of a shoulder on the low temperature side of the glass transition. Annealing results in a substantial increase in the half-peak width, but a lowering of the peak height of this composite transition. The temperature of the transition maximum is observed to increase from 49° to 65°C. There is a clearly discernible, but not totally resolved, transition originating in a Hytrel-rich phase. This is clear evidence that the annealed blend is considerably more heterogeneous than the unannealed material.

Kaplan[14] has predicted that two-phase materials with an average dispersed phase diameter of around 15 nm will show high levels of damping at temperatures between the glass transitions of the component polymers. The tan δ–temperature curve for the annealed 75% Hytrel blend may be exhibiting behaviour similar to that predicted by Kaplan[14]. Whilst relatively little evidence exists for the proposed[14] mechanism, a distribution ofcompositions could quite readily explain the results.

Figure 7 shows the E' and E'' *versus* temperature plots for the 75% by wt Hytrel samples. The E' curves for both

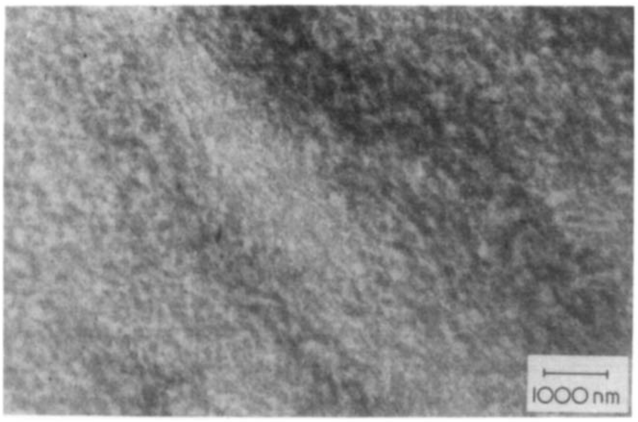

Figure 6 Electron micrograph of the unannealed 75% by weight Hytrel blend

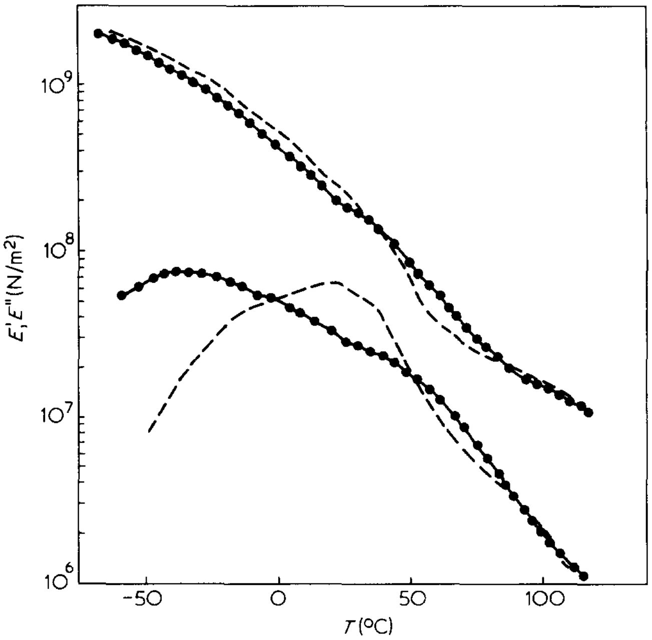

Figure 7 Dynamic storage modulus and dynamic loss modulus *versus* temperature plots for the unannealed (— — —) and the annealed (●) blend containing 75% of Hytrel by weight

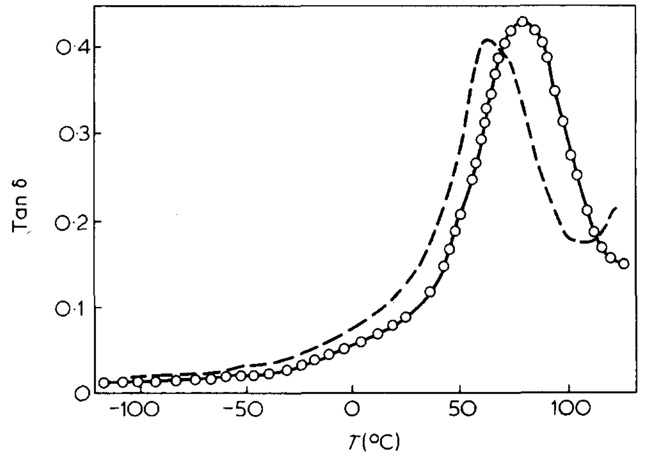

Figure 8 Tanδ *versus* temperature plots of the unannealed (— — —) and the annealed (○) blend containing 45% of Hytrel by weight

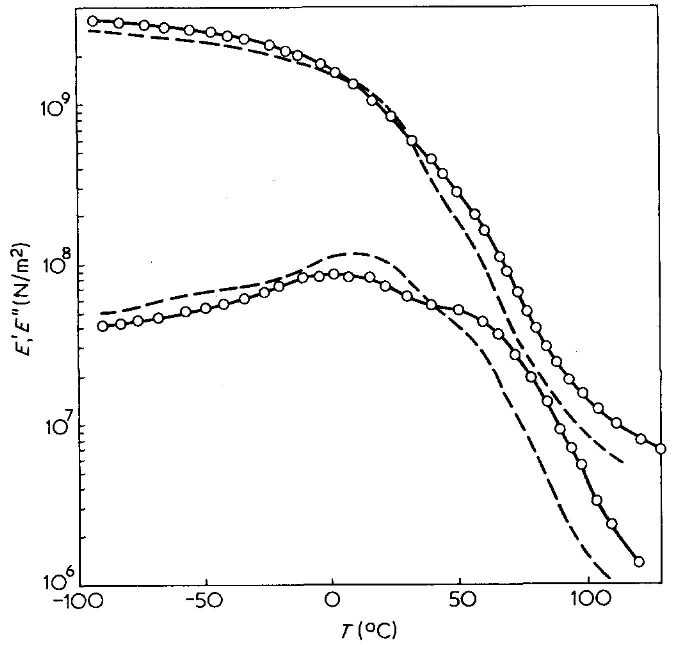

Figure 9 Dynamic storage modulus and dynamic loss modulus *versus* temperature plots for the unannealed (— — —) and the annealed (○) blend containing 45% of Hytrel by weight

the annealed and the unannealed samples show a slope change at around the Hytrel glass transition temperature and again at approximately 50°C which are ascribed to Hytrel-rich and PVC-rich phases, respectively. The E'' *versus* temperature curves both reflect the two-phase morphology of these samples. The non-heat treated sample exhibits a broad peak in the loss modulus spectrum. In contrast the annealed sample shows clear evidence of peak resolution although the higher temperature dispersion is still in the form of a shoulder.

Annealing is also observed to result in an increase in V_L (*Table 1*). It was shown earlier[7] that the onset of microphase separation in these blends does not produce a discontinuous change in the plot of V_L *versus* composition because the wavelength of the sonic pulse is several centimetres. The increase in V_L most likely results from an enhanced degree of crystallinity of the 4GT segments. Nishi *et al.*[5] have argued that crystallization of the hard segments in a 50% Hytrel blend is not hindered by the presence of PVC chains. Some crystallization of PVC segments may also occur.

Figure 8 shows the tan δ *versus* temperature curves for the 45% Hytrel blend in the annealed and unannealed forms. On annealing, the glass transition temperature is observed to move to a higher value, but the peak height and width are only marginally increased (*Table 1*). The annealed sample exhibits a slight tail on the tan δ curve at about 0°C on the low temperature side of the transition. The unannealed blend is thought[7] to be reasonably compatible and shows no evidence of a low temperature tail. Annealing is believed to result in the formation of a relatively heterogeneous mixture, but with a domain size which is still too small[15] to be resolved, in at least the tan δ–temperature dispersion, by dynamic methods. Further evidence for this argument comes from the E' and particularly the E'' *versus* temperature plots in *Figure 9*. E' is observed to be higher in the annealed sample over most of the temperature range investigated. This may again arise from 4GT and PVC crystallite formation. The effect is more marked above T_g. The morphology of this blend is better reflected in the E'' *versus* temperature plots. The non-heat-treated sample exhibits a loss maximum centred at 10°C which is indicative of extensive mixing between the Hytrel soft segments and PVC. The shoulder at about 50°C indicates the presence of a PVC-rich phase. The loss modulus curve of the annealed sample shows greater evidence of resolution into two relaxation regions associated with PVC-rich and Hytrel-rich regions at around 60°C and 5°C, respectively.

The annealed sample again exhibits an increased value of V_L (*Table 1*). It seems likely that 4GT and PVC crystallite formation will account at least for part of this increase. However, as the change in V_L is quite large, it is conceivable that annealing may also have resulted in partial phase inversion with PVC becoming a co-continuous phase[7].

REFERENCES

1 Witsiepe, W. K. *Adv. Chem. Ser.* 1973, **129**, 39
2 Cella, R. J. *J. Polym. Sci. (Polym. Symp.)* 1973, **42**, 727
3 Buck, W. H. and Cella, R. *Polym. Prepr.* 1973, **14**, 98
4 Buck, W. H., Cella, R. J., Gladding, E. K. and Wolfe, J. R. *J. Polym. Sci. (Polym. Symp.)* 1974, **48**, 47
5 Nishi, T., Kwei, T. K. and Wang, T. T. *J. Appl. Phys.* 1975, **46**, 4157
6 Nishi, T. and Kwei, T. K. *J. Appl. Polym. Sci.* 1976, **20**, 1331
7 Hourston, D. J. and Hughes, I. D. *J. Appl. Polym. Sci.* 1977, **21**, 3099
8 Beamish, A. and Hourston, D. J. *Polymer* 1976, **17**, 577
9 Shen, M., Mehra, V., Niinomi, N., Koberstein, J. T. and Cooper, S. L. *J. Appl. Phys.* 1974, **45**, 4182
10 Wetton, R. and Williams, G. *Trans. Faraday Soc.* 1965, **61**, 2123
11 Neilsen, L. E. 'Mechanical Properties of Polymers and Composites, Vol. 1', Marcel Dekker, New York, 1974
12 Tanaka, K. *Rep. Prog. Polym. Phys. Jpn.* 1962, **5**, 138
13 Takayanagi, M. *Mem. Fac. Eng. Kyushu Univ.* 1963, **23**, 1
14 Kaplan, D. S. *J. Appl. Polym. Sci.* 1976, **20**, 2615
15 Deanin, R. D., Deanin, A. A. and Sjoblom, T. 'Recent Advances in Polymer Blends, Grafts & Blocks', (Ed. L. H. Sperling), Plenum, New York, 1974