Improvement of the Impact Strength of a Blend of Poly(vinyl Chloride) with Copolyester Thermoplastic Elastomer by Heat Treatment

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Synopsis

Dynamic mechanical properties and impact strength of a blend of poly(vinyl chloride) with a copolyester thermoplastic elastomer were studied. The microscopic structure of the blend was dependent on the thermal history of the specimen. By an appropriate heat treatment, the blend underwent phase separation with an attendant severalfold increase in room-temperature impact strength. The mechanism of energy dissipation involves both crazing and shear flow processes.

INTRODUCTION

Recent studies of compatible mixtures of polystyrene and poly(vinyl methyl ether) have revealed the existence of upper and lower cloud-point temperatures for these systems.[1-6] (The term upper or lower cloud-point temperature follows the terminology of upper or lower critical solution temperature.) The complex phenomena of compatibility and phase separation can be best analyzed with the use of phase diagram and thermodynamic criteria for stable, metastable, and unstable binary mixtures. When a compatible mixture is brought into the miscibility gap, phase separation can occur via two different mechanisms, namely, nucleation and growth, and spinodal decomposition. The two modes of phase separation result in different geometric patterns of the separated phases,[7] and it is possible to control morphology, to some extent, by selecting the proper condition of thermal treatment. These principles have been demonstrated successfully in the study of PS–PVME mixtures near the lower cloud-point temperatures.[6]

An appreciation of the above principles becomes even more important in the study of polyblends below the upper cloud-point temperatures because phase separation in these systems can be controlled by kinetic considerations and the true picture of phase equilibrium is often obscured. On the other hand, recognition of this phenomenon has led us to think that the properties of a kinetically stable (though not necessarily thermodynamically stable) polyblend can be altered by manipulating its thermal history which changes the compositions and relative abundance of the phases in the mixture. In this

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report, we wish to illustrate the above thesis by presenting some results concerning the effect of heat treatment on the impact strength and dynamic mechanical properties of a 75/25 (by weight) mixture of poly(vinyl chloride) and a copolyester thermoplastic elastomer. A more extensive investigation including pulsed nuclear magnetic resonance, dynamic mechanical, thermomechanical, calorimetric, and morphologic studies over a wider range of composition will be reported in a later publication.

EXPERIMENTAL

A copolyester thermoplastic elastomer was supplied by the E. I. du Pont de Nemours Company, designated Hytrel-3495. It is a copolymer[8,9] formed by randomly joining poly(tetramethylene ether) glycol terephthalate (PTMEGT), the soft segments, and tetramethylene terephthalate (4GT), the hard segments which are capable of undergoing crystallization. The weight per cent of the hard segments is approximately 30%, and the average block length of 4GT segments is about 3.[8] The number-average molecular weight of the copolyester is about 25,000–30,000.

Poly(vinyl chloride), Geon 103EP, was obtained from B. F. Goodrich Chemical Company. The inherent viscosity of the polymer is 1.02 measured in cyclohexanone at 30°C.

The two polymers were mixed on a differential-speed two-roll mill at 150°C with the incorporation of 1.5 phr Ferro-GH-148 (Ba, Cd, Zn phosphate) from Ferro Corporation as stabilizer for PVC. The mixture was pressed at 150°C to appropriate thickness for various measurements and cooled in air to room temperature at a cooling rate of approximately 30°C/min. Specimens of PVC and Hytrel were prepared under identical conditions for the purpose of comparison. Heat treatment of the sample was carried out at 130°C for various time intervals and then cooled to room temperature slowly, ca. 0.2°C/min. The crystallinity of the blend, measured by differential scanning calorimetry, did not change significantly after heat treatment.

Impact strengths of the samples were measured by Izod impact tester according to ASTM D256. Specimen dimensions were 2.5 × 0.5 × 0.25 in. Sample temperature was controlled to ±1°C with a regulated flow of cold nitrogen from a liquid nitrogen reservoir.

Dynamic mechanical measurements were carried out with a Vibron Dynamic Viscoelastometer, Toyo Instrument Company, Model DDV II. The temperature range of our study was from −170° to 150°C, and the frequency employed was 110 Hz.

Results and Discussion

Visual Observation

Molded sheet of Hytrel is not transparent; the opacity arises from the existence of crystalline regions of hard segments in the copolymer. The mill-mixed blend is only slightly opaque. The heat-treated mixture shows discoloration characteristic of PVC, but the specimen retains the same degree of transparency as the mill-mixed blend.

Dynamic Mechanical Properties

Figures 1a and 1b show the temperature dependence of the dynamic Young's modulus E' and the mechanical loss tangent tan δ, respectively, for rigid PVC, copolyester thermoplastic elastomer (Hy), and their mixture before and after heat treatment. The maxima in the tan δ curve for PVC occur at around 94° and −10°C, in agreement with previous studies reported in the
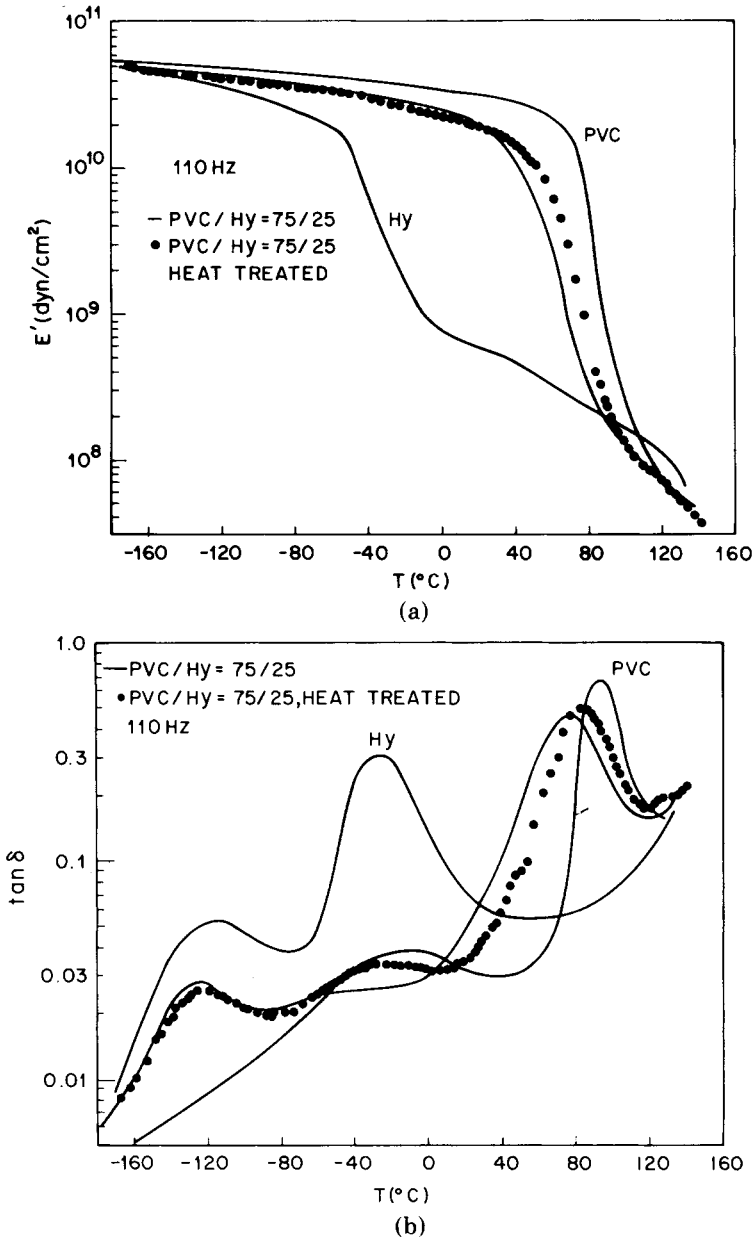

Fig. 1. Dynamic mechanical properties of rigid PVC, PVC/Hy = 75/25 mixture, heat-treated PVC/Hy = 75/25 mixture (●) and copolyester thermoplastic elastomer Hy from −170°C to 140°C at 110 Hz: (a) dynamic storage modulus E' vs. temperature T; (b) mechanical loss tan δ vs. temperature T.

literature.[10] The high-temperature maximum is related to relaxation associated with glass transition, and the broad low-temperature peak is ascribed to local mode motion of the main chain. The thermoplastic elastomer also shows two maxima, at −28° and −115°C, respectively.[11] The former loss peak has been attributed to the motion of the soft segment accompanying glass transition.[8] The origin of the low-temperature peak is most likely due to the local motion of the $[(CH_2)_4O]_x$ group since it is also observed in other polymers containing similar groups.[12,13] The dynamic Young's modulus E' of the copolyester decreases very gradually after glass transition. This is an indication that a network of hard segments remains intact and contributes to the sustainment of high modulus. The modulus drops rapidly above 120°C when the melting temperature of the crystalline hard segments is approached.

Heat treatment at 130°C for 5 hr causes only a very slight change in the dynamic mechanical properties of both PVC and Hytrel. For the purpose of clarity in graphic presentation, these results are not included.

The mill-mixed blend show three regions of mechanical relaxation. A distinct low-temperature peak exists at −122°C which, as previously mentioned, originates from the local motion of the soft segment of the copolyester. A prominent loss maximum occurs at about 78°C. An abrupt change in E' accompanies this relaxation which is undoubtedly associated with glass transition of the mixture. In the region from 0° to −60°C where the glass transition of Hytrel and the local motion of PVC occur, the loss tangent curve of the blend is almost flat. These observations suggest the following conclusions. First, the appearance of a single major glass transition for the mixture is a manifestation of the extensive mixing of the segment of PVC and Hytrel. We wish to avoid the use of the word "compatible" here because it may carry the connotation of being thermodynamically stable, which may be incorrect for this system. Whether the mixture consists only of a single phase is a subject reserved for discussion in a later publication. Secondly, the conclusion of intimate mixing is supported by the observed change in the secondary dispersion of PVC. This is a strong evidence that the local environment of PVC segments has been altered by the presence of polyester segments. In fact, a more careful examination indicates that the local relaxation is now represented by weak shoulder in the tan δ curve around −30° to −60°C. The shift of this loss mechanism to a lower temperature is consistent with similar observations in plasticized PVC systems.[14]

The tan δ curve for the mixture heat treated at 130°C for 5 hr also shows three regions of mechanical relaxation. The low-temperature dispersion remains essentially unchanged. The glass transition occurs at a higher temperature, about 85°C, and the shoulder between 0° and −60°C becomes more prominent. A higher glass transition temperature means that the composition of the phase in question has become richer in PVC. Correspondingly, a second phase, rich in copolyester, must be present in order to preserve material balance. Again, the details of phase relationships will not be elaborated in this paper, but the simple argument suffices to illustrate that the phases have changed.

The amount of the copolyester-rich phase in the heat-treated mixture appears to be small since a loss peak associated with the glass transition of this phase is not obvious in the tan δ curve. (Contribution of this phase to tan δ is

TABLE I
Impact Strength of Rigid PVC, PVC/Hy = 75/25 Mixture
and Effect of Heat Treatment at 130°C

	Izod impact strength, ft-lb/in.	
	R.T.	−30°C
PVC	0.91	0.61
Heat-treated PVC	0.95	0.71
PVC/Hy = 75/25	2.05	0.69
Heat-treated PVC/Hy = 75/25	9.25	1.48

TABLE II
Effect of Heat Treatment Time at 130°C for the Impact Strength of PVC/Hy = 75/25

	Izod impact strength, ft-lb/in.	
	R.T.	0°C
1 hr	13.90	4.04
5 hr	9.25	4.60
24 hr	0.69	0.50

in the shoulder region.) The average size of the copolyester-rich phase also seems to be very small since there is no difference in the transparency of the specimen before and after heat treatment. It is conceivable that the existence of a network of hard segments of the copolyester limits the extent of phase separation.

The enhanced shoulder in the tan δ curve between 0° and −60°C may be interpreted, in part, as a reflection of the local environment of PVC segment which has become more PVC-like because the major phase is very rich in PVC.

Impact Strength

Effect of Heat Treatment. The Izod impact strengths of rigid PVC, PVC–copolyester blend, and the heat-treated mixture are listed in Table I. The blend has about the same Izod impact strength at −30°C as that of PVC, ~0.6 ft-lb/in. But the impact strength at room temperature is higher, namely, 2.05 ft-lb/in. compared to 0.95 ft-lb/in. for PVC. Heat treatment for 5 hr at 130°C increases the impact strengths to 1.48 ft-lb/in. at −30°C and to 9.25 ft-lb/in. at room temperature. The same heat treatment does not change the impact strength of PVC to a significant extent.

In the previous section on dynamic mechanical properties, we have presented evidence that a change in the composition of the phases has resulted from heat treatment of the blend. If phase separation is the underlying cause for the improvement of impact strength, it may be anticipated that the kinetics of phase separation would play an important role. We have measured, therefore, the impact strengths after heat treatment for different time intervals. The results are shown in Table II. The impact strength at room temperature reaches a high value of 13.9 ft-lb/in. after 1 hr at 130°C but decreases to 0.69 ft-lb/in. after 24 hr. A similar trend was seen for test results

at 0°C.   There appears to be an optimum condition for heat treatment, prob-
ably related to both phase composition and domain size, in attaining maxi-
mum improvement in the impact strength.

Fracture Surface. The dramatic change in the impact strength of the
mixture after heat treatment suggests strongly that the mechanism of energy
dissipation is no longer the same.   Therefore, we have examined by microsco-
py the fracture surfaces after impact failure at room temperature.   Three
typical photographs are shown in Figure 2.   The fracture surfaces of PVC
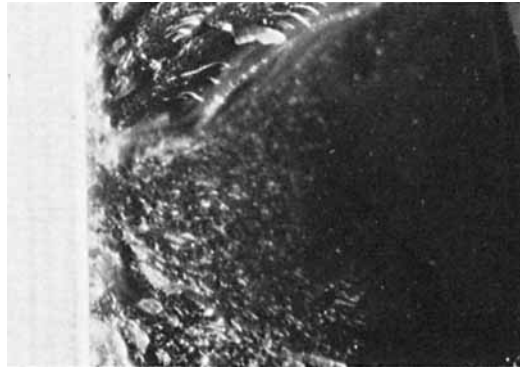
(a)
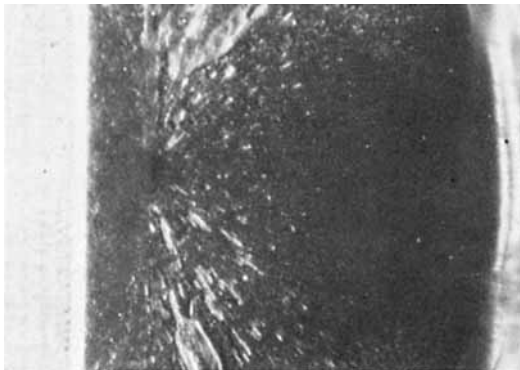
(b)

(c)

Fig. 2. Fracture surfaces of Izod impact test specimen: (a) rigid PVC; (b) PVC/Hy = 75/25
mixture; (c) heat-treated PVC/Hy = 75/25 mixture.

and the polyblend are smooth and have the typical appearance of brittle fracture. In contrast, the fracture surfaces of heat-treated mixtures having high impact strengths are rough and show stress whitening commonly seen in the crazing of rubber-reinforced glassy polymers.[15] This observation is consistent with the phase separation behavior, i.e., the emergence of a rubbery, copolyester-rich phase. However, a second mechanism also appears to be operative here. Deformation by shear flow[16] may also contribute to energy dissipation because we have noticed a reduction in the cross-sectional areas of the specimens adjacent to the fracture surfaces. After heat treatment for 24 hr, the impact fracture appears to revert to a brittle mode. Impact tests at $-30°C$ always result in brittle fracture for all samples.

It may be mentioned in passing that the beneficial effect of heat treatment on impact strength is not gained without some penalty to another mechanical property. The ultimate elongation becomes lower, 60% versus 130% without heat treatment, probably as a consequence of weakened interface between phases.

CONCLUSIONS

Our preliminary studies have shown that the properties of a blend of PVC with copolyester thermoplastic elastomer are sensitive to the thermal history of the specimen. By means of an appropriate heat treatment, the impact strength at room temperature can be improved by almost a factor of seven. The mechanism of energy dissipation in the heat-treated mixture appears to consist of both crazing and shear flow.

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