

Miscible Blends from Plasticized Poly(vinyl Chloride) and Epoxidized Natural Rubber

K. T. VARUGHESE and P. P. DE, *Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India*,
S. K. SANYAL, *Chemical Engineering Department, Jadavpur University, Calcutta 700032, India*, and S. K. DE, *Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India*

Synopsis

Miscible blends from plasticized poly(vinyl chloride), and epoxidized natural rubber having 50 mol% epoxidation level were prepared in a Brabender Plasticorder by the melt-mixing technique. Changes in Brabender torque and temperature, density, dynamic mechanical properties, and differential scanning calorimetry of the samples were examined as a function of blend composition. The plasticized poly(vinyl chloride)/epoxidized natural rubber blends behaved as a compatible system at all composition ranges as evident from their single glass-rubber transition temperature (T_g) obtained from dynamic mechanical analysis as well as from differential scanning calorimetry. Profound changes in the nature of the glass-rubber transition were noted with respect to blend composition. The T_g -width values of blends lie between those of plasticized poly(vinyl chloride) and epoxidized natural rubber.

INTRODUCTION

Poly(vinyl chloride), PVC, is known for its efficiency to form miscible systems with several other low and high molecular weight substances acting as plasticizers. The high molecular weight substances provide superior permanence in physical properties than their low molecular weight counterparts, which in turn impart higher flexibility than the former. In both cases, specific interaction through hydrogen bonding between the components is suggested to be the basis of miscibility.¹⁻³

In a laboratory, blending of PVC with other polymers can be achieved easily by the melt-mixing of the components in a Brabender Plasticorder. It has been reported^{4,5} that blends of rigid PVC with epoxidized natural rubber (ENR) having 50 mol% epoxidation level form mutual miscible systems, in which the ENR reduces Brabender torque⁵ and melt viscosity of rigid PVC.⁶ Both melt-mixed⁵ and solution-cast⁴ blends have been reported to exhibit a single glass-rubber transition temperature (T_g) lying between that of PVC and ENR.

Since plasticized PVC systems form the bulk of commercial utilization of PVC, in the present study we have included blends of plasticized PVC with ENR with special reference to Brabender mixing, and phase behavior in dynamic mechanical analysis and differential scanning calorimetry (DSC).

TABLE I
Details of Materials Used

Materials	Characteristics/ literature data	Source
Poly(vinyl chloride), PVC	Suspension polymerized PVC (NOCIL PVC Polymer S67-311)K Value 66-69	NOCIL, Bombay
Tribasic lead sulfate(TBLS)	Lead-based stabilizer for PVC	Waldies Ltd., Calcutta
Diocetylphthalate (DOP)	Plasticizer for PVC	Perkin Chemical Industries, Calcutta
Epoxidized natural rubber (ENR)	50 mol% epoxidized natural rubber. Mooney viscosity $ML_{(1+4)}100^{\circ}C, 140$. Specific gravity 1.03. Glass transition temperature $-20 \pm 2^{\circ}C$.	Malaysian Rubber Producers' Research Association, Brickendonbury, U.K.

EXPERIMENTAL

Details of the materials used and the formulations of the mixes are given in Tables I and II, respectively. The mixes are denoted by PP_{100} , PP_{70} , PP_{50} , and PP_{30} corresponding to the weight percentage of plasticized PVC in the blends. P_0 corresponds to 100 wt% of ENR.

Prior to the blending of plasticized PVC with ENR, the powdered PVC resin was initially mixed with 6 phr of the stabilizer, tribasic lead sulfate (TBLS) and 40 phr of the plasticizer, dioctylphthalate, in a Brabender Plasticorder (model PLE 330) using a cam-type mixer at a rotor speed of 100 rpm and temperature of $110^{\circ}C$ for 15 minutes.

The blending of plasticized PVC with ENR was performed at $180^{\circ}C$ maintaining the rotor speed at 60 rpm in the Brabender Plasticorder. Torque and temperature developed were measured directly from the recorder. At the start, plasticized PVC was allowed to melt for two minutes, and ENR was added thereafter. The total mixing time of ENR with molten-plasticized PVC was 6 minutes in all cases. The molten mix was then quickly removed from the chamber and sheeted out in the tight nip of a laboratory two-roll mill. The sheeted-out stock was compression-molded at $180^{\circ}C$ for 3 minutes. The hot mold with the blended material inside was then quenched in a stream of cold

TABLE II
Formulations of Plasticized PVC-ENR Blends

Blend Code	PP_{100}	PP_{70}	PP_{50}	PP_{30}	P_0
Weight percentage of plasticized PVC ^a	100	70	50	30	0
Weight percentage of ENR	0	30	50	70	100

^a Containing 6 phr of TBLS and 40 phr of DOP

water for one minute before removing the sample. Density of all samples was measured at 25°C.

Dynamic mechanical properties were measured using a Rheovibron model DDV III-EP at a strain amplitude of 0.0025 cm and a frequency of 3.5 Hz. The procedure was to cool the sample to -100°C and record the measurements during the warm-up. The temperature rise was 2°C/min.

DSC measurements were run on a Dupont differential scanning calorimeter model 910 in nitrogen atmosphere. T_g s of the samples were taken as the midpoint of the step in the scan, run at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Brabender Torque and Stock Temperature

Mixing parameters that may influence the phase morphology and physical properties of the Brabender-mixed products are rotor speed, mixing time, mixing temperature, and the total volume of the mixing components. These parameters have been maintained for all compositions of plasticized PVC-ENR blends. Changes in the torque and the stock temperature developed during the blending process with mixing time are given in Figure 1. In all cases, torque gradually reduces with mixing time and shows steady values from the fifth minute of mixing. Increasing the proportion of ENR raises considerably the initial and final torque in blends. This is attributed to the much higher viscosity of ENR than plasticized PVC.

The progress of the stock temperature as a function of the mixing time is represented by the dashed lines in Figure 1. The observed lowering of stock temperature from the mixing temperature (180°C) is due to the quick addition of ENR into molten PVC. However, the vigorous shearing causes the stock temperature to rise steeply above the mixing temperature even at the end of the first minute of mixing. As the blending progresses, the stock temperature

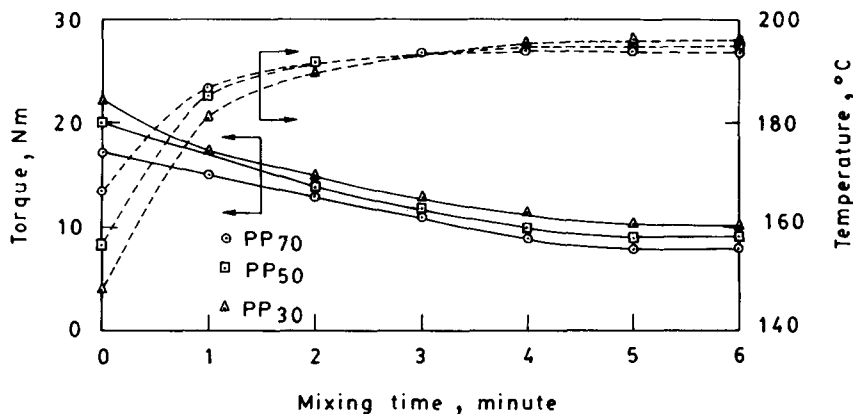


Fig. 1. Effect of mixing time on the Brabender torque and temperature of plasticized PVC-ENR blends. \circ , PP₇₀; \square , PP₅₀; \triangle , PP₃₀.

undergoes a gradual rise till a final steady value is attained. The maximum rise in stock temperature (ΔT), for PP₇₀, PP₅₀ and PP₃₀ has been found to be 14°, 15°, and 16°C, respectively. The attainment of steady values of torque and high stock temperature indicate the completion of the exothermic mixing of plasticized PVC and ENR in the Brabender Plasticorder.

The deviation in the values of torque and stock temperature with the increase of ENR in plasticized PVC-ENR blends is an opposite trend to the rigid PVC-ENR blends reported earlier.⁵ In the latter case, ENR molecules extensively increase the segmental mobility of PVC by breaking down the intermolecular bonding between C—Cl dipoles through the so-called association-dissociation process;⁷ this will result in decreased viscosity or torque in blends. Whereas, in plasticized PVC-ENR blends, the breakage of intermolecular bonding between the C—Cl dipoles is not frequent because of their low content. Moreover, the viscosity of ENR is much higher than plasticized PVC. Hence a high torque is noted for high ENR blends.

Density

Experimental values of density of all samples are shown in Table III. It is found from Figure 2 that the experimental values of blends lie above the calculated values (dashed line). This phenomenon could be understood in terms of packing densification in plasticized PVC-ENR blends. This is in agreement with our previous results of rigid PVC-ENR blends.⁵ The similar nature of density dependence on blend composition has also been reported by Zakrezewski⁸ for miscible NBR-PVC blends.

Dynamic Mechanical Properties

Dynamic storage modulus (E'), loss modulus (E''), and damping ($\tan\delta$) of different compositions of plasticized PVC and ENR are shown in Figures 3–5. In addition to the α -transition, ENR (P₀) has shown two minor transitions of short-scale motions of molecular chain segments at -45°C and -82°C in the glassy region; this may be the result of any structural defects in the material.⁵ PP₁₀₀ shows no secondary transition of β -peak, which appears to have been suppressed due to the interaction with plasticizer.⁹⁻¹⁰ In blends, the low temperature peaks present at the glassy zone in loss modulus and damping curves are diminished with the increase in the composition of plasticized PVC.

TABLE III
Density, T_g , and T_g Width (DSC) in Plasticized PVC-ENR Blends

Samples	Density (g/cm ³)	T_g (°C)			T_g width (DSC)(°C)
		E''	$\tan \delta$	DSC	
PP ₁₀₀	1.232	9.2	40.7	-2.0	42.0
PP ₇₀	1.170	-3.5	16.6	-8.0	26.0
PP ₅₀	1.118	-7.4	12.8	-13.2	23.0
PP ₃₀	1.063	-11.2	6.7	-14.0	22.0
P ₀	0.982	-9.2	-1.0	-17.0	11.0

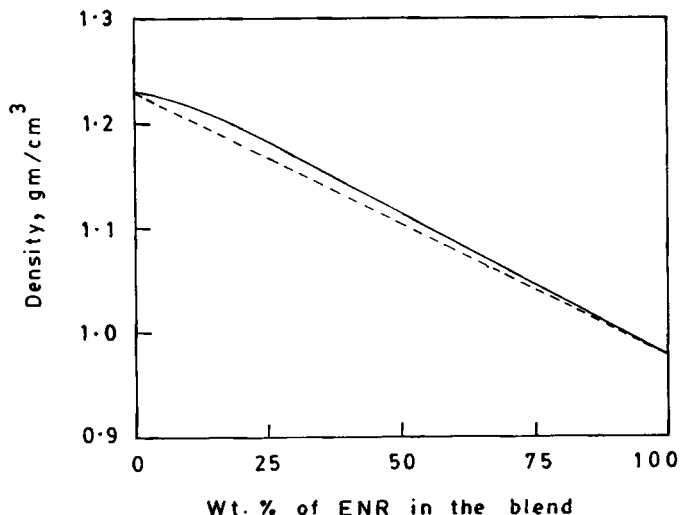


Fig. 2. Density changes of plasticized PVC-ENR blends.

For all compositions, blends exhibit only a single glass-rubber transition temperature (T_g) corresponding to the cooperative segmental motions of molecular chains. This suggests a single-phase morphology in plasticized PVC-ENR blends. Dynamic storage modulus rapidly decreases at the T_g zone due to the decrease in stiffness of the samples. Concomitantly, loss modulus and damping sharply rise until they attain the maxima and then fall with the increase in temperature. The temperature corresponding to the maximum in damping or loss modulus is chosen as the T_g of the samples (Table III). As a general trend in polymer systems, the temperature corresponding to the loss modulus maximum, in all cases, is found to be lower than that of the damping maximum. From Figures 4 and 5, it is quite evident that the blends have only one T_g , which occurs in between the T_g s of the individual components. This indicates that the system is compatible at all compositions. The values of the maxima also taken as T_g , in loss modulus and damping with respect to temperature of blends are found to be intermediate between those of the individual components. The progressive rise in $\tan\delta_{\max}$ of blends from plasticized PVC to ENR indicates the increasing viscous dissipation or mechanical loss of energy with the increasing level of ENR in blends. A detailed examination of the loss peak and damping peak reveals variation in broadening showing a profound change in the nature of the glass-rubber transition in terms of blend composition. This aspect will be further demonstrated along with the similar results of DSC thermograms discussed later in this report.

DSC Thermograms

Additional evidence for the mutual solubility of plasticized PVC and ENR is available from the DSC thermograms shown in Figure 6. Blends exhibit a single T_g , which progressively shifts to lower temperature as ENR content

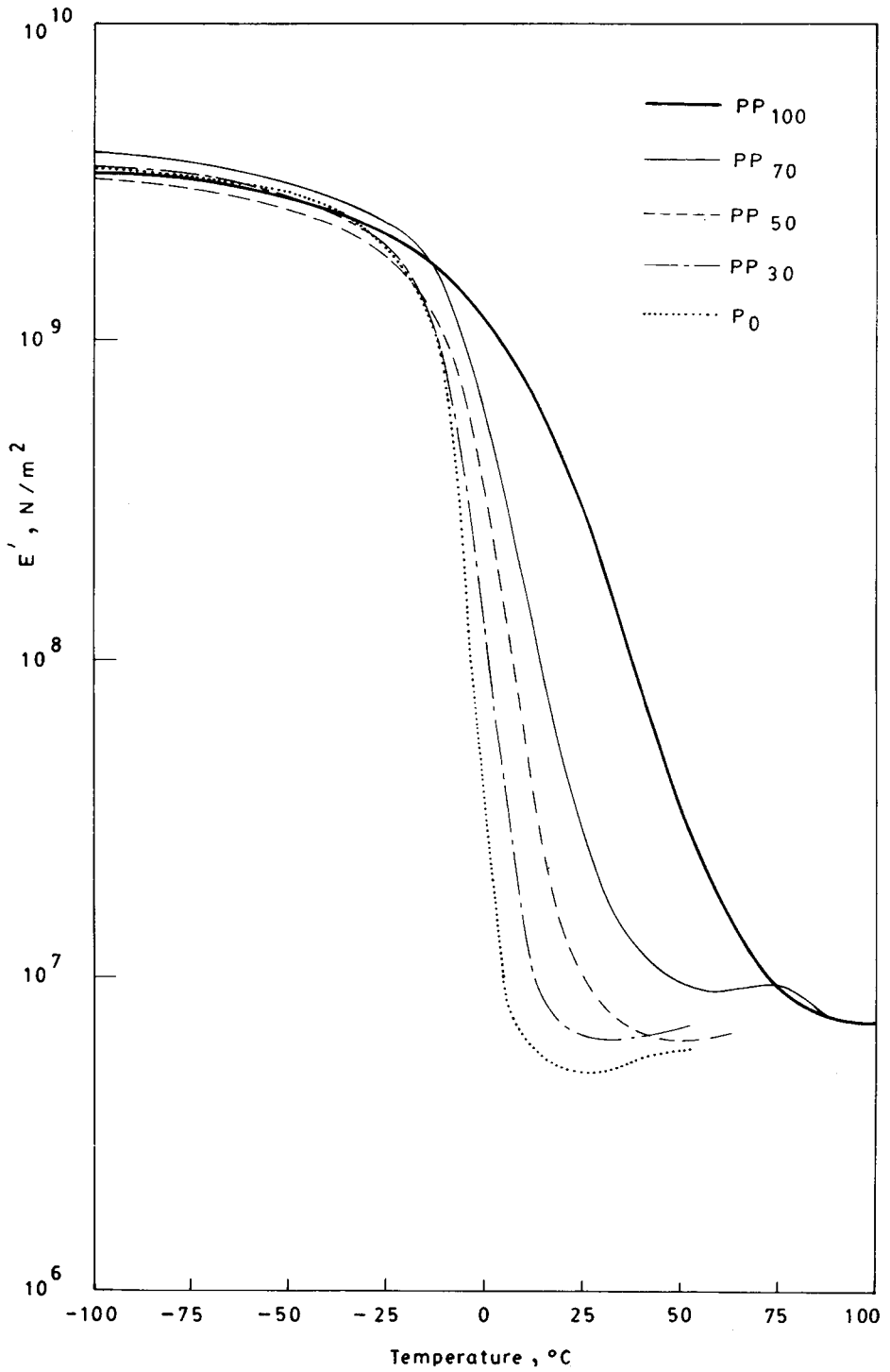


Fig. 3. Effect of temperature on storage modulus of plasticized PVC-ENR blends.

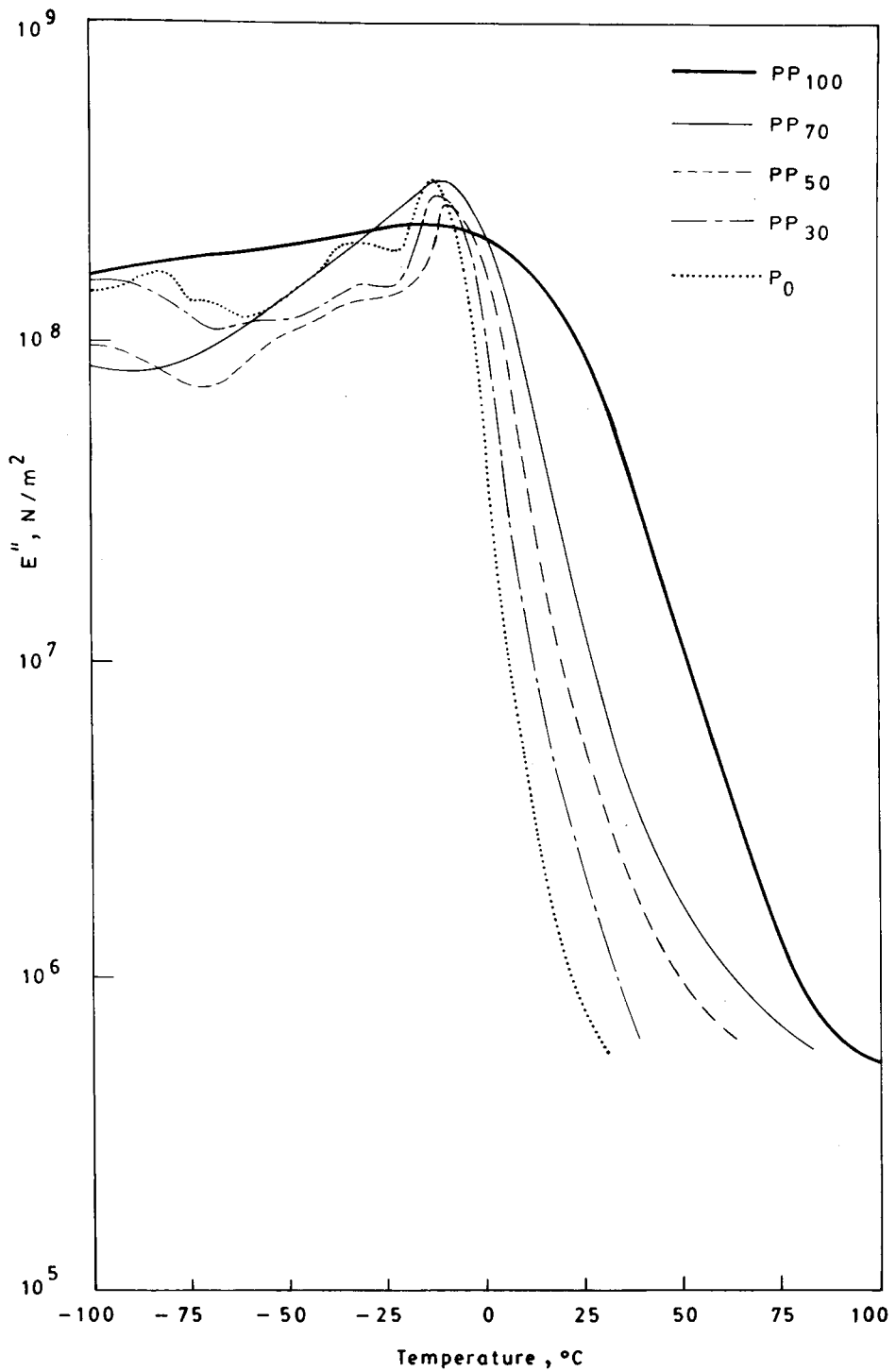


Fig. 4. Effect of temperature on loss modulus of plasticized PVC-ENR blends.

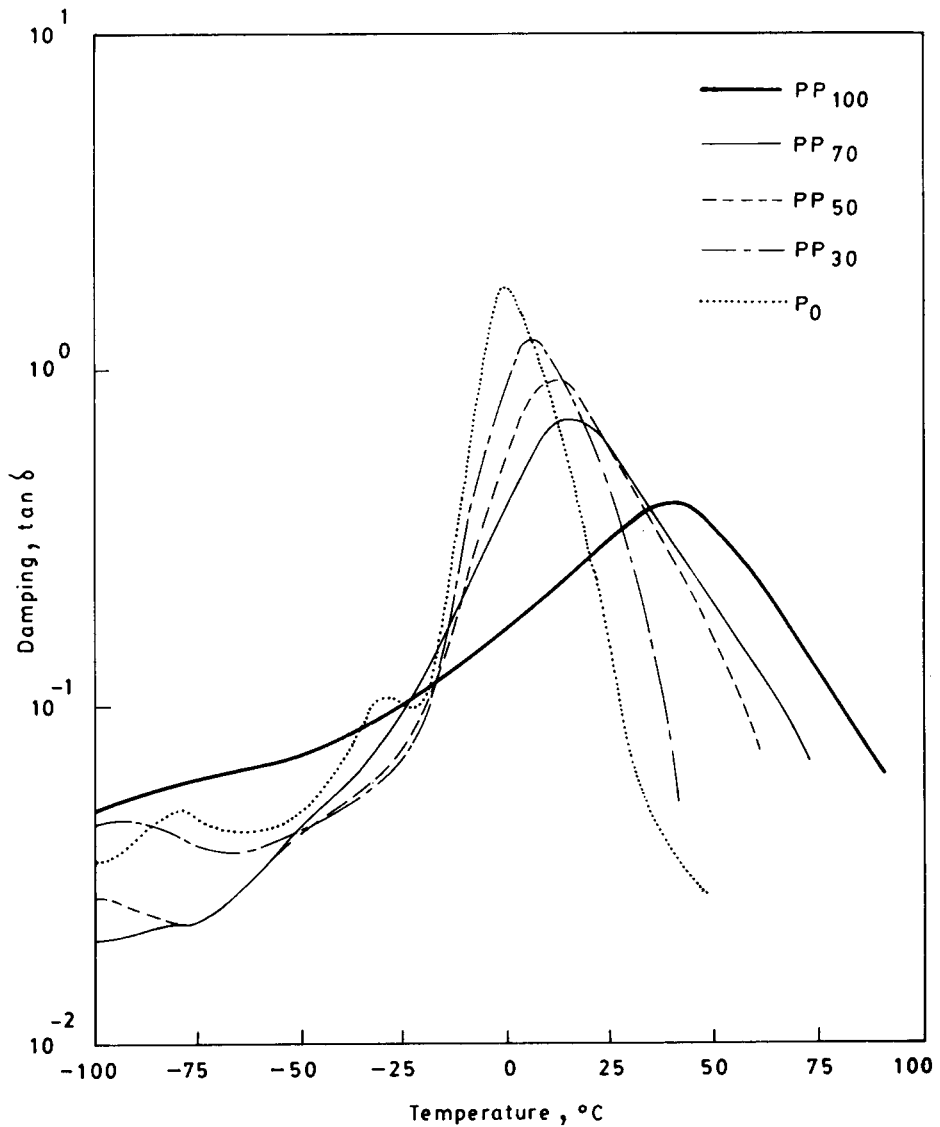


Fig. 5. Effect of temperature on damping ($\tan \delta$) of plasticized PVC-ENR blends.

increases. As in the case of dynamic mechanical behavior, the glass-rubber transition zone exhibits variations in broadening with respect to blend compositions in the DSC thermograms. The magnitude of this has been measured and is shown in Figure 7 and Table III. The minor low temperature transitions (-82°C and -45°C) observed for ENR in the results of dynamic mechanical analysis are absent in the DSC thermograms.

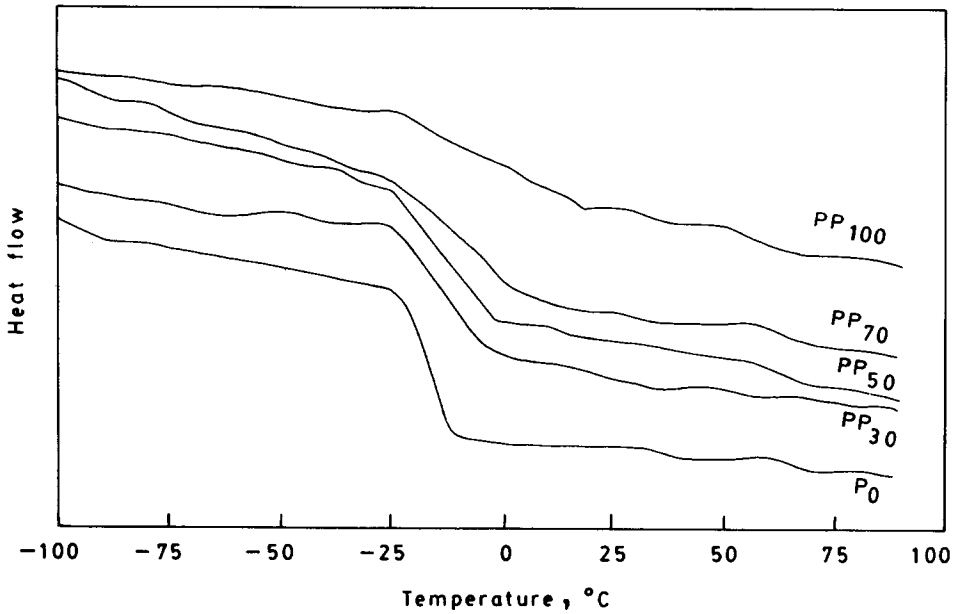


Fig. 6. DSC thermograms of plasticized PVC-ENR blends.

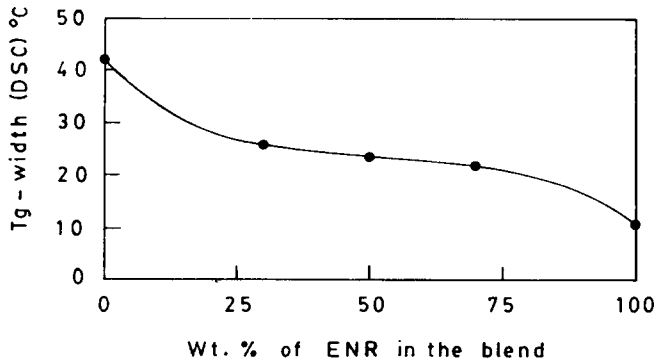


Fig. 7. Effect of blend ratio on T_g width (DSC) of plasticized PVC-ENR blends.

Effect of Blend Composition on Glass-Rubber Transition Behavior

A salient feature in the glass-rubber transition of samples in this study is the change in the nature of glass-rubber transition with respect to the blend composition. Figures 5 and 6 confirm broadening of T_g zone in blends intermediate between that of the pure components. PP_{100} and P_0 show, respectively, the maximum and the minimum broadening of T_g zone. The T_g width, defined

as the temperature covering the glass-rubber transition region, measured from DSC thermograms, is plotted as a function of blend composition (Fig. 7). It is seen that the addition of ENR into plasticized PVC remarkably reduces the T_g width from 42°C to 26°C. This is in fact a slight deviation from the rigid PVC-ENR system⁵ in which the 30 wt% of ENR in blends showed highest T_g width, which was attributed to the perturbation of the aggregated PVC particles¹¹⁻¹⁵ from molecular level mixing of PVC and ENR. However, other miscible systems, in which blends have T_g width intermediate from that of the blend components are not yet known. Most of the miscible polymer systems are reported to have higher T_g width than that of the blend components.¹⁶⁻¹⁸ This is believed to result from fluctuations in compositions over the T_g region.^{16,17} Our results show such composition fluctuations prominent in PP₁₀₀ and moderate in blends. In PP₁₀₀, this may result from the molecular aggregates (microdomains) of PVC¹¹⁻¹⁵ perturbing the true homogeneous or molecular level distribution of dioctylphthalate in PVC. Since ENR is miscible with PVC, the dioctylphthalate present in plasticized PVC may also have a very good affinity toward ENR. The drastic reduction in T_g width of plasticized PVC with the incorporation of ENR may be due to the uniform distribution of dioctylphthalate among ENR macromolecules, which has joined with PVC particles. The mutual miscibility of PVC and ENR eventually causes dioctylphthalate to reach an equilibrium distribution at the end of the blending process. Moderate broadening of T_g zone in blends, however, indicates minor level inhomogeneity at the molecular level mixing of PVC and ENR. The remarkable reduction in T_g width from plasticized PVC to plasticized PVC-ENR blends suggests a more defined single-phase morphology in the latter.

The T_g s of the sample obtained from loss modulus versus temperature, damping versus temperature, and DSC thermograms are given in Table III. The results indicate that plasticized PVC and plasticized PVC-ENR blends have lower values of T_g than the respective rigid PVC and rigid PVC-ENR blend reported earlier.⁵ This suggests greater low temperature flexibility in plasticized PVC-ENR blends than rigid PVC-ENR blends. The effect of blend composition of T_g is depicted in Figure 8. In every case, the results have been tested with the commonly used Fox relationship.¹⁹

$$1/T_g b = W_1/T_g 1 + W_2/T_g 2 \dots \quad (1)$$

where $T_g b$, $T_g 1$, and $T_g 2$ are the T_g s of the blend, component 1 and component 2, respectively, and W_1 and W_2 are the weight fractions of the component 1 and 2, respectively. The nature of the experimental plots based on loss modulus, damping, and DSC thermograms differ from one another. Moreover, the experimental results show deviation from Fox values in every case. This deviation may result from the contribution of the excess volume of mixing to the free volume.^{20,21} The closer values of T_g s of plasticized PVC and ENR, however, does not cause any difficulty in the appearance of prominent single glass-rubber transition in blends. Concavity,²⁰⁻²³ a salient feature in the T_g composition curve of miscible polyblends, is not regular or prominent in the T_g composition curves of miscible plasticized PVC-ENR system.

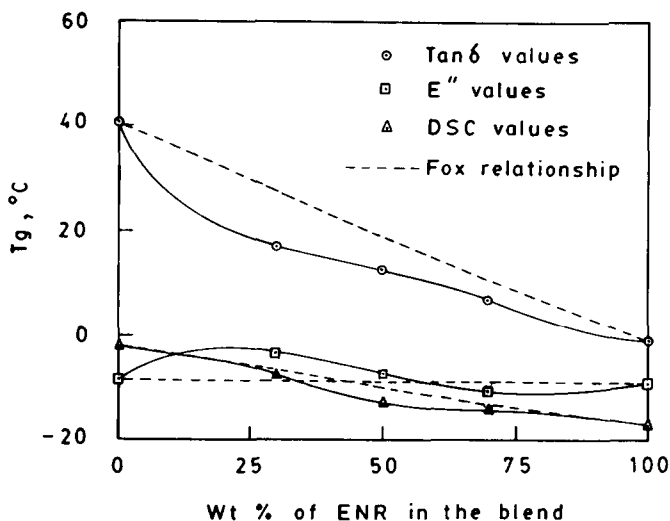


Fig. 8. Effect of blend ratio on T_g of plasticized PVC-ENR blends.

CONCLUSIONS

In consideration of the above discussions and analyses, it is concluded that the melt-mixed blends of plasticized PVC and ENR (epoxidation level 50 mol%) have a phase morphology close to a single-phase system. These blends have a single T_g lying between the T_g s of the blend components as evident from dynamic mechanical analysis and DSC thermograms. Plasticized PVC has the maximum broadening in glass-rubber transition of all the samples. The drastic reduction in T_g width of plasticized PVC with the incorporation of ENR may be due to the uniform distribution of dioctylphthalate among ENR molecules, which has joined with PVC particles. This reduction in T_g width from plasticized PVC to plasticized PVC-ENR blends suggests a more defined single-phase morphology in the latter. Since the T_g of plasticized PVC-ENR blends is much lower than that of rigid PVC-ENR blends,⁵ the former have greater low temperature flexibility.

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