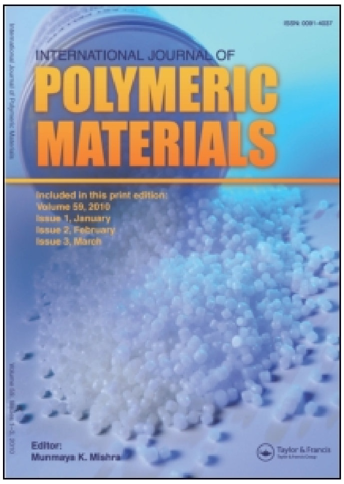

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Dynamic Mechanical Properties of Poly(vinyl chloride)/Impact Modifier Blends

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The dynamic mechanical properties of PVC/Impact Modifiers blending systems have been studied using the DDV-III-EA viscoelastomer. It is revealed that butadiene-acrylonitrile copolymer (26% AN) is miscible with PVC, ethylene-vinylacetate copolymer (28% VAc) is partially miscible with PVC, while chlorinated polyethylene is compatible with PVC. The dynamic mechanical properties of the blends depend on blending temperature.

KEY WORDS PVC, BAN, CPE, impact modifiers, blend, dynamic mechanical properties.

INTRODUCTION

Poly(vinyl chloride) (PVC) is a most important plastics commodity, but the rigid PVC products are relatively poor in impact behavior, which restricts its use in wider applications. Butadiene-acrylonitrile copolymer (BAN), ethylenevinylacetate copolymer (EVA), chlorinated polyethylene (CPE) are important impact modifiers for PVC. When blended with the impact modifiers, the toughness of PVC products is improved.[1-3] Dynamic mechanical properties of PVC with respective BAN-26, EVA-28, CPE, are studied in the paper, which could be instructive for research of PVC modification.

EXPERIMENTAL

Materials

PVC (η = 1.8) supplied by TianJin Dagu Chemical Plant, BAN-26 (containing 26% AN) supplied by LianZou Chemical Industry Company, EVA-28 (containing 28% VAc) supplied by ShangHai Chemical Industry Research Institute, CPE (containing 36% chlorine) supplied by JiangSu Chemical Additive Plant.

Sample Preparation

1) PVC/BAN-26 blends. PVC and stabilizer were mixed by stirrer with high speed for about 15 minutes. The dry mixed powder and milled BAN-26 were then blended

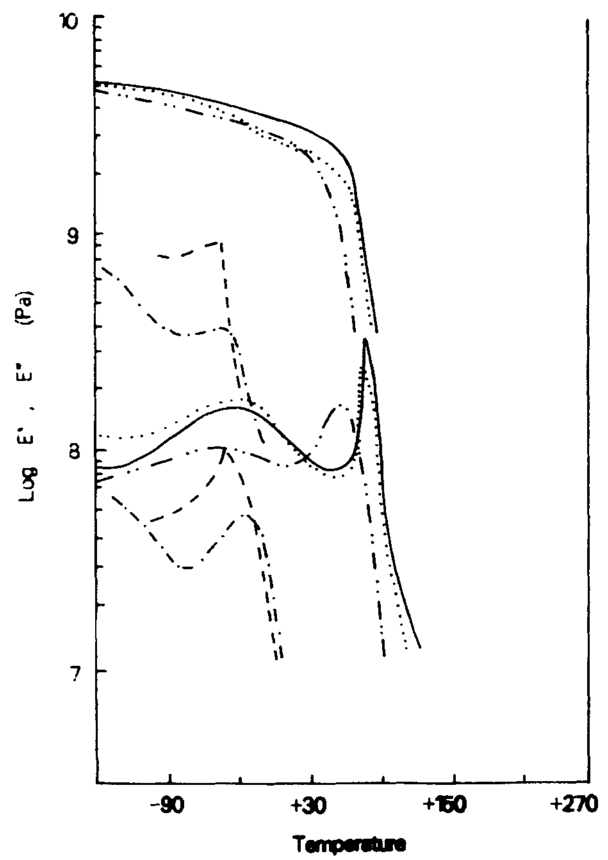

FIGURE 1 Dynamic viscoelastic spectra of PVC/BAN-26 and PVC/EVA-28 blends (——) PVC; (----) BAN-26; (—·—) EVA-28; (—··—) PVC/BAN-26: 87/13; (··· ···) PVC/EVA-28: 93/7.

on a two roll plasticator at a given temperature and for a given time. The blankets were removed from the roll and were molded to the desired thickness in a preheated press. The sample was cooled in the mold under pressure for 10 minutes.

2) PVC/EVA-28 blends. In the experiment, EVA-28 and plasticized PVC with stabilizer were blended on a two roll plasticator. The remaining procedure was the same as PVC/BAN-26 blend's.

3) PVC/CPE blends. The blends were prepared by dry mixed components of PVC, CPE and stabilizers, and the roll milling done at a given temperature and for a given time. The remaining procedure was the same as PVC/BAN-26 blend's.

Dynamic Mechanical Properties Experiments

The dynamic mechanical properties of the blend were measured at 35 Hz, 2°C/min., over the temperature range $-150 \sim +200$°C, by means of Toyo Rheovibron DV-III-EA. E'-storage modulus, E''-loss modulus.

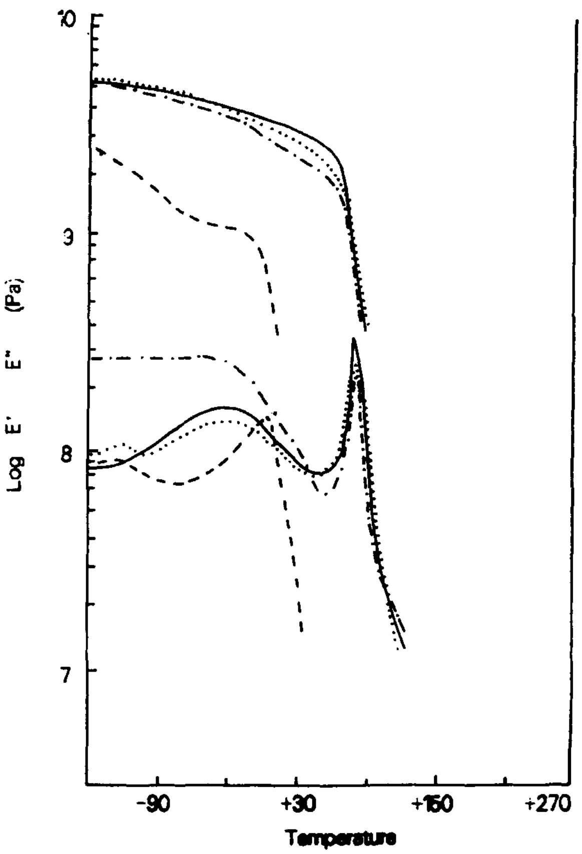

FIGURE 2 Dynamic viscoelastic spectra of PVC/CPE and PVC/PE blends (——) PVC; (······) PVC/PE: 89/11; (----) CPE; (—·—) PVC/CPE 89/11.

RESULTS AND DISCUSSION

Influence of Structure of Impact Modifiers

The dynamic mechanical properties of PVC/BAN-26, PVC/EVA-28, PVC/CPE, PVC/PE blends are shown in Figures 1 and 2. In the figures, two maxima in the *E*" curve of PVC occur at approximately 87 and −24°C. The high temperature peak is attributed to the motion of PVC chain segment which accompanies the glass transition, the very broad low temperature peak is the β relaxation of PVC, which is ascribed to the local-mode motion of the main chain. The following information is obtained from Figures 1 and 2:

1) For PVC/BAN-26 blend (Figure 1), in the *E*', *E*" curve of the blend, a single glass transition is observed between the Tg's of the two components, which is broader than that of the transition of the pure components. 2) Two transitions are observed in the *E*', *E*" curve for PVC/EVA-28 blend (Figure 1): the high temperature transition with its maximum located at 84.8°C and the low temperature

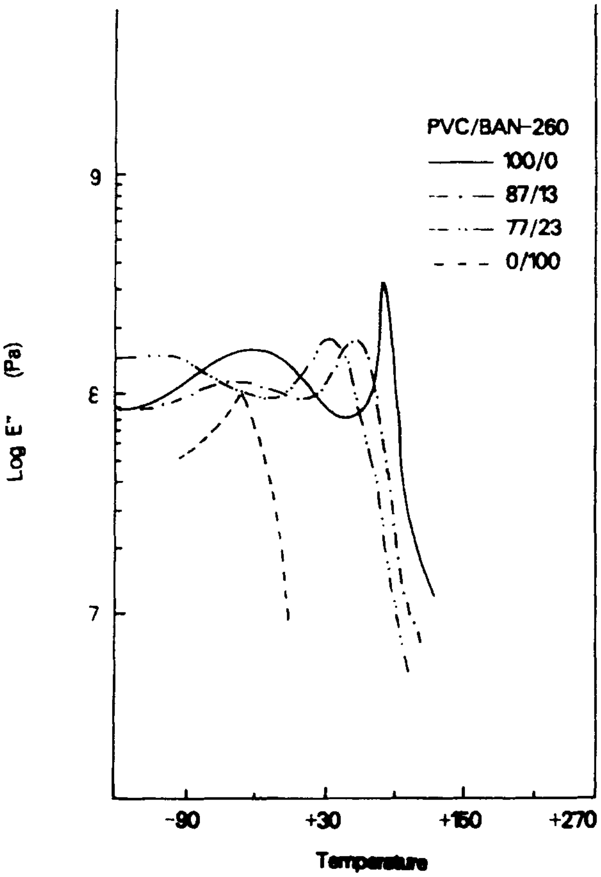

FIGURE 3 Loss modulus vs. temperature for PVC/BAN-26 blends with compositions as indicated.

transition with its maxima located at −21.2°C are the glass transition of the respective PVC and EVA-28 components in the blend. Therefore, the Tg values of the two components in the blend shift closer to each other than found with the pure components. 3) The PVC/CPE blend exhibits two transitions in the *E*′ curve at the same temperature as found with the pure components, 87 and 4°C for PVC and CPE, respectively. The feature of α relaxation of CPE and β relaxation of PVC occur indistinctly in the *E*″ curve (Figure 2). 4) For PVC/PE blend (Figure 2), three transition peaks are found in the *E*″ curve, with their maxima located at the same temperature as α relaxation of pure PE ($T = -80$°C), β and α relaxation of pure PVC respectively.

These show that the dynamic mechanical properties of the blends vary with the chemical structure of impact modifiers. In PVC/BAN-26 blend, the specific interaction of α hydrogen (proton giving) of PVC with AN group (proton acceptor) of BAN-26 leads to a single glass transition. Some broadening of the peak suggests a certain degree of heterogeneity in the blend. The data indicate

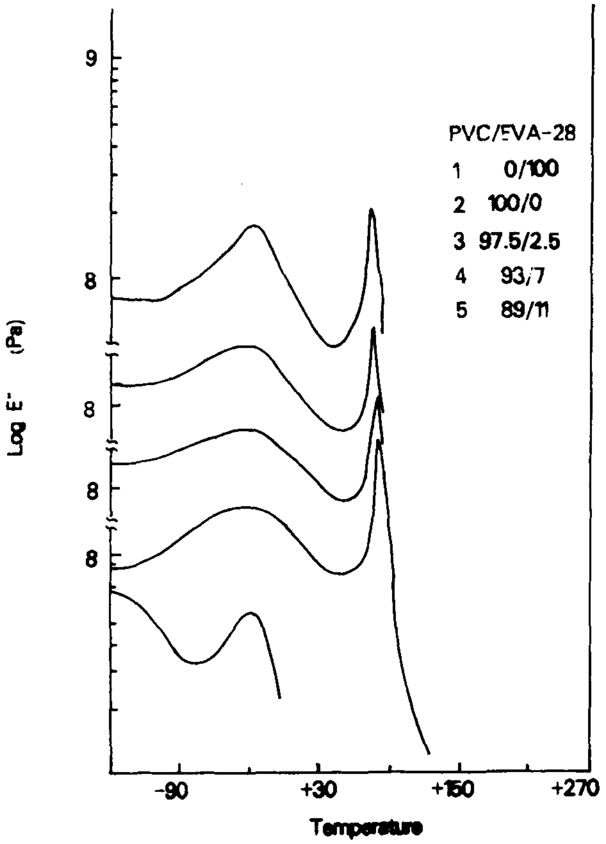

FIGURE 4 Loss modulus vs. temperature for PVC/EVA-28 blends with composition as indicated.

that PVC is miscible[4] with BAN-26. PVC is weakly capable of hydrogen bonding with EVA-28 because the polarity of carbonyl in the chain of EVA-28 is smaller than that of CN group in the chain of BAN-26. Therefore the Tg of the PVC component shifts down and the Tg for EVA-28 component shifts up slightly in the blend. We conclude that PVC is partially miscible[4] with EVA-28. PE differs markedly from PVC in its chemical structure, so the characteristic peak of the two components in the blend appears distinctly in the E' and E'' curve at same temperature as with the pure components. This suggests that PVC is incompatible with PE, which results in poor interfacial bonding. The chain of CPE containing 36% chlorine usually consists of some high chlorine content segments and some low chlorine content segments, the former being diffused to interface between the two phases during blending to provide good interfacial bonding, which means PVC is compatible[4] with CPE.

Influence of Blend Composition

The dynamic mechanical data of the blends vary with blend composition as shown in Figures 3–5 and Tables I and II. In the PVC/BAN-26 blends, Tg values of the

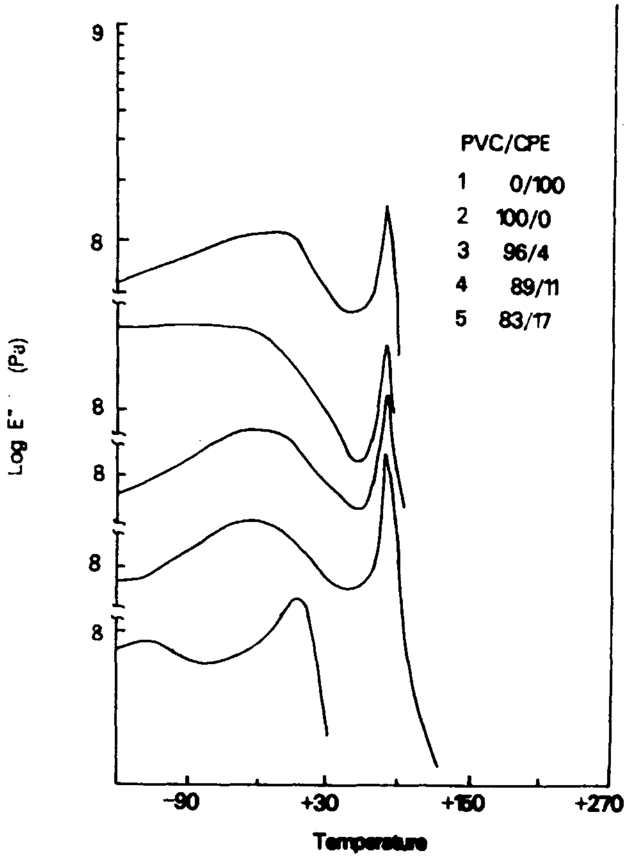

FIGURE 5 Loss modulus vs. temperature for PVC/CPE blends with compositions as indicated.

TABLE I

Tg of PVC/BAN-26 blends and blend components

PVC/BAN-26	Tg (°C)
100/0	87
87/13	54.7
77/23	36
0/100	−43.1

Blend time: 5 min.
Blend temperature: 170°C.

blends reduce rapidly with increasing BAN-26 content and β relaxation of PVC gradually disappears (Table I and Figure 3). This agrees with what is found in PVC/BAN-32 blend.[5] This might indicate that the specific interaction of PVC and BAN-26 results in reduction of interaction of PVC component in the blend and altered the local mobility of PVC chain. In PVC/EVA-28 blends, two transition

TABLE II

Tg of PVC/EVA-28 blends and blend component

	Tg (°C)	
PVC/EVA-28	Tg EVA-28	Tg PVC
100/0	—	87
97.5/2.5	−25	86.5
93/7	−21.2	84.8
87/13	−19.1	82.1
0/100	−29.2	—

Blend time: 5 min.
Blend temperature: 165°C.

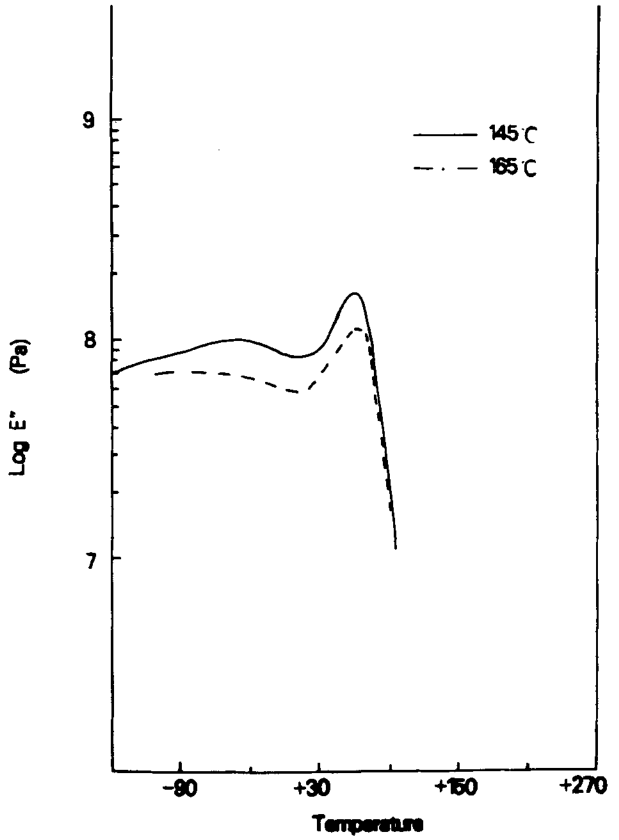

FIGURE 6 Loss modulus vs. temperature for PVC/BAN-26 blends with blend temperature as indicated, composition: 87/13.

peaks of the blends gradually shift closer to each other with increasing EVA-28 content (Figure 4 and Table II). When PVC is toughened with CPE (Figure 5), the location of the high temperature peak is constant and some mixing of β peak of PVC and α peak of CPE takes place in the *E*" curve as CPE content increases.

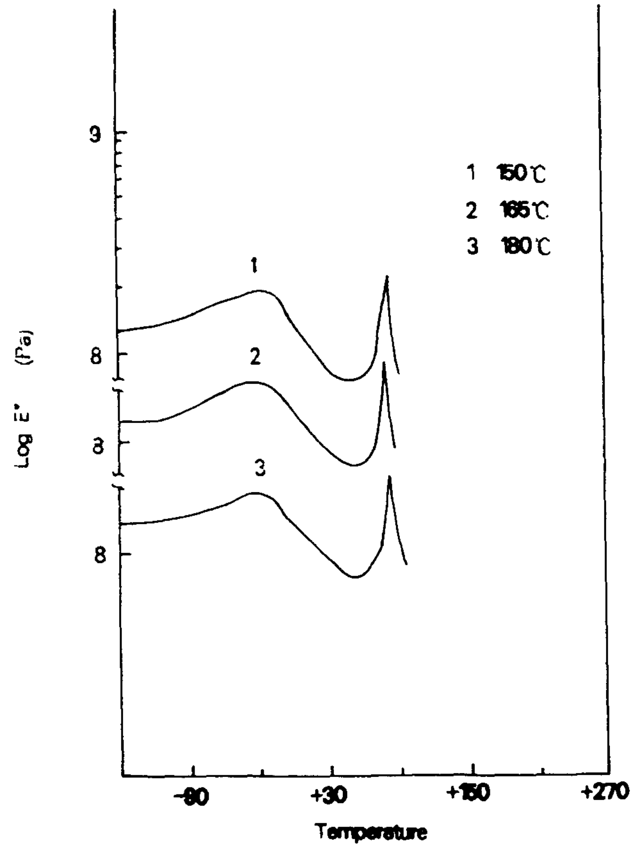

FIGURE 7 Loss modulus vs. temperature for PVC/EVA-28 blends with blend temperature as indicated, composition: 93/7.

The disappearance of the characteristics of β peak of PVC and α peak of CPE for 11% wt content CPE blend is unusual. The result is not consistent with that found in torsion pendulum experiments.[3]

Influence of Blend Temperature

As shown in Figures 6–8 and Table III: 1) For PVC/BAN-26 blends, the transition peak shifts to high temperature as blend temperature increases from 145°C to 160°C (Figure 6). Note that it is difficult to plasticize PVC below 145°C. 2) For PVC/EVA-28 blend, the two transition peaks in the *E*" curve shift close to each other slightly as the blend temperature rises from 150°C to 165°C. But the result is opposite when blend temperature increases from 165°C to 180°C (Figure 7 and Table III). 3) For PVC/CPE, blend as shown in Figure 8, the location of the high temperature peak is not influenced by blend temperature. The characteristic of α peak for CPE and β peak for PVC disappears at 175°C, but the *E*" values overlapping temperatures of α peak for CPE and β peak for PVC increase both above

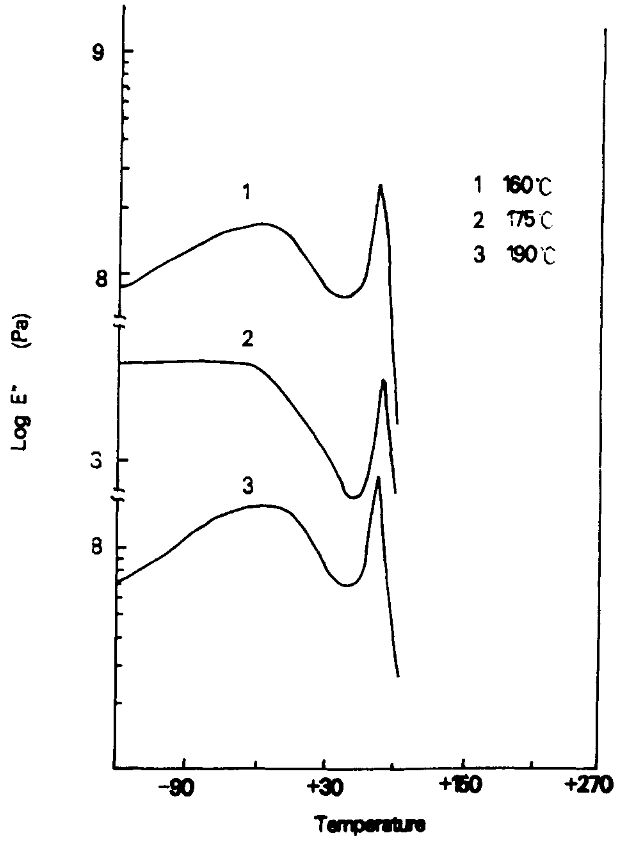

FIGURE 8 Loss modulus vs. temperature for PVC/CPE blends with blend temperature as indicated, composition: 89/11.

TABLE III

Tg of PVC/EVA-28 blend and blend temperature

Blend temperature (°C)	Tg (°C)	
	Tg EVA-28	Tg PVC
150	−25.1	86.8
165	−21.2	84.8
180	−23.2	85.6

and below 175°C. The results indicate that at an appropriate blend temperature PVC is miscible with specific impact modifiers. However, when the blends are mixed at too low or too high temperatures, the miscibility (or compatibility) of PVC-impact modifier is reduced.

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