JOURNAL OF APPLIED POLYMER SCIENCE VOL. 20, 2737–2755 (1976)

Polyblends. II. Isochronal Viscoelastic Parameters for Polyblends of Butadiene–Acrylonitrile Elastomers and Copolymers of Vinyl Stearate and Vinyl Chloride

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Synopsis

Isochronal viscoelastic parameters were obtained for the polyblends of nitrile rubbers with internally and externally plasticized poly(vinyl chloride) (PVC) whose mechanical properties were studied in the previous paper. Thus, the room-temperature mechanical properties of the previous paper were extended to include a wide temperature range in this work. Phase immiscibility, indicated by the observance of two glass transition temperatures, using differential scanning calorimetry, was observed for most of the polyblends. In contrast, blend compatibility was indicated by mechanical measurements, because the inflection temperatures of the isochronal curves (T_i) shifted with blend composition. It was concluded that mechanical spectroscopy-monitored volume elements large enough to include contributions to viscoelastic response from both phases; this caused the curves to shift with composition. On the other hand, the much shorter-range segmental responses characteristic of T_g produced transitions at the discrete temperature intervals representative of each phase. Using a relation between torsional stiffness at room temperature and tensile strength, failure strengths with respect to temperature were estimated and compared at varied free-volume increments ($T - T_g$) up to 50°C. Approximate equivalence was found by this procedure for fillers of bulk PVC and those containing 21 wt-% of both internal and external plasticizer, in analogy with findings for mechanical property optimization of the previous paper. Low-temperature properties and viscoelastic response of the polyblends containing vinyl stearate copolymers were greatly improved over their neat state. In addition, data from isochronal temperature–composition diagrams suggested viscoelastic equivalence, but greater ease of processability for the blends containing vinyl ester, compared to the others.

INTRODUCTION

The main purpose of the preceding paper[1] was to determine mechanical properties at room temperature of polyblends of several nitrile rubbers (NBR) with polymeric substances containing vinyl chloride. In this paper, their mechanical properties were monitored over a wide temperature interval. Emphasis was on the differences, if any, that existed between mechanically determined glass transitions and those obtained from thermal analysis. By the latter technique, the coexistence of a relatively miscible phase with discrete phases could also be qualitatively ascertained. Correlation of the data with requirements for compatibility[2–4] as the mixed phases passed from glass–glass[5] to glass–rubber[6] and finally rubber–rubber[7] with increase in tem-

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perature was, therefore, a major concern of this work. In addition, an empirical correlation between tensile strength and torsional modulus at ambient temperature was used to compare tensile strengths at various free-volume increments above T_g, that is, at $(T - T_g)$, for the various blend systems under investigation.[8,9]

Finally, an estimation of processing and use temperature range for the blended systems was graphically illustrated from isochronal temperature–composition diagrams.[10] Thermal and viscoelastic data for the starting vinyl stearate–vinyl chloride copolymers and DOP mixtures, which have been extensively studied recently,[11,12] were available for direct comparison with those of the polyblends. In the next paper,[13] the experimental content of this and the previous paper, together with additional data, will be considered with respect to several theories of polycomposite behavior and analyzed in terms of the compatibility criteria.

EXPERIMENTAL

Viscoelastic Data

Experimental procedures for polyblend preparation were reported in the previous paper.[1] The torsional modulus method of Williamson[14] was used in this work rather than the Clash-Berg method[12,15] to permit a greater temperature range in monitoring the rubbery plateau region of these soft compositions. The procedures used followed ASTM Standards D1043-61T. Measurement duration was 10 sec, and the temperature range was usually −70° to 120°C. At temperatures above the inflection temperature T_i, where Poisson's ratio becomes 0.5, the torsional moduli were assumed to equal 3G.[12] Therefore, the two methods yield Young's modulus.

Isochronal data obtained by the Williamson apparatus for selected vinyl stearate–vinyl chloride starting copolymers of this work were compared with similar data from the often used[12] Clash-Berg apparatus. The latter was operated at 5 sec. It was observed that the torsional moduli E_t at −70°C were generally 4.5 to 5.0 × 10^5 psi by Williamson, but only 3.0–3.4 × 10^5 by Clash-Berg. To convert Williamson moduli E_w to those of Clash-Berg, E_c, at temperatures between T_i and $T_i - 50°$, the relationship found was

$$E_c = 1.0 - [(1 - f)T_i - T]E_w$$

with $f = 0.67$; at still lower experimental temperatures, fE_w gave corrected values. At $T_i + T$, the two methods were identical. Therefore, Clash-Berg T_f was about 10–15°C below that by the uncorrected Williamson method. The inflection temperatures by the two methods were similar (±2°C) in line with the small difference in measurement frequency. However, at temperatures greater than T_i, Clash-Berg moduli were inaccurate below about 500 psi (3.4 × 10^7 dynes/cm^2), while the Williamson procedure yielded reasonable values as low as 90 psi (6.2 × 10^6 dynes/cm^2).[14] The failure of the Williamson method to correlate directly with the generally used Clash-Berg method in the high-modulus region was offset by its advantages in accurately describing the viscoelastic properties of the largely soft elastomeric polyblends of this work. However, the factor introduced above placed both methods in reasonable agreement.

Differential Scanning Calorimetry

The procedures followed for homopolymers and internally plasticized copolymer systems[16] were used here, but with certain modifications. Samples, in the form of films, were weighed into solvent cups, which were then sealed. Temperatures were programmed from −90° through 150°C, using liquid nitrogen cooling for all samples. Manual return to −90° or programmed cooling at 10°/min made no difference in the value of the transitions. Side-chain crystallization was entirely absent from these polyblends.[16] Rough estimations of the two observed T_g values were obtained from the scans by reading from a linear calibration curve, referenced to the melting point of indium. The rough T_g values were remeasured as true values by direct-dial read-out using the procedure of reference 16. Programs were repeated several times. Unmixed polycomposites were prepared by weighing two to four discrete pieces of film of both blend starting materials (i.e., plasticized polymer and elastomer) directly into the weighing pans. Samples prepared in this way revealed any heat capacity–temperature effects produced by the bulk presence of both phases and indicated the correct T_g of each component in the mixture. The T_g of the unmixed polycomposite and the fine resolution of its scan could be compared with an experimental polyblend of the same composition to provide an insight into the blend homogeneity.

An IBM 1130 computer was used for all of the curve fitting and most of the calculations in this work.

RESULTS AND DISCUSSION

General Features

Viscoelastic parameters of the starting polymers, the plasticized mixtures, and the derived polyblends are listed in Table I. This table lists parameters for the experiments presented in Tables I and II of the previous paper.[1] However, data for vinyl acetate copolymers, polyblends using Hycar 1452-P50, and vulcanized samples have been deleted here; data for these are either presented in the tables and figures that follow or they are so similar to the values in Table I that their presentation was deemed unnecessary. Glass transition temperatures were obtained using differential scanning calorimetry (DSC), and mechanical transitions were determined by the Williamson method.[14] The temperature T_f corresponded to a modulus[17] of 135,000 psi, while T_i was taken at 14,500 psi (1×10^9 dynes/cm^2), the latter considered to be the approximate inflection temperature[18] of the modulus–temperature curves. Some of the transitions presented here were listed in Table II of the previous paper.[1]

The designations of the viscoelastic parameters of Table I of this paper follow those first used by Tobolsky[18–20] and Iobst and co-workers[21] on plasticized PVC, and particularly those of Jordan et al.[11,12] on internally plasticized PVC. The meaning of these designations may be more readily seen by reference to the slash marks in Figure 1. The slope s was taken at the inflection temperature T_i, whereas s_1 and s_2 are slopes of the moduli E_{t1} and E_{t2}. The temperatures of these moduli were arbitrarily selected as 50°C below and 50°C above T_i, respectively.[12] They correspond to the pseudoequili-

TABLE I

Glass Transition Temperatures and Viscoelastic Parameters From Modulus–Temperature Curves

Expt. no.[a]	w_{NBR}[b]	Glass transitions, °C[c] T_{g1}	T_{g2}	Mechanical transitions, °C[d] T_f	T_i	$-s$	E_{f1}, $\times 10^{-5}$, psi	$-s_1$	E_{f2}, psi	$-s_2$	$E_{f23°}$, psi	$E_{f120°}$, psi
Starting Copolymers: Vinyl Stearate–Vinyl Chloride Copolymers												
1′	0		81	82	88	0.13	5.0	0.0041	550	0.036	5.50×10^5	1500
2′	0.207[e]		41	33	48	0.061	3.9	0.0029	350	0.0074	2.46×10^5	240
3′	0.356[e]		13	10	28	0.089	3.0	0.0058	185	0.0064	26,000	82
4′	0.467[e]		8.0	−8.0	12	0.049	2.6	0.0067	110	0.0093	1,350	29
Starting Mixtures: Vinyl Chloride and Di-2-ethylhexyl Phthalate (DOP)												
5′	0.207[f]		14	14	37	0.058	2.8	0.0097	680	0.0037	80,000	500
6′	0.356[f]		−20	−29	−3	0.044	4.0	0.012	1010	0.017	2,450	350
7′	0.467[f]		−44	−49	−32	0.057	5.0	0.012	600	0.0049	578	150
Starting Elastomers: Hycar 1411 (8′), Hycar 1452P-50 (9′), and AN25 (10′)												
8′	0.336[g]	−23		−24	−20	0.64	5.3	0.0047	460	0.0090	520	270
9′	0.303[g]	−43		−38	−27	0.15	3.8	~0	180	0.012	181	21
10′	0.249[g]	−51		−49	−37	0.14	4.3	0.012	300	0.011	222	40
Polyblends: Vinyl Stearate (0.207 Weight Fraction) and Vinyl Chloride (0.793 Weight Fraction) Copolymer with Hycar 1411												
1	0.25	−3	57	9	28	0.069	4.0	0.0053	420	0.0046	31,000	270
2	0.38	−10	41	−7	20	0.060	3.7	0.0099	420	0.0032	9,000	270
3	0.50	−18	26	−14	8	0.042	4.3	0.0043	440	0.0031	1,740	290
4	0.75	−18	40	−22	−9	0.105	5.8	0.0013	540	0.0079	850	270
Polyblends: Vinyl Stearate (0.356 Weight Fraction) and Vinyl Chloride (0.644 Weight Fraction) Copolymer with Hycar 1411												
5	0.25	−18	13	−15	16	0.056	3.1	0.011	220	0.0076	3,700	52
6	0.38	−18	13	−21	12	0.058	3.5	0.0088	240	0.0054	1,550	120
7	0.50	−23	12	−19	3	0.027	3.9	0.0024	340	0.0104	880	130
8	0.75	−18	13	−25	−18	0.070	3.9	0.0014	440	0.0094	540	170
Polyblends: Vinyl Stearate (0.467 Weight Fraction) and Vinyl Chloride (0.533 Weight Fraction) Copolymer with Hycar 1411												
9	0.25	−18	10	−21	9	0.051	3.2	0.0098	103	0.016	1,030	13
10	0.50	−18	7	−23	−1	0.045	3.1	0.0045	220	0.016	700	87

				Polyblends: Di-2-ethylhexyl Phthalate (0.207 Weight Fraction) and Poly(vinyl Chloride) (0.793 Weight Fraction) Mixture with Hycar 1411								
11	0.25	−4	14	−5	19	0.033	4.3	0.014	680	0.0041	10,300	450
12	0.38	−18	2	−14	6	0.031	5.2	0.0056	840	0.013	4,700	450
13	0.50	−18	14	−19	−2	0.033	4.8	0.0039	950	0.018	2,900	450
14	0.75	−18	9	−25	−17	0.070	4.8	0.0030	750	0.018	950	400
				Polyblends: Di-2-ethylhexyl Phthalate (0.356 Weight Fraction) and Poly(vinyl Chloride) (0.644 Weight Fraction) Mixture with Hycar 1411								
15	0.25	−23	n/v[h]	−30	−13	0.058	5.4	0.0013	840	0.0070	1,120	320
16	0.38	−19	n/v[h]	−28	−15	0.044	5.6	0.0056	800	0.0050	940	370
17	0.50	−20	n/v[h]	−30	−17	0.049	4.7	0.0047	620	0.0074	770	350
18	0.75	−18	n/v[h]	−26	−20	0.061	5.5	~0	500	0.0055	560	270
				Polyblends: Di-2-ethylhexyl Phthalate (0.467 Weight Fraction) and Poly(vinyl Chloride) (0.533 Weight Fraction) Mixture with Hycar 1411								
19	0.25	−44	n/v[h]	−38	−30	0.075	5.0	0.0076	680	0.0051	660	310
20	0.38	−41	n/v[h]	−38	−27	0.086	5.0	0.047	440	0.0066	520	300
21	0.50	−41	n/v[h]	−36	−26	0.085	5.8	0.0030	520	0.0050	540	330
22	0.75	−24	n/v[h]	−30	−24	0.18	5.0	0.0020	480	0.0067	500	250
				Polyblends: Poly(vinyl Chloride) Homopolymer with Hycar 1411								
23	0.25	9	61	29	60	0.035	2.9	0.014	740	0.0088	1.80×10^5	660
24	0.50	−18	67	−10	14	0.014	5.0	0.0017	1600	0.022	10,500	500
25	0.58	−5	62	−14	5	0.027	5.0	0.0013	1100	0.017	5,500	500
26	0.66	−15	62	−17	−2	0.048	5.0	0.0025	850	0.024	2,650	390
27	0.75	−18	65	−19	−8	0.065	5.5	0.0025	670	0.014	1,210	400

[a] Sample numbers correspond to the experiments listed in the previous paper. Primed numbers are those of Table I of that paper; the rest are from Table II. This table is a selected listing of the available data; some not listed will appear in the tables and figures that follow.

[b] Weight fraction of nitrile rubber in the polyblend, except as specified for the starting materials.

[c] Obtained using differential scanning calorimetry.

[d] Temperature corresponding to a torsional modulus of: T_f, 135,000 psi; T_f, 14,500 psi (1.0×10^9 dynes/cm^2).

[e] Weight fraction of vinyl stearate in the copolymer. The corresponding mole fractions were: expt. 1′, 0; expt. 2′, 0.005; expt. 3′, 0.10; expt. 4′, 0.15.

[f] Weight fraction of DOP in the mixture with PVC.

[g] Mole fraction of acrylonitrile in the nitrile rubber.

[h] n/v = not visible.

TABLE II
Constants of the Various Equations

Expt. no. Range[a]	Type	Estimated mechanical transitions, °K: Homopolymers T_{i2}[b]	T_{i1}[b]	Equations (1), (3), (4): K, °K	γ_A/γ_B[c]	Intercept σ_{bo}, psi, eq. (5)	Slope α, psi, eq. (5)
1–4	T_i	321.7	252.1	−19.36	0.4	60.82 ± 312.2	243.7 ± 36.6
	T_f	306.7	249.3	−74.20	0.9		
5–8	T_i	300.7	249.6	−0.01	0	−1096 ± 123.5	348.1 ± 171.7
	T_f	281.0	250.3	−62.48	−1.2		
9–10	T_i	287.6	254.2	0.03	0.4	−1309 ± 39.4	320.6 ± 5.8
	T_f	264.2	249.3	−33.46	−1700		
11–14	T_i	311.5	251.5	−41.20		−4624 ± 994	841.4 ± 122
	T_f	287.2	248.9	−55.89			
15–18	T_i	269.6	253.2	−23.64		−11379 ± 474.1	1950 ± 70.6
	T_f	243.9	249.3	−9.03			
19–22	T_i	240.8	252.7	−0.03		−8858 ± 8005	1587.1 ± 1268
	T_f	226.0	249.2	−0.03			
23–27	T_i	365.3	250.8	−74.10	2.3[f]	−1872 ± 340	482.7 ± 37.2
	T_f	354.4	249.0	−142.1	1.0[f]		
VS, 0.207[d]	T_i	321.6	245.7	−64.90	0.9	−1289 ± 1342	413.8 ± 188.3
	T_f	304.9	236.2	−63.40	0.8		
VS, 0.356[d]	T_i	300.3	244.4	−36.72	0.4	−4366 ± 1928	882.1 ± 307.9
	T_f	281.3	237.0	−53.65	1.1		
VS, 0.467[d]	T_i	268.8	227.5	0.04	0	−2971 ± 101	587.9 ± 15.4
	T_f	264.5	235.2	−35.61	1.5		
DOP, 0.207[d]	T_i	309.4	246.5	−62.80		−4019 ± 665	798.3 ± 94.2
	T_f	285.1	235.9	−57.10			
DOP, 0.356[d]	T_i	268.9	246.6	−33.30		−5436 ± 855	1056 ± 138.4
	T_f	244.8	234.2	−11.66			
DOP, 0.467[d]	T_i	240.5	246.0	−5.45		−3972 ± 176	815.1 ± 30.6
	T_f	223.9	234.8	9.08			
PVC, 1.00[d]	T_i	362.0	245.4	−69.30	0.7[f]	−1049 ± 739	364.6 ± 85.9
	T_f	354.3	236.2	−110.3	1.0[f]		

[a] Experiment numbers are from Table I. Consequently these numbers designate the polyblend system being correlated.

[b] Calculated as the limits of eq. (2). The values are close to the appropriate experimental values (primed quantities) of Table I.

[c] Ratios were taken for polyblends of VS–VCl copolymers and polyblends of DOP–PVC mixtures with NBR from Table I which had the same plasticizer content. For instance, ranges 1–4 and 11–14 were compared as were 5–8 with 15–18 and 9–10 with 19–22.

[d] These polyblend systems are not described in Table I. The nitrile rubber was Hycar 1452P-50.

[e] These constants correlate tensile strengths and torsional moduli at 23° for all of the data collected in this work.

[f] Subscript A, PVC; subscript B, VS—VCl copolymers, expt. ranges 1—4 and 28—31, respectively.

[g] Subscript 1, uncured; subscript 2, cured.

[h] These constants apply to eq. (5) only.

brium glassy and rubbery region of the curves. Moduli were also taken at room temperature, 23°C ($E_{t23°}$), and at 120°C ($E_{t120°}$); some of these were presented and discussed in the previous paper.[1] With the aid of these parameters, enough information is available to reconstruct approximate modulus–temperature curves for all of the listed data.

The flex temperature T_f for the polyblends remained fairly constant from system to system as NBR increased (Table I). These T_f values were usually a little higher than T_f for the parent elastomers (experiments 8′, 9′, 10′). In

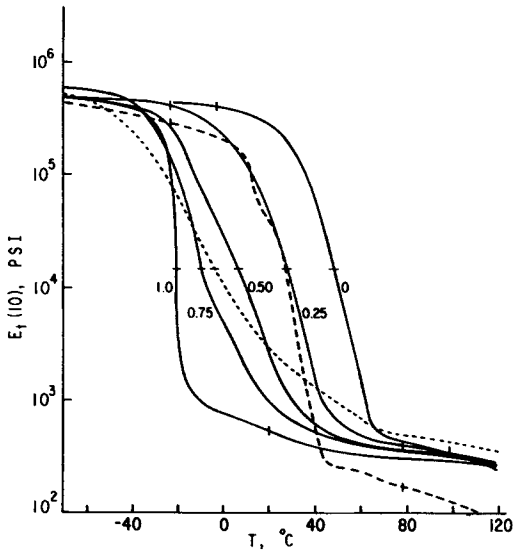

Fig. 1. Ten-second modulus–temperature curves for typical polyblends studied in this work. Pictured are polyblends of copolymers of vinyl stearate and vinyl chloride, containing 0.207 weight fraction vinyl stearate, with Hycar 1411. These data correspond to experiments 2′, 1, 3, 4, and 8′ of Table I. The weight fraction of NBR is indicated. Dashed line is for the starting copolymer containing 0.356 weight fraction of vinyl stearate (experiment 3′, Table I). Dotted line is for the mixture di-2-ethylhexyl phthalate (DOP) and poly(vinyl chloride) (PVC) containing 0.356 weight fraction of DOP (experiment 3′, Table I). Horizontal slashes designate T_i; vertical slashes indicate E_{t1} and E_{t2}, respectively, for selected systems.

contrast, the inflection temperature T_i shifted with temperature. This transition corresponded best to the main mechanical transition temperature of the polyblend because it is in the region of precipitous decrease in modulus (Fig. 1). Thus, these systems behaved as plasticized mixtures. They may, therefore, be considered compatible by the standards discussed in the previous paper. The question of compatibility and the type of blend morphology will be considered below in connection with observations by differential scanning calorimetry.

The magnitude of $-s$ in Table I provides an indication of the breadth of the modulus temperature curves. Values of $-s$ for the polyblends in most sections resembled those for the copolymers and the DOP–PVC mixtures (experiments 2′–4′ and 5′–7′); they are much smaller than for the elastomers. Because $-s$ for DOP–PVC was unusually small,[18–20] reflecting reinforcement by an out-of-phase crystalline network,[22] the analogy to the phase-separated polyblends is obvious. Likewise, in internally plasticized copolymers,[11,12] aggregates of main- and side-chain units produced through mutual insolubilization were deemed responsible for the lower slopes of the softer starting copolymers (experiments 2′, 3′, and 4′). Again, by analogy, small values of $-s$ for the polyblends suggests phase immiscibility.[3] However, because the slopes $-s_1$ and $-s_2$ were low for all systems, the transition region did not exceed 100° (Fig. 1).

The increases in the moduli of the polyblends at the highest temperature studied in this work, 120°C ($E_{t120°}$, Table I), where both phases were in their rubbery state, were produced by the fillers in the order PVC > DOP–PVC >

VS–VCl. This was the approximate order of E_{t2} decline for PVC and the copolymers. Consequently, it is a manifestation of the increase in the inflection temperature T_i as the free volume available to the filler decreased. The relatively high values of E_{t2} for PVC–DOP mixtures (experiments 5′–7′) and their polyblends again reflect crystallinity contributions to modulus and isochronal curve broadening. However, the elastomers raised the plateau region for the softest starting copolymers (experiments 3′ and 4′, compared to experiments 5–10). This suggests a greater contribution of entanglement and crosslinking from the networks in the elastomer than from the copolymer. In fact, entanglement coupling should have been eliminated in the latter by dilution by side chains.[23]

To illustrate the effect produced by this probable pseudoequilibrium network, the viscoelastic properties of the starting compositions and their polyblends can be compared by reference to Figure 1. The vinyl stearate content of the copolymers may be adjusted to give a transition region similar to those of specific polyblends. The dashed line represents a 36 wt-% vinyl stearate copolymer, which partially fits the transition region of a polyblend containing 75 wt-% of a vinyl stearate (0.21 weight fraction)–vinyl chloride copolymer and 25 wt-% Hycar 1411. However, the rubbery plateau for the neat copolymer is very low, suggesting a decrease in the relative fraction of its network coupling points. Note that a DOP–PVC mixture of the same wt-% plasticizer (36%, dotted line) had better low-temperature properties than did the polyblend or copolymer, yet retained an effective rubbery plateau. The superior properties introduced by crystalline networks in DOP–PVC mixtures compared to amorphous internally plasticized systems have been extensively treated[11,12,17–22] and will not be discussed further here. However, the improvement to the copolymers induced by polyblending is obvious.

Relation Between Mechanical and Glass Transitions

Figures 2 and 4 are differential scanning calorimetry scans of the starting copolymers and DOP–PVC mixtures, respectively. Figures 3 and 5 are scans for selected polyblends using Hycar 1411. Figure 3 represents data for bulk PVC and copolymer blends; Figure 5 shows data for the same PVC and for DOP–PVC mixtures. These curves are typical of all of the polyblend data. The dashed lines in Figures 3 and 5 are scans for the unmixed polycomposites. These were prepared by weighing a few large pieces of both blend compositions in the same pan. These data were intended to sharply define the T_g contributions of each phase and to produce scans showing at the highest resolution possible the effect of the separated phases. The onset temperatures were taken as T_g, as described previously.[11,16] The occurrence of transitions (vertical slashes) at the same temperature in these curves and in the experimental polyblends provides clear evidence for incompatibility in the latter.

Several features of the scans in Figures 2 through 5 are noteworthy. The scans of the starting bulk PVC, elastomer, and copolymers (Fig. 2) were relatively well defined; those for DOP–PVC mixtures (Fig. 4) were diffuse. As can be seen, these features were carried over into the polyblend scans (Figs. 3 and 5). The polyblend scans were considerably more diffuse than those of

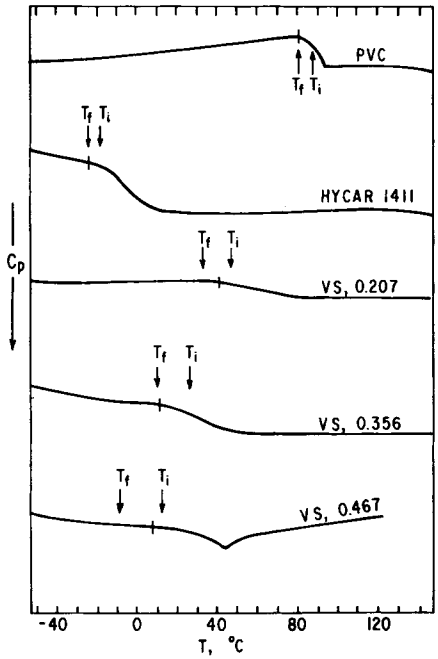

Fig. 2. DSC traces of the starting homopolymer, nitrile rubber, and copolymers. The weight fraction of vinyl stearate in the copolymers is indicated. Vertical slashes indicate T_g. Temperatures of T_i and T_f (Table I) are given.

the unmixed polycomposites (dashed lines), reflecting a more intimate microstructure in the former case, but the presence of two distinct T_g values lying close to those of the unmixed polycomposites was always noted. In the two lower curves in Figure 5, the T_g values of the elastomer and DOP mixture nearly coincide; consequently, only one T_g can be observed for these polyblends and polycomposites. In Figures 3 and 5, the T_g of the pure starting polymer, copolymer, or mixture is denoted by the letter x. While the mechanical transitions T_f and T_i, marked by arrows in all figures, lay close to the temperature region for T_g in the starting compositions (Figs. 2 and 4), both of these transitions were close to the T_g of the elastomer phase in the 50/50 polyblends shown in Figures 3 and 5. Of special importance, T_i was not close to the T_g of the polymeric filler in the two upper curves in Figures 3 and 5. It is also noteworthy that the scans for the polyblends resolve the elastomeric transition (T_{g1}, Table I) with greater clarity than that of the filler (T_{g2}, Table I). This was observed even for those polyblends containing the smallest weight fraction of elastomer in Table I. This appears to provide evidence over that of the shifting T_i in Figure 1 that the nitrile rubber constitutes the continuous phase in these polyblends. Phase incompatibility is clearly indicated by the T_g behavior.

A different picture is presented when the mechanical transitions are plotted as a function of the weight fraction of elastomer in the polyblends. Selected data are shown in Figure 6. It can be seen that both T_i and T_f declined monotonically with the weight fraction of NBR, designated w_1. In contrast, T_g data (dotted lines) from DSC remained close to the T_g of the starting components. It is also seen that T_{g1} and T_f had similar values, espe-

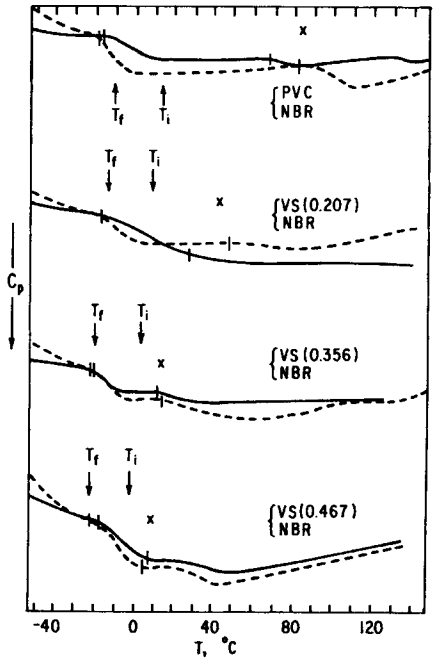

Fig. 3. DSC traces of selections of the polyblends (solid lines) and the unmixed polycomposites (dashed lines). All data are for approximately 0.5 weight fraction polyblends and polycomposites using Hycar 1411 as the nitrile rubber. The weight fraction of vinyl stearate in the copolymers is given in the brackets. Vertical intersections at left designate T_{g1}; those to the right T_{g2}. Temperature of T_i and T_f (Table I) are also indicated. The temperature marked x is the T_g of the starting copolymers.

cially at high w_1. Clearly, the mechanical transitions are showing the behavior of plasticized systems; as demonstrated earlier, they indicate that these polyblends, and the others of this work, are compatible.

The seeming contradiction, in which the polyblends are compatible by mechanical spectroscopy and incompatible by thermal analysis, may be resolved by considering that the mechanical transition reflects the properties of a large volume element of the microstructure than does DSC. The glass transition is produced by short-range cooperative segmental motions of about 30–40 chain units[24] and so would be sensitive to motion in each separate phase. The mechanical spectroscopy used in this work, in contrast perhaps to that of other workers,[2,25,26] appeared to monitor larger volume elements; these would incorporate regions of both phases if the morphology were ultrafine.[25,27–29] Under these conditions, the isochronal curves would reflect contribution to moduli from segmental interaction of both phases, including their respective interphases, so that T_i would tend to shift with temperature as observed and so produce the appearance of compatibility.[25] It may be tentatively concluded that these polyblends are incompatible at phase dimensions approaching molecular,[27–29] but are compatible at supermacromolecular phase dimensions. Acceptance of this conclusion implies that an ultrafine phase morphology of intermingled anisomorphic domains characterizes the microstructure of these polyblends.[25,27–29] Ultrafine but more ordered, nonductile, iso-

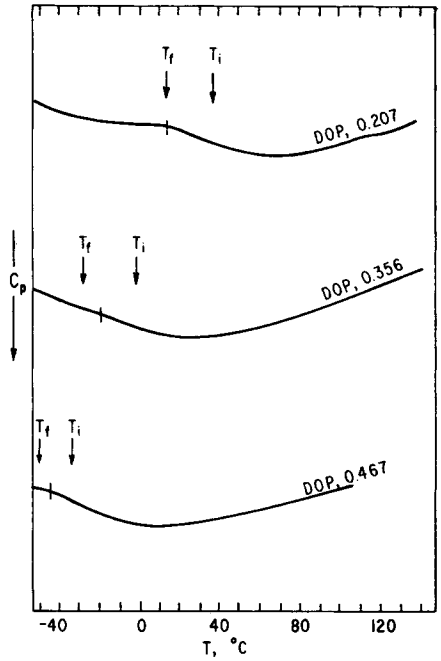

Fig. 4. DSC traces of the starting di-2-ethylhexyl phathalate (DOP)–poly(vinyl chloride) mixtures. The weight fraction of DOP in the mixtures is indicated. Vertical slashes indicate T_g. Temperatures of T_i and T_f (Table I) are also given.

morphic inclusions seem to introduce incompatibility as judged by results from electron microscopy and mechanical spectroscopy measurements.[2,30–40]

Because of elastomers appear to behave like plasticizers for the modified polymeric component of these mixtures, it might be instructive to treat the data by expressions in the literature that relate T_g to plasticizer content for the case of polymers solvated classical by solvents. By the use of one such expression, the empirical relation between T_i (or T_f) and the weight fraction of NBR was found in this work to be

$$T_i = w_1 T_{i1} + w_2 T_{i2} + K(w_1 w_2) \tag{1}$$

where temperature T is in degrees Kelvin and w is the weight fraction of the respective phases; subscript 1 signifies the nitrile rubber and subscript 2 stands for the DOP or VS modified polymer phase. This meaning of the subscripts will be followed for the balance of this paper. This equation is of the same form as the general empirical equation relating T_g and the weight fraction of a monomeric liquid plasticizer[41,42] or an internal fatty ester plasticizer.[11,12,43,44] In eq. (1), K is an empirical constant, reflecting the efficiency of the elastomer in reducing the respective transition temperature as composition changes. In this work, if K were zero, NBR would be acting merely as a diluent. This, in fact, was observed when vinyl stearate was studied as a simple internal plasticizer for vinyl chloride.[11] To obtain the values of K for the systems under investigation, all T_i and T_f data (Table I) were curve fitted by

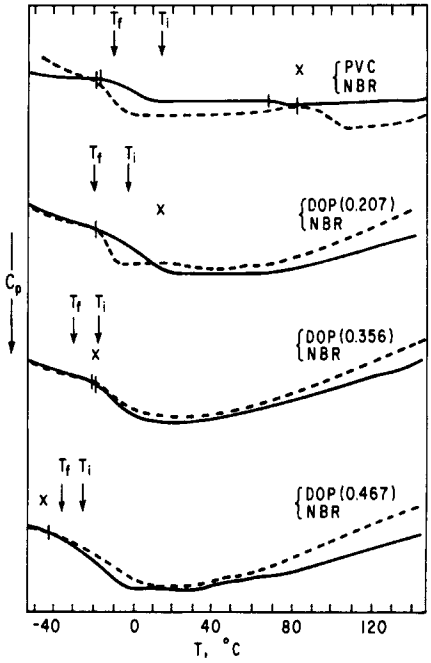

Fig. 5. DSC traces of the polyblends (solid lines) and the unmixed composites (dashed lines). All data are for approximately 0.5 weight fraction polyblends and polycomposites using Hycar 1411 as the nitrile rubber. The weight fraction of DOP in the initial DOP–PVC mixtures is given in the brackets. Vertical intersections at left indicate T_{g1}; those to the right, T_{g2}. The temperature of T_f and T_i (Table I) are also indicated. The temperature marked x is the T_g of the starting mixture.

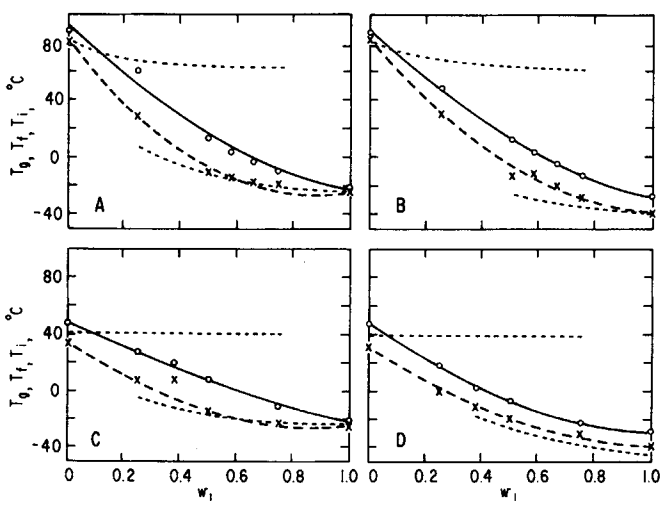

Fig. 6. Plot of T_g, T_f, or T_i vs. the weight fraction of nitrile rubber, w_1, in polyblends of poly(vinyl chloride) (PVC) with (insert A) Hycar 1411 and (insert B) Hycar 1452P-50. Corresponding data are presented for polyblends of vinyl stearate–vinyl chloride copolymers, containing 0.207 weight fraction of vinyl ester, with (insert C) Hycar 1411 and (insert D) Hycar 1452P-50. T_i (solid line) and T_f (dashed line) calculated using eq. (1) and the constants of Table II. Upper dotted line approximates the T_g of the homopolymer or copolymer phase; lower dotted line approximates the T_g of the NBR phase.

computer as functions of w_1. The data were significant in accordance with the following relation, shown here for T_i:

$$T_i = T_{i1} - kw_1 + k'(w_1)^2 \tag{2}$$

From the constant k, the parameter K was obtained[11] as

$$k = -k + (T_{i2} - T_{i1}) \tag{3}$$

Values of K, T_{i2}, and T_{i1} for a selection of the polyblends studied in this investigation are listed in Table II. T_{i2} and T_{i1} are estimates by means of eq. (2) of the values of the transition temperatures of the starting components (polymers and elastomers) making up the polyblends. These values are close to the appropriate experimental values (primed quantities) of Table I. The constant k is not given but was used to calculate K by eq. (3). The larger the negative value of K in the table, the greater the concavity of the curves in Figure 6 and, hence, the greater the efficiency of the elastomer in reducing T_i or T_f. However, comparison between different systems can be made only when data are compared at a common reference difference of $T_{i2} - T_{i1}$. It was desired to compare the efficiency of an NBR in lowering the T_i or T_f of a copolymer plasticized by its co-units with its efficiency in lowering the T_i or T_f of a polymer plasticized by the same fraction of external plasticizer. To do this, the values of K exhibited by the two systems were related through the respective $(T_{i2} - T_{i1})$ values by eq. (4):

$$\gamma_A/\gamma_B = K_A/[(T_{i2} - T_{i1})_A/(T_{i2} - T_{i1})_B]K_B \tag{4}$$

where the A subscript was assigned to the copolymers and B to the DOP–PVC mixtures as fillers. Values of the comparison ratio γ_A/γ_B are also listed in the table.

In eq. (4), when the elastomer used with B is more effective in lowering the T_i of B than that of A, then $\gamma_A/\gamma_B < 1.0$; for the reverse case, $\gamma_A/\gamma_B > 1.0$. When the two systems are equal in effectiveness, $\gamma_A/\gamma_B = 1$. For cases where $K_A < K_B$ and $K_A \simeq 0$, $\gamma_A/\gamma_B \simeq 0$; for the reverse case, when $K_B \rightarrow 0$, $\gamma_A/\gamma_B \simeq \infty$. A negative value for the ratio indicates antiplasticization because $T_{i1} > T_{i2}$ and the relation becomes useless for the purpose intended.

While all possible types of behavior are displayed by γ_A/γ_B in Table II, in general, it may be seen that the elastomers reduced T_i and T_f of the DOP–PVC mixtures a little more efficiently than those of the copolymers. In general, the difference between internal and external plasticizer effect are small enough that additivity of free volume alone can account for most of the observed ratio similarities. Ratios approaching zero or large numbers do seem to indicate the intrusion of other factors, however. Because the ratio γ_A/γ_B was 1.5 for DOP–PVC mixtures (designated system A, using K from ref. 11 of −171.1°K) and PVC plasticized by Hycar 1411 elastomer (experiments 23–27, Table II) as system B, the liquid plasticizer was considerably more efficient than NBR in plasticizing PVC, as has been observed.[45,46] Thus, the constants of Table II, by permitting T_i or T_f to be calculated for any blend composition, satisfy the criteria for compatibility even to following relationships derived for monomeric plasticizers. As a consequence, the poor low-temperature properties of vinyl stearate copolymers[12] (experiments 2′–4′, Table I) can be improved by polyblending with a low-T_g elastomer.

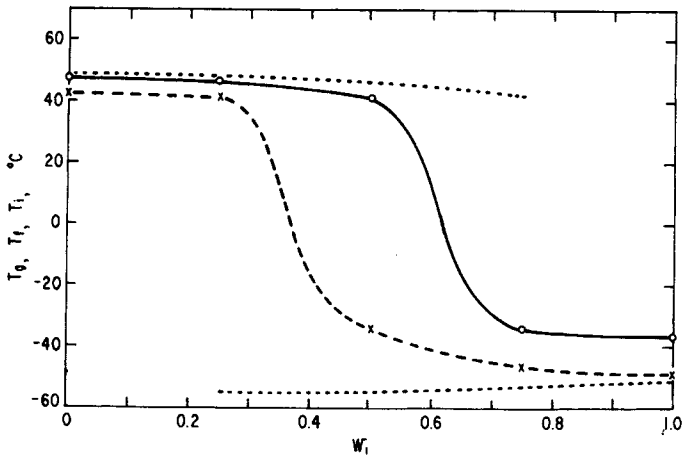

Fig. 7. Plot of T_g, T_f, or T_i vs. the weight fraction of nitrile rubber, w_1, in polyblends with copolymers of vinyl acetate and vinyl chloride containing 0.60 mole fraction of vinyl acetate. The nitrile rubber was AN 25. T_i is solid line; T_f is dashed line. Upper dotted line approximates the T_g of the polymer phase; lower dotted line approximates the T_g of the nitrile rubber phase.

Finally, transition temperature data are correlated (Fig. 7) for vinyl acetate–vinyl chloride copolymers. Here, the decline in the mechanical transition was decidedly not monotonic. There is a suggestion that these systems are not mechanically compatible and that phase inversion occurs in the vicinity of a weight fraction of 0.5 NBR. Whether this is a function of the specific morphology or a reduced ductility of these copolymers of high vinyl acetate content is unknown at present.

Comparison of Mechanical Properties at $T - T_i$

The only accurate basis for comparing the effect of temperature on the ultimate mechanical properties, such as tensile strength, is at the same free-volume increment $T - T_g$.[8,9] For soft elastomers at their equilibrium moduli, where Poisson's ratio is 0.5, arguments using the WLF equation show that $\eta/\eta_{T_g} = E/E_{T_g}$ in this temperature region.[47] The range T–T_g corresponds to T–T_i for the polyblends of this work, because T_i is the temperature where the filler undergoes its transition. Above T_i, therefore, a mixed rubber is present, although the bulk viscosities of the components vary widely. Tensile strengths in this work were computed using an empirical relation between torsional modulus E_t and experimental tensile strength. The relation was

$$\sigma_b = \sigma_{b0} + a(\ln E_{t23°}) \tag{5}$$

where σ_b is the tensile strength at break in psi, and $E_{t23°}$ is found in Table I. The constants σ_{b0} and a for the various polyblend systems are listed in Table II. Consequently eq. (5) assumes that linear viscoelasticity persists at all strains to break. This has often been found[8,9] and treated theoretically[48] for certain elastomers.

An example of the comparison is given in Table III for all of the polyblends of the 0.207 weight fraction vinyl stearate–vinyl chloride copolymer and Hycar 1411 (experiments 1–4, Table I). Torsional moduli E_t were read from

TABLE III
Torsional Moduli and Computed Tensile Strengths at Several $T - T_i$ for One Typical Polyblend System

Expt. no.[a]	w_{NBR}	T_i, °C[b]	$T - T_i = 12$ ln E_t, psi[c]	$T - T_i = 12$ σ_b, psi[d]	$T - T_i = 25$ ln E_t, psi[c]	$T - T_i = 25$ σ_b, psi[d]	$T - T_i = 50$ ln E_t, psi[c]	$T - T_i = 50$ σ_b, psi[d]
1	0.25	28	7.24	1825	6.40	1560	6.04	1533
2	0.38	20	8.16	2049	6.40	1621	6.04	1533
3	0.50	8	7.90	1986	6.75	1706	6.09	1545
4	0.75	−9	8.24	2070	7.09	1789	6.29	1594
		ave.[e]	7.89	1983	6.60	1669	6.11	1551

[a] Corresponds to the order of Table I.
[b] ln E_t at T_i = 9.58 psi; $\sigma_{b(\text{ave.})}$ at $T - T_i = 0$ computed from this quantity and the appropriate specific correlation constants of Table II, when possible.
[c] Taken from the modulus–temperature curves.
[d] Computed from the specific correlation constants of Table II.
[e] Average values of stress to break, $\sigma_{b(\text{ave.})}$, as used in Fig. 11.

the experimental modulus temperature curves at each value of $T - T_i$ as shown. The failure stresses were computed using eq. (5) and the specific constants given in Table II (experiments 1–4). As can be seen, at each $T - T_i$ in the table, E_t and σ_b remained fairly constant as NBR content increased. Average values, characteristic of the polyblend system, could be taken as shown. Similar results were found for all systems in Tables I and II.

Selected comparisons are shown in Figure 8. Here, the average values of computed break stress, at several $T - T_i$, are plotted as a function of the

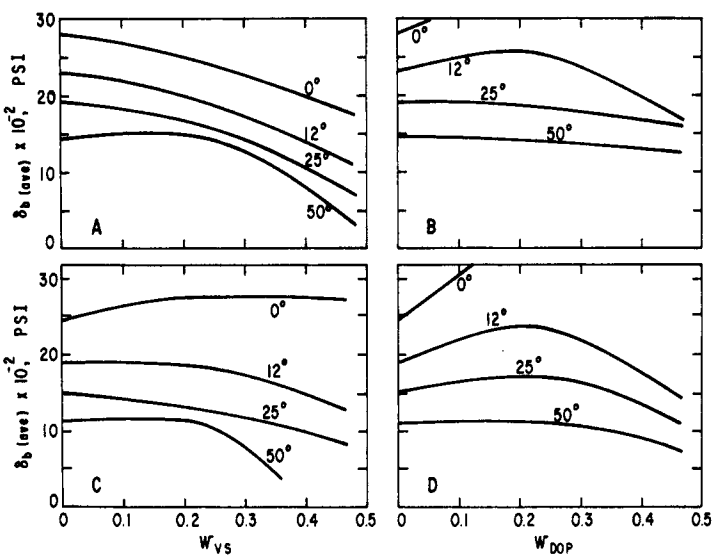

Fig. 8. Computed average break strength $\sigma_{b(\text{ave})}$ at several $T - T_i$ (as indicated in the figure) vs. the weight fraction of vinyl stearate, w_{VS}, in the copolymers (A), (C) or di-2-ethylhexyl phthalate (DOP) and in mixtures (B), (D). Hycar 1411 was used in (A) and (B); Hycar 1452P-50 in (C) and (D). The constants of eq. (5) given in Table II were used to calculate σ_b and thus $\sigma_{b(\text{ave})}$ for each polyblend system as illustrated in Table III.

weight fraction of vinyl stearate in the starting copolymers in inserts A and C and of DOP in the starting mixtures in inserts B and D. Hycar 1411 was the elastomer in inserts A and B; Hycar 1452P-50 was used in inserts C and D. Failure tensile strengths stayed relatively constant for bulk PVC ($w_{VS} = 0$) through a weight fraction of 0.207 for the vinyl stearate in a VS–VCl copolymer using both elastomers (inserts A and C); they then declined monotonically at higher vinyl ester contents. In contrast, DOP data, inserts B and D, went through a slight maximum at the same weight fraction of liquid plasticizer. Some decline in strength was also observed here at higher plasticizer contents. Clearly, use of more plasticizer in the filler than a critical amount (~ 20 wt-%) will reduce mechanical properties as the temperature is raised. Similar results were found for the other systems in Table I. It may be concluded that approximate mechanical equivalence of bulk PVC and fillers containing up to 0.207 weight fraction of either internal or external plasticizer persists over temperature ranges of at least 50°C. This parallels the findings of the previous paper[1] for data compared at room temperature. The overall data suggest that failure in these elastoplastics follows an extension of the principles of linear viscoelasticity when they are in a mixed rubbery state above T_i.[8,9,48]

Isochronal Temperature Composition Diagrams

Isochronal temperature–composition diagrams relating modulus both to temperature and to the weight fraction of filler in the polyblends, w_2, are shown in Figure 9. These were first used by Yannas for gelatin plasticized by glycerol[10] and later by Jordan[12,43] to describe internally plasticized vinyl chloride copolymers. In this plot, the indicated moduli (isothenes), in dynes/cm^2, are shown which demark convenient regions of viscoelastic behavior with respect to both temperature and composition of the polyblend. Thus, moduli higher than 10^{10} dynes/cm^2 are in the glassy region, whereas those lower than 10^7 are approaching the terminal region of viscoelastic behavior. The dashed line in all inserts represents the usual upper region of temperatures studied with the torsional modulus instrument (120°C). The isothene, 10^9, corresponds to T_i for all systems. Vertical sectioning (called isopleths) gives the modulus of a given polyblend with respect to temperature. Consequently, this roughly represents the isochronal temperature curves of Figure 1. Horizontal sectioning (called isotherms) give the effect of composition on moduli at fixed temperatures. Isotherms at 23°C were extensively described in the previous paper. Alternatively, the diagram as a whole may be considered and compared with the diagrams of different systems for indications of relative processing ease and use-temperature ranges. Thus, these diagrams summarize much of the information on viscoelasticity contained in both papers of this series.

Insert A of Figure 9 is a diagram of Hycar 1411 filled by vinyl stearate–vinyl chloride copolymers, while in insert B the fillers were DOP–PVC mixtures, and in C, bulk PVC was used. In insert A, the isopleths at most w_2 had similar magnitudes. Those in inserts B and C are more varied, increasing in temperature at high filler contents. Because the isothenes of insert A are generally lower than those in inserts B and C, processing of this system should be easier than that of the latter compositions. Greater ease of pro-

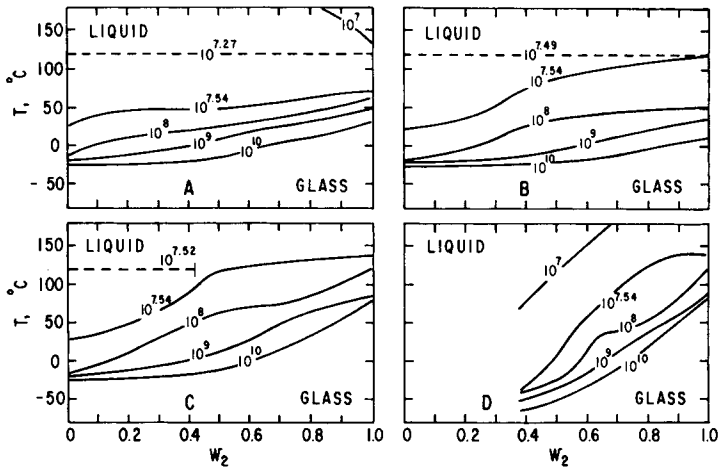

Fig. 9. Isochronal temperature–composition diagrams for polyblends of Hycar 1411 and vinyl stearate–vinyl chloride copolymers containing 0.207 weight fraction vinyl stearate (A), DOP–PVC mixtures containing 0.207 weight fraction of DOP (B), and poly(vinyl chloride) (C). Diagrams for DOP–PVC mixtures containing no NBR are shown in (D).

cessing was actually observed for the copolymer polyblends, as indicated by the lower milling and molding temperature used in the previous paper.[1] Processing of PVC in nitrile rubber has long been a problem,[49] only recently relieved by use of powdered rubbers.[45] While DOP has long been added to PVC–NBR blends to act as a processing aid,[46] the data of insert B, when compared with the data of insert A, tend to challenge its usefulness. However, the systems in insert B have greater high-temperature utility than those of insert A.

Isotherms at 23°C summarize the major findings concerning viscoelasticity and mechanical equivalence of the previous paper. Since these were adequately reviewed there, they will not be discussed further. It should again be stressed, however, that to attain a given modulus at constant temperature (say, 10^8 dynes/cm^2 at 23°C), more NBR is needed for PVC alone (insert C) than is required for both types of pre plasticized filler compositions (inserts A and B).

Finally, the contrasting behavior of PVC plasticized by DOP (insert D) is to be noted. Isothenes here were more sensitive to composition than in the polyblends. The spread of the isothenes with rising temperature reflects broad modulus–temperature curves and wide use-temperature ranges. The diagrams do suggest the need for higher processing temperatures, especially at low DOP contents. It is clear that more elastomer will be needed for a given level of plasticization of bulk PVC (insert C) than of DOP in DOP–PVC mixtures (insert D), reflecting the difference in the glass temperatures of the elastomer (T_g − 23°C) and DOP (T_g − 87°[11]). Similar diagrams could be constructed for the other elastomer polyblends, but the results would be similar to these.

SUMMARY AND CONCLUSIONS

The significant parameters from isochronal modulus–temperature curves have been presented in tabular form and by other means for all of the poly-

blend systems studied in the previous paper.[1] Glass transition temperatures of each phase, obtained by differential scanning calorimetry, indicated phase immiscibility. The range of the segmental motions responsible for glass transitions was considered to be narrow enough to focus on each separate phase. In contrast, the shifting of the inflection temperature T_i with composition satisfied an accepted criterion for compatibility. An empirical relation involving a single parameter, satisfactory for describing the relation between T_g and concentration of monomeric plasticizer, also successfully described T_i for the polyblends with change in elastomer content. Polyblends reinforced by vinyl acetate–vinyl chloride copolymers appeared to be completely incompatible, however. From a relation between torsional modulus at ambient temperature and tensile strength, break stresses at various free volume increments above T_i, $(T - T_i)$, were estimated for the polyblends and compared. Approximate equivalence was found for bulk PVC and fillers containing 20 wt-% of both internal and external plasticizer, over temperature differences of 50°C. Polyblending improved the viscoelastic and low-temperature properties of the vinyl stearate copolymers investigated. As fillers for the NBR elastomers, they compared favorably with bulk PVC and DOP–PVC mixtures. This conclusion was supported, and better processibility suggested, for the vinyl ester copolymer systems from data presented in diagrams relating modulus to both temperature and polyblend composition.

The authors thank Mrs. Ruth D. Zabarsky for the operation of the computer. Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

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Received August 5, 1975
Revised December 3, 1975