JOURNAL OF APPLIED POLYMER SCIENCE VOL. 20, 2757–2778 (1976)

Polyblends. III. Correlation of the Viscoelastic Data for Polyblends of NBR and Plasticized Vinyl Chloride Compositions with Theories of Polycomposite Behavior

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Synopsis

Viscoelastic data obtained on the polyblends described in the previous two papers together with some new data have been correlated with various theories derived for the viscosity and continuum properties of polycomposites, to gain insight into the nature of compatible domain interactions. Unmodified theories of Mooney, Eilers and Van Dyck, Guth and Smallwood, and Kerner did not correlate with the observed viscoelastic data. However, when the Kerner relation was substantially altered (after allowing for phase inversion following procedures of Halpin and Tsai as modified by Nielsen), an adequate description of torsional modulus behavior at ambient temperature was obtained. To characterize tensile modulus (100%), however, a new expression was necessary. Both procedures invoked a critical modulus for the blend with respect to composition at which phase inversion was initiated. The critical volume fraction associated with this modulus increased inversely with the T_g of the filler; when the filler T_g was below the ambient temperature, the blends behaved as mixed rubbers, and torsional modulus ratios followed the lower Kerner relation at all blend compositions. It was concluded that polyblends having isochronal modulus–temperature curves that shift with composition over the temperature scale yet are anomalously broad as in the present work should be classified as systems exhibiting restricted molecular mixing. The restricted molecular mixing character exhibited by the polyblends could be explained by a plurality of mixed-phase responses to deformation produced in a morphology of interlocking microdispersions. Favorable polarity effects and high filler ductility were considered responsible for the domain interactions. No evidence was found for true molecular compatibility in the blends. An analysis of temperature effects on the blend viscoelasticity resulted in a temperature analog of the composition behavior.

INTRODUCTION

The two previous papers[1,2] have presented data on the mechanical and viscoelastic properties of polyblends of several elastomeric butadiene-acrylonitrile copolymers with polymeric fillers whose properties were, in turn, modified by plasticization. Mechanical properties were obtained at room temperature in the first paper and over a wide temperature range in the second. In this paper, the available and some additional data will be correlated with several modified theories describing viscosity and continuum properties of polycomposites. To accomplish this, the effect was studied of a complete range of inclusion volume fractions on composite moduli at ambient temperatures. To provide this range, new polyblends were prepared especially for this work. These yielded more mechanical data at high filler contents where presumably elastomeric phase continuity had been inverted.[3-5] The volume fraction of filler needed to produce phase inversion was expected to be a function of both blend composition and plasticizer content of the particulate filler. Consequently, the wide ranging variation of moduli with blend type and composition obtained in this work should provide much greater insight on the factors contributing to mechanical compatibility.[6-12] Mechanical compatibility was observed for the polyblends in the first two papers,[1,2] but results of thermal analysis disputed this observation. However, the existence of compatibility was restricted in these papers either to systems of mixed elastomers at ambient temperature or to blends where the soft phase was largely continuous. Because the blend moduli were functions of both plasticizer content and temperature, the effect of the latter will also be qualitatively treated in this work.

EXPERIMENTAL

The polyblends of this paper were prepared and their mechanical and viscoelastic properties determined by reported procedures.[1,2] Literature values of the densities of polybutadiene and polyacrylonitrile were used to compute densities for the copolymers by assuming additivity of volumes. Densities of poly(vinyl stearate) and poly(vinyl chloride) were computed by the group additivity method of Van Krevelin;[13] the densities of the copolymers were then estimated by the procedures used for the nitrile rubbers. By using literature values of density for DOP and the calculated density for PVC, the densities of the DOP–PVC mixtures were estimated. From the known weight fraction of the blends and the densities of the blend components, volume fractions were then computed. No attempt was made to estimate the volume fraction of the dispersed phase by assuming that a portion of the continuous phase was present as an entrapped contaminant.[14,15] Most of the computations of this paper were done with an IBM 1130 computer.

RESULTS AND DISCUSSION

Compositions, tensile properties, viscoelastic properties, and modulus ratios are listed in Table I for new polyblends having decreased NBR content. These were introduced to provide greater detail to mechanical properties in the higher filler composition region, where the rigid phase was expected to be largely continuous.[3-5] The new data were concentrated on two polyblend systems using Hycar 1411. These were selected to be representative of the blended systems having the highest filler moduli. Because much of the following discussion will concern blends of lower filler content, data previously reported[1,2] on such systems were reproduced here for convenience. In addition, a good deal of the data evaluated will come from the two previous papers. Modulus ratios, considered in this paper for the first time, are defined as follows: unless otherwise designated, E/E_1 is the ratio of the 100% modulus[1] of the polyblend to that of the starting elastomer; E_t/E_{t1} is the ratio of the torsional modulus of the polyblend at room temperature, $E_{t23°}$,[2] to the

TABLE I

Compositions, Tensile Properties, Viscoelastic Properties, and Modulus Ratios of Selected Polyblends

	Vinyl polymer in polyblend		Tensile properties			Viscoelastic properties				Modulus ratio[c]	
Expt. no.[a]	Weight frn.	Volume frn.	Strength, psi	Modulus × 10^{-5}, psi[b]	% Elong.	T_f, °C	T_i, °C	$E_{t23°}$ × 10^{-5}, psi	$E_{t120°}$, psi	ln E/E_1	ln E_t/E_{t1}
			Homopolymer: Poly(vinyl Chloride) Blended with Hycar 1411								
1	1.0	1.0	6270	1.90	4.1	82	88	5.50	1500	7.38	6.96
2	0.90	0.874	6520	1.75	14.7	65	78	5.20	900	7.29	6.91
3	0.80	0.754	4500	1.10	144	45	70	2.76	690	6.83	6.27
4	0.75	0.697	4040	0.625	66.3	29	60	1.80	660	6.26	5.85
5	0.70	0.642	3880	0.564	122	27	56	1.51	800	6.16	5.67
6	0.60	0.535	3220	0.235	208	9	43	0.520	660	5.29	4.61
7	0.55	0.484	2950	0.126	168	1	39	0.235	460	3.66	3.81
8	0.50	0.434	2380	0.0153	198	−10	14	0.105	500	2.56	3.01
9	0.42	0.357	2320	0.0109	293	−14	5	0.0550	500	2.22	2.36
10	0.34	0.283	2030	0.00701	357	−17	−2	0.0265	390	1.77	1.63
11	0.25	0.204	1580	0.00537	364	−17	−8	0.0121	400	1.51	0.844
12	0	0	159	0.00119	520	−24	−20	0.00520	270	0	0
		Copolymer: Vinyl Stearate, 0.05 Mole Fraction (0.207 Weight Fraction) and VCl Blended with Hycar 1411									
13	1.0	1.0	5830	1.50	11.4	33	48	2.46	240	7.14	6.16
14	0.90	0.882	2970	0.591	65.7	28	42	1.68	340	6.21	5.78
15	0.85	0.824	3095	0.521	217	25	40	1.48	340	6.08	5.65
16	0.80	0.768	2610	0.265	135	14	35	0.660	320	5.41	4.84
17	0.75	0.713	2510	0.0182	278	9	28	0.310	270	2.73	4.09
18	0.62	0.575	2380	0.0120	399	−9	20	0.0900	270	2.31	2.85
19	0.50	0.453	1910	0.00719	356	−14	8	0.0174	290	1.80	1.21
20	0.25	0.216	1640	0.00415	600	−22	−9	0.00850	270	1.25	0.492

[a] Experiments 1, 4, 8–12, 13, and 17–20 were described in the two previous papers. The limited data repeated here are for convenience in treating the data of this paper.

[b] Initial modulus reported for all samples exhibiting yield; for the rest (experiments 8–12 and 17–20), the modulus at 100% elongation is reported.

[c] Designations are as follows: E/E_1 is the ratio of the experimental tensile modulus to that of the NBR; E_t/E_{t1} is the corresponding ratio for torsional moduli at 23° C.

same modulus for the elastomer. As before, w is the weight fraction, while subscripts 1 and 2 designate elastomer and filler, respectively. Volume fractions were designated v; these were estimated by the procedure given in the experimental section. Copolymers used as fillers are sometimes given the shorthand notation exemplified by VS (0.207) VCl. This designates a copolymer of vinyl stearate and vinyl chloride containing 21 wt-% of vinyl stearate (5 mole-%).

An examination of the data for the PVC-filled systems in Table I shows that the mechanical properties of the polyblends containing relatively small amounts of NBR (experiments 1–5) somewhat resembled those of tough impact materials[6,8,16–18] in having high initial modulus but substantial elongation. Even T_i of these blends did not appear to shift substantially with composition. This suggests that the polyvinyl component was the continuous phase in these systems. Consequently, these appeared to show more parallel mixing response, based on Takanagi models,[9] compared to previous systems where series response seemed to predominate.[19,20] At higher NBR contents, the properties resembled those of plasticized systems, as was discussed extensively in the previous paper.[2] The same mixing behavior did not seem to be present in the polyblends containing vinyl stearate copolymers (experiments 13–18), however. Clearly, as composition changed, there appeared to be a transition from mechanically incompatible systems to compatible systems in the first series but not in the second. A detailed investigation of these trends, and others not anticipated above, will be pursued in the sections that follow.

Hard Dispersions in a Liquid Matrix

For a dispersion of hard spheres in a liquid or rubber-like matrix, Mooney[21] developed the relation

$$\ln \eta/\eta_1 = k_e v_2/[1 - (v_2/v_m)] \qquad (1)$$

where k_e is the Einstein coefficient with the value of 2.5 for dispersed spheres, v_2 is the volume fraction of filler, and v_m is a sedimenting volume defined as the critical maximum volumetric packing fraction above which the available liquid is no longer able to wet the filler properly because of its tight packing. This condition heralds phase inversion. Equation (1) applies only when Poisson's ratio ν for the matrix is 0.5, i.e., when a hard filler is dispersed in a soft rubber-like matrix. Under these conditions, $\eta/\eta_1 = E/E_1 = E_t/E_{t1}$.[22]

An equation similar to the Mooney equation is that of Eilers and Van Dyck[23]:

$$E/E_1 = [1 + (kv_2/1 - S'v_2)]^2 \qquad (2)$$

where E_i are Young's moduli and where, according to Robinson,[24] $2k$ will be approximately equal to k_e (the Einstein coefficient), while $S' = 1/v_m$. This equation is also limited to systems where $\nu = 0.5$.

The best-known equation is that of Guth[25] and Smallwood.[26] This equation, however, is of limited utility, being accurate only for a few systems and then only to $v_2 \simeq 0.3$. The equation is

$$E/E_1 = 1.0 + k_e v_2 + 14.1\,(v_2)^2 \qquad (3)$$

All of these equations suffer from being applicable only when $\nu = 0.5$ and, therefore, useful only in describing reinforcement of rubber. The equation of Kerner,[27] which assumes a specific morphology, is more versatile in providing an approximate method for calculating the elastic moduli of both elastomers filled by rigid inclusions and rigid matrices filled by soft inclusions. On the other hand, the more exact and more general treatment of Hashin and Shtrikman,[28,29] based on variational principles,[30,31] is independent of phase morphology but leads to bounds. However, for binary component polycomposites, the Hashin-Shtrikman limiting highest lower bound and lowest higher bound are algebraically identical to single-valued Kerner expressions for, respectively, filled elastomers and rigid matrixes containing soft inclusions. Thus, the general form of the Kerner equation, for spheres embedded in a matrix, is

$$E/E_1 = \frac{v_2E_2/[(7-5\nu_1)E_1+(8-10\nu_1)E_2]+v_1/[15(1-\nu_1)]}{v_2E_1/[(7-5\nu_1)E_1+(8-10\nu_1)E_2]+v_1/[15(1-\nu_1)]} \qquad (4)$$

While this equation was originally derived for shear modulus, it is equally applicable[32,33] to other moduli, such as Young's E or torsional E_t of this work.

For a soft dispersed phase in a rigid matrix, eq. (4) can be simplified to

$$E_1/E = 1.0 + (v_2/v_1)[15(1-\nu_1)/(7-5\nu_1)] \qquad (5)$$

where $\nu_1 = 0.2$ to 0.5. This is, therefore, the lowest upper bound of the Hashin-Shtrikman relation. It expresses the upper limiting condition of the modulus ratio for the stated morphology. Most experimental moduli will fall below this bound.

The highest lower bound of the Hashin-Shtrikman equation, again of Kerner form, expressing the limiting case of a hard dispersed phase in a soft matrix, is

$$E/E_1 = 1 + (v_2/v_1)[15(1-\nu_1)/(8-10\nu_1)] \qquad (6)$$

Because of its limiting nature, experimental modulus ratios for real systems should lie above this bound. A general defect of the majority of these equations is that they consider only one phase geometry. Exceptions are the general equations of Hashin-Shtrikman which are not limited to specific geometry or number of phase components.[28,29] The rest, eqs. (1)–(6), are all limited to a dispersion of spheres in either a soft or hard matrix and assume perfect adhesion between the components; the irregular and aggregated morphologies[9,14,15,34,35] characteristic of real polycomposites can lead to results not predicted by the various theories.

Figure 1 compares the theoretical expressions with experimental data (circles) for various polycomposites. Relations are between torsional modulus ratios at 23°C and the volume fraction of polymeric filler, v_2. The maximum packing volume v_c (described below) used instead of v_m in the Mooney and Eilers and Van Dyck expressions, eqs. (1) and (2), were 0.413 in insert A and 0.667 in insert B. It is apparent that none of these expressions described the experimental data for any present polycomposite, at least for any sustained range of v_2. The use of an experimentally determined v_m in the Mooney or Van Dyck expression would have achieved a better fit of the curves up to v_m. However, a fit over all v_2 would not be possible by the limiting nature of these

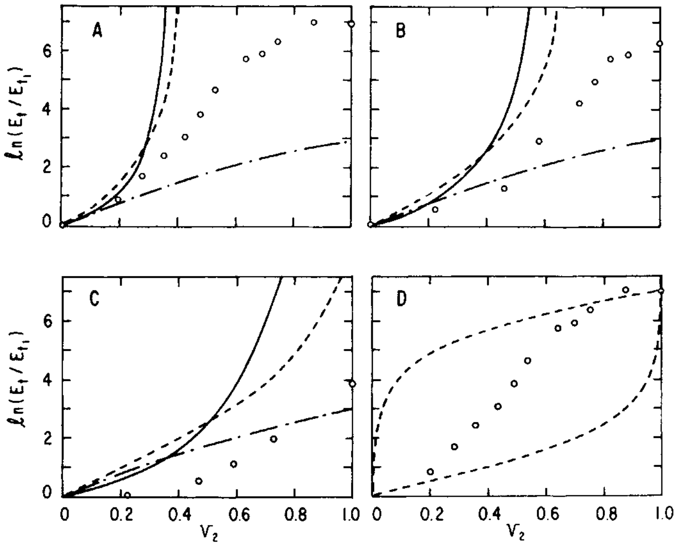

Fig. 1. Comparison of torsional modulus ratios E_t/E_{t1} vs. volume fraction of polymeric filler, v_2, for selected experimental polyblends (circles) with several theoretical equations. Relations are: solid line, Mooney equation, eq. (1); dashed line in (A), (B), and (C), equation of Eilers and Van Dyck, eq. (2); broken line, equation of Guth and Smallwood, eq. (3); dashed lines in (D), upper and lower curves calculated using the Kerner equations, eqs. (5) and (6). The polymeric fillers used were: (A) and (D), PVC; (B), VS (0.207) VCl; (C), VS (0.356) VCl. Poisson's ratio for the upper bound of the Kerner equation was assumed to be 0.3. Critical volume fractions (Mooney and Eilers and Van Dyck) are from Table III.

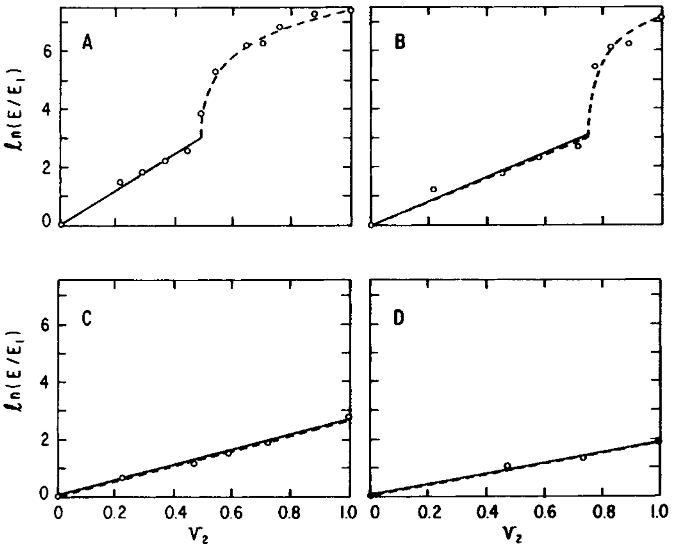

Fig. 2. Relation between tensile modulus ratio ln (E/E_1) and volume fraction of polymeric filler, v_2, in polyblends employing Hycar 1411. The polymeric filler was PVC (A) and copolymers of vinyl stearate and vinyl chloride containing vinyl stearate weight fractions of 0.207 (B), 0.356 (C), and 0.467 (D). Solid lines are eq. (7); dashed lines are eq. (10).

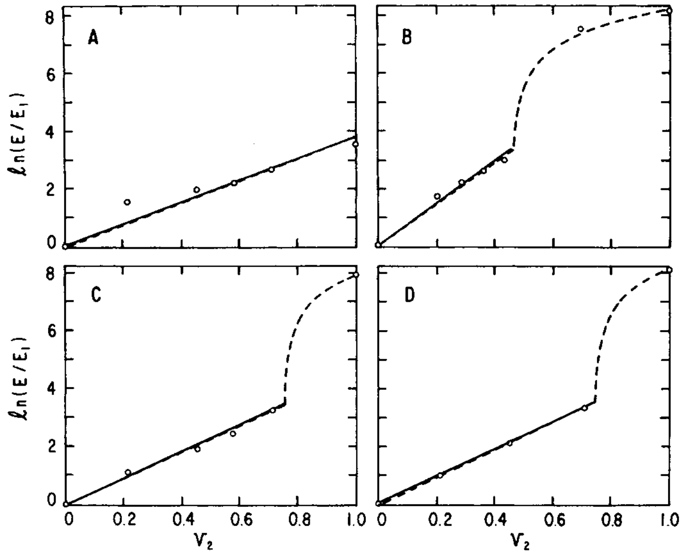

Fig. 3. Relation between tensile modulus ratio ln (E/E_1) and volume fraction of polymeric filler, v_2, in polyblends employing Hycar 1411 (A), Hycar 1452P-50 (B) and (C), and AN 25, unvulcanized (D). The polymeric filler was DOP (0.207) PVC (A), PVC (B), and VS (0.207) VCl (C) and (D). Solid lines are eq. (7); dashed lines are eq. (10).

equations, which fail at v_m. The fact that v_c and v_m do not coincide will be seen to be significant as v_c is discussed in the sections below. In view of insert D, the experimental data resemble more the quantities produced by mixed contributions from each phase, at least over much of the experimental range of filler volume fractions. The discussion of the balance of this paper will be primarily concerned with a more careful examination of these mixed contributions to modulus.

The Tension Modulus Ratio E/E_1

Typical data for the tension modulus ratios E/E_1 as a function of the volume fraction of filler v_2 are shown in Figures 2 and 3. The relation for the linear portion of the data (solid line in the figure) is

TABLE II
Values of the Constant k of Eq. (7)

	k, eq. (7)			
Polyblend system	0[a]	0.207[a]	0.356[a]	0.467[a]
VS–VCl, HY 1411	6.19	3.99	2.69	1.91
DOP–PVC, HY 1411		3.82	2.59	1.63
VS–VCl, HY 1452P-50	7.31	4.49	3.29	2.79
DOP–PVC, HY 1452P-50		4.50	3.45	2.45
VS–VCl, AN 25, uncured	6.48	4.77	2.41	2.79
VS–VCl, AN 25, cured	4.42	2.48	1.76	1.31

[a] Weight fraction of plasticizer in the starting copolymer or mixture.

$$\ln E/E_1 = kv_2 \tag{7}$$

where $k \simeq \ln (E_2/E_1)$ in Figure 2, inserts C and D, and Figure 3, insert A. Equation (7) described all blend data having T_i below room temperature (see Table I and data in the previous two papers[1,2]). Computer values of k, with the intercept forced through zero, for all of the polyblend systems studied in this investigation[1,2] are listed in Table II. The constant k decreased as the plasticizer content of the filler increased in all systems. Systems using Hycar 1452P-50 have larger values of k than those using Hycar 1411, because E_1 is smaller for the former system (i.e., $E_2/E_1 \simeq k$ increases). Surprisingly, vulcanization lowered k compared to unvulcanized blends; cured systems at any v_2 were, therefore, softer though possessing higher tensile strengths.[1] In general, the magnitudes of k values were similar and decreased as free volume increased with increase in plasticizer content, in line with a lower E/E_1 at $v_2 = 1$.

The most curious feature of the relations shown in inserts A and B of Figure 2 and B, C, and D of Figure 3 is the obvious discontinuity that occurred when E/E_1 approached about 20 ($\ln E/E_1 \simeq 3$). This was observed when T_i became greater than ambient with increase in v_2; consequently, it was only observed for systems, like those enumerated above, whose fillers had a T_g greater than ambient and, therefore, were hard. It is in this composition region that elongation became less than 100% so that the reported values of E (Table I of this paper and polyblends I) were initial moduli. Consequently, the discontinuity reflected the abrupt decrease in the free volume of the blends as the filler itself began to dominate properties in these systems. In composition regions governed by eq. (7) in Figures 2 and 3, the elastomer was acting merely as a diluent in reducing moduli.

The discontinuous increase in E and, therefore, in the modulus ratio E/E_1 had its origins in the free volume available to the polymeric filler at ambient temperature and to its volume fraction in the blend, v_2. The former effect can be expressed through the parameter $T_g - T_{23}$, where T_g is the glass transition of the filler and T_{23} is room temperature. Hardness of a polymer will increase somewhat with positive values of $T_g - T_{23}$ but will approach a limit as the equilibrium free volume v_f of the glass is reached.[36] When $T_g - T_{23}$ is negative, the filler will be relatively soft. In the polyblends under discussion, this represented the case of mixed rubbers, where T_i of the filler was less than room temperature and eq. (7) applied over all v_2 (Fig. 2, inserts C and D, and Fig. 3, insert A). The relation between $T_g - T_{23}$ and the value of k of eq. (7), as listed in Table II, is shown in Figure 4, insert A, for VS–VCl copolymers and DOP–PVC mixtures blended with Hycar 1411. The relation is

$$T_g - T_{23} = (T_g - T_{23})_0 + \delta k \tag{8}$$

where T_g is the glass transition of the starting polymer, copolymer, or plasticized mixture. Values of the constants $(T_g - T_{23})_0$ and δ are given in Table III for all of the polyblended systems studied. The triangle point in Figure 4, insert A, is the value of $T_g - T_{23}$ and k for bulk PVC. The critical value of k, or $\ln (E_2/E_1)_c$, designated k_c, where phase inversion became possible in any blended system, occurred near $T_g - T_{23} \simeq 0$ (dashed line in the figure). This corresponded to a critical volume fraction for phase inversion, designated v_c, such that

TABLE III
Constants of the Various Equations

System[a]	Eq. (8), tensile		Eq. (8), torsion		Critical vol. fraction		Critical modulus[b]		C,
	δ, °K	$(T_g - T_{23})_0$, °K	δ', °K	$(T_g - T_{23})_0'$, °K	v_c	v_c'	E_c, psi	E_c', psi	eq. (20)[c]
PVC, HY 1411	17.77	-53.08	14.06	-36.94	0.483	0.413	2360	7190	0.136
VS, HY 1411	17.77	-53.08	14.06	-36.94	0.749	0.667[d]	2360	7190	0.235
DOP, HY 1411	27.54	-113.3	18.27	-71.07		0.868		25,400	0.154
PVC, HY 1452P-50	14.32	-48.20	14.10	-37.24	0.460	0.382	1590	2540	0.187
VS, HY 1452P-50	14.32	-48.20	14.10	-37.24	0.750	0.877	1590	2540	0.259
DOP, HY 1452P-50	25.88	-129.9	20.48	-93.67		0.928		17,500	0.191
PVC, AN-UC	12.17	-43.12	15.05	-25.71	0.547		1520		0.163
VS, AN-UC	12.17	-43.12	15.05	-25.71	0.743	0.853	1520	1225	0.243
PVC, AN-C	24.19	-47.67	12.85	-13.75	0.446	0.190	1180	1200	0.151
VS, AN-UC	24.19	-47.67	12.85	-13.76	0.795	0.868	1180	1200	0.236
HY 1411									0.0556[e]
HY 1452P-50									0.0844[e]
						ave.	1663	7332	

[a] The system pertains to polyblends of the plasticized components at all compositions, as in Table II. Definitions are as follows: PVC, poly (vinyl chloride); VS, vinyl stearate–vinyl chloride copolymers; DOP, DOP–PVC mixtures; HY, Hycar, a B. F. Goodrich product; AN, NBR containing 0.25 mole fraction of acrylonitrile; UC, uncured; C, sulfur cured. Critical vol. fraction modulus data limited to plasticizer content of 0.207.

[b] Calculated using $E_c = E_0 e^{kv_c}$, where E_0 is E_1 or E_{t1}. Values of E_0 are (listed as NBR, tensile modulus (100%) in psi, and torsional modulus at 23° C in psi): 1411, 119, 520; 1452P-50, 55, 181; AN 25-UC, 44, 222; and AN 25-C, 164, 400.

[c] Proportionality constant relating the initial torsional modulus ratio E_t/E_{t1} and the WLF equation.

[d] The quantity v_c' for polyblends of VS (0.356) VCl and HY 1411 was 0.903.

[e] Intercepts in eq. (21) are: HY 1411, -1.007; HY 1452P-50, -1.164.

$$v_c = [(T_g - T_{23})_0/\delta]/k \qquad (9)$$

Consequently, using v_c and eq. (7), it was possible to compute the modulus ratio E_c/E_1 and the critical modulus E_c necessary to indicate the onset of phase inversion for any of the filled systems under investigation. For tension modulus, these values are given in Table III.

A similar relation was obtained for torsional moduli at room temperature, E_t. However, the relationship between ln (E_t/E_{t1}) and v_2 was not always linear (the curve being concave downward) so that k' values, obtained by computer using eq. (7), were sometimes forced average values. This introduced more error into the parameters of eqs. (8) and (9) (primed quantities in Table III) than had been found for the corresponding 100% modulus computations.

Values of α and α' and the derived v_c and v_c' values were similar for each blend system in Table III; however, $(T_g - T_{23})_0$ were somewhat variable. Considerable variability existed for individual values of both E_c and E_c' in the table. The variability reflects failure of eqs. (7), (8), and (9) to predict a common critical modulus marking phase inversion for all of the systems. However, the averaged values of E_c and E_c' are reasonable. Their difference is in the expected direction for the two types of modulus.[2]

Equation (7) expresses the relation between the tensile modulus ratio, ln (E/E_1), and the volume fraction of filler, v_2, only in the composition range where both phases were soft and rubber-like. Consequently, it expresses the additive effect of the bulk viscosity of the mixed rubber phases. An equation, eq. (10), that adequately computed the modulus ratio for the entire composition range made use of eq. (9) to calculate the critical volume v_c for the onset of the discontinuous increase in modulus and then estimated the tension modulus ratios for the inverted-phase region at $v_2 > v_c$:

$$\ln E/E_1 = \ln [v_a(E_c/E_1) + v_b(E_2/E_1)] - k[v_c + v_2(1 - v_c/v_2)] + kv_2 \qquad (10)$$

When $v_2 \leqslant v_c$, $E_c = E$, and when $v_2 > v_c$, E_c remains E_c. When $v_2 < v_c$, v_2 remains v_c in eq. (11):

$$v_b = (v_2 - v_c)/(1.0 - v_c) \qquad (11)$$

$$v_a = 1.0 - v_b \qquad (12)$$

The critical volume v_c is from eq. (9), and E_c is taken as $E_c = E = E_1e^{kv_2}$ for $v_2 < v_c$ and $E_c = E_1e^{kv_c}$ for $v_2 > v_c$. These quantities are given in Tables I to III. The dashed lines in Figures 2 and 3 show that eq. (10) was reasonably successful in describing both the mixed-rubber region below v_c and the rapid rise in modulus ratios above this critical volume fraction at which the phases seem to invert. Equation (10) stresses the importance of a critical modulus of the filler–matrix system necessary to initiate the onset of phase inversion. It also expresses the importance of the relative hardness of the filler as determined by its plasticizer content in increasing v_c. When v_c becomes $\geqslant 1.0$, mixed rubbers prevail, T_i is below ambient, and the single-parameter eq. (7) can describe the moduli at all v_2 values.

Equation (10) is really an equation expressing a discontinuity. Consequently, it can be decomposed into its two-component expressions. Thus, when the rubber phase was continuous, $v_2 < v_c$, series response appeared to prevail,[9,14] and

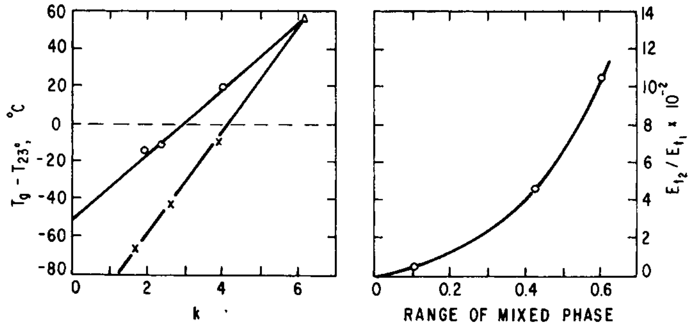

Fig. 4. (a) Relation between $T_g - T_{23}$ and k of eq. (7): (O) VS–VCl copolymers; (x) DOP–PVC mixtures; (△) PVC. The nitrile rubber is Hycar 1411. Dashed line marks $T_g - T_{23} = 0$ above which phase inversion is possible. (b) Observed torsional moduli ratios for starting polyblend components versus the phase overlap region where viscoelastic properties depend on the geometric rule of mixtures.

$$\ln (E/E_1) = \ln (E_c/E_1) - k[v_c + v_2 - v_c] + kv_2 = kv_2 \qquad (13)$$

where in this region $E_c = E$. In the overlap region, where $v_2 > v_c$, more parallel behavior was prevailing, and

$$\ln (E/E_1) = \ln [v_a(E_c/E_1) + v_b(E_2/E_1)] \qquad (14)$$

because the right-hand terms of eq. (10) cancel out in this region. It can be seen that, in spite of the observation of the previous papers,[1,2] which described these systems as mechanically compatible, an incompatible region does exist whose range is a function of the initial hardness and ductility of the filler. The manner in which these effects influence torsional modulus will be considered next. Torsional moduli reflect the lowest strain state of the blends. Their analysis will be accomplished using a modification of the Kerner equation.[27] This modification considers mixed phase behavior.

The Torsional Modulus Ratio E_t/E_{t1}

For purposes of describing the behavior of the torsional modulus ratio E_t/E_{t1}, the expressions for the upper and lower moduli ratios estimated by the Kerner equation[27] can be recast (Halpin[32] and Tsai[33]), yielding for the lower moduli ratios

$$E_t/E_{t1} = (1 + ABv_2)/(1 - Bv_2) \qquad (15)$$

where, for spherical particles or for rigid filler particles of a random shape,

$$A = (7 - 5\nu_1)/(8 - 10\nu_1) = k_e - 1.0$$

$$B = (E_{t2}/E_{t1} - 1)/(E_{t2}/E_{t1} + A)$$

Here, Poisson's ratio is $\nu_1 = 0.5$. After phase inversion has occurred,

$$E_t/E_{t1} = (1 - B'v_2)/(1 + A'B'v_2) \qquad (16)$$

where $A' = 1/A$ and $B' = E_{t1}/E_{t2} - 1/(E_{t1}/E_{t2} + A')$. Equations (15) and (16) suffer in that conditions anticipating phase inversion are not considered. Nielsen has modified the equations for this condition[3-5] by introducing a crit-

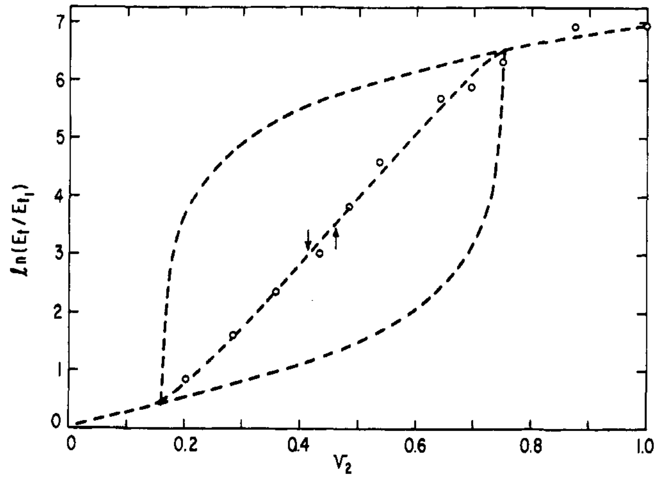

Fig. 5. Halpin-Tsai version, eqs. (16) and (17), of Kerner equation, eq. (4), as modified by Nielsen, eq. (18), fitted to polyblends of PVC and Hycar 1411. Ordinate is the torsional modulus ratio E_t/E_{t1}; abscissa is the volume fraction of PVC. Circles are experimental values. The range of mixed phases, 0.60, is from Fig. 4, insert B. Downward arrow is the critical average packing volume fraction v_c' (Table III); upward arrow is the midpoint of the fitted range.

ical maximum volumetric packing fraction v_m as the essential parameter. With this modification, eqs. (15) and (16) now become, for the lower relation,

$$E_t/E_{t1} = (1 + ABv_2)/(1 - B\psi v_2) \tag{17}$$

with $\psi = 1 + [(1 - v_m)/v_m^2]v_2$. A similar insertion of ψ can be made in the numerator of eq. (16).

Nielsen[3-5] considered that in the vicinity of v_m, both phases would be con-

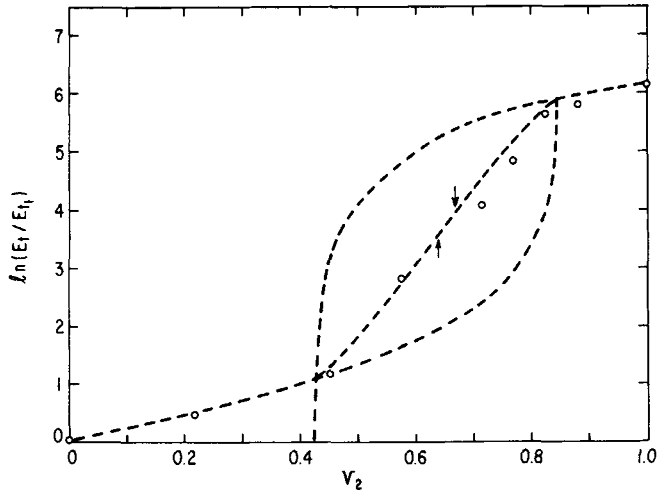

Fig. 6. Halpin-Tsai version, eqs. (16) and (17), of Kerner equation eq. (4), as modified by Nielsen, eq. (18), fitted to polyblends of Hycar 1411 and VS (0.207) VCl. Abscissa is the torsional modulus ratio E_t/E_{t1}; ordinate is the volume fraction of polymeric filler, v_2. Circles are experimental values. The range of mixed phases, 0.425, is from Fig. 4, insert B. Downward arrow is the average critical packing volume fraction v_c' (Table III); upward arrow is the midpoint of the range.

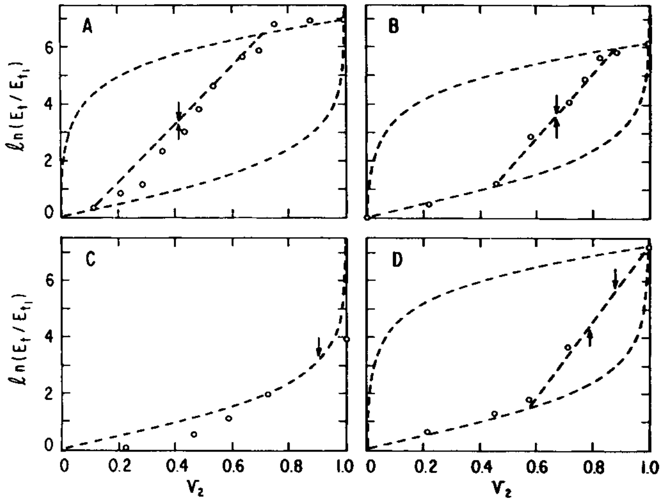

Fig. 7. Approximate Kerner-Nielsen plots of torsional modulus ratio ln (E_t/E_{tl}) vs. volume fraction of polymeric filler, v_2, for polyblends of PVC (A), VS (0.207) VCl (B), and VS (0.356 VCl (C), all with Hycar 1411 and VS (0.207) VCl with Hycar 1452P-50 (D). Downward arrow is the average critical packing volume fraction v_c' (Table III); upward arrow is the midpoint of the fitted range. The range is from Fig. 4, (B).

tinuous in a narrow composition range called, for convenience, the overlap region. In the overlap region, he assumed[4] that the geometric rule of mixtures would prevail, so that

$$\log E_t = v_U \log E_{tU} + v_L \log E_{tL} \tag{18}$$

In this equation, v_U and v_L are volume fractions of rigid material given by the

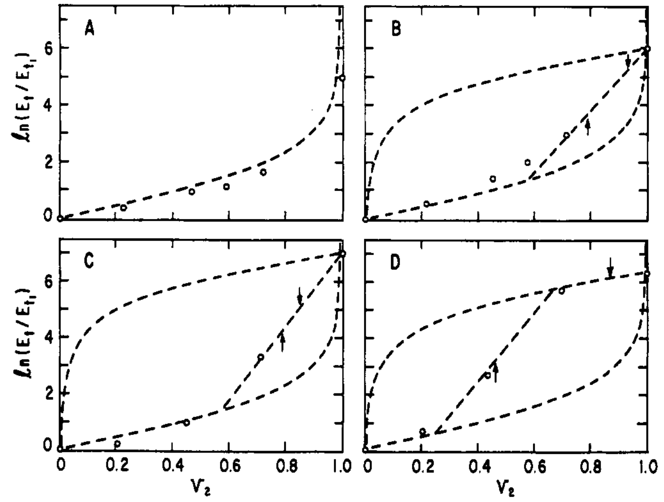

Fig. 8. Approximate Kerner-Nielson plots of torsional modulus ratio ln (E_t/E_{tl}) vs. volume fraction of polymeric filler, v_2, for polyblends of VS (0.356) VCl (A), DOP (0.207) PVC (B), both with Hycar 1452P-50, and VS (0.207) VCl with AN 25, unvulcanized (C), and vulcanized (D). Downward arrow is the average critical packing volume fraction v_c' (Table III); upward arrow is the midpoint of the range. The range was taken from Fig. 4, (B).

Kerner higher-moduli expression, eq. (16), and the lower moduli, eq. (17), respectively, in the overlap region.

When eqs. (16) and (17) were used with v_c' (Table III) to fit the experimental data (Table I), the agreement was poor. The experimental overlap region (Fig. 1) was far too large to agree with the predicted range, and v_c' did not correspond to the phase inversion region. A correlation was obtained empirically (Fig. 4, insert B) of the observed range of the experimental overlap region with E_{t2}/E_{t1} for the experimental data in Table I (using Hycar 1411) and some data from Table III for VS (0.356) VCl. The appropriate overlap region was taken from this figure, and the limit of the range was assumed to represent the maximum volumetric packing fraction v_m. With the aid of this quantity, the upper and lower modulus ratios of the modified Kerner equation were constructed using eq. (17) and eq. (16) modified by ψ. The mixed-phase line was also drawn using eq. (18). The curves were then graphically shifted for the best approximate fit to the experimental data, keeping the overlap region the same. Using the values of $1 - v_m$ and v_m obtained after curve shifting, which were the initial and final volume fractions of the mixed-phase range, the modified Nielsen-Kerner equations, eqs. (16) and (17), were again used to reconstruct the upper and lower sets of modulus ratios. The mixed phase line, eq. (18), now fell close to the experimental data as can be seen in Figures 5 and 6. It may be observed that the midpoint of the fitted range in both figures lies close to v_c', computed from eq. (9) from data in Table III (arrows in the figure). Consequently, with torsional moduli data, v_c' appeared to denote the average composition of the mixed-phase contribution rather than the onset of phase inversion, as with the 100% modulus ratios discussed in the section above. The sensitivity of torsional moduli to low-strain states appears to be responsible for the behavior differences.

The rather laborious method just described for exactly fitting experimental data to the Kerner equation in Figures 5 and 6 was replaced (Figs. 7 and 8) by an approximate method having more predictive power. With ν fixed as 0.5 and v_m taken as unity for both relations, the Halpin-Tsai parameters used for all calculations became, for the lower curve, $A = 1.50$, $B = 0.9950$, and $AB = 1.493$; and, for the upper curve, $A' = 1/A = 0.6667$, $B' = 0.9970$, and $A'B' = 0.6647$. Using appropriate starting material moduli taken from the previous paper,[1] the curves shown in Figures 7 and 8 were thereby constructed. With v_c' of Table III taken as the midpoint of the overlap range for each blended system (the range from Fig. 4, insert B), a line was drawn from the initial v_2 of the lower curve to the terminal v_2 of the range in the upper curve. This procedure can be seen (Fig. 7, inserts A and B) to give almost as good a fit as the more exact procedure discussed above (Figs. 5 and 6). The balance of the data in the figures shows reasonably good fit of the theoretical curves to the experimental data, regardless of the type of polyblend. In cases where v_c' was greater than the midpoint of the range (Fig. 4, insert B), the upper curve v_2 was taken as unity (Fig. 7, insert D and Fig. 8, inserts B and C). In Figure 8, insert D, representing vulcanized polycomposites, the procedure outlined above failed; the overlap line was adjusted graphically although the proper range was maintained.

In general, these drastic modifications of the original Kerner equation[27] were able to describe the viscoelastic behavior with respect to blend composition of the polyblend systems studied in these papers. That is, the experimental data for systems of strongly contrasting moduli lay close to both bounds predicted using variational principles or assumed isotropic dispersions by Hashin and Shtrikman,[28–31] but only over a limited range of experimental volume fractions. In a large range of filler volume fractions, apparent continuity of both phases was present. This was significant because the moduli of the fillers used in this work could be reduced at will by plasticization, either internal or external. The general effect of increased filler plasticization was to reduce the range of mixed-phase contributions to viscoelastic response and to shift the ranges to higher volume fraction of filler. When the T_g of the polymeric filler fell below room temperature, the lower Kerner relation was closely followed (Fig. 7, insert C and Fig. 8, insert A).

Mechanical compatibility, whose recognition was based on shifting T_i and general mechanical behavior, was shown to be followed by all of the blended systems in the previous papers. Clearly, this criterion was really only applicable when the data lay close to this lower Kerner relation, i.e., when $T_g - T_{23}$ of eq. (8) became negative or where the NBR content was large in the other systems. In systems where the difference $T_g - T_{23}$ was positive and where the NBR content was relatively low (Table I), phase incompatibility eventually resulted. Consequently, through much of the composition range of those blends filled by hard inclusions, mixed-phase contributions determined the mechanical behavior. Both mechanical and thermal spectroscopy now lead to the conclusion that the present polyblend systems are incompatible, whether reinforced with vinyl copolymers or with externally plasticized PVC. The illusion of molecular compatibility based on viscoelastic data[2] resulted from significant contributions from both ultrafinely dispersed mixed phases. This suggests a morphology of discrete interlocking microdispersions. This morphology would cause T_i to shift with composition as in true molecular mixing. However, the broadness of the individual isochronal modulus–temperature curves, observed as NBR content changed in any blended system,[2] provides clear evidence that the environment of the domain-matrix stress fields were supermolecular. This gives rise to gradual inflections in the modified Kerner-Nielsen plots of Figures 5–8. In truly molecularly mixed systems, on the other hand, only a very narrow overlap region, denoting phase inversion, is encountered.[4] Isochronal curves having large slopes at T_i then characterize the viscoelastic data. This was found for truly molecularly dispersed amorphous interpolymers.[37]

It is pertinent that poly(vinyl chloride), molecularly plasticized by monomeric DOP but containing macromolecular, out-of-phase reinforcing crystallites, produced anomalously broad isochronal modulus–temperature curves, indicating only partial molecular mixing.[38–40] It is suggested that the type of mixing characteristic of polyblends of vinyl chloride containing polymers or plasticized mixtures blended with nitrile rubbers be classified as restricted molecular mixing. This classification serves to differentiate their type from the type shown by polycomposites whose viscoelasticity data exhibit two loss maxima. Systems like the latter are clearly incompatible, regardless of which phase constitutes the matrix.[6,8] Incompatibility in polycomposites seems to result from using nonductile fillers such as polystyrene, poly(methyl methacrylate), or polyacrylonitrile. The effect appears to be relatively insensitive to the type of polycomposite[6,15-17,19,20,35,41-45] and details of their morphology,[8,15,35,46,47] but exceptions are to be noted.[19,48,49] However, unfavorable polar interactions were also lacking in the cited systems; favorable polarity was sometimes,[6,50] but not always,[51,52] found in compatible polycomposites containing PVC.

Empirical Torsional Modulus–Temperature Relations

The discussion just completed has shown that the appearance of mechanical compatibility depends on the difference between T_g of the blend filler and the temperature of observation at ambient temperature T_{23}. This indicates that whenever the temperature of observation is below T_g of the filler of any polyblend, mechanical incompatibility will result at some volume fraction of inclusion above $1 - v_m$. On the other hand, when the temperature of observation is above T_g of the particulate filler, the systems should exhibit the behavior of mixed rubbers and become apparently compatible. However, true molecular compatibility should never be encountered in any polyblend, regardless of temperature, because of the high probability of positive free energies of mixing between polymer pairs.[7,53] In further support of these ideas, when selected mixed rubbers were cooled to −20°C, all tested samples exhibited stress whitening, presumably because of craze development in the polymeric filler phase. A special designation of restricted molecular mixing was, therefore, proposed for polycomposite systems like those studied in this work.

In this section and those that follow, an approximate analysis of isochronal moduli–temperature curves is presented which embodies the principles outlined above concerning the effect of plasticization on filler modulus and composite morphology. This analysis avoids the assignment of constants to assumed mechanical models for mixing as in the method of Takayanagi.[9,54,55] This method suffers in that constants assigned to the parameters of each model can fit experimental data with equal facility but lead to opposing interpretation of the extent of parallel and series character in a given polyblend. The discussion below avoids this problem. However, only a qualitative approximation of actual behavior is intended.

Because T_{g1} and T_f are the approximate temperatures where the nitrile rubber underwent its glass transition,[2] the temperature region between T_{g1} and T_i represents the behavior of an increasingly soft elastomer filled by a hard filler. Beyond T_i, both phases became rubbery and the modulus ratio was expected to follow eq. (7) with $k \simeq \ln (E_2/E_1)$. In the temperature interval T_i–T_{g1}, the moduli gradually decreased from some high value at T_{g1} to 14,500 psi at T_i. The effect of a decreasingly efficient filled rubber in the temperature interval T_i–T_{g1} can be described as

$$E(T) = (T - T_{g1}/T_i - T_{g1})E_{Ti} + [1 - (T - T_{g1}/T_i - T_{g1})]E_{Tg1} \qquad (19)$$

where E_{Ti} = 14,500 psi = 1.0×10^9 dynes cm^2, E_{Tg1} = 500,000 psi = 3.45×10^{10} dynes/cm^2 and $T = T_{g1} < T < T_i$. Temperatures were in °K. The inflection temperature T_i was calculated from eq. (1) and the constants of Table II of the previous paper.[2] Values of T_g for the three elastomers[2] (T_{g1}) were: Hycar 1411, −23°C; Hycar 1452P50, −43°C; and AN 25, −51°C. Equation (19) was used to estimate modulus–temperature curves in the tem-

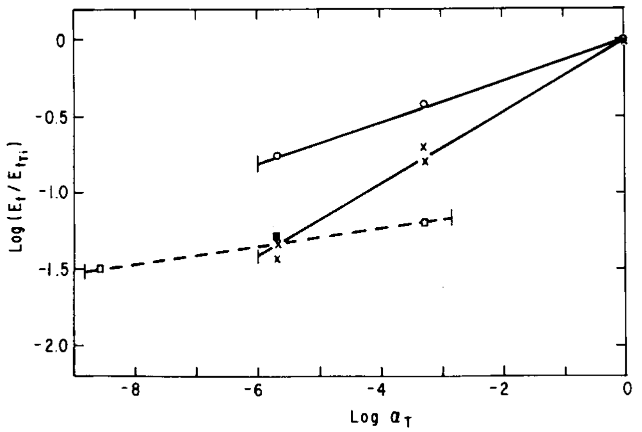

Fig. 9. Initial relation between torsional modulus ratio ln (E_t/E_{tT_i}) and the WLF equation for polyblends with Hycar 1411. For the solid lines, circles designate PVC, while the x's designate all VS–VCl copolymers studied in this work. Range of the linear correlation is about T–T_i = 25°C as shown by vertical slashes. Dashed line is the correlation of Hycar 1411 with T–T_i interval, 12° to 50°C, as shown by vertical slashes.

perature region between T_{g1} and T_i; the results will be discussed below.

The torsional modulus ratio from T_i to $T_i + 100$, designated E_t/E_{tT_i}, was proportional to the viscosity ratio of the Williams-Landel-Ferry equation[56a]

$$\log (E_t/E_{tT_i}) = C \log (\eta/\eta_{T_g}) = C \log \alpha_T = C\,\frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \tag{20}$$

for moduli above T_i for every polyblend system studied, through log α_T of about −6. For the nitrile rubbers themselves, the rate of change of modulus ratio became very small because of the effect of the rubbery plateau. In fact, the relation between log (E_t/E_{tT_i}) and T_i for the nitrile rubbers followed

$$\log (E_t/E_{tT_i}) = C_0 + C' \log \alpha_T. \tag{21}$$

These two relations can be seen graphically in Figure 9. Values of the constants C, C', and C_0 are given in Table III for all of the polyblend systems studied in this work. Consequently, for a limited $T - T_i$ (not exceeding 100° [56a]), the WLF equation could be invoked to compute the ratio and, thus, the torsional modulus as a function of temperature above T_i. However, the impact of the nitrile rubber network phases and the relatively smaller effect of entanglement coupling[56b,c] are neglected using eq. (20). To estimate these effects, eq. (22) was developed:

$$E(T) = E_{T_i}[e^{2.303C \log \alpha_T}] + Fw_1[E_{Ti}(e^{2.303C_0 + C' \log \alpha_T})] \tag{22}$$

The factor F is given as

$$F = [(T - T_i)/100] \log \{w_1 Z_c + [w_2/(T - T_i]Z_e\} \tag{23}$$

where $Z_c = M_c/M_0$, the ratio of molecular weight between crosslinks of the rubber to the molecular weight of the chain unit, and Z_e is the same ratio for entanglement coupling of both copolymer and elastomer units. In eq. (22), the term at the left computes modulus by the WLF relation; the terms at the right attempt to modify these computed moduli to qualitatively account for

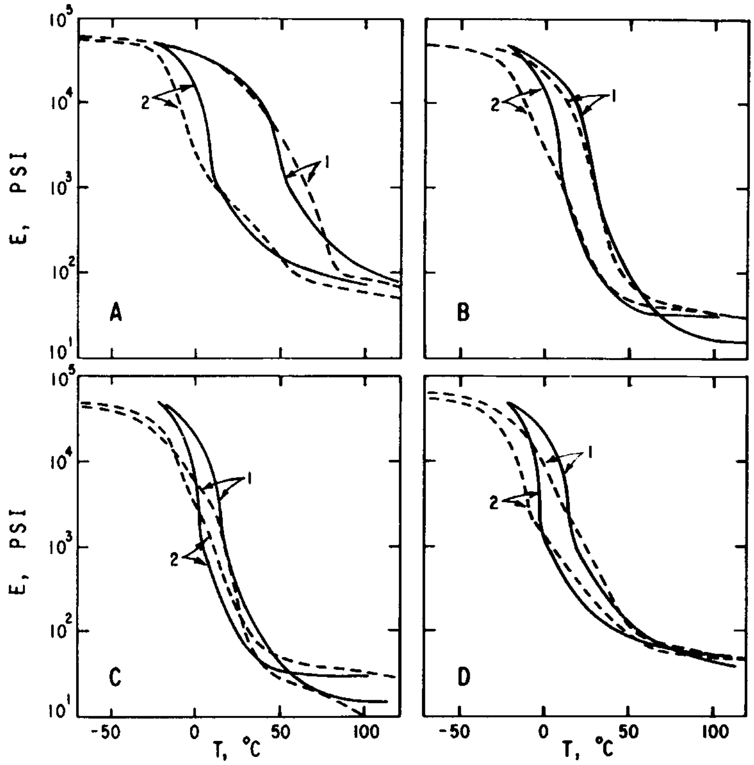

Fig. 10. Torsional modulus–temperature curves for various polyblends of Hycar 1411. The polymeric filler used was: (A), PVC; (B), VS (0.207) VCl; (C), VS (0.356) VCl; and (D), DOP (0.207) PVC. The weight fraction of NBR was, right-hand pair of curves, 0.25; left-hand pair, 0.50, except in (A), where the NBR in the left-hand pair was 0.58. Solid lines calculated according to eqs. (19), (22), and (23); dashed lines are experimental.

the gradual increase in importance of the rubbery phase as temperature increases. The form of the factor F specifies an increasing contribution of the nitrile rubber phase and a decreasing contribution of entanglement coupling of the polymer as temperature increases to a limit not exceeding $T - T_i$ of 100°C.

Cognizance was taken in the use of eqs. (22) and (23) of the considerable theoretical difficulties in estimating quantitatively the magnitudes of the modulus and the degree of network perfection present in the rubbery modulus region of even simple polymers and copolymers.[56a–d] The entanglement terms in eqs. (22) and (23) are intended only as empirical correlation constants. The purpose of the equations was to disengage and describe the main molecular contribution of the domains to modulus behavior under the influence of changing temperature. Success in the use of these expressions, therefore, can only be gauged by their fit to the experimental data. To this end, the quantity Z_e was assumed to be 1000 in all calculations, and Z_c was assigned the value of 100 for systems using Hycar 1411 and 500 for systems using the less crosslinked Hycar 1452P-50.[1] These assignments were considered reasonable in view of literature values.[56c]

Calculated modulus–temperature curves (solid lines) are compared with a selection of experimental curves (dashed lines) in Figures 10 and 11 for vari-

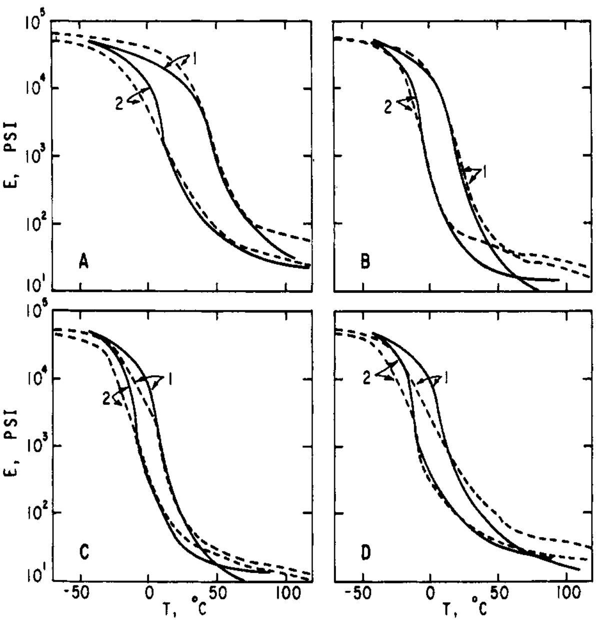

Fig. 11. Torsional modulus–temperature curves for various polyblends of Hycar 1452P-50. The polymeric filler used was: (A), PVC; (B), VS (0.207) VCl; (C), VS (0.356) VCl; and (D), DOP (0.207) PVC. The weight fraction of NBR was, right-hand pair of curves, 0.25, and left-hand pair, 0.50. Solid lines were calculated according to eqs. (19), (22), and (23); dashed lines are experimental.

ous polyblend systems. Each insert contains two curves describing two different NBR concentrations for a single pictured polyblend system. The data in Figure 10 are for Hycar 1411 polyblends; those in Figure 11, for Hycar 1452P-50.

The portion of the curves between T_{g1} and T_i, calculated using eq. (19), are plainly delineated in both figures. The form of the equation expressed the trends of modulus in this region; a better fit could have been obtained from a more realistic assignment of $E_{T_{g1}}$ and by using a somewhat lower T_{g1} for Hycar 1411. The curves suggest that additive mixed-phase contributions of a hard (500,000 psi) and a relatively soft phase (14,500 psi) determined modulus in this region for all systems. Inflection temperatures were accurately given,[2] shifting each curve down the temperature scale with increasing NBR as illustrated. For the temperature interval in the immediate vicinity of T_i (to $T-T_i \simeq 25°$), the increased free volume becoming available to the hard domains in this region alone determined the moduli. At higher temperatures, the increasing influences of the elastic and entanglement network were fairly well anticipated by eqs. (22) and (23). While a better fit could have been obtained by adjusting Z_c and Z_e, no useful purpose would have been served by this procedure.

A number of the required features of the mechanical properties of the experimental polyblends are reflected in the calculated curves. The broadness of the curves, which increased as the hardness of the filler increased, was predicted (compare insert A with inserts C and D, Fig. 10, and insert A with inserts C and D, Fig. 11). This broadness depends on the shifting of T_i with filler plasticization, while T_{g1} stays constant. This provides evidence for discrete phase microdispersity as was discussed above. The magnitude of the plateau region increased as NBR increased in VS–VCl filler polyblends (inserts B and C, Fig. 10, and inserts B and C, Fig. 11) but stayed relatively constant for PVC and DOP–PVC filled systems (inserts A and D, respectively, in both figures). The calculated curves reflected this behavior. The superior high temperature properties of these latter filled systems compared to those using VS–VCl copolymers is also illustrated. Finally, the modulus behavior at high temperature depended strongly on Z_e, as might be expected (compare Figs. 10 and 11). It may be concluded that increasing temperature changes each polyblend from an initial state of mixed glasses, through a filled elastomer region featuring mixed parallel and series response, to mixed elastomers above T_i. At high temperatures, the degree of network perfection and the bulk viscosity of liquid-like dispersions determined mechanical properties. The several empirical equations just described appear to reflect the experimental trends closely enough to describe the qualitative molecular responses to temperature changes occurring in the polyblends.

SUMMARY AND CONCLUSIONS

Various theoretical equations derived to describe the viscoelasticity of filled elastomers and other expressions useful for polycomposites exhibiting both parallel and series response to deformation were tried on the polyblends of these investigations. The properties of these polyblends were affected by NBR content and by the extent of the plasticization of the particulate filler used. New mechanical and viscoelastic data were introduced to provide greater experimental detail for compositions having reduced NBR content. Several of the theoretical treatments failed. A substantial modification of the Kerner equation, proceeding from expressions accounting for phase inversion, finally proved useful in describing torsional modulus ratios as filler composition increased. Tensile modulus ratios (100%) followed a different empirical expression, however.

A critical volume fraction, associated with the composition region where phase inversion occurred, was an essential parameter for relating both bypes of modulus to composition. The range of mixed-phase contributions decreased as T_g of the added polymer decreased and shifted to higher polymer compositions, finally vanishing when the T_g of the inclusion fell below room temperature. The latter systems alone, by following the lower Kerner relation, suggested completely mechanically compatible behavior. The main conclusions of this work were that these systems represent a class of polycomposite materials exhibiting restricted molecular mixing. Discrete intermingling macromolecular phases seem to constitute a morphology permitting almost additive phase response to deformation. This intermingling type of morphology was postulated to account for isochronal curve broadening and still to allow for the observed shifting of the mechanical glass transition temperature with changing composition. No evidence was found for true molecular compatibility. The contribution of temperature to the properties of the polyblends was also shown to be an analog of the composition trends.

The authors express their special thanks to Mrs. Ruth D. Zabarsky for the computer calculations used in this work. 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