

Polyblends. I. Mechanical Properties of Polyblends of Butadiene-Acrylonitrile Elastomers and Copolymers of Vinyl Stearate and Vinyl Chloride

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Synopsis

Several nitrile rubber elastomers were polyblended, across the composition range, with selected polymeric compositions containing vinyl chloride. The compositions incorporated were (a) bulk poly(vinyl chloride) (PVC); (b) copolymers of vinyl stearate and vinyl chloride containing, respectively, 0.21, 0.36, and 0.47 weight fraction of the vinyl ester; and (c) mixtures containing the same weight fractions of di-2-ethylhexyl phthalate (DOP) with PVC. Mechanical, viscoelastic, optical, and volatility properties were studied on all blends in this first paper. To accurately compare the mechanical properties of polyblends of different systems, a criterion of mechanical equivalence was taken as the observance of similar stresses at break for compositions selected to have identical 100% moduli. Optimum mechanical equivalence, therefore, occurred at the largest ratios of 100% modulus to break stress for all systems compared. Optimum mechanical property equivalence was observed for NBR blends with PVC and for similar blends of both internally and externally plasticized systems containing 0.21 weight fraction of plasticizer. However, considerably more nitrile rubber was needed for PVC blends to acquire the properties of the plasticized systems. Mechanical equivalence was observed, but was not optimum for systems having more plasticizer because tensile strengths were lower. Polyblending with NBR improved the toughness and low-temperature properties of starting vinyl stearate copolymers. Improved toughness was indicated by the expansion of areas under stress-strain curves. Refractive index matching appeared to explain the transparency of the best films and their relative freedom from haze. On heating at 85°C, poly(vinyl chloride) and the copolymer polyblends suffered no volatility loss. Volatility of DOP from the blends was 1.5 times greater than for PVC-DOP mixtures. Because modulus-temperature curves and mechanical T_g values of the filler component shifted with composition, the mechanical behavior of these blends was in harmony with an accepted standard of interdomain compatibility.

INTRODUCTION

This paper and those that follow^{1,2} will consider the mechanical properties of polyblends of mostly unvulcanized nitrile rubbers (NBR) with poly(vinyl chloride) (PVC), together with blends incorporating copolymers of vinyl stearate and vinyl chloride,^{3,4} and mixtures of PVC and di-2-ethylhexyl phthalate (DOP). Mixtures of PVC and NBR in bulk and, presumably, in the presence of external or internal plasticizers for the PVC are considered to be compatible⁵⁻⁷ over wide compositional ranges of their blends. However, similar

composite systems having even greater morphological intimacy are often found to be incompatible. The relative ductility of the hard inclusions in all polycomposites having soft matrixes appears to be important in specifying the nature of the mechanical response which defines the extent of compatibilization. Thus, rubbers reinforced with carbon,^{8a} silicas,^{8b} and hard vinyl^{8c} are incompatible blends. Incompatible blends also result when low-ductility organic fillers such as polystyrene, poly(methyl methacrylate), and polyacrylonitrile are inserted into low-moduli elastomers in polyblends,⁹⁻¹¹ in graft,¹²⁻¹⁵ and block copolymers,^{16a,17} and in interstitial,¹⁸⁻²² and interpenetrating polymer networks.²³⁻²⁷

In contrast, when more ductile inclusions are present in the soft matrix, greater compatibility is usually observed. For instance, ductile PVC^{28,29} in nitrile rubbers,³⁰⁻³² in ethylene-vinyl acetate copolymers,³³ or in butylene- α -methylstyrene elastomers³⁴ yields compatible systems. Certain epoxy resins in NBR³⁵ and crystalline polyethylene in ethylene-acrylate ester copolymers³⁶ are also compatible. Consequently, the appreciably different phase morphologies^{16b,37-40} resulting from the various synthetic routes outlined above, while contributing in various degrees to compatibilization, have not been found to be solely responsible for the two distinctly different types of mechanical behavior. However, favorable polar interactions, especially in PVC-NBR polyblends,^{5-7,30} can be, but are not always,^{34,36} important in achieving miscibility.⁶

The two most important criteria for incompatibility in bulk polycomposite materials are the persistence of the glass temperature of the blend components and the stepped nature of the storage modulus-temperature curves^{5-7,17,41} of the blends. Similarly, two loss maxima are found that vary in intensity as composition changes.^{17,41} Systems considered compatible, on the other hand, are characterized by a single glass transition (or loss maximum) and families of modulus-temperature curves that shift to lower temperatures as the softer component prevails.^{5,6,42} Hence, they behave like plasticized polymers. Because of their ultrafine microstructure,^{16b,43} with dimensions in the range of a few hundred to several thousand angstroms, many of these materials are optically transparent^{5,6,44} even when refractive indexes are unmatched. Exceptions are fiber-reinforced materials⁴⁵ not considered in this report. While this rules out appearance as a criterion of compatibility in unstressed samples, whitening at high stresses in samples where the hard phase is continuous does constitute a reliable appearance criterion.⁴⁴

In the work to be described here and in the papers that follow,^{1,2} ductility of the hard phase could be increased at will from that of the bulk state of PVC by narrowing the difference between T_g for the reinforcing inclusions and ambient temperature. Consequently, mixed rubber polyblends, differing only in bulk viscosity, resulted at high plasticizer contents. Therefore, these systems should be essentially composition analogs in reflecting effects usually brought about by temperature on polymers and blends. Also, the two types of PVC plasticizers, internal through vinyl stearate and external through DOP, should differ mainly in volatility and in their relative plasticizing efficiencies.^{3,4,46,47}

Specifically, in this paper, the mechanical properties at room temperature were studied for NBR polyblends at four blend compositions across the range. The nitrile rubbers were blended with the following systems: (a)

bulk poly(vinyl chloride); (b) three copolymers of vinyl stearate and vinyl chloride, containing 0.207, 0.356, and 0.467 weight fraction of vinyl ester, respectively; and (c) three mixtures of PVC and DOP having the same plasticizer weight fractions. Three nitrile rubbers, having different compositions and mechanical properties, were employed as the rubbery phase. Two were newly introduced powdered nitrile⁴⁸ rubbers of contrasting high and low Mooney viscosity and crosslink density. The other was a cold-recipe, low-nitrile NBR, prepared in these laboratories. It was the rubber base used to compare the properties of gum and unvulcanized polyblends. Finally, some properties of blends of vinyl acetate copolymers with vinyl chloride were contrasted with the results on the above. Ultimate strengths and rupture energies at ambient temperature; equivalence of mechanical properties as systems and their compositions are changed; transparency, and volatility are described in this first paper. The paper that follows¹ treats isochronal modulus-temperature properties, while a third² correlates the present, and some additional, data with selected theories^{41,42,49} of viscoelastic behavior for poly-composite materials, with respect to the points about compatibility discussed in the section above.

EXPERIMENTAL

Monomers and Copolymers

Copolymers were prepared as in reference 47 from monomers of the same purity. (Because of possible health hazard, vinyl chloride monomer must be handled with proper precautions to prevent exposure by the operator or other personnel.)

Elastomers

Newly developed powdered Hycar nitrile rubbers from B. F. Goodrich⁴⁸ were used. These materials were specially designed to provide good intimacy and speed of mixing in thermoplastic polyblending. The two Hycars used were selected, from the screening of a series, to represent property extremes. Hycar 1411 was a medium nitrile (0.336 mole fraction acrylonitrile, by elemental analysis), high Mooney (ML-4 at 212°F, 115), crosslinked rubber, only 11% soluble after Soxhlet extraction for 24 hr with toluene. Hycar 1452P-50 was a low Mooney (50) of similar nitrile content (0.303 mole fraction of acrylonitrile) but was 89% soluble after similar Soxhlet extraction. The other elastomer was prepared in 90% yields in these laboratories by a standard cold recipe⁵⁰ held at 30°C for 24 hr. Composition of this copolymer, designated AN25, was 0.249 mole-% acrylonitrile; it was 92% soluble after Soxhlet extraction with toluene. Molecular weights were obtained on all soluble copolymers by membrane osmometry.³

Preparation of the Polyblends

All ingredients of the polyblend (polymer, external plasticizer, when used, elastomer, and PVC stabilizers) were thoroughly premixed. They were then band mixed on a roll mill, typically at 300–320°F, for about 5 min. The

TABLE I
Compositions, Mechanical Properties, and Molecular Weights of the Starting Polymers and Copolymers

Expt. no.	Elastomer designation	Composition ^a		Molecular weights		Tensile properties			Bayshore rebound, %			
		m_b	w_b	\bar{M}_n	\bar{X}_n	Strength, psi	Modulus, ^b psi	% Elongation				
1		0		Copolymers: Vinyl Stearate and Vinyl Chloride			6270	1.90×10^5	4.1	46		
2		0.05	0.207	54,200	724	5830	1.50×10^5	11.4	51			
3		0.10	0.356	59,900	686	2280	2000	117.0	49			
4		0.15	0.467	57,500	577	1180	800.0	155.0	32			
5				Mixtures: Poly(vinyl Chloride) and Di-2-ethylhexyl Phthalate (DOP)			4300	4180	118.0	45		
6						2550	1450	168.0	17			
7						1490	591.0	273.0	16			
8	Hycar 1411c	0.336		Elastomers: Goodrich Hycar Powdered Rubbers and AN 25			26,700	498	159.0	119.0	520	25
9	Hycar 1452P-50c	0.303				58,300	1080	25.0	55.0	1270	40	
10	AN 25d	0.249				51,600	960	60.0	44.0	1350		
11		0.40		Copolymers: Vinyl Acetate and Vinyl Chloride								
12		0.60	0.674d	49,700	673	6030			2.28×10^5	4.0		
13		0.80	0.846d	94,900	1210	5200			1.92×10^5	9.9		
				153,100	1860	1860			0.52×10^5	14.0		

^a The letter m designates mole fraction; w , weight fraction. The subscript b designates, in experiments 1-4, vinyl stearate; in experiments 5-7, DOP; in experiments 8-10, acrylonitrile; in experiments 11-13, vinyl acetate. Compositions were obtained from elemental analysis, except for the DOP mixtures.

^b Secant moduli, except where elongations exceeded 100%, where the 100% modulus was reported.

^c Solubilities, after Soxhlet extraction in toluene, were as follows: expt. 2, 57%; expt. 8, 10.5%; expt. 9, 88.5%; expt. 10, 91.8%; expt. 11, 30.0%; expt. 12, 62.1%; expt. 13, 66.4%.

^d Prepared at this laboratory by emulsion polymerization of 0.25/0.75 acrylonitrile-butadiene feed stock at 30°C.

^e Feed composition.

milled samples were placed in a hydraulic press and molded at the same temperature for 10 min at moderate pressure, then for 10 min more at 20 to 30 times this pressure; and cooled to room temperature by passing cold water through the water jacket of the press. However, blends employing copolymers containing 35.6 wt-% vinyl stearate were usually milled and molded at 280°F, while those containing 46.7% of the internal plasticizer were milled and molded at 200–220°F. Harsher thermal treatment was thus required for the blends employing DOP; consequently, they were somewhat darker than those using vinyl stearate of the same concentration. The blends were straw colored, the color being largely contributed by the elastomers. Hycar 1452P-50 produced the lightest-colored materials. Most of the molded samples were judged free of internal stresses since no dimensional changes occurred on reheating selected samples to high temperatures. However, the starting elastomers and the polyblends richest in elastomer shrank considerably on release from the mold.

The PVC stabilizer used was a 1-to-2 mixture of a cadmium–barium stabilizer (Vanstay-R.R., R. T. Vanderbilt Co., New York) and an epoxidized oil (G-62, Rohm and Haas). This stabilizer was mixed so as to constitute 3 wt-% of the total blend used in each recipe, and the elastomer concentration was reduced by this amount. For purposes of data correlation, the stabilizer concentration was included as part of the rubber. This seemed to be reasonable because the mechanical properties of the elastomers containing stabilizer were identical with those containing none.

Gum vulcanizates were prepared using a recipe containing 5% zinc oxide (Kadox-15, New Jersey Fine Co.), 1.5% sulfur (NBS standard 371), 1% stearic acid (NBS standard 372), and 1% benzothiazyl disulfide (ALTAX Goodyear Tire and Rubber Co.). All samples were milled for 5 min, the vulcanizing materials were added, and milling was continued for another 5 min at 300–320°F. Molding was done at 300–320°F for 20 min at 20 tons pressure.

Mechanical Properties

All samples were equilibrated at 23°C and 50% R.H. for at least 24 hr before testing. Tensile data were obtained with an Instron tensile tester using ASTM D638-61T. Cross-head speed for all samples was 20 in./min. Shore A hardness measurements were performed according to ASTM D1706-61.

Viscoelastic Properties

A Williamson torsional wire stiffness apparatus⁵¹ was used. This apparatus monitors the rubber plateau region of soft samples with greater accuracy than the Clash-Berg apparatus.⁴ A comparison of the use of the two instruments will be reserved for the next paper.¹

Optical Properties

The appearance of films measuring 1 in. × 2.5 in. × $\frac{1}{16}$ in. were judged in the following manner. Transparency was classified by placing the films on a page of standard printing and judging the transmission in a scale of values

TABLE II
Compositions, Tensile Properties, and Viscoelastic Properties of Selected Polyblends^a

Expt. no.	Composition		Tensile properties			Viscoelastic properties			Bayshore rebound, %
	NBR, weight fraction	Polymer, weight fraction	Strength, psi	Modulus, 100% psi	% Elong.	$T_g^b, ^\circ\text{C}$	E_{123}^c, psi	E_{1120}^c, psi	
		Copolymer: Vinyl Stearate, 0.05 Mole Fraction (0.207 Weight Fraction) and VCI Blended with Hycar 1411							
1	0.25	0.75	2510	1820	278	9	28	31,000	270
2	0.38	0.62	2380	1200	399	-9	20	9000	270
3	0.50	0.50	1910	719	356	-14	8	1740	290
4	0.75	0.25	1640	415	600	-22	-9	850.0	270
		Copolymer: Vinyl Stearate, 0.10 Mole Fraction (0.356 Weight Fraction) and VCI Blended with Hycar 1411							
5	0.25	0.75	1650	793	342	-15	16	3700	52
6	0.38	0.62	1560	536	429	-21	12	1550	120
7	0.50	0.50	1500	375	469	-19	3.0	880	130
8	0.75	0.25	878.0	229	595	-25	-18	540	170
		Copolymer: Vinyl Stearate, 0.15 Mole Fraction (0.467 Weight Fraction) and VCI Blended with Hycar 1411							
9	0.25	0.75	928	449	396	-21	9	1030	13
10	0.50	0.50	863	334	478	-23	-1	700	87
		Mixture: Di-2-ethylhexyl Phthalate (DOP) (0.207 Weight Fraction) and PVC Blended with Hycar 1411							
11	0.25	0.75	3280	1760	290	-5	19	10,300	450
12	0.38	0.62	2460	1060	294	-14	6	4700	450
13	0.50	0.50	1850	871	238	-19	-2	2900	450
14	0.75	0.25	1280	565	330	-25	-17	950	400
		Mixture: Di-2-ethylhexyl Phthalate (DOP) (0.356 Weight Fraction) and PVC Blended with Hycar 1411							
15	0.25	0.75	2270	642	381	-30	-13	1120	320
16	0.38	0.62	2010	537	380	-28	-15	940	370
17	0.50	0.50	1600	576	354	-30	-17	770	350
18	0.75	0.25	945	264	474	-26	-20	560	270
		Mixture: Di-2-ethylhexyl Phthalate (DOP) (0.467 Weight Fraction) and PVC Blended with Hycar 1411							
19	0.25	0.75	1410	359	391	-38	-30	660	310
20	0.38	0.62	1360	337	401	-38	-27	520	300
21	0.50	0.50	1100	262	460	-36	-26	540	330
22	0.75	0.25	758	198	518	-30	-24	500	250
		Homopolymer: Poly (vinyl Chloride) Blended with Hycar 1411							
23	0.25	0.75	4040	62,500	66 ^d	29	60	1.80×10^5	660

24	0.50	0.50	2380	1530	198	-10	14	10,500	500	16
25	0.58	0.42	2320	1090	293	-14	5	5500	500	16
26	0.66	0.34	2030	701	357	-17	-2	2650	390	12
27	0.75	0.25	1580	537	364	-17	-8	1210	400	11
Copolymer: Vinyl Stearate, 0.05 Mole Fraction (0.207 Weight Fraction) and VCI Blended with Hycar 1452P-50										
28	0.25	0.75	2190	1450	326	1	19	7000	200	
29	0.38	0.62	2020	658	482	-10	4	1050	210	16
30	0.50	0.50	1520	380	604	-18	-6	680	150	
31	0.75	0.25	772	173	1369	-29	-21	345	80	
Homopolymer: Poly(vinyl Chloride) Blended with Hycar 1452P-50										
32	0.25	0.75	3590	96,070	84 ^d	31	49	2.29 × 10 ⁵	560	
33	0.50	0.50	1550	1086	250	-12	13	6000	230	
34	0.58	0.42	2055	738	471	-10	4	1750	220	
35	0.66	0.34	1602	505	557	-19	-4	980	170	
36	0.75	0.25	1139	292	720	-27	-12	510	140	
Copolymer: Vinyl Stearate, 0.05 Mole Fraction (0.207 Weight Fraction) and VCI Blended with AN 25, Uncured										
37	0.25	0.75	2220	1290	286	-5	17	6400	180	
38	0.50	0.50	1404	374	562	-18	-9	600	170	
39	0.75	0.25	525	125	851	-40	-28	280	110	
Copolymer: Vinyl Stearate, 0.05 Mole Fraction (0.207 Weight Fraction) and VCI Blended with AN 25, Cured										
40	0.25	0.75	2530	1230	316	-3	21	11,000	320	
41	0.50	0.50	1900	384	348	-19	-4	790	400	
42	0.75	0.25	940	207	386	-31	-20	545	360	
43	1.00	0	531	164	302	-39	-33	450	400	
Copolymer: Vinyl Acetate, 0.60 Mole Fraction (0.674 Weight Fraction) and VCI Blended with AN 25										
44	0.25	0.75	4310	1.95 × 10 ⁵ ^d	9.6	41	46	3.80 × 10 ⁵	110	
45	0.50	0.50	1200	4670 ^d	51.0	-34	41	62,500	75	
46	0.75	0.25	269	926 ^d	85	-46	-34	1650	50	

^a In addition to the experiments listed, blends of Hycar 1452P-50 with vinyl stearate copolymers and DOP mixtures, corresponding to experiments 5 through 22, were prepared. Similarly, blends of AN 25 corresponding to experiments 37 through 42 with PVC and with vinyl stearate copolymers of, respectively, 0.10 and 0.15 mole fraction vinyl stearate, both cured and uncured, were prepared. Blends of the remaining vinyl acetate copolymers of Table I were prepared like experiments 44 through 46. The properties of some of these will be presented as part of the data in the tables and figures that follow.

^b Temperature corresponding to a torsional modulus of T_f , 135,000 psi; T_f , 14,500 psi.

^c Torsional modulus at, respectively, 23°C and 120°C.

^d Secant moduli.

designated 1, opaque; 2, near opaque; 3, clear; and 4, very clear. Haze was classified by the extent of transmission through a film held against the window. Designations were: A, opaque; B, translucent; C, much haze; D, considerable haze; and E, slight haze.

Refractive Index

Refractive indexes were done at 30°C with an Abbé refractometer (Carl Zeiss #33062) on thin films (0.01 mm or less), prepared mostly as mechanical flashing. Films deposited by solvent evaporation were used for a few starting copolymers.

Volatility

Molded films, prepared without the addition of the stabilizers described above, and cut to sizes approximately 10 cm × 5 cm × 0.04 cm (and weighing about 2.5 g) were suspended in a closed, unventilated oven at about 85°C. These were weighed daily over a two-week period. Initial samples resembled the stabilized films in appearance; they darkened to only a small extent during the heating period. However, both Hycar elastomers contained a small weight fraction of a volatile component (Hycar 1411, 0.4 wt-%; and Hycar 1452P-50, 0.71 wt-%) that was completely distilled off in three days at 85°C. All volatility data were corrected for this component.

An IBM computer was used for all computations in this paper.

RESULTS AND DISCUSSION

General Features

In Table I are listed the compositions, number-average molecular weights, and mechanical properties of the starting homopolymers, copolymers, plasticized mixtures, and nitrile rubbers used in this work. Mechanical properties of the homopolymers and copolymers were similar to those previously described³; those of experiments 1 and 2 indicate systems having glass temperatures above room temperature. The tensile data for the elastomers are typical of the poor properties of unfilled, unvulcanized rubber,⁵² even though Hycar 1411 was somewhat superior to the others. The high Bayshore values reflect the high storage modulus of the complex moduli in these hard or leather-like copolymers, while considerable damping was present in the elastomers and highly plasticized PVC.

Table II lists the compositions, mechanical properties, and some limited viscoelastic properties of a selection of the polyblends prepared in this work. The first six sections (experiments 1 through 27) list all of the available data for the polyblends using Hycar 1411. The same polyblend compositions were studied for Hycar 1452P-50, but the data are only partially listed to conserve space. Incomplete data are also presented in the table for AN 25 blends, both vulcanized and unvulcanized, as well as for the blends made from vinyl acetate copolymers. Some data missing from the table are available from the tables and figures that follow. It should be noted that moduli for the stiffer

PVC systems were made similar to those of the plasticized systems by increasing the nitrile content of the blend.

From the modulus-temperature curves, the quantities T_f (corresponding to a modulus of 135,000 psi) and T_i (corresponding to a modulus of 14,500 psi, or 10^9 dynes/cm², ref. 48) were taken. The latter temperature has correlated well with T_g ($T_g = T_i - 10.4^\circ\text{C}$) for internally and externally plasticized compositions of PVC.⁴ In these polyblends, T_f was found to represent the softening temperature of the rubber phase, while T_i was taken to be the mechanical glass transition of the harder filler component. The quantities E_{t23° and E_{t120° are the torsional moduli at 23°C (ambient) and 120°C, respectively. These moduli, when considered in conjunction with T_f , yield some indication of the use-temperature range of the polyblends.

For the blends listed in each section of the table (Table II), tensile moduli and strengths decreased steadily as NBR content increased, while elongations usually increased. However, the rate of change of mechanical properties fell as more plasticizer (internal or external) was introduced into each starting copolymer or mixture. Although the softening temperature (T_f) of the rubber component remained approximately constant ($\sim -20^\circ$ to -30°C), that of the plastic component (T_i) showed a steady decrease with increase in NBR for the data in each section. In like fashion, ambient torsional moduli E_{t23° decreased steadily, the rate of change decreasing with plasticizer content. However, the rate of change of the high-temperature modulus E_{t120° varied little with composition, although the magnitude of the observed value changed from system to system. Thus the mechanical and viscoelastic behavior of the polyblends presented in Table II is appropriate to conventionally plasticized homopolymers. The data are, therefore, in harmony with the criteria for compatible polyblends discussed in the introduction, wherein modulus-temperature curves were seen to shift with composition. At higher temperatures, the mechanical behavior was that of blended rubbers of different bulk viscosity. The properties of blended rubbers were also found, to a considerable extent, in those systems (experiments 5 through 22) for which T_g of the starting copolymer or mixture was less than room temperature.

The stiffness of these polyblends at room temperature was more sensitively described by torsional stiffness (E_{t23°) than by tensile modulus at 100% elongation. The former value lies close to the initial tensile modulus and so reflects the state of the blend at the lowest levels of strain. Stiffness for the individual systems (noted by averaging over each section in Table II) declined roughly in the order PVC > vinyl stearate copolymers > DOP mixtures, reflecting the initial state of aggregation of the filler component. The order of stiffness contributed by the elastomers was Hycar 1411 > Hycar 1452P-50 > AN 25, reflecting the crosslink density and nitrile content of the rubbers. The reinforcing influence of the filler at high temperatures (E_{t120°) varied in the order PVC > DOP mixture > VS copolymers, but each value was in turn influenced by the elastomer, decreasing in the order given above. The data for Bayshore hardness were inconclusive because high rebound was found for the stiffer systems, reflecting their Hookean elasticity. Because the rebound of the starting elastomers indicated high damping,⁵³ the Bayshore values for the softer systems in the table suggest poor network density or perfection.

Finally, very poor mechanical properties and high T_i values were found for

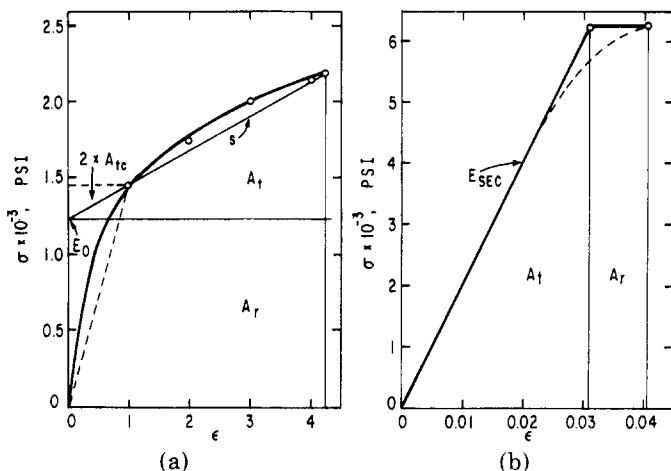


Fig. 1. Schematic representation of models used for estimating tensile areas. (a) Soft polymers, mixtures, and polyblends; (b) stiff starting polymers and copolymers.

vinyl acetate–vinyl chloride copolymer polyblends (experiments 44–46). Because the glass transitions of the starting copolymer seem to remain observable (as T_i) in the first two blends (experiments 44–45), there is a suggestion of incompatibility in these polyblends. Whether phase aggregation was extreme here and led to low tensile strengths and brittle failures is not known at present.

In the sections that follow, more detailed consideration will be given to the rubber toughening effect, the extent of mechanical equivalence of the different blends, optical properties, and the degree of plasticizer volatility.

Approximate Relative Stress–Strain Areas

For all of the data in Tables I and II, tensile stresses were taken incrementally at unit elongations up to failure. Most of the resultant stress–strain curves had the appearance of the solid curve shown schematically in Figure 1, insert 1. Most curves were characterized by a rapid rise in stress to about unit strain, then yielded, with deformation stabilization,⁵⁴ to a slightly curved arc as shown, which persisted up to failure. A few, having high initial moduli and tensile strengths (like experiments 1 and 2, Table I), resembled that of Figure 1, insert 2. To obtain approximate areas, the experimental data were treated in the following manner. All curves were fitted with a rectangle and triangle whose areas were designated A_r and A_t , respectively, as shown in the figure. Areas of the dashed triangle (A_{tc}) in insert 1 were also obtained and arbitrarily factored to provide an empirical correction for curve overlap. The algebraic sum of areas yielded an approximation of the total area A . While considerable error was, of course, entailed in this simple procedure, an estimation of the relative toughness⁵⁵ of the starting polymers and the derived polyblends could be obtained from these approximate rupture energies.^{56,57}

Area correlations with composition are shown in Figure 2, insert A, for polyblends prepared from Hycar 1411 and bulk PVC (dashed line), together with polyblends of copolymers of vinyl stearate at all three weight fractions of

vinyl stearate. Area data for polyblends incorporating DOP-PVC mixtures are shown in insert B. All of the copolymers exhibited a maximum stress-strain area near a weight fraction of NBR of 0.5. The PVC data were skewed to higher NBR values, while those for DOP-PVC were displaced to lower weight fractions of elastomer. This behavior was similar to that found for the influence of temperature on the rupture energies of poly(methyl methacrylate).⁵⁴ Moreover, the areas for all plasticized fillers decreased with increased plasticizer as shown. The curve displacement with w_1 was in line with the relative free volume contributions of the three filler types, which increases in the order PVC, VS copolymers, DOP mixtures. The vertical order

TABLE III
Area Ratio Data for Selected Polyblend Systems

Expt. no. ^a	Polymer system ^b	Composition		Approx. area, lb/in. ²	Area ratios ^c		
		NBR, weight fraction	Polymer, weight fraction		A_m/A_p	A_{VS}/A_{DOP}	A_m/A_r
Polyblends with Hycar 1411							
1	VS, 0.207	0.25	0.75	5031	9.13	0.88	7.53
3	VS, 0.207	0.50	0.50	3674 ^d	6.67	1.69	5.50
5	VS, 0.356	0.25	0.75	3378	3.34	0.79	5.05
7	VS, 0.356	0.50	0.50	3579	3.54	1.20	5.36
9	VS, 0.467	0.25	0.75	2294	3.10	0.86	3.43
10	VS, 0.467	0.50	0.50	2499	3.38	0.99	3.73
11	DOP, 0.207	0.25	0.75	5706	1.61		8.53
13	DOP, 0.207	0.50	0.50	2177	0.61		3.26
15	DOP, 0.356	0.25	0.75	4289	2.62		6.42
17	DOP, 0.356	0.50	0.50	2990	1.83		4.47
19	DOP, 0.467	0.25	0.75	2657	1.34		3.98
21	DOP, 0.467	0.50	0.50	2531	1.28		3.79
24	PVC, 1.0	0.50	0.50	2635	17.2		3.94
26	PVC, 1.0	0.66	0.34	3771	24.6		5.64
Polyblends with Hycar 1452P-50							
28	VS, 0.207	0.25	0.75	5038	9.15	0.82	7.07
30	VS, 0.207	0.50	0.50	4967	9.02	1.56	6.97
33	PVC, 1.0	0.50	0.50	2637	17.17		3.70
35	PVC, 1.0	0.66	0.34	5073	33.03		7.12
Polyblends with AN25, Uncured							
37	VS, 0.207	0.25	0.75	3982	7.23	0.85	5.85
38	VS, 0.207	0.50	0.50	4277	7.76	1.52	6.29
11'	PVC, 1.0	0.50	0.50	857.0	1.56	0.53	1.26
Polyblends with AN25, Cured							
40	VS, 0.207	0.25	0.75	4700	8.53		6.40
41	VS, 0.207	0.50	0.50	2811	5.10		3.83
12'	PVC, 1.0	0.50	0.50	1604	2.91		2.18

^a Corresponds to order of Table II; primed numbers are for data not listed in Table II.

^b VS designates vinyl stearate; DOP, dioctyl phthalate; PVC, poly(vinyl chloride). Numbers are the respective weight fractions in the copolymers or mixtures.

^c Subscripts have the following meaning: m , polyblend; p , starting polymer, copolymer, or mixture; r , starting nitrile rubber. A_{VS}/A_{DOP} is the ratio of the copolymer polyblend area to that of the corresponding DOP mixture. The ratio of uncured to cured is given in column 10 of samples 37, 38, and 11'.

^d Point off of the curve in Fig. 2.

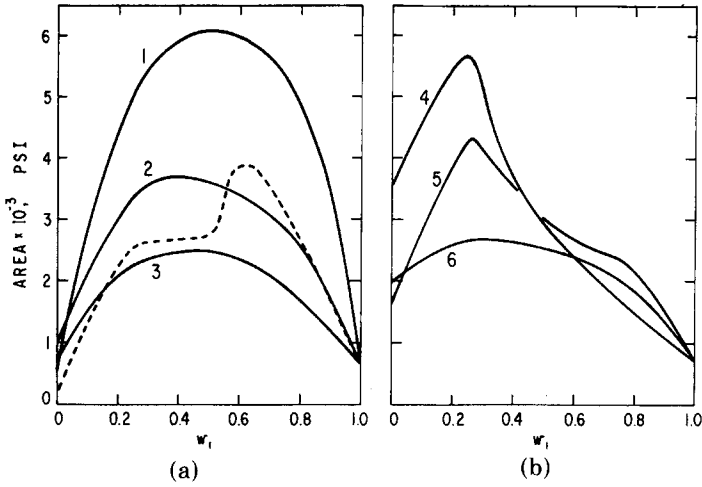


Fig. 2. Estimated stress-strain areas vs. the weight fraction of Hycar 1411. (a) Copolymers of vinyl stearate and vinyl chloride. Weight fraction of vinyl stearate in the copolymers is as follows: curve 1, 0.207; curve 2, 0.356; curve 3, 0.467. (b) Mixtures of DOP and PVC. Weight fraction of DOP in the mixture is as follows: curve 4, 0.207; curve 5, 0.356; curve 6, 0.467. Dashed line is PVC homopolymer.

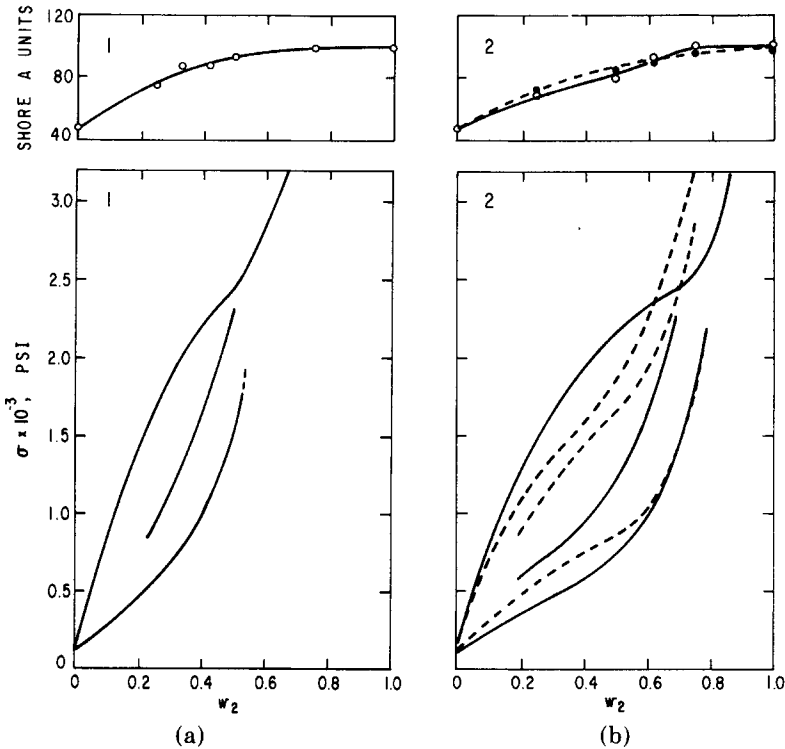


Fig. 3. Tensile stress σ vs. weight fraction w_2 of polymer copolymer or mixture in polyblends of Hycar 1411. (a) Data for poly(vinyl chloride); (b) Vinyl stearate copolymers and DOP-PVC mixtures (dashed line), both compositions containing 0.207 weight fraction of plasticizer. In both (a) and (b), the lowest of the three sets of curves is 100% modulus, the middle set is stress at 300% extension, and the upper set is the stress at break. The upper inserts are the corresponding data for Shore hardness.

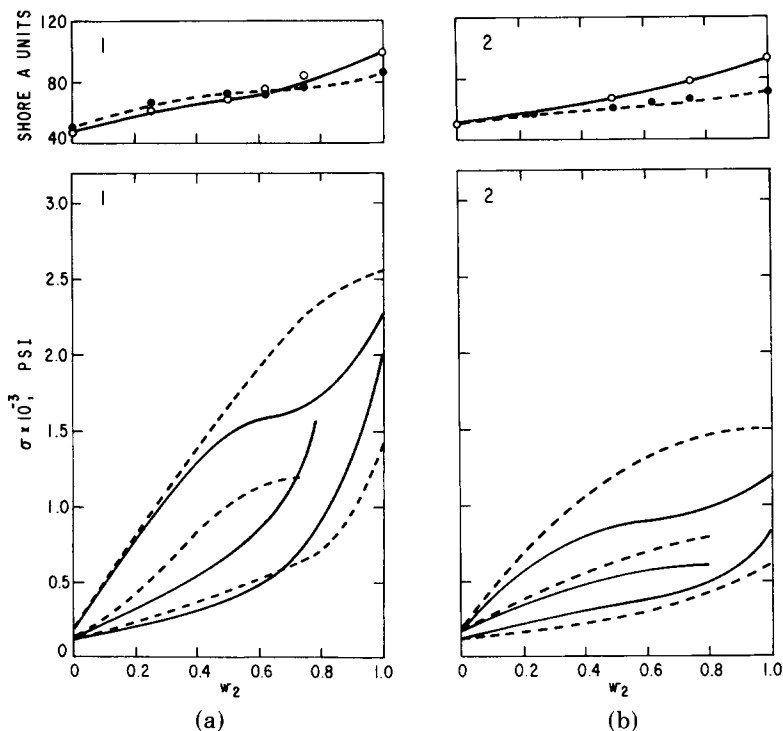


Fig. 4. Tensile stress σ vs. weight fraction w_2 of polymer, copolymer, or mixture in polyblends of Hycar 1411. (a) Data for vinyl stearate copolymers (solid lines) and DOP-PVC mixtures (dashed lines), both compositions containing 0.356 weight fraction of plasticizer. (b) The same as (a) except that the weight fraction of plasticizer was 0.467. In both (a) and (b), the lowest of the three sets of curves represents 100% modulus, the middle set is stress at 300% elongation, and the upper set is the stress at break. The upper inserts are the corresponding data for Shore hardness.

for each composition (curve maximum $1 > 2 > 3$ and $4 > 5 > 6$) paralleled the order of ultimate strengths found for the starting compositions.^{3,4} The improvement in toughness compared to the starting copolymers and elastomers is obvious; these data illustrate the dual role that both elastomer and filler played in dissipating deformation energy at high strains, thereby retarding failure.

Table III lists rupture energy improvement ratios for selected polyblends. Subscripts m , p , and r designate the polyblend mixtures, starting polymers, and rubbers, respectively. The ratios are, therefore, numerical improvement factors whose magnitude indicates the rupture energy improvement of the blend over that of the starting polymer or elastomer. As was already seen in Figure 2, improvement for all blends was in the order of decreasing plasticizer in the filler; it was relatively insensitive to elastomer type or extent of cure.

Equivalent Mechanical Properties

Plots of 100%, 300%, break stress, and Shore A units as functions of weight fraction of the polymeric filler, w_2 , are presented in Figures 3 through 7. The mechanical equivalence can be readily ascertained from the plots. Two or

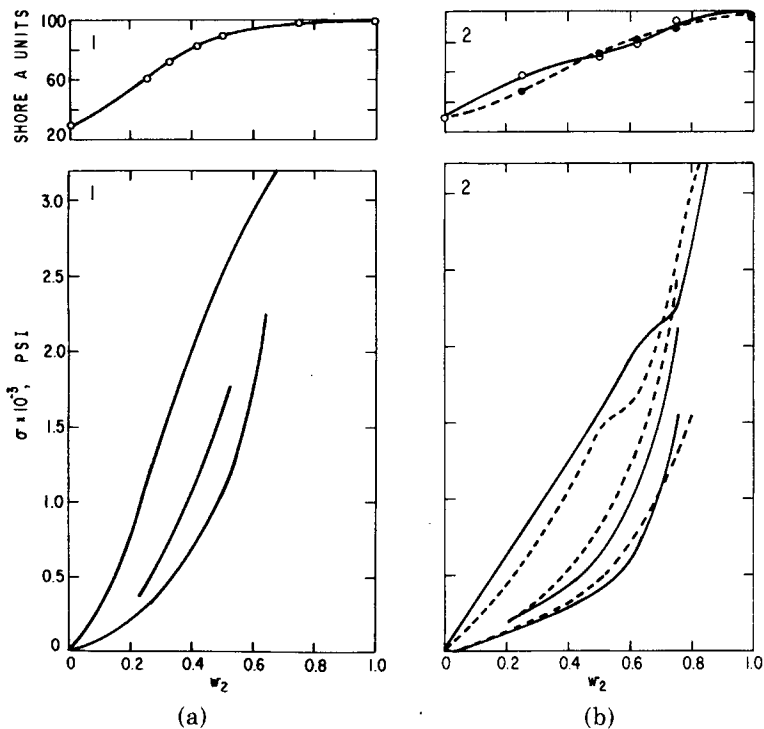


Fig. 5. Tensile stress σ vs. weight fraction w_2 of polymer, copolymer, or mixture in polyblends of Hycar 1452P-50. (a) Data for poly(vinyl chloride); (b) Vinyl stearate copolymers (solid line) and DOP-PVC mixtures (dashed line), both compositions containing 0.207 weight fraction of plasticizer. In both (a) and (b), the lowest of the three sets of curves is 100% modulus, the middle set is stress at 300% elongation, and the upper set is the stress at break. The upper inserts are the corresponding data for Shore hardness.

more compositions that are being compared are designated mechanically equivalent when they have similar values of tensile strength σ_b for a preselected value of stress at lower strain. Optimum mechanical properties will occur at the highest ratios of initial and failure stress for the systems being compared.

The trends of these data have already been discussed and should be obvious from the figures. It should be noted that considerably less nitrile rubber was necessary for the same mechanical equivalence using plasticized systems than using unplasticized PVC. A filler-plasticizer content of about 20 wt-% appeared to lie close to the optimum amount for equivalence with unplasticized PVC; higher plasticizer contents produced softer but weaker samples. Similarly, vulcanizing the blends (Fig. 7) raised tensile strengths without affecting 100% moduli. As will be seen, the copolymers had the same low volatility and migrating character as that possessed by blends of unplasticized PVC. While the foregoing remarks are generalizations, the individual plots should permit intelligent selection of individual systems in terms of end use.

A comparison of the mechanical properties of the polyblends of this work with those of other nitrile rubber systems is given in Figure 8. The tensile strengths of the thermoplastic polyblends of this work (systems 6-9) compare

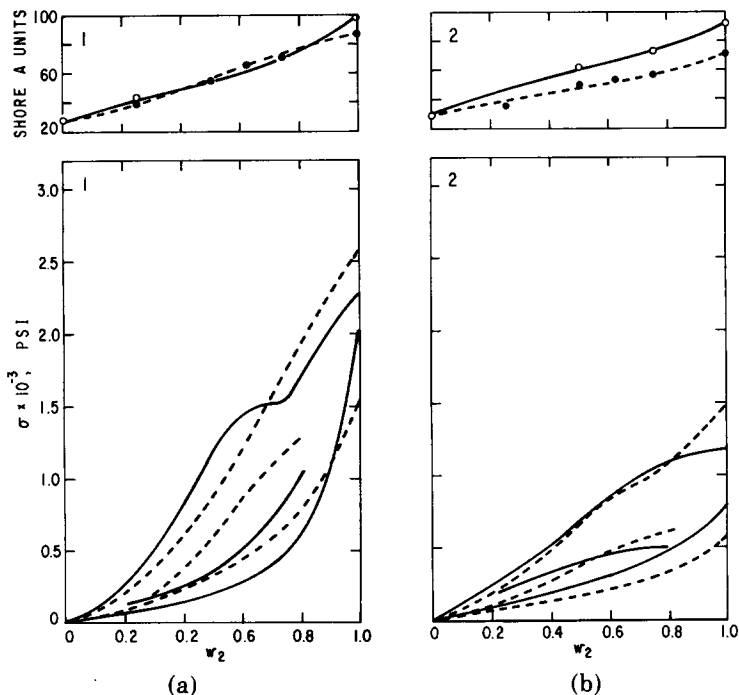


Fig. 6. Tensile stress σ vs. weight fraction w_2 of polymer, copolymer, or mixture in polyblends of Hycar 1452P-50. (a) Data for vinyl stearate copolymers (solid lines) and DOP-PVC mixture (dashed lines), both compositions containing 0.356 weight fraction of plasticizer. (b) The same as (a), except that the weight fraction of plasticizer was 0.467. In both (a) and (b), the lowest of the three sets of curves represents 100% modulus, the middle set is stress at 300% elongation, and the upper set is the stress at break.

favorably with black-filled, vulcanized polyblends of PVC, systems 4-5, but are lower than those of highly reinforced nitrile rubbers, systems 1-3. The 100% and 300% stress and Shore A hardness values of the polyblends, in general, classify them as plastic materials, as noted previously.

Optical Properties

Films, $\frac{1}{16}$ -in. thick, for many of the polyblends containing vinyl stearate or DOP were very transparent and relatively low in haze compared to those incorporating unplasticized poly(vinyl chloride). This was especially true when Hycar 1452P-50 was the elastomer used. It can be seen in Figure 9 that refractive index matching^{5-7,12} may be largely responsible for the behavior. The fact that Hycar 1452P-50, which has a low gel content, yielded reasonably transparent films having reduced haze and color even with unplasticized PVC (insert c) suggests that a large fraction of domains smaller than that required to scatter light ($\sim 1000 \text{ \AA}$) were present when this filler was used. This could have resulted from greater blend intimacy because of the lower bulk viscosity of the elastomer. Domains of this order are common, though admixed with larger sizes, in PVC-NBR polyblends.⁴³ Vinyl acetate copolymers (insert d) produced generally opaque films, the effect increasing with vinyl ester content. Poor index matching or large domains could be responsi-

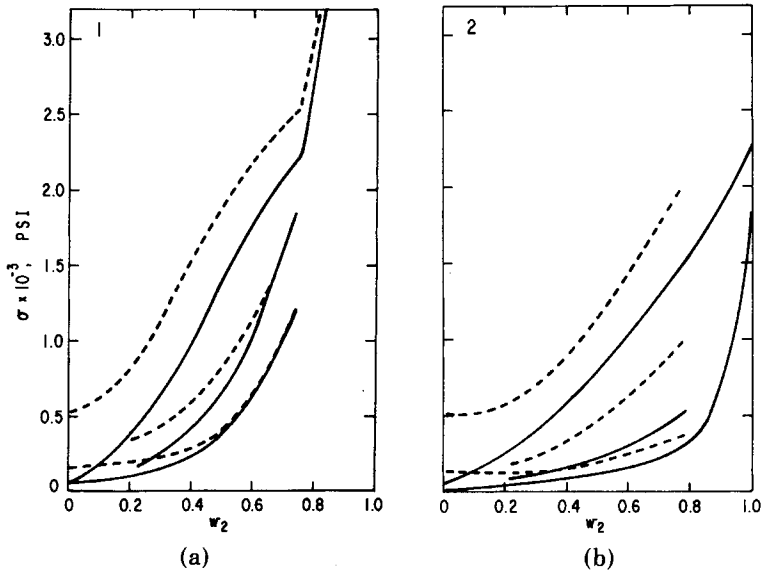


Fig. 7. Tensile stress σ vs. weight fraction w_2 of vinyl stearate copolymers in polyblends of AN 25. The solid line represents uncured samples; the dashed line, sulfur-cured gum stocks. Weight fraction of vinyl stearate in (a) is 0.207; in (b) it is 0.356.

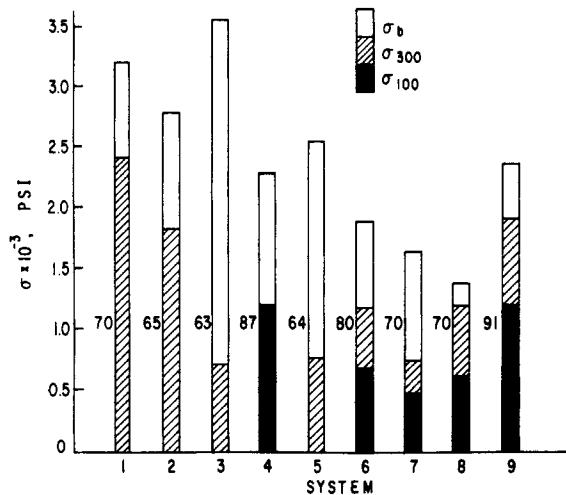


Fig. 8. Tensile stress σ for various nitrile rubber systems. System 1, Perbunan N3307; acrylonitrile content, 33%; black filled, 32%; reference 62a. System 2, Perbunan N2818; acrylonitrile content, 28%; black filled, 33%; reference 62b. System 3, nitrile rubber, Bayer; acrylonitrile content, 33%; silica filled, 33%; reference 8b. System 4, nitrile rubber; acrylonitrile content, 30%; polyblend thereof, NBR 70%–PVC 30%; vulcanized, black 29%; reference 63. System 5, nitrile rubber; acrylonitrile content, 30%; polyblend thereof, NBR 70%–PVC 30%; vulcanized gum; reference 48. System 6, data from graph, Fig. 3; polyblend, NBR 70%–PVC 30%; Hycar 1411. System 7, data from graph, Fig. 3; polyblend, NBR 70%–VS (5 mole-%)–VCL copolymer, 30%; Hycar 1411. System 8, data from graph, Fig. 3; polyblend, NBR 70%–DOP (5 mole-% or 21 wt-%)–PVC mixtures, 30%; Hycar 1411. System 9, experiment 2, Table II.

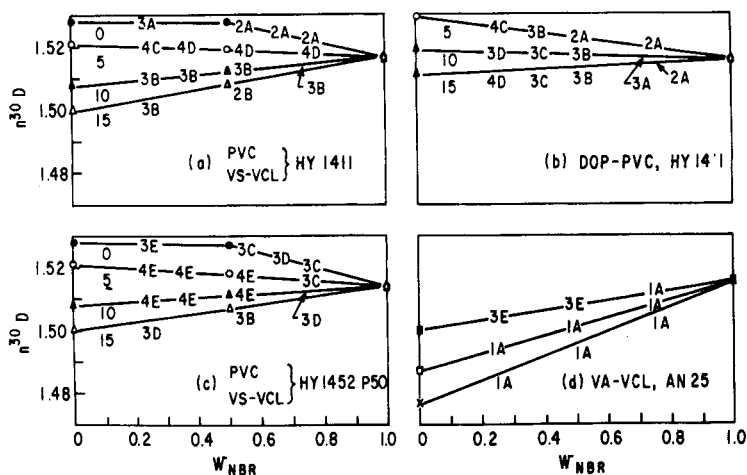


Fig. 9. Comparison of refractive index n^{30}_D of starting compositions and selected polyblends with respect to both transparency (numbers) and haze (letters). Designations are: *Transparency*: 1, opaque; 2, near opaque; 3, clear; 4, very clear. *Haze*: A, opaque; B, translucent; C, much haze; D, considerable haze; E, slight haze. Numbers at left of each insert designate the approximate mole fraction of plasticizer in the starting compositions. Abscissa relate to the weight fraction of NBR. Data for DOP-PVC mixtures with Hycar 1452P-50 resembled those of insert c.

ble for the behavior. Unfortunately, the optical classification method used in this work (see experimental section) was rather subjective. However, work was recently initiated at this laboratory, using both transmittance and scanning electron microscopy, which should produce a complete morphological description of these polyblends.

TABLE IV
Rate Constants at 85°C for the Loss of DOP from the DOP-PVC Mixtures and from the Polyblends

Expt. no.	Zero-order, k , M $\text{kg}^{-1} \text{hr}^{-1} \times 10^5$	First-order, k' , $\text{hr}^{-1} \times 10^5$	$\frac{k'm}{k'_{\text{DOP}}}$	$t_{1/2}$, ^a days	$\frac{(t_{1/2})_{\text{DOP}}^a}{(t_{1/2})_m}$
5 ^b	3.52 ± 0.056	6.68 ± 0.11		314	
6 ^b	7.10 ± 0.21	7.86 ± 0.023		268	
7 ^b	10.54 ± 0.51	7.84 ± 0.15		236	
13	2.35 ± 0.030	8.99 ± 0.42	1.34	234	1.34
17	5.83 ± 0.034	13.01 ± 0.079	1.66	163	1.64
21	8.04 ± 0.19	13.67 ± 0.34	1.74	155	1.52
RC-1 ^{c,d}	$1.24^e \pm 0.070$	$1.37^e \pm 0.077$		1534	
RC-2 ^{c,d}	$4.59^e \pm 0.32$	$5.58^e \pm \text{—}$		414	
RC-3 ^{c,d}	$31.3^e \pm 0.23$	$59.7^e \pm 8.3$		61	
3	$\sim 0^f$	$\sim 0^f$			
7	$\sim 0^f$	$\sim 0^f$			
8	$\sim 0^f$	$\sim 0^f$			

^a Half-time in days calculated for zero-order kinetics.

^b Table I. Other experiments are from Table II.

^c Data of Reed and Connor,⁵⁹ DOP, 0.356 weight fraction.

^d Film thickness, 0.0102 cm; the balance of the experiments had film thicknesses corrected to 0.040 cm.

^e Temperatures were: RC-1, 56°C; RC-2, 69°C; RC-3, 85°C.

^f These data and all other data in the table corrected for volatilization of the stabilizer.

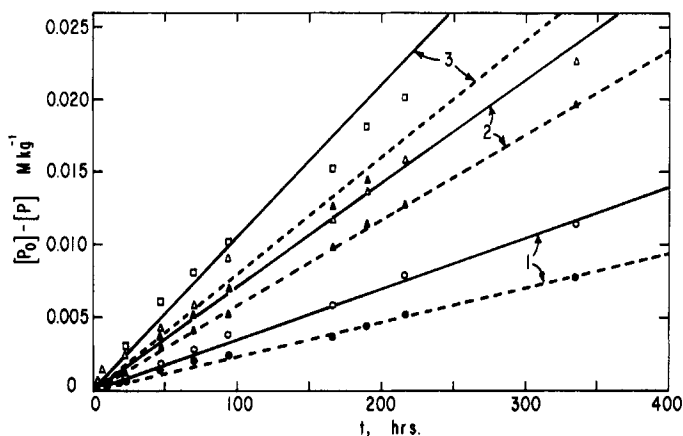


Fig. 10. Zero-order plots of loss of di-2-ethylhexyl phthalate (DOP) from DOP-PVC mixtures (solid lines) and 50:50 polyblends (dashed lines) with Hycar 1411. The weight fraction of DOP in the mixture (before polyblending) was: 1, 0.207; 2, 0.356; 3, 0.467.

Volatility of the Polyblends

The abundant volatility data collected in this work (see experimental section) was treated statistically by use of conventional rate expressions. Zero- and first-order rate constants were generally statistically significant; their values are listed in Table IV. No weight loss was found for either PVC or the vinyl stearate copolymers polyblended with Hycar 1411; only DOP was volatile. A plot of the zero-order rate data for both DOP-PVC mixtures (experiments 5, 6, and 7, Table I) and 50-50 NBR plasticized PVC mixtures (experiments 13, 17, and 21, Table II) are shown in Figure 10. Relative loss of DOP from the blends compared to those of the mixtures was obtained from the ratio of the respective first-order rate constants and the ratio of half-times using zero order rate data. Dioctyl phthalate loss from the blends was about 1.5 times that from neat PVC-DOP mixtures. The reasons for this difference are obscured by the lack of knowledge concerning the various processes contributing to volatility in these systems. The experimental methods used here precluded⁵⁸ any serious analysis of diffusional effect.

Using the literature data of Reed and Connor⁵⁹ for DOP evaporation from PVC at several temperatures, activation energies were computed (Fig. 11) and found to be 25.7 kcal/mole. Curve 1 represents data for a film thickness of 0.0102 cm (as used by Reed and Connor); curve 2 was recomputed from the film thickness studied in this work (0.04 cm). Consequently, the Arrhenius equation may be modified to allow for film thickness:

$$k = f' A_0 e^{-\Delta H/RT} \quad (1)$$

where $f' = 0.0102$; with f being the new film thickness. This equation, when used with the above activation energy to compute the rate constant for experiment 6, gave the tabled value. Consequently, it was the intercept of eq. (1) that was sensitive to film thickness; and, hence, the thickness of the film made the major contributions to rate. The magnitude of the activation energy (Fig. 11), which is related to the cohesive energy density, specifies that volatility of DOP will be severe only at high temperatures, unless the films are

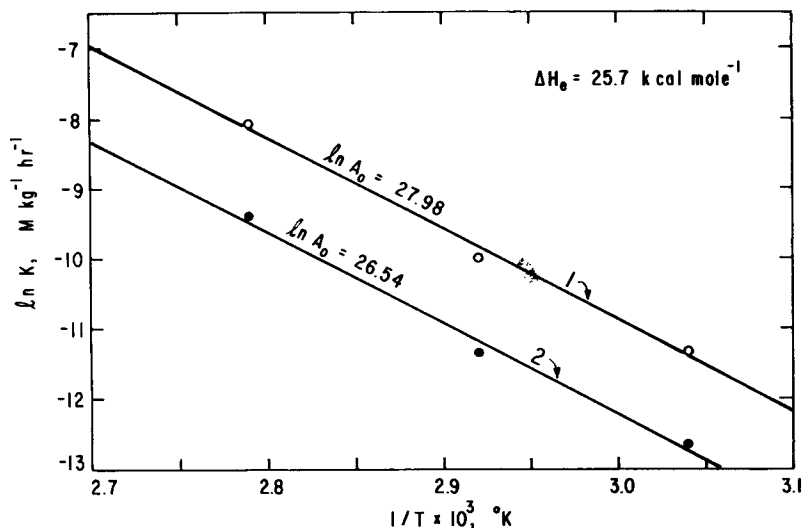


Fig. 11. Arrhenius plot of zero-order rate constants from the data of Reed and Connor⁵⁹ at two different film thicknesses, namely: curve 1, 0.0102 cm; curve 2, 0.04 cm. The latter was the film thickness used in this work.

very thin. However, extraction of DOP from plasticized PVC films at low temperatures, especially by oils and detergents,^{60,61} is very severe. In contrast, loss of volatiles from blends made using vinyl stearate copolymers or unplasticized PVC was zero in Table IV; extraction loss should also be negligible in these systems.

SUMMARY AND CONCLUSIONS

Several NBR elastomers were polyblended with selected systems of polymers, copolymers, and mixtures containing vinyl chloride across the composition range. Systems studied were (a) PVC, (b) vinyl stearate-vinyl chloride copolymers, (c) DOP-PVC mixtures, and (d) vinyl acetate-vinyl chloride copolymers. Their mechanical, viscoelastic, optical, and volatility properties were measured. Approximately optimum mechanical equivalence was obtained for PVC and internally and externally plasticized polyblend systems containing 0.21 weight fraction of plasticizing component. At higher plasticizer levels (0.36 and 0.47 weight fraction), the polyblends were somewhat inferior in tensile strength when compared at the same initial stresses. All of the polyblends had higher rupture energies than their starting components. Noteworthy were the increased stress-strain areas of the blends incorporating vinyl stearate-vinyl chloride copolymers, especially those containing 0.21 weight fraction of the vinyl ester. The transparency of $\frac{1}{16}$ -in. thick films and their relative freedom from haze appeared to be largely contributed by refractive index matching. Volatility was severe at high temperatures ($>100^{\circ}\text{C}$) for samples containing DOP. It was absent from blends of simple PVC and from those reinforced by vinyl stearate copolymers. It may be concluded that, to at least a first approximation, the low-temperature and ordinary mechanical properties of polyblends containing selected vinyl stearate-vinyl chloride copolymers approach those of DOP-PVC mixtures.

The criteria of compatibility were discussed in terms of viscoelastic properties. Incompatible systems had stepped modulus temperature curves; for compatible ones, the isochronal curves shifted with temperature. Because the inflection temperatures of the isochronal curves of these polyblends were of the latter type, and thus behaved like plasticized polymers, they were considered to be compatible. While tendencies toward compatibilization were recognized as stemming from polar contributions of the PVC, ductility of the plastic component and its regulation through plasticization were held to be chiefly responsible for the behavior. Filler ductility also seemed to be a factor in improving compatibility in other polyblends.

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