

## Polymer Compatibility II. The System Poly(methyl Methacrylate)-Poly(vinyl Acetate). Preparation and Impact Behavior

BERNARD SCHNEIER, *Center for Industrial Research (CIR)  
Ltd., Haifa, Israel*

### Synopsis

Blends of poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) were prepared by mixing the polymers in the melt and in the absence of a solvent. PMMA was the major constituent of the blend. Traces of gel permeation chromatograms showed that the starting materials retain their polymeric character after Brabender processing. Data obtained from notched Izod impact strength tests at 23°C showed that blends may exhibit values ranging from about 0.3 to 0.9 ft-lb/in. notch. Differences in mix conditions afford blends which, from a phenomenologic viewpoint, consist of a mixture of two glassy polymers or of a rubbery polymer dispersed in a glassy matrix. Micrographs of a crack pattern in companion blends consisting of PMMA/PVAc 85/15 are consistent with impact strength test results.

### INTRODUCTION

Equation (1)<sup>1</sup> provides a value whose magnitude apparently differentiates between polymer mixtures listed<sup>2,3</sup> as either compatible as solids or incompatible:

$$\Delta H_M = \{x_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 [x_2 / (1 - x_2) M_2 \rho_2 + (1 - x_1) M_1 \rho_1]^2\}^{1/2} \quad (1)$$

where  $x$  refers to the weight fraction of components 1 and 2 present in the mixture ( $x_1 + x_2 = 1.0$ ), and  $M$ ,  $\rho$ , and  $\delta$ , refer, respectively, to the molecular weight of an average monomer unit, polymer density, and solubility parameter. The usefulness of eq. (1) in pointing up polymer pairs compatible as solids was tested<sup>1</sup> using the data of Bohn<sup>2</sup> and Molau.<sup>4</sup> Using these lists as criteria, eq. (1) appears useful in providing the investigator a basis for differentiating between polymer pairs that may or may not be compatible as solids.

Bohn<sup>2</sup> and Krause<sup>3</sup> have assembled lists of polymer pairs on which compatibility studies have been reported. The lists contain polymer pairs for which, according to them, compatibility as solids may be considered to be definitely established at least in some regions of proportions. The system poly(methyl methacrylate) (PMMA)/poly(vinyl acetate) (PVAc) is listed as incompatible by Bohn<sup>2</sup> and borderline by Krause.<sup>3</sup> According to calculations based on eq. (1), the system would be expected to be compatible as solids.

Literature information on the system PMMA/PVAc is based on films prepared by casting mixtures of the two polymers from solution. Friese<sup>5</sup> reported that homogeneous solutions and transparent films were obtained with mixtures of PMMA and PVAc when chloroform or toluene were used as solvents, but that phase separation and noncompatible films were obtained when ethyl acetate, benzyl acetate, or dimethylformamide were used. Jenckel and Herwig<sup>6</sup> found that when chloroform was used as a solvent, clear solutions were obtained with mixtures of the two polymers. They studied also the dynamic mechanical properties of the mixtures as determined by a torsion pendulum and observed that the damping curves exhibited two maxima. Based on these results, Bohn<sup>2</sup> classified the system as being incompatible as solids. It may be noted that others<sup>7,8</sup> also consider that results from dynamic mechanical property testing provide evidence for the presence of a single- or two-phase system.

In the studies reported here, the polymers were mixed in the absence of a solvent. The mixtures of PMMA and PVAc were blended in the melt using a Brabender Plastograph as a mixer, and were mixed at various temperatures for 1 hr past the final flux point. It has been mentioned previously<sup>1</sup> that in Bohn's list, in most instances, compatible polymer pairs have been prepared in the melt. Mixing in the melt is not a necessary condition, nor does it assure obtaining polymer pairs compatible as solids. Nevertheless, in the molten state, the polymers exhibit reduced viscosity, affording the possibility of adsorption at the surfaces and mutual diffusion. It is realized that thermodynamic equilibrium may not have been reached because of a slow rate of diffusion and limits of time and shear inherent in any mixing operation. However, it was observed that in each instance, using autographic tracings of torque-time and melt temperature-time as criteria, little or no change occurred after approximately the first 15 min of mixing. Based on these values of constant torque and temperature, the assumption was made that some upper limit of molecular mixing had been reached. External mixing conditions for the three sets of blends were the same in each instance, except that mix temperature was varied. The fused products were molded at 150°C into rectangular-shaped specimens and films for testing.

In these studies, PMMA was selected as component 1, eq. (1). For PMMA, values of 100.23, 1.17, and 9.71 were used, respectively, for  $M$ ,  $\rho$ , and  $\delta$  and, in turn, 86.09, 1.19, and 9.56 for PVAc. The weight fraction of polymer was calculated as follows: the term  $(1 - x_1)$  was set equal to 0.90, and the product of this term and  $M_1\rho_1$  provided the weight fraction of PMMA present in the mixture; then, the term  $(1 - x_2)$  was set equal to 0.10, and the product of this term and  $M_2\rho_2$  provided the constituent weight fraction of PVAc. The calculations were repeated for values of  $(1 - x_1)$  equal to 0.85 and 0.80. The amount of PMMA present in the blends comprised 91.15%, 86.64%, and 82.08% of the composition. They are reported below as PMMA/PVAc 90/10, 85/15, and 80/20.

## EXPERIMENTAL

**Materials.** The PMMA used was Diakon injection molding-grade powder (ICI Plastics Division, Welwyn Garden City, Herts, England). This material, supplied in pellet form, was used as received. Poly(vinyl acetate) (BDH Chemicals Ltd., Poole, England, Product No. 30572, molecular weight approximately 45,000) was supplied in free-flowing granular form. This component was stored at room temperature in a desiccator containing calcium chloride; as needed, portions were removed to prepare the blends.

**Preparation of Blends.** In a standard manner, a physical mixture of weighed amounts of the two polymers was added to a Brabender Plastograph equipped with a roller mixer Type 30 (capacity 30 cc) operating at a roller mixer speed of 30 rpm and containing a stock temperature thermocouple connected to a recorder. The weight on the chute during mixing was 15 kg. For a given ratio of PMMA to PVAc, the weight of material added to the mixer was adjusted so that, during mixing, small movement of the loading chute was observed in order to assure that the mixing chamber was completely filled. The blends were mixed for 1 hr past the flux point, removed, cooled to room temperature, and granulated with a cutting mill (H. Dreher Machine Co., Aachen, West Germany). The blends were then molded at 150°C against Mylar or Teflon by preheating for 5 min without pressure, pressing for 5 min, and cooling under pressure to room temperature to provide test specimens.

**Measurements.** Impact strength was measured at 23°C and 50% R.H. (ASTM D256). Test specimens (63.5 mm long  $\times$  12.7 mm wide  $\times$  4 mm thick) were conditioned in this environment for a minimum of 48 hr after notching, prior to testing.

Gel permeation chromatograms were obtained on the Waters Ana-Prep instrument equipped with seven sample columns. Tetrahydrofuran solutions of PMMA, 1/4%, and of PVAc, 1/2%, were injected in a 2-min period. Flow rate was 1 ml/min.

## RESULTS AND DISCUSSION

Table I lists the compositions and Brabender mix conditions used to prepare the three sets of PMMA/PVAc blends reported here. The results, taken from the autographic recordings of torque during the period of initial melt fusion of the blends, point up an apparently unusual behavior. Generally, when a polymer is fused in a Brabender Plastograph, the fusion curve is characterized by an initial torque which then falls to some minimum value; at this stage, the mass is powdered and melting begins. For pure PMMA, for example, when the external mix conditions were the same as those shown for sample 90/10-1, torque increased from 680 to 2400 m-g in about 1/2 min; after melting, the trace indicated a torque of 2075 m-g which varied slightly thereafter. In contrast, recordings obtained during fusion

TABLE I  
Effect of Composition and Brabender Mix Temperature On Initial Melt Fusion Behavior of Blend

PMMA/PVAc	Weight, g <sup>a</sup>		Temperature, °C		Brabender torque, <sup>b</sup> m-g, after specified mix period, min <sup>c</sup>										
	PMMA	PVAc	Head	Melt	0.0	0.5	1.0	1.5	2.0	2.5	3.0	4.0	5.0	6.0	7.0
90/10-1	30.1150	2.8851	215	206	500	900	1300	1400	1630						
90/10-2	30.1150	2.8851	195	183	1250	1600	2200	2550	2620						
85/15-3	29.0313	4.4694	208	194	450	800	1000	1220	1350						
85/15-4	29.0313	4.4694	190	177	1300	1600	1730	1830	1850						
80/20-5	27.3934	6.6074	195	183	400	600	550	530	600	650	900	1200	1330		
80/20-6	27.3934	6.6074	180	169	400	800	670	610	540	520	530	700	1030	1600	1820

<sup>a</sup> Weight adjusted to provide slight movement of the load chute during mixing.

<sup>b</sup> Addition time, about 1 min; weight on load chute during mixing, 15 kg; roller mixer speed, 30 rpm.

<sup>c</sup> After addition time.

TABLE II  
Effect of Blend Composition on Change of Brabender Torque with Mix Time After Fusion

PMMA/PVAc	Melt temp., °C	Brabender torque, <sup>a</sup> m-g, during specified mix period after fusion, min <sup>b</sup>													
		0	1	2	3	4	5	10	15	20	25	30	40	50	60
90/10-1	206	1630	1610	1500	1450	1380	1390	1330	1300	1280	1300	1280	1300	1250	1260
90/10-2	183	2620	2500	2350	2300	2300	2300	2150	2020	2080	1950	1960	1980	1980	1920
85/15-3	194	1350	1320	1260	1200	1130	1070	1030	1030	1010	1000	1000	1000	1000	1000
85/15-4	177	1800	1700	1630	1610	1590	1580	1540	1560	1560	1550	1550	1520	1560	1550
80/20-5	183	1330	1300	1260	1230	1190	1180	1120	1100	1120	1130	1130	1180	1180	1170
80/20-6	169	1820	1770	1670	1650	1620	1610	1550	1560	1570	1600	1600	1570	1600	1600

<sup>a</sup> Weight on load chute during mixing, 15 kg; roller mixer speed, 30 rpm.

<sup>b</sup> Torque during blending step after initial melt fusion (Table I).

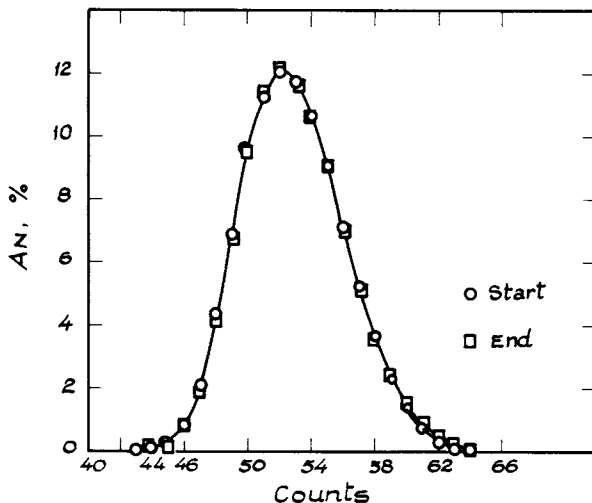


Fig. 1. Relative change in MWD of PMMA before and after processing.

of the various blends exhibited a gradual increase of torque with time. Based on the available data, the results indicate that melt fusion of the blends proceeds at a slower rate than is normally observed with pure polymers. In addition, although the rate of fusion decreases with increasing PVAc content, for a given polymer pair, fusion rate is not affected by melt temperature.

Recalling that PVAc was added in the form of a free-flowing granular powder and that its  $T_g$  is around  $30^\circ\text{C}$ , it is considered likely that during the fusion step, PVAc is converted into a molten mass before PMMA. The surfaces of the mixer blades may be coated at this point. PVAc, then, exhibits the properties of a low-viscosity mass (low torque values) and reduces the capability of the mixer to grind the PMMA pellets to a powdery form. Consequently, the amount of heat generated by friction during the grinding step is also reduced. As the amount of molten PMMA increases, the melt viscosity of the blend increases too (higher torque values), which aids in entrapping additional powdered material.

Table II shows the change in torque observed during the blending of the polymer pairs in the melt. The data show the effect of blend composition and melt temperature on the change of Brabender torque during the mix period subsequent to the initial fusion step (Table I). The results show that after about 15 min of mixing, torque changes slightly up to the end of the 1-hr mix period. The assumption was made that under the conditions of mechanical mixing in the melt used here, some upper limit of interaction has taken place between segments of the two polymers.

Gel permeation chromatography was used to characterize molecular weight distribution of the starting polymers before and after processing. The purpose of the study was to determine if Brabender mixing of the individual polymers for 1 hr at  $180^\circ\text{C}$  gave rise to formation of lower

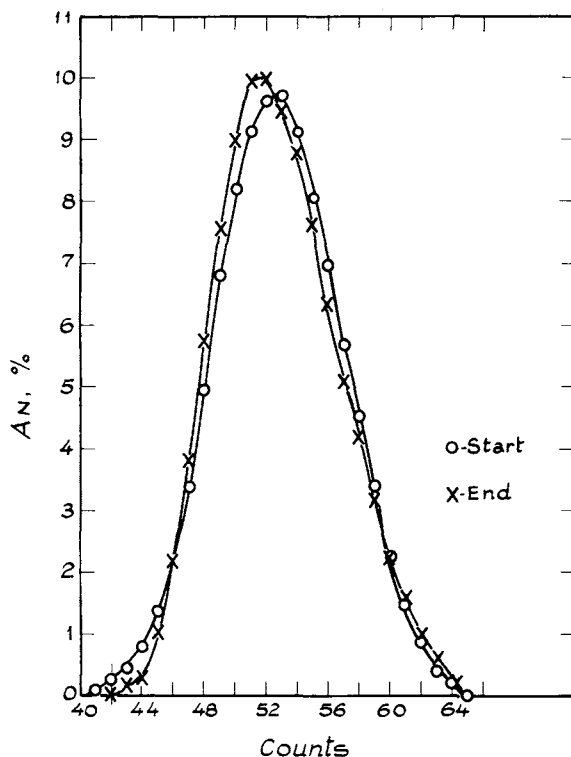


Fig. 2. Relative change in MWD of PVAc before and after processing.

molecular weight species and, consequently, a plasticization effect. In these studies, tetrahydrofuran solutions of the individual polymers were prepared, injected into the apparatus, and traces of the individual chromatograms were collected. At each count number, the vertical height,  $a_n$ , from the baseline to the elution curve was measured, and the sum of the vertical heights,  $\Sigma a_n$ , was obtained. The ratio,  $A_N = a_n / \Sigma a_n$ , represents, then, the relative change in molecular weight distribution of the polymers before and after processing. The results are shown in Figures 1 and 2. Figure 1 shows that the molecular weight distribution of PMMA is not affected by processing conditions. Recalling that the larger molecules emerge at a lower count number and the smaller ones at the end of the separation, Figure 2 shows that, for PVAc, a broader molecular weight distribution is obtained after processing. In addition, there is a shift at the highest end to lower molecular weight species. However, it may be concluded that the starting materials retain their polymeric character after processing.

Studies were conducted to determine the effect of polymer blend composition and mix temperature on the Brabender torque and on the impact properties of the blends. In these studies, PMMA and blends of PMMA and PVAc were mixed for 1 hr at various temperatures. The processing

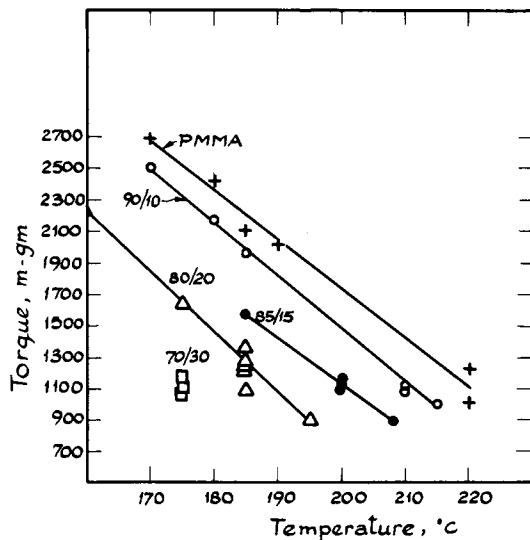


Fig. 3. Effect of melt temperature of PMMA, alone and in blends containing PVAc, on Brabender torque after 1 hr of mixing. Numbers refer to blend composition expressed as ratio of PMMA to PVAc.

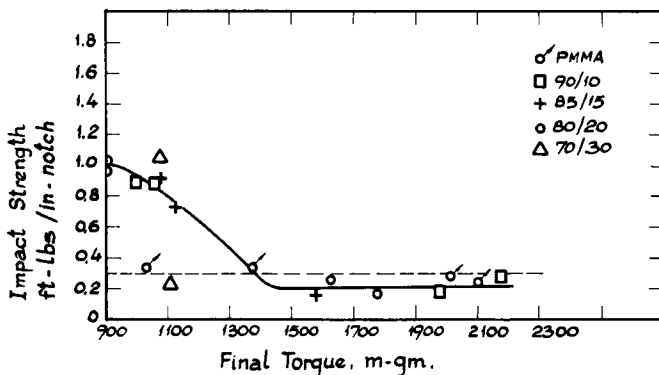


Fig. 4. Effect of Brabender torque on Izod impact strength of PMMA and blends. Numbers refer to blend composition expressed as ratio of PMMA to PVAc.

data are given in Table III and are presented in Figure 3. The results show that for PMMA, alone and in combination with PVAc, torque decreases with increase in mix temperature. In addition, at a constant mix temperature, torque decreases as the PVAc content of the blend increases. Finally, an examination of Table III shows that, for a given blend, mixing at a constant temperature provides a melt which exhibits an approximately constant value of torque, except in the case of blend 80/20. Five batches of blend 80/20 were mixed at 185°C. In three instances, the torque was approximately constant, ranging from 1220 to 1270 m-g. Values of 1360 m-g and 1080 m-g were obtained also. The reason for the variation is



TABLE III  
Effect of Composition and Mix Temperature on Brabender Torque and Impact Strength of Polymer Blends

Polymer blend PMMA/PVAc	Brabender data <sup>a</sup>		Izod impact strength, ft-lb/in. notch
	Melt temp., °C	Torque, m-g	
100/0	170	2680	—
	180	2415	—
	185	2110	0.24
	190	2010	0.28
	210	1380	0.33
	220	1220	—
	220	1010	0.33
90/10 <sup>b</sup>	170	2500	—
	180	2165	0.28
	185	1985	0.18
	210	1120	—
	210	1060	0.89
	215	1000	0.88
85/15 <sup>b</sup>	185	1580	0.15
	200	1160	—
	200	1130	0.74
	200	1080	0.92
	208	900	—
80/20 <sup>b</sup>	160	2220	—
	170	1780	0.17
	175	1630	0.25
	185	1360	—
	185	1270	—
	185	1230	—
	185	1220	—
	185	1080	—
	195	900	0.94
	195	900	1.02
70/30 <sup>c</sup>	175	1170	—
	175	1100	0.22
	175	1060	1.04

<sup>a</sup> After 1 hr of mixing.

<sup>b</sup> Composition is given in Table I.

<sup>c</sup> Composition is PMMA, 25.4694 g; PVAc, 10.5307 g (70.75% PMMA).

unknown. The melt obtained from the Brabender mixer was moulded and impact strength specimens were prepared.

Figure 4 shows that, for various PMMA/PVAc blends, the notched Izod impact strength at 23°C is affected more by Brabender mix conditions than by the composition of the blend. The data (Table III) show that the impact strength of pure PMMA is about 0.3 ft-lb/in. notch within the range of mix conditions used here. Low values were obtained on the blends if the torque after 1 hr of mixing was greater than 1500 m-g. On the other hand, if the mix temperature is adjusted to provide a torque of about 1100

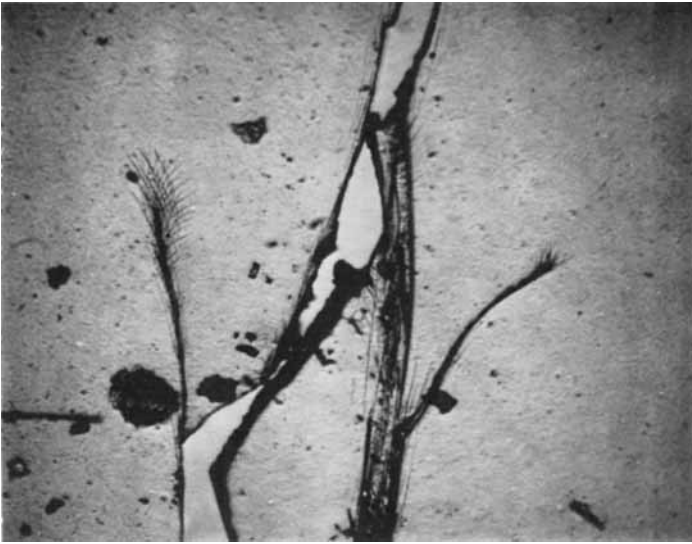


Fig. 5. Crack initiation and termination pattern observed with polymer blends 85/15-3 and 85/15-4 (150 $\times$ ).



Fig. 6. Termination of crack in blend 85/15-4 (620 $\times$ ).

m-g or less, in seven out of eight instances the blends exhibit an impact strength of about 0.9 ft-lb/in. notch. Phenomenologically, the results suggest that the high impact-strength materials are heterogeneous and consist of a rubber polymer dispersed in a glassy matrix; for the low impact-strength materials, the blends consist of two glassy polymers.

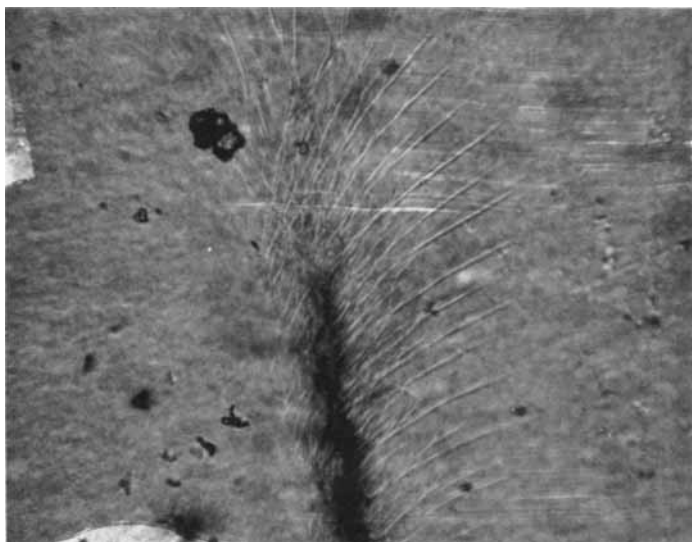


Fig. 7. Termination of crack in blend 85/15-3 (620 $\times$ ).

The data in Table II show that, for a particular PMMA/PVAc blend, adjustment of the melt temperature affords systems which exhibit a torque greater or less than 1500 m-g. As expected, for each polymer pair, as mix temperature increases, torque decreases. The dynamic mechanical properties of the blends will be reported and compared with those obtained on the pure materials.<sup>9</sup>

Figures 5-7 show micrographs illustrating the difference in propagation of the fracture pattern exhibited by polymer blends containing 85/15 PMMA/PVAc. Since the samples were only about 0.015 mm thick, transmitted light was used without significant loss of sharpness. In these studies, the specimens were fractured by applying a flexural stress normal to the surface of the film; the film surface was examined. Figure 5 illustrates the straight nature of crack initiation observed in both blends. Figure 6 shows that termination of the crack in blend 85/15-4 occurs abruptly with well-defined glass-like protuberances from the surface of the film. There is little evidence of crazing or branching along the crack front. Figure 7 shows that the crack pattern in blend 85/15-3 is characterized by a multiplicity of branches emanating from the crack. There appears to be a lack of dependence of the direction of the fibrous-appearing branches to the direction of the crack. The micrographs are consistent with results obtained from impact strength as well as dynamic mechanical property tests.<sup>9</sup>

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