

Polymer Compatibility III. The System Poly(methyl Methacrylate)-Poly(vinyl Acetate). Characterization Studies

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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. The polymer blends were tested, using various methods, to determine if they are compatible as solids. Data obtained from dynamic mechanical and DSC measurements show that, when they are mixed under given Brabender mix conditions, the blends exhibit properties characteristic of polymer pairs compatible as solids. If the mix conditions are altered, a two-phase system is evidenced. Using micrographs obtained by light microscopy in phase contrast as criteria, two companion blends containing PMMA/PVAc 80/20 would be classified as incompatible as solids because of the differences in refractive index of PMMA and PVAc. The micrographs also show that, in the system that would otherwise be listed as compatible, the PVAc domains appear to be relatively uniform in size and distribution through the PMMA matrix. In its companion blend, large, irregularly shaped particles of PVAc which are poorly dispersed in the PMMA matrix are evident.

INTRODUCTION

Literature information on the system poly(methyl methacrylate) (PMMA)/poly(vinyl acetate) (PVAc) is based, in part, on films prepared by casting mixtures of the two polymers from solution^{1,2} and, in part, on blends prepared by mixing the polymers in the melt and in the absence of a solvent.³ Friese¹ 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 dimethyl formamide were used. Jenckel and Herwig² found that when chloroform was used as a solvent, clear solutions were obtained with mixtures of the two polymers. Using a torsion pendulum, they studied also the dynamic mechanical properties of the mixtures and observed that the damping curves exhibited two maxima. These results indicated that the system is incompatible as solids.

In the studies reported here, the polymers were mixed in the absence of a solvent.³ The mixtures were blended in the melt using a Brabender Plasto-

graph as a mixer and were mixed at various temperatures for 1 hr past the final flux point. It was observed³ 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. For the three sets of blends discussed here, external mixing conditions were the same in each instance except that mix temperature was varied. The fused products were molded at 150°C into films for testing.

It has been shown³ that, for various PMMA/PVAc blends, the notched Izod impact strength at 23°C ranges from about 0.3 to 0.9 ft-lb/in. notch. Adjustment of the external Brabender mix condition was sufficient to alter the impact strength characteristics of the blends.

Phenomenologically, the results suggested that the high impact-strength materials are heterogeneous and consist of a rubbery polymer dispersed in a glassy matrix; for the low impact-strength materials, the blends consist of two glassy polymers. Micrographs³ of the fracture pattern obtained on blends containing 85/15 PMMA/PVAc were consistent with results obtained from impact strength tests. In this report, the dynamic mechanical properties and DSC heat absorption curves obtained on PMMA and PVAc, alone and in combination, are presented. In addition, differences in the apparent homogeneity of polymer blends consisting of PMMA/PVAc 80/20 are illustrated.

EXPERIMENTAL

Materials and Preparation of Blends. These items have been reported previously.³

Measurements. Dynamic mechanical measurements in tension were made using a Vibron dynamic viscoelastometer, Model DDV II (Toyo Instrument Co.) at a frequency of 3.5 Hz over the temperature range of approximately 20° to 100°C. In addition, dynamic mechanical measurements in shear were made on blends labelled 85/15 using an inverted torsional pendulum over the temperature range of 80° to 320°K. The design and use of this torsion pendulum is described elsewhere.⁴

Calorimetric measurements were made using a Perkin-Elmer DSC-1B differential scanning calorimeter. Uniformly, the test conditions were: scan speed, 20°C/min; range setting, 8; nitrogen flow, 30 ml/min; chart speed, 1 in./min; sample weight, 4.5 mg.

A large Zeiss Universal Research Microscope was used in phase contrast to determine morphologic differences between two polymer blends 80/20-5 and 80/20-6. Specimens were embedded in epoxy resin which was cured at room temperature and, then, were sectioned with the use of a microtome. Micrographs of cross sections of the test specimens, approximately 0.015 mm thick, were taken.

RESULTS AND DISCUSSION

Figures 1 and 2 show in a semilogarithmic plot the tensile dynamic properties of PMMA and PVAc, both alone and in combination, as determined with the use of a Vibron at a frequency of 3.5 Hz. Table I and Figure 1 show the effect of temperature on the dynamic storage moduli of these materials. The modulus-temperature curve indicates that below 36°C, PVAc is brittle as evidenced by its high modulus, 7×10^{10} dynes/cm²; at 48°C, its modulus is comparable to that of PMMA, 1.03×10^{10} dynes/cm². For PMMA, the onset of a transition occurs around 100°C. Dynamic storage modulus declines from 1.4×10^{10} to about 1.0×10^{10} dynes/cm² in the range between 26° and 100°C.

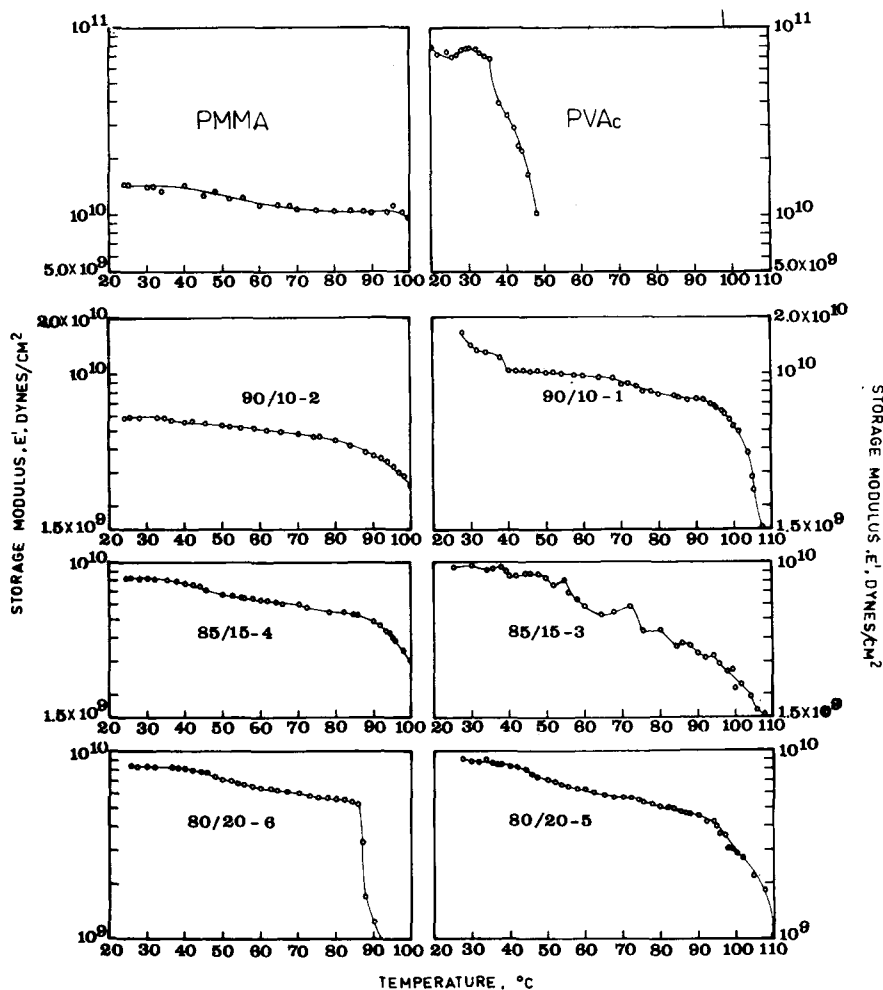


Fig. 1. Change in dynamic storage modulus with temperature for PMMA, PVAc, and blends of the two polymers. Numbers refer to blend compositions and preparative conditions given in Tables I and II, ref. 3.

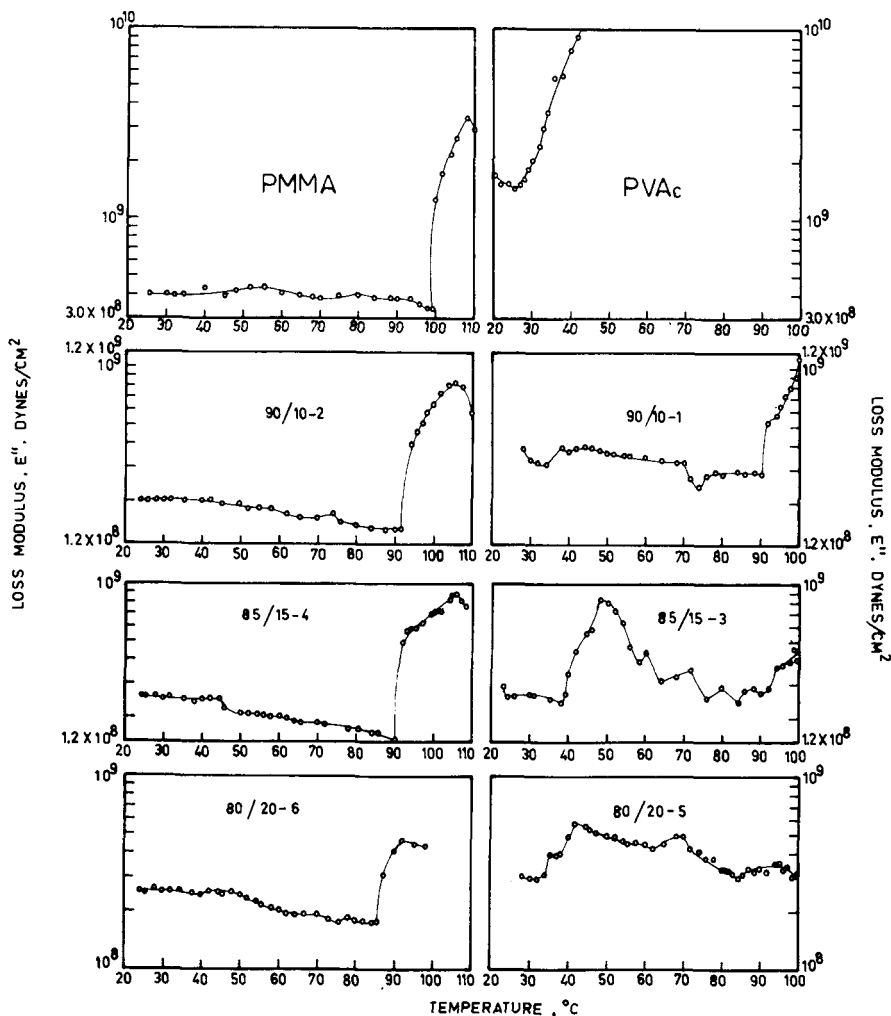


Fig. 2. Effect of temperature on dynamic loss modulus of PMMA, PVAc, and blends of the two polymers. Numbers refer to blend compositions and preparative conditions given in Tables I and II, ref. 3.

Based on a criterion of dynamic storage moduli, the data in Figure 1 and Table I show that the polymer pairs divide into two groups. The graph of the modulus-temperature curve obtained on blends 90/10-2, 85/15-4, and 80/20-6 mirrors that observed for pure PMMA. As the amount of PVAc in the blend increases, the start of a transition region is shifted to a lower temperature. In addition, data points show a smooth progression as modulus changes with temperatures; on the other hand, data obtained on blends 90/10-1, 85/15-3, and 80/20-5 show evidence of multiple peaks. For the latter blends, reproducibility of data points is difficult.

Using these and supplementary data presented previously³ and below, the results show that the polymer blends 90/10-2, 85/15-4, and 80/20-6 exhibit properties that are characteristic of polymer pairs that are com-

TABLE I
Effect of Temperature on Storage Modulus of PMMA, PVAc, and
Blends of the Two Polymers^a

Temp., °C	Storage modulus, ^b (dynes/cm ²) × 10 ⁻⁹							
	PVAc	Blend 90/10-1	Blend 85/15-3	Blend 80/20-5	PMMA	Blend 90/10-2	Blend 85/15-4	Blend 80/20-6
26	70.5	—	9.56	9.00	14.5	5.94	8.23	8.24
30	70.5	14.1	9.77	8.87	14.1	5.88	8.20	8.24
34	70.5	13.3	9.12	9.02	14.1	5.83	8.15	8.24
38	39.7	12.1	9.46	8.53	—	5.68	7.95	8.19
42	29.7	10.3	8.53	8.33	—	5.60	7.63	7.91
46	16.4	10.2	8.76	7.61	—	5.50	7.12	7.71
50		10.1	8.19	7.04	12.8	5.36	6.76	7.17
60		9.71	6.91	6.23	11.8	5.11	6.35	6.44
80		7.88	4.43	5.16	10.7	4.48	5.41	5.63
84		7.71	3.62	4.91	10.7	4.20	5.31	5.41
88		7.32	3.65	4.64	10.7	3.85	5.04	1.71
92		7.39	3.17	4.24	10.4	3.54	4.64	0.92
96		6.60	2.96	3.68	11.0	3.22	3.83	0.87
100		5.23	2.14	2.87	9.15	2.57	3.03	0.85

^a Composition of blends is given in Tables I and II, ref. 3.

^b Vibron dynamic viscoelastometer, Model DDV II, at a frequency of 3.5 Hz.

patible as solids. The companion blends 90/10-1, 85/15-3, and 80/20-5, respectively, exhibit properties of incompatible polymer systems. This classification will be used hereafter to avoid repetition.

The results given in Table I and Figure 1 show that below about 48°C, a polymer pair incompatible as solids exhibits a storage modulus higher than its companion set. The modulus of 90/10-2 is less than that of either 85/15-4 or 80/20-6. The reason is unknown. The latter two polymer blends are characterized by a similar modulus at 23°C, about 8.2×10^9 dynes/cm². Table I shows that moduli of the companion blends, 85/15-3 and 80/20-5, are higher at room temperature and exhibit this value only at 50°C and 43°C, respectively. Above these temperatures, modulus of the incompatible polymer blend decreases at a faster rate than that of its companion compatible pair. Recall that within the temperature range of 23° to 48°C, the modulus of PVAc is higher than that of PMMA. The data indicate that in the incompatible polymer blends, PVAc segments retain the capability to manifest a high inherent storage modulus independent of the PMMA constituent. The data suggest that aggregation of PVAc segments occurs. As shown below, microscopic examination supports this view.

Figure 2 shows the effect of temperature on the dynamic loss modulus for the three sets of polymer blends as well as for the starting materials. The data (Table II) show that within the temperature range of 26° to 94°C, PMMA exhibits a loss modulus of about 4×10^8 dynes/cm²; a glassy-to-rubbery transition takes place at 100°C. PVAc exhibits a transition around 26°C, and at this temperature, loss modulus is almost four times higher than found for PMMA. For blends 90/10-2, 85/15-4, and 80/20-6,

TABLE II
Effect of Temperature on Loss Modules of PMMA, PVAc, and
Blends of the Two Polymers^a

Temp., °C	Loss modulus, ^b (dynes/cm ²) × 10 ⁻⁸							
	PVAc	Blend 90/10-1	Blend 85/15-3	Blend 80/20-5	PMMA	Blend 90/10-2	Blend 85/15-4	Blend 80/20-6
26	15.7	—	2.62	2.90	4.09	2.02	2.59	2.50
30	20.2	3.37	2.94	2.93	4.01	2.06	2.57	2.50
34	36.6	3.19	2.55	3.16	4.04	2.04	2.57	2.54
38	57.6	3.87	2.47	4.01	—	2.01	2.47	2.46
42	93.6	3.80	4.52	5.67	—	2.02	2.59	2.53
46	138.0	3.87	5.82	5.25	—	1.93	2.28	2.47
50	—	3.63	8.04	4.93	4.30	1.93	2.16	2.44
60	—	3.49	4.49	4.55	4.12	1.89	2.03	2.06
80	—	2.84	2.97	3.36	3.94	1.52	1.76	1.80
84	—	2.93	2.50	3.09	3.81	1.47	1.70	1.79
88	—	2.93	2.96	3.25	3.83	1.43	1.61	3.08
92	—	5.25	2.95	3.22	3.79	1.42	4.92	4.67
96	—	7.26	3.84	3.31	3.53	4.64	5.97	4.42
100	—	11.3	4.17	3.73	12.8	6.51	7.37	4.20

^a Composition of blends is given in Tables I and II, ref. 3.

^b Vibron dynamic viscoelastometer, Model DDV II, at a frequency of 3.5 Hz.

to their transition temperature, the plot corresponds closely to that found for PMMA. In contrast, curves of the data obtained on the heterogeneous blends, 90/10-1, 85/15-3, and 80/20-5, exhibit two maxima. The first peak occurs between 34° and 38°C, corresponding to the presence of the constituent PVAc polymer. The peak height and breadth do not appear to vary consistently with PVAc content, indicating a nonuniformity in the environment of the PVAc segments.

Differences in the size and distribution of the PVAc particles may account for the difference in impact strength exhibited³ by the two sets of polymer blends. The dynamic mechanical test data show that PVAc exhibits a loss modulus of 1.57×10^9 dynes/cm² at 26°C, considerably higher than that of PMMA. Loss modulus is related to the resistance of a body to viscous deformation when an external sinusoidal stress is applied. In the process, energy is dissipated. Loss modulus is high when energy dissipation is large. PVAc, then, exhibits the capability of converting the energy imparted to the specimen under rapid loading conditions to heat more efficiently than PMMA and at a temperature close to that employed in the impact strength test.³ The data indicate that, in the compatible polymer blends, the mobility of the PVAc chains is restricted in some manner by the presence of the PMMA constituent.

Figure 3 shows the dynamic properties in shear obtained on the two starting polymers and the blends 85/15-3 and -4. The data were obtained with the aid of a torsion pendulum over the temperature range of about 85° to 320°K.⁴ Jenekel and Herwig² determined the change in logarithmic decrement with temperature between about -35°C and +125°C. Within the temperature range common to both studies, damping curves on PMMA

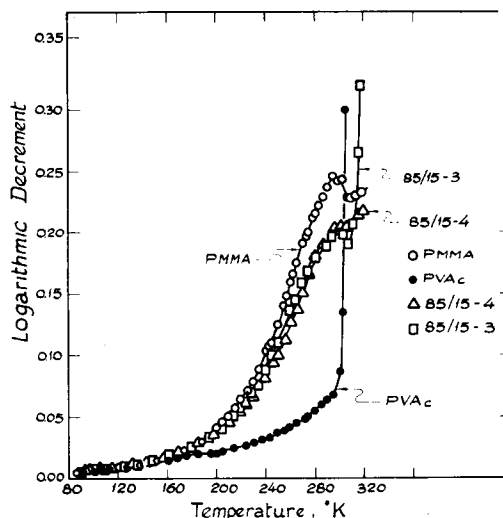


Fig. 3. Logarithmic decrement as a function of temperature for PMMA, PVAc, and blends 85/15-3 and 85/15-4. Composition and preparation of these blends are listed in Tables I and II, ref. 3.

and PVAc reported here are very similar to those presented by them. The onset of a transition region for PVAc about 300°K is indicated by the steep increase in the damping curve. The data indicate the presence of a relaxation maximum for PMMA around 295°K. The damping curve obtained on blend 85/15-4 resembles that of pure PMMA over the temperature range of -80° to 320°K. From -80° to 295°K, the curve obtained on blend 85/15-3 is similar to that of pure PMMA and to its companion set. However, at 309°K, a sharp rise in damping is observed corresponding to the presence and effect of the PVAc constituent. The data show that confirmatory results of dynamic mechanical testing in tensile and in shear are obtained on blends consisting of 85/15 PMMA/PVAc.

Figure 4 shows the traces of the DSC heat absorption curves obtained on PMMA and PVAc, alone and in combination, over the temperature range of 40° to 120° C. Portions of the curves obtained over the range of -80° to $+40^{\circ}$ C showed only the usual change of heat content with temperature. For PVAc, the data show a marked endotherm around 55° C. An endotherm of varying area is observed also on blends 80/20-5, 85/15-3, and 90/10-1. A definite change in slope is difficult to discern from data obtained on PMMA or on the blends 90/10-2, 85/15-4, or 80/20-6. These data also are in agreement with those obtained previously.

Figures 5-8 show in phase contrast microscopy differences in the size and distribution of the polymer constituents in blends containing PMMA/PVAc 80/20. In these micrographs, PVAc particles appear light because the refractive index of PVAc is less than that of PMMA, 1.47 and 1.49,⁵ respectively. Using light microscopy as a criterion, the results show the existence of two phases. Figures 5 and 6, obtained on blend 80/20-6, show that the PVAc domains appear to be relatively uniform in size and

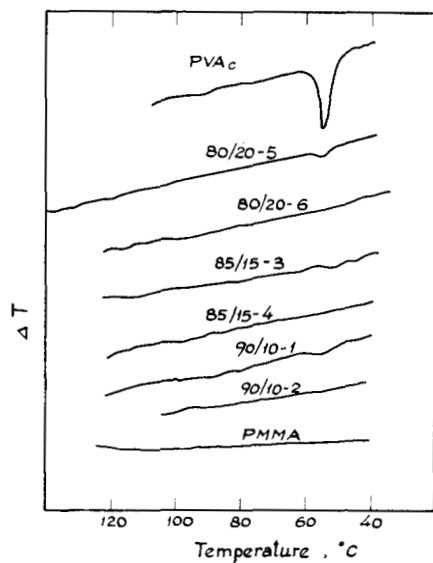


Fig. 4. DSC curves for PMMA, PVAc, and blends of the two. Numbers refer to blend compositions given in Tables I and II, ref. 3.

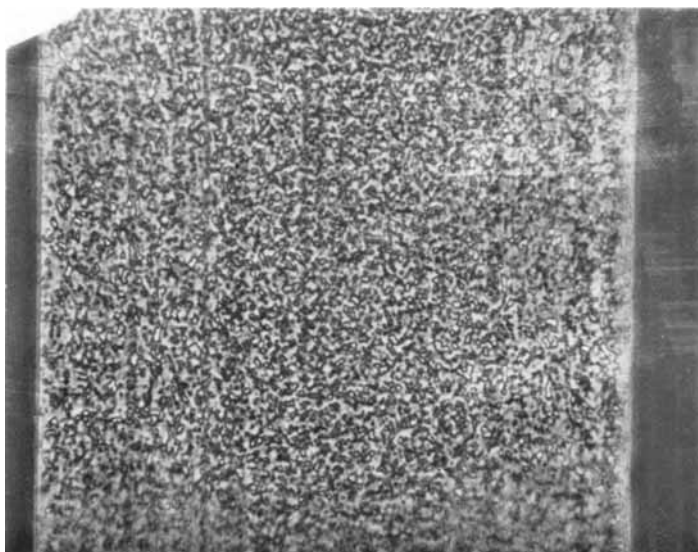


Fig. 5. Phase contrast micrograph of cross section of film 80/20-6 (700 \times).

distribution throughout the blend; in addition, they appear to be of the same size and shape as the PMMA matrix. Figure 7 and 8, obtained on blend 80/20-5, show that the PVAc domains are very poorly dispersed in the PMMA matrix. Large, irregularly shaped particles of PVAc are evident.

It is generally reported that if a film prepared from a blend of two polymers is cloudy, the polymer pair is incompatible as solids. The difference in refractive index between PMMA and PVAc is sufficient to reduce the

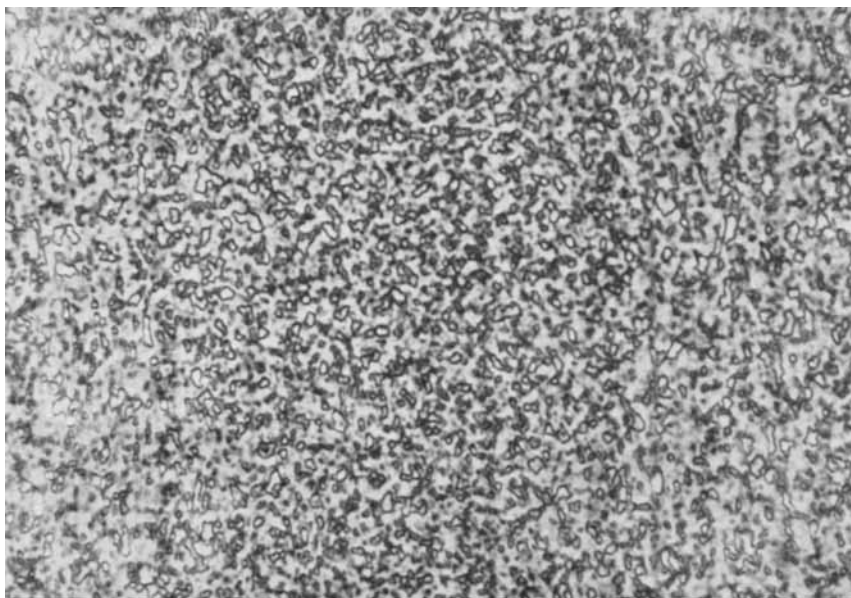


Fig. 6. Magnified section of Fig. 5 (1400 \times).

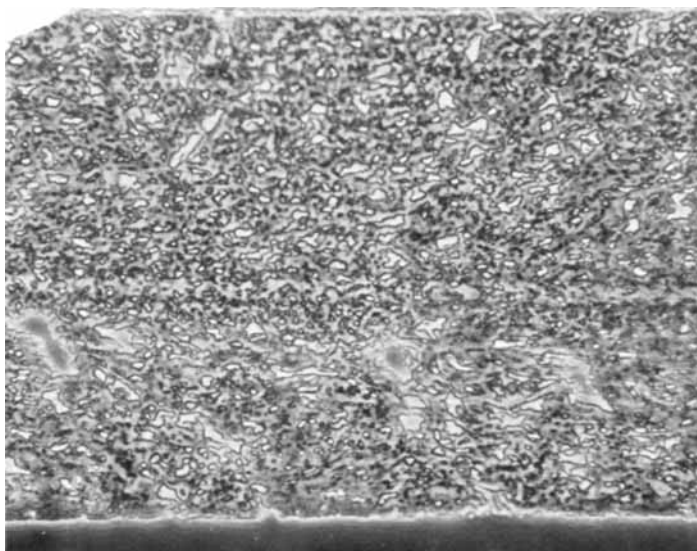


Fig. 7. Phase contrast micrograph of cross section of film 80/20-5 (700 \times).

transparency of films prepared from these blends. As the PVAc content of the blend increased, translucency decreased. However, other methods used in compatibility studies, such as dynamic mechanical property tests and differential scanning calorimetry, indicate that under certain conditions the polymers apparently exhibit an affinity for each other. Evidently, depending upon the method used in the compatibility studies, the size and distribution of the constituent polymers in the blend are important

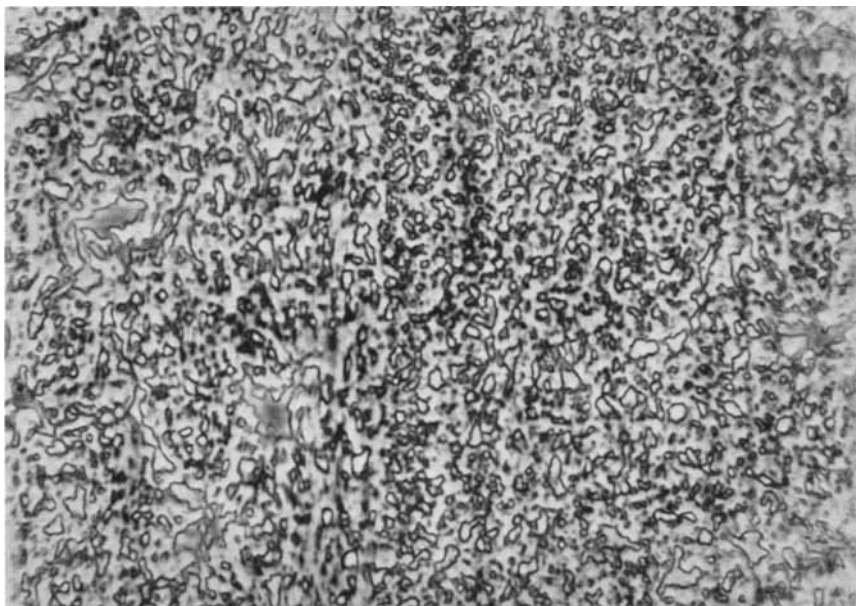


Fig. 8. Magnified section of Fig. 7 (1400 \times).

factors in assessing whether or not the system would be classified as compatible. Yu's view,⁶ which is apparently confirmed here, is that the finer the size of the dispersed phase in the continuous phase, the better the compatibility. If the investigator is interested in systems that are compatible as solids, eq. (1)³ may provide him with a basis for selecting polymer pairs. These studies show clearly, though, that attention must be directed also to the preparative methods. It is not obvious, however, why the seemingly slight differences in mix conditions afford materials with radically different properties.

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