

## Heterogeneous Polymer Systems. I. Torsional Modulus Studies

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### I. INTRODUCTION

Variations in the scheduling of monomer addition may be employed in emulsion polymerization to produce substantial alterations in chemical and physical structure, such as the following.

1. Monomers may be charged simultaneously, resulting in production of as homogeneous copolymers as are permitted by the polymerization kinetics.

2. Monomers may be charged sequentially, to produce polymers of greater heterogeneity. The particles may contain mixed polymers and/or graft copolymers, or they may consist of isolated regions, such as concentric shells, of the homopolymers. If new particle initiation is possible, the second stage monomer addition may produce new homopolymer particles, resulting in a mixture of particles of the two homopolymers.

In addition to the mechanics of emulsion polymerization, the following factors should influence the nature of the polymer produced: (1) the specific physical nature of each polymer, e.g., its glass temperature ( $T_g$ ) and whether it is crystalline or amorphous, (2) the molecular weights of the polymer constituents, (3) the ratio of the total amounts of each polymer present and the continuity or discontinuity of the phases, (4) equilibrium considerations and the effect of temperature, (5) the polarity and shape factors of the polymer species as reflected by whether they are good or poor solvents, or non-solvents, for one another, and (6) the degree of mixing of the substituents. If the polymers exist in regions instead of being molecularly dispersed, the size and shape of these as well as the nature of their boundaries are probably important.

### II. PRESENT STUDY

#### A. Torsional Modulus Studies

The shear modulus versus temperature curves of polymer films allow certain insights into film struc-

ture, and this technique has been applied to a variety of films prepared from emulsion polymers and certain other model systems.

#### B. Polymer-Polymer Compatibility Studies

Since the structure of the various films should depend upon the mutual compatibility of the constituents, this aspect has also been examined. In general, two chemically different polymers are incompatible;<sup>1,2</sup> the few observed exceptions have been either extremely similar polymers or highly polar polymers having favorable chain-chain interactions, such as the isomeric polymethyl acrylate and polyvinyl acetate. Incompatibility is evident in the separation of relatively dilute solutions (1-3 g./dl.) of the mixture into two distinct layers and the heterogeneous layered films obtained by evaporating the solvent.

### III. EXPERIMENTAL

#### A. Apparatus

The torsional or shear moduli of the various films were obtained with a torsion wire type of apparatus similar to Williamson's,<sup>3</sup> so constructed that four samples could be run simultaneously in a constant temperature cabinet. A circulating fan and thermoregulator-controlled heaters were used for temperature control ( $\pm 2^\circ\text{C}$ ). Dry ice was placed in the cabinet to reduce the temperature. All samples were stored and tested over indicator desiccants, either  $\text{CaCl}_2$  or  $\text{P}_2\text{O}_5$ .

#### B. Materials

The following polymers were used: polymethyl methacrylate, polymethyl acrylate, polyethyl acrylate, poly-*n*-butyl acrylate, poly-*n*-butyl methacrylate, polystyrene, and polyvinyl acetate, abbreviated respectively as: PMMA, PMA, PEA, PnBA, PnBMA, PS, and PVAc. The combinations PMA/PMMA, PMA/PS, and PMA/PVAc were

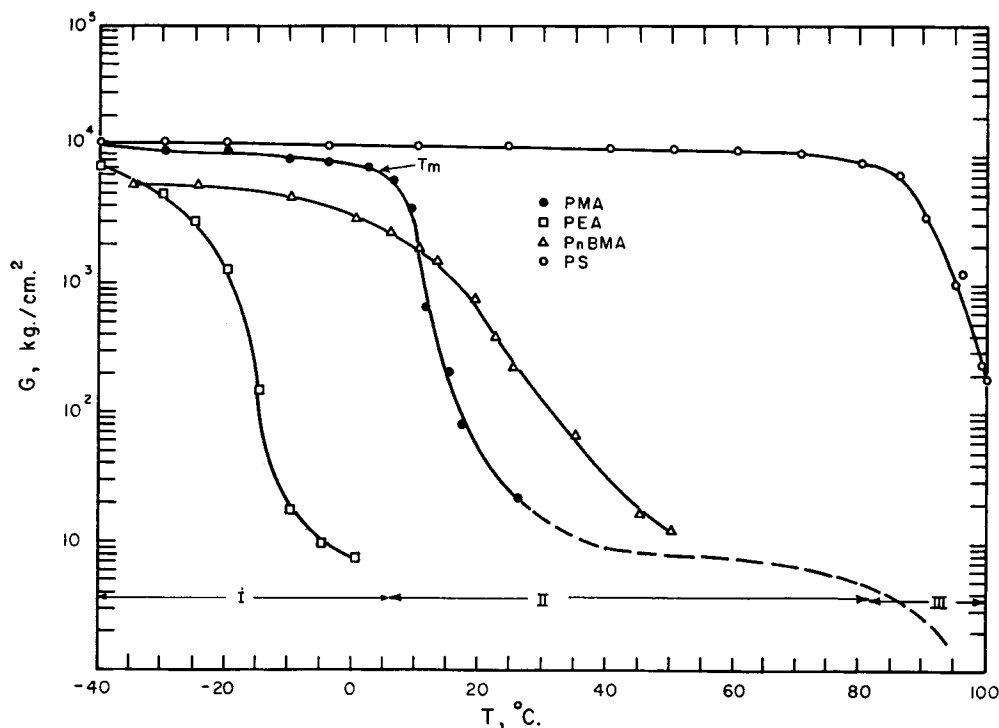


Fig. 1. Torsional modulus-temperature curves for PMA, PnBMA, PEA, and PS.

selected to demonstrate the effects of moderate, poor, and high compatibility. Homopolymers and random copolymers were synthesized. Heterogeneous samples were prepared by (1) mixing of two homopolymer emulsions, (2) dissolving two polymers together, and (3) emulsion polymerizing a monomer in the presence of a preformed different type of polymer. The three mixing methods will be abbreviated as ME, MS, and TS, to imply mixed emulsions, mixed solutions, and two-stage polymerization.

The following notation, illustrated for compositions of 75 wt.-% PMA and 25 wt.-% PMMA, will be used. The random copolymer is indicated as PMA-PMMA 75-25; the mixed emulsion film as

PMA/PMMA 75/25 ME; the mixed solution film as 75/25 PMA/PMMA MS (or with the solvent in parentheses); the two-stage polymer as PMA-(MMA) 75-(25) (the preformed polymer given first, followed by the second monomer in parentheses).

All the polymers were emulsion polymerized by conventional redox techniques. Sodium lauryl sulfate, 3% (weight of polymer) was the usual emulsifier. Table I contains relevant data. Intrinsic viscosities,  $[\eta]$ , were obtained in benzene at 30°C.

The two-stage polymers were prepared by adding the second monomer with emulsifier (3%) and water at 25-30°C. to the preformed polymer, stirring for 3-16 hr., and then adding catalyst. Conversions were of the order of 99%; final concentrations, about 25%.

Bulk samples of the homopolymers were obtained by freeze-drying the diluted (5-10% solids) emulsion. PnBA, however, was precipitated from emulsion with ethanol.

### C. Film Preparation

Films were prepared by casting from emulsion on glass or casting from solution on mercury. For mixed solution (MS) films, sufficient solvent was used, so that no obvious two-phase separation of the

TABLE I  
Emulsion Homopolymers

Polymer	[ $\eta$ ]		$T_m \pm 2^\circ\text{C.}$	$T_g, ^\circ\text{C.}$
	Conversion, %	in benzene at 30°C.		
PMMA	>99.5	1.93	105	105
PMA	>99	1.45	4	8
PEA	>99.5	2.80	-28	-22
PnBA	97	3.51	$-55 \pm 5$	-54
PnBMA	>99.5	2.58	13	19
PS	97	3.51	$86 \pm 5$	100
PVAc	>99.5	—	30	30

ternary solution was observed. As predicted by solution theory, two-layered films were frequently formed. Removal of the final traces of solvents, which is essential for obtaining meaningful physical measurements, was done by evaporation in high vacuum.

#### IV. EXPERIMENTAL RESULTS

##### A. Homopolymers

Figure 1 shows plots on a log scale of the shear modulus ( $G$ ) versus temperature ( $T$ ) for PMA, PEA, PnBMA, and PS. These show the shape characteristic of noncrystalline homopolymers which consists of the three distinct regions, indicated on the PMA curve by I, II, and III. In region I, corresponding to temperatures below the transition region, the modulus is high and relatively temperature-insensitive. With increasing temperature, a point is reached ( $T_m$ , the modulus transition temperature) at which the polymer changes from a solid or "glassy" state to a rubbery or "liquid" one, and  $G$  tends to decrease markedly. This marks the onset of the rubbery region II, where the reversible "high elasticity" associated with long-chain molecules is developed. Deformation occurring when molecule segments slip irreversibly past one another accounts for region III. Thus, the interpretation of shear modulus data involves an understanding of the factors affecting glassy transitions and viscoelastic properties of polymers.

With torsional modulus techniques,  $T_m$  is conveniently obtained from a plot of the strain angle

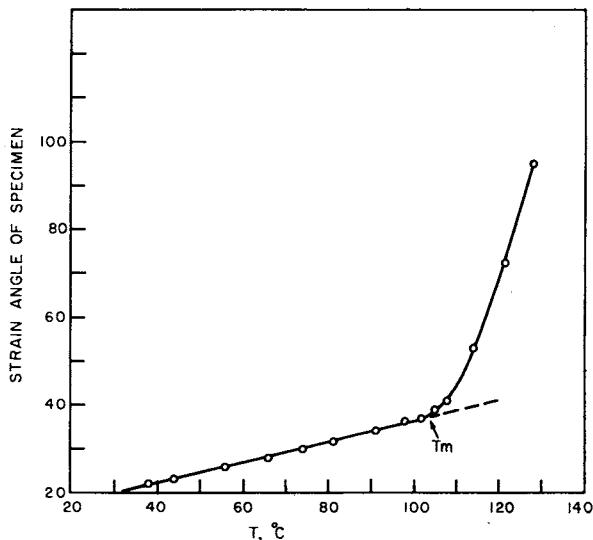


Fig. 2. Determination of  $T_m$  for PMMA.

of the specimen versus temperature obtained under conditions of constant total strain angle for specimen and wire. Figure 2 shows such a plot for PMMA ( $\bar{M}_v = 3.8 \times 10^5$ ).

Our measurements of a number of polymers show that  $T_m$  correlates very closely with  $T_g$ , the dilatometric<sup>4</sup> glass temperature. For PMMA,  $T_m = T_g = 105^\circ\text{C}$ . The dynamic torsion measurements of Schmieder and Wolf<sup>5</sup> also support this conclusion. Table I lists comparisons of  $T_m$  with the most recent values for  $T_g$  obtained in our laboratories (not necessarily from the same samples used in these studies).

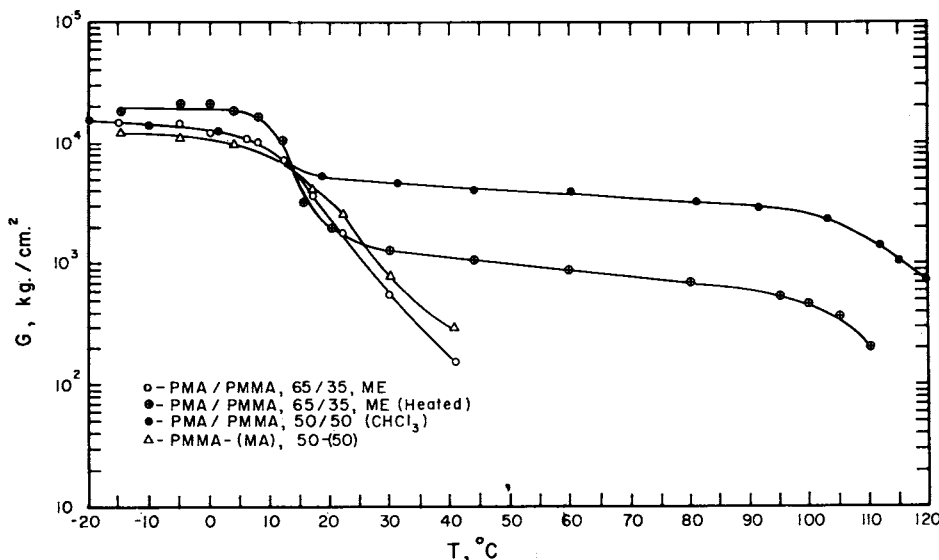


Fig. 3. Torsional modulus-temperature curves for 50/50 and 65/35 PMA/PMMA systems.

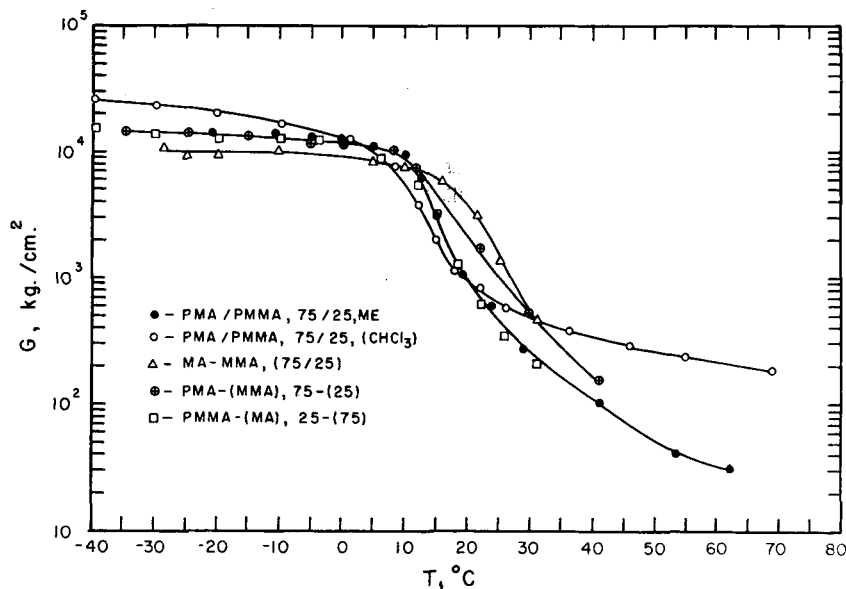


Fig. 4. Torsional modulus-temperature curves for PMA/PMMA, 75/25 systems.

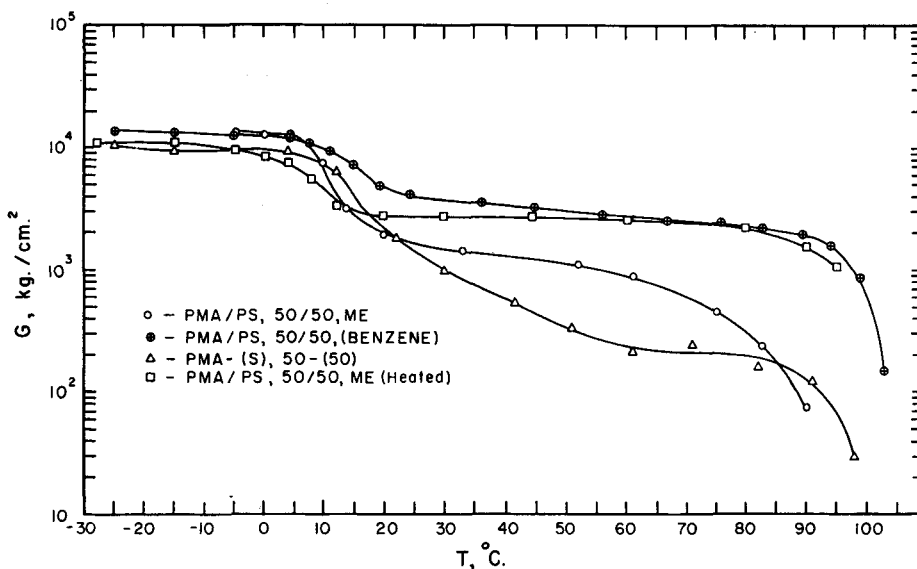


Fig. 5. Torsional modulus curves for 50/50, PMA/PS systems.

### B. PMA/PMMA Combinations

Figures 3 and 4 show  $\log G$  versus  $T$  curves for nine PMA/PMMA combinations. All of the heterogeneous systems show a transition in the range expected for PMA (4°C.), whereas the copolymer (75% MA, 25% MMA) shows a transition at a higher temperature, 15°C., in good agreement with the calculated value of 17°C.<sup>6</sup> The influence of sample history is demonstrated for the mixed emulsion films, examined as prepared and after heating to more than 105°C., the glass temperature of

PMMA. The heating produced a marked stiffening in the sample.

A mixed emulsion film of 50/50 composition was prepared but was too brittle to allow measurement. A PMA/PMMA 50/50 film was cast from chloroform and gave a curve slightly below that of the analogous 75/25 film shown in Figure 4.

Transitions determined as described above are summarized in Table II for these and subsequent figures.  $T_l$  and  $T_u$  refer to lower and upper transition temperatures.

TABLE II  
 Description of Films and Summary of Transitions

Sample	Composition	Transitions, °C.		Film clarity
		$T_l$	$I_u$	
PMA/PMMA	65/35, ME	5	—	Transparent, very clear
PMA/PMMA	65/35, ME (heated)	6	98	Transparent, very clear
PMA/PMMA	50/50 (CHCl <sub>3</sub> )	3	105	Transparent, sl. hazy
PMMA-(MA)	50-(50)	6	—	Transparent, very clear
PMA/PMMA	75/25, ME	5	—	Transparent, very clear
PMA/PMMA	75/25 (CHCl <sub>3</sub> )	2	—	Transparent, sl. hazy
MA-MMA	75-25	15	—	Transparent
PMA-(MMA)	75-(25)	4	—	Transparent, very clear
PMMA-(MA)	25-(75)	2	—	Transparent, very clear
PMA/PS	50/50, ME	6	60-65	Whitish, sl. translucent
PMA/PS	50/50, ME (heated)	1	76	Whitish, sl. transparent
PMA/PS	50/50 (benzene)	7	88	Translucent, white
PMA-(S)	50-(50)	6	85-92	Transparent, faint haze
PEA/PMMA	50/50, ME	-28	—	Transparent, very clear
PEA/PMMA	21/79 (CHCl <sub>3</sub> )	-28	~50	Transparent, hazy
PEA-(MMA)	79-(21) GCP	-28	~50	Hazy
PMA/PVAc	50/50, ME	6	30	Transparent
PMA/PVAc	50/50 (acetone)	2	—	Transparent, very clear
PMA-(VAc)	50-(50)	0-5	~20	Transparent
PEA/PnBMA	50/50, ME	-31	5-20	Transparent
PEA/PnBMA	50/50 (CHCl <sub>3</sub> )	-31	~21	Transparent, textured
PEA-(n-BMA)	50-(50)	-30	—	Transparent
PnBMA-(EA)	50-(50)	-30	—	Transparent

### C. PMA/PS Combinations

Figure 5 compares data for four samples containing equal parts by weight of PMA and PS. The curve for the film cast from benzene showed transitions at 7 and 88°C. and had the highest plateau region observed for this polymer pair. The film, however, consisted of two layers and had poor physical properties.

Data for a composition obtained by emulsion polymerizing styrene in the presence of an equal weight of a PMA emulsion polymer are shown. This two-stage polymer was examined for grafting. Ungrafted PS was extracted from the purified dried sample with cyclohexane at 60°C., then the insoluble material was freeze-dried and extracted with methyl Cellosolve. It was found that 31% of the PMA and 15% of the PS could not be removed by solvent extraction and thus were presumed to be involved in a graft copolymer. (The extraction procedure was shown to produce complete separation on a freeze-dried mixture of equal parts of PMA and PS). Fractions were analyzed by C-H analysis. The weight fraction composition of the pure graft was 0.35 PS and 0.65 PMA. A film cast from chloroform was tough, opaque white, had a pearly lustre and no apparent layering.

An MA-PS 50-50 random copolymer did not

form a continuous film from emulsion at room temperature.

For the PMA/PS system all mixed emulsion and mixed solution films were nontransparent and whitish, whereas two-stage polymers were transparent.

### D. PEA/PMMA Combinations

The data are shown in Figure 6. For the PEA/PMMA 50/50 ME sample a transition was found at -28°C. which corresponds to PEA homopolymer. A pronounced plateau follows. It is apparent that an upper transition is setting in gradually, but from the data a specific temperature could not be assigned. This film was very clear and looked homogeneous.

Data were taken on a PEA/PMMA 21/79 film prepared from chloroform. Two transitions resulted, one at -28°C. and the other, more difficult to locate, at about 50°C.

The third curve is for a PMMA-(EA) 21-(79) graft polymer prepared by Gluckman et al.<sup>7</sup> by polymerization of the acrylate in the presence of a backbone containing mercaptan groups.

Note that the polymer begins to soften slowly above the PEA glass transition. A second transition appears to set in gradually after about 60°C

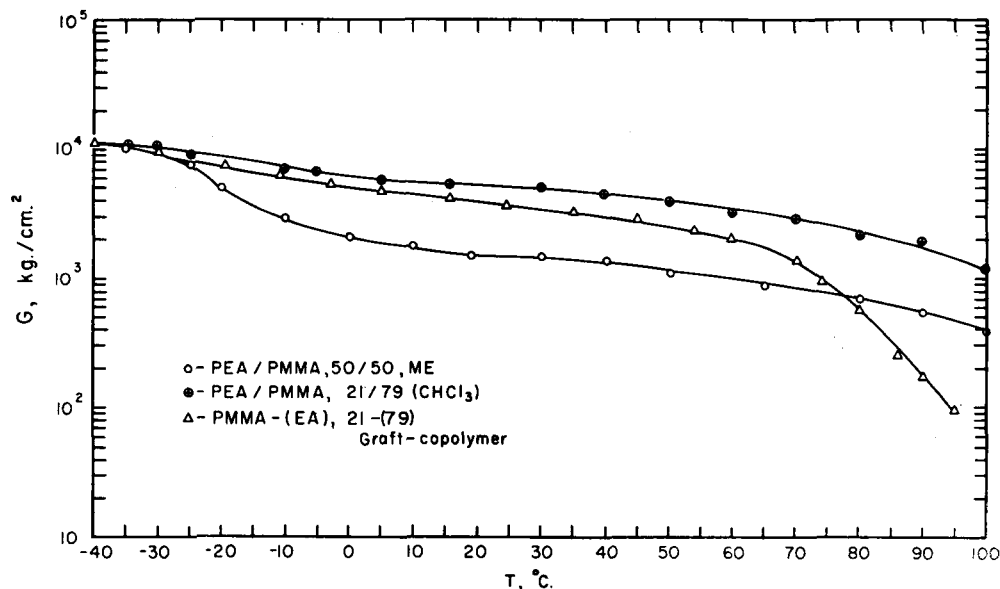


Fig. 6. Torsional modulus-temperature curves for PEA/PMMA systems.

which is considerably below the  $T_g$  for PMMA. The general shape of the curve looks very similar to that for mixtures.

### E. The PMA/PVAc Combination

Data are shown in Figure 7 for four samples. All these films were clear and transparent. For PMA/PVAc 50/50 ME, two glassy transitions are readily observed, one at 6 and the other at 30°C. The latter, which corresponds to PVAc, could not be located precisely because the rate of change of  $G$  with temperature between 6 and 32°C. was sub-

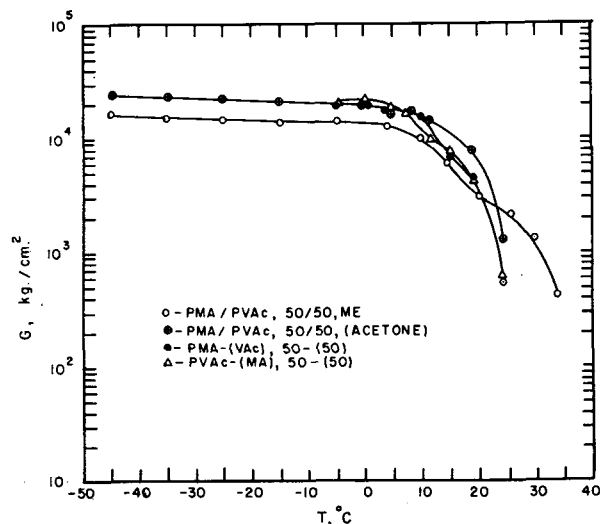


Fig. 7. Torsional modulus-temperature curves for PMA/PVAc, 50/50 systems.

stantial. Even though this system is one in which the polymers are highly compatible, the particles have essentially retained their individual identities. For PMA/PVAc 50/50 (acetone) a single glass temperature was found at about 2°C.; the torsional curve appeared slightly smeared but no other indication of the presence of a second polymer was found. For PMA-(VAc) 50-(50), two transitions were indicated, but the second was not very distinct. One was that typical of PMA; the second was indicated by a pronounced decrease in  $\log G$  above about 20°C. Results with PVAc-(MA) 50-(50) differed but slightly from its converse.

The fact that the glass temperatures of PMA and PVAc are so relatively close (only 22 degrees apart) tends to complicate interpretation of the torsional data. Presumably, the factors which make these isomeric polymers miscible are those regulating the  $T_g$  itself, e.g., chain flexibility and polarity.

### F. PEA/PnBMA Combinations

Data for four samples, all transparent, are shown in Figure 8. Table II lists transition points.

## V. INTERPRETATION OF DATA

A limited interpretation of the results is possible in the light of a knowledge of the properties of the constituents of the films, the method by which they are combined, and some reasonable postulates concerning film structure.

### A. Mixtures of Homopolymer Emulsions

Films deposited from mixed homopolymer emulsions exhibit properties generally interpretable in terms of the expected structure. Homopolymers of PEA or PMMA produce continuous films upon deposition from emulsion; PMMA and PS do not.<sup>8</sup> It is expected, therefore, that mixtures of one of the film formers (soft polymers) and one of the non-filming (hard) polymers should form continuous films at room temperature provided sufficient soft polymer is present to bind the harder component. The inclusion of about 25% of the hard polymer gives a film slightly stiffened in comparison with the

tion, all polyacrylate–polymethacrylate combinations gave transparent films.

### B. Solution Mixtures

The structure of films deposited from solutions is undoubtedly somewhat more variable. With two incompatible polymers the resulting film was often visibly inhomogeneous, the components being present in layers or regions. For the one combination of compatible polymers (PVAc, PMA) a single glass transition point was observed—consistent with the hypothesis that homogeneity was obtained.

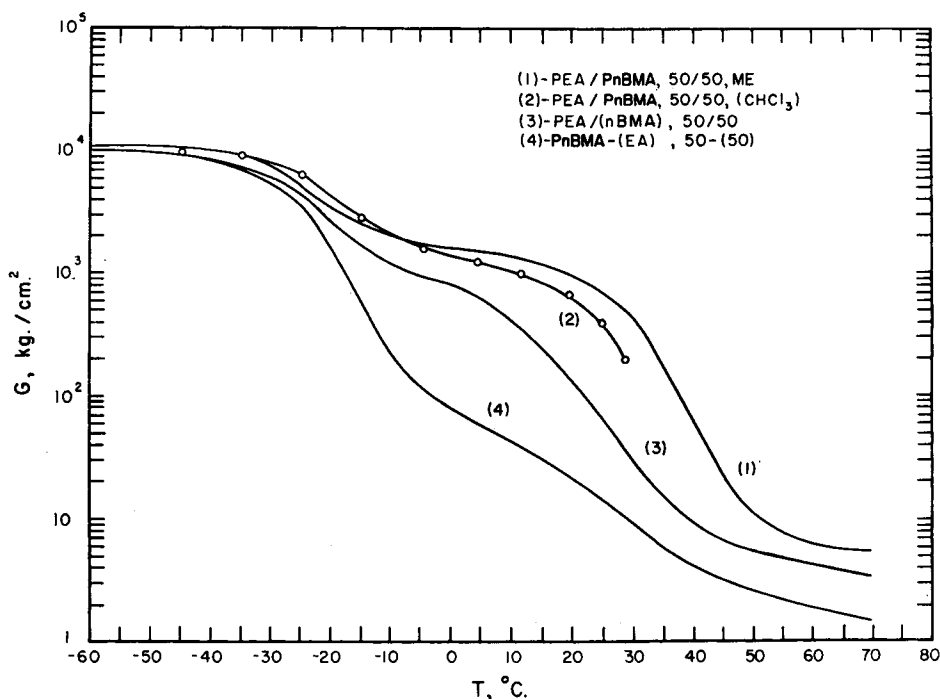


Fig. 8. Torsional modulus-temperature curves for PEA/PnBMA, 50/50 systems.

film of the soft homopolymer, as if by inclusion of a pigment. Upon heating of the film, such that some fusion of the particles of the hard component might occur, a pronounced stiffening is found. Only in those cases in which the film has been heated or large proportions of the hard polymer are present is there observed a glass transition point attributable to this component.

All the mixed emulsion films examined undoubtedly contained two phases, even when the polymers were compatible (PVAc, PMA), since the polymer viscosities were never sufficiently low to permit thorough mixing. Despite the phase separa-

Films prepared from mixed solutions of a rubbery and a glassy polymer consistently show very high modulus values for the glassy-rubbery region. The glassier polymer apparently forms a continuous network which may segregate in a layer or may interpenetrate the network of the softer polymer. Thus, casting films from solution may result in continuous networks for both polymers, provided a sufficient amount of each is present. Polymer molecules dissolved in a solvent have considerable mobility and, as the solvent evaporates, are relatively free to seek a favorable environment. They may aggregate as regions or layers, depending upon

the rate processes and thermodynamic equilibria involved.

### C. Two-Stage Emulsion Polymerizations

When a monomer is polymerized in the presence of a preformed polymer emulsion, penetration of monomer into polymer particle occurs if the polymer is swollen by the monomer. It is probable that an outside layer is formed which is rich in the polymer of the second-stage monomer and that new homopolymer particles are formed, especially if emulsifier concentration is high. The order of polymerization is thus important in determining film structure and properties, as is shown in Figure 4, which gives results for two samples of 25% MMA, 75% MA, prepared in the two orders of addition. The stiffness of the film is a reflection of the hardness of the second-stage polymer. Where large proportions of the hard polymer are present from the second-stage polymerization, film formation may be prevented. It is interesting to note, however, that clear films of incompatible polymers (PMA, PS) may be prepared from two-stage emulsions of this type. Films from mixed homopolymer emulsions of the same overall composition are opaque.

As in the case of films from mixed emulsions, these mixed polymers do not represent equilibrium configurations; thus heating and working of the films might result in substantial changes in their properties.

### D. Interpretation of Modulus-Temperature Curves

All the torsional modulus data obtained thus far for two-component polymer mixtures of limited compatibility, formed by mixing solutions or mixing emulsions, or by two-stage emulsion polymerization, show that the glassy transition point of the softer polymer is essentially unaffected by the presence of the second polymer. It is concluded that regions of the individual polymers, that are sufficiently large for the polymers to retain their intrinsic identities, must exist in these films.

In the region between the two  $T_g$ 's, a two-phase system of rubbery polymer A and glassy polymer B exists. (The presence of a third phase of a solution of A and B at the boundaries is not considered here.) If the hard polymer is present in sufficient amounts and distributed so as to provide a large number of entanglements, the development of rubberlike elasticity and substantial viscous flow are retarded until the temperature is raised above the  $T_g$  of the second polymer. Then the system is composed of two rubbery polymers.

It is interesting that in a sense it is possible to imitate the modulus behavior of a crystalline polymer. In the case of a crystalline polymer the permanent network entanglements (i.e., "permanent" below the melting point of the polymer) are supplied by the crystallites, a different phase of the same polymer, rather than by a second polymer.

Torsional measurements help provide insight into the nature of heterogeneous systems; however, data obtained by methods involving greater stresses and/or faster stressing rates (e.g., creep studies, tensile measurements, and dynamic torsional studies) should prove highly enlightening.

The authors wish to acknowledge the synthesis of the polymers by Dr. B. Larsson, the use of PEA/PnBMA data of G. Bauldauf, and the use of the data of R. Graham on the PEA-(MMA) graft copolymer.

### References

1. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, New York, 1953, Chap. 13.
2. Kern, R. J., and R. J. Slocombe, *J. Polymer Sci.*, **15**, 183 (1955).
3. Williamson, I., *British Plastics*, 87 (Sept. 1950).
4. Loshaek, S., *J. Polymer Sci.*, **15**, 391 (1955).
5. Schmieder, K., and K. Wolf, *Kolloid-Z.*, **134**, 149 (1953).
6. Wood, L. A., *J. Polymer Sci.*, **28**, 319 (1958).
7. Gluckman, M. S., M. J. Kampf, J. L. O'Brien, T. G. Fox, and R. K. Graham, *J. Polymer Sci.*, **37**, 411 (1959).
8. Brown, G. L., *J. Polymer Sci.*, **22**, 423 (1956).

### Synopsis

Torsional modulus-temperature data have been obtained on heterogeneous polymer compositions prepared by several procedures. Both the state of aggregation of the component chain molecules and their degree of compatibility are significant variables. Modulus curves similar to those for crystalline polymers can be obtained from incompatible polymers having glass temperatures sufficiently far apart. Detailed interpretations are presented for modulus curves of both individual homopolymers and bicomponent heterogeneous polymer mixtures.

### Résumé

Des données sur la relation module de torsion-température ont été obtenues pour des compositions de polymère hétérogènes, réalisées par différents procédés. L'état d'aggrégation des molécules de la chaîne ainsi que leur degré de compatibilité sont des variables significatives. Des courbes similaires de module à celles dans le cas de polymères cristallins peuvent être obtenues avec des polymères incompatibles ayant des températures de transition vitreuse assez différentes. Des interprétations détaillées sont présentées pour des courbes de module des homopolymères individuels ainsi que des mélanges de polymère hétérogènes à deux composants.



### Zusammenfassung

Torsionsmodul-Temperatur-Daten wurden an heterogenen, auf verschiedene Art bereiteten Polymermischungen bestimmt. Sowohl der Aggregationszustand der Kettenmolekülkomponenten als auch ihr Verträglichkeitsgrad sind wichtige Variable. Nichtverträgliche Polymere, die genügend auseinanderliegende Glastemperaturen besitzen,

liefern Modulkurven, die denen kristalliner Polymerer ähnlich sind. Eine ausführliche Interpretation der Modulkurven wird sowohl für Homopolymere für sich als auch für die aus zwei Komponenten bestehenden, heterogenen Polymermischungen gegeben.

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