

Generalized Model Representation Relating the Degree of Mixing to the Rheological Behavior of a Mechanical Mixture of Two Polymer Components*

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Synopsis

On assuming that the two polymer components are poorly compatible or incompatible and from semimicro heterogeneous systems composed of homogeneous phases of each component, two kinds of generalized models which relate the degree of mixing of the two phases to the mechanical behavior of the systems were proposed. In this phenomenological theory, the chemical interaction between the two polymer components was neglected, and the stress or strain distribution along the boundaries between the two phases was much simplified. This might give serious error when the mixed phases become small and the surface effect, instead of volume effect, becomes significant. The mechanical mixtures can be classified by the manner of mixing of the two phases of A and B components as follows: A islands in B matrix, B islands in A matrix, A matrix-B matrix, and A islands-B islands mixing. The mechanical properties of the mixed systems are affected not only by those of each component and their volume fraction in bulk, but strongly by the manner of mixing. The terminology used here, as the degree of mixing, is one of the representations of the manner of mixing in terms of distribution function of partial volume fractions of each component in the mixed system.

The analysis of some mixed systems of two polymer components gave the following results. The mixed systems cast from acetone solution of poly(vinyl acetate) and poly(methyl methacrylate) give mechanical mixtures of the islands-in-matrix type mixing. A phase conversion from PMMA islands in PVAc matrix to PVAc islands in PMMA matrix occurs at about 70% volume fraction of PMMA due to the hexagonal close packing of PMMA islands in PVAc matrix with increase of volume fraction of PMMA. On the other hand, the systems cast from mixtures of acetone solution of PVAc and lightly crosslinked PMMA fine particles give mechanical mixtures of the matrix-matrix type mixing. The mixed systems of polystyrene and 30/70 butadiene-styrene copolymer, which have been classified by Tobolsky as polyblends, might also be a type of mechanical mixture classifiable as matrix-matrix mixing. However, the manner of mixing should be much modified by the chemical interaction between the two components.

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INTRODUCTION

The mechanical properties of polymer mixtures depend on the degree of mixing of the mixed components.¹ If two polymers mixed are completely compatible, the blended system behaves like a random copolymer of the two monomeric components, having a single glass-transition temperature which shifts with the monomer ratio.^{2,3} The only example of such a completely compatible system observed is that obtained by blending poly(vinyl chloride) with butadiene-acrylonitrile rubber within some range of fraction of the components, where a sort of solvation may occur due to a strong interaction between polar radicals, such as $-\text{CN}$ and $-\text{Cl}$.^{4,5}

If the mixed polymers are poorly compatible or incompatible, which is more often the case in actuality, a sort of mechanical mixture rather than a solution results. This common type of mixing usually shows the existence of two glass-transition temperatures which correlate, more or less, to the original glass-transition temperatures of each component and suggest that the mechanical mixture leaves homogeneous phases of each component.^{6,7}

In the following phenomenological theory, it is intended to relate the rheological properties of this type of mechanical mixture to the degree of mixing by using two types of generalized models. The theory proposed is based on semimicro heterogeneity of the mixed system, neglects chemical interactions between the two polymers mixed, and simplifies greatly the stress or strain distribution along the boundary of the mixed phases.

THEORY

Simple Models Based on the Additivity of Contribution Either of Partial Stress or of Partial Strain to the Total Stress or Strain

One of the simplest models to describe the mechanical mixture of two polymer components may be given by a particle of B polymer component floating in a unit cubic lattice of A polymer component, as shown in Figure 1a, so as to minimize the contact surface between the two phases. The radius of the particle may be decided, as a mean value, from its volume fraction.

This simple model may be approximated to two types of mechanical models combining the two phases as shown in Figures 1b and 1c. The former mechanical model represents a simple additivity of contribution of partial stress of each element sliced vertically to the total stress, and the latter that of partial strain of each element sliced horizontally to the total strain. In these models, rigid adhesion between the two phases and no interference between the sliced elements are assumed, i.e., actual stress or strain distribution along the spherical surface of each phase is much simplified.

The relaxation modulus, $E(t, T)$ of the combined systems at time t and temperature T is given by the following equations.

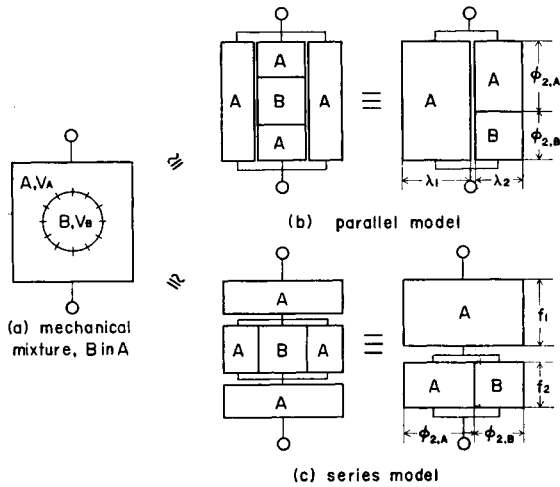


Fig. 1. Two types of mechanical models corresponding to a simple mechanical mixture, B sphere in A unit cubic lattice.

For the parallel model in Figure 1b:

$$\begin{aligned}
 E(t, T) &= \lambda_1 E_A(t, T) + \lambda_2 \{ \varphi_{2,A} / E_A(t, T) + \varphi_{2,B} / E_B(t, T) \}^{-1} \\
 \lambda_1 + \lambda_2 &= 1 \\
 \varphi_{2,A} + \varphi_{2,B} &= 1 \\
 \lambda_2 \varphi_{2,B} &= V_B \\
 \lambda_1 + \lambda_2 \varphi_{2,A} &= V_A
 \end{aligned}
 \tag{1}$$

where λ_1 and λ_2 are volume fractions of the elements coupled in parallel, $\varphi_{2,A}$ and $\varphi_{2,B}$ are volume fractions of A and B polymer phases in the λ_2 element, V_A and V_B are volume fractions of A and B components in the bulk, and E_A and E_B are relaxation moduli of each polymer component, respectively.

For series model in Figure 1c:

$$\begin{aligned}
 E(t, T) &= [f_1 / E_A(t, T) + f_2 / \{ \varphi_{2,A} E_A(t, T) + \varphi_{2,B} E_B(t, T) \}]^{-1} \\
 f_1 + f_2 &= 1 \\
 \varphi_{2,A} + \varphi_{2,B} &= 1 \\
 f_2 \varphi_{2,B} &= V_B \\
 f_1 + f_2 \varphi_{2,A} &= V_A
 \end{aligned}
 \tag{2}$$

where f_1 and f_2 are volume fractions of the two elements coupled in series, and $\varphi_{2,A}$ and $\varphi_{2,B}$ are volume fractions of A and B polymer phases in the f_2 element, respectively.

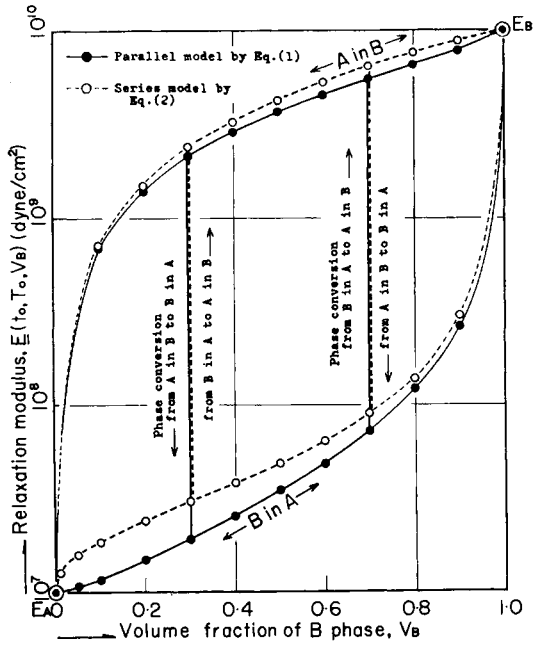


Fig. 2. Volume fraction dependence of relaxation modulus of a simple mechanical mixture, B sphere in A unit cubic lattice or A sphere in B unit cubic lattice.

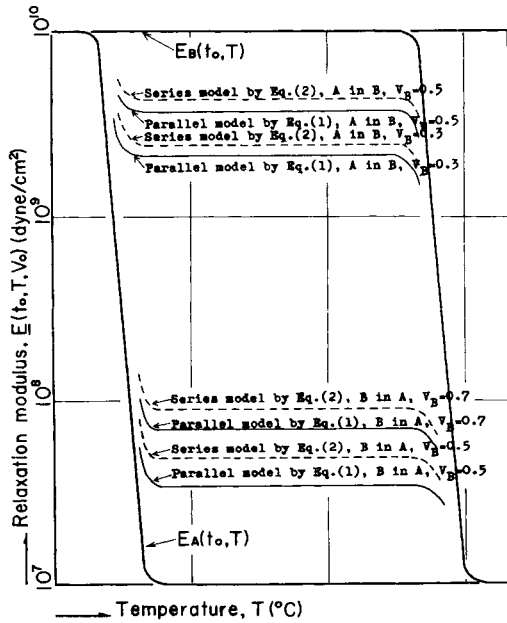


Fig. 3. Temperature dependence of relaxation modulus of a simple mechanical mixture, B sphere in A unit cubic lattice or A sphere in B unit cubic lattice.

When the sphere B floating in the unit cubic lattice of A is approximated as a cube having the same volume as the sphere, the V_B dependence of $E(t, T)$ calculated from either eqs (1) or (2) at given time t_0 and temperature T_0 is shown in Figure 2, where $E_A(t_0, T_0)$ and $E_B(t_0, T_0)$ are assumed as 1×10^7 and 1×10^{10} dynes/cm.², respectively. Similarly, the temperature dependence of $E(t, T)$ at given time t_0 and volume fraction V_B , is shown in Figure 3, where $E_A(t_0, T)$ and $E_B(t_0, T)$ are assumed as illustrated in the figure.

As shown in the figures, the mechanical properties of the system are greatly affected by those of the component which occupies the medium phase, not the sphere phase. The drastic changes of relaxation modulus with changing volume fraction V_B at about 70 or 30%, as seen in Figure 2, are caused by the phase conversion from B in A to A in B or from A in B to B in A due to the hexagonal close packing of B spheres in A medium or A spheres in B medium, respectively. It may be noted that the mixture under 30%, or beyond 70% volume fraction of a component has two different natures, i.e., one is a stable mixture governed by the phase selectability of each component, the other is unstable and constrained by the excess amount of volume fraction beyond the limit of hexagonal close packing.

There exists some difference between the results calculated from eqs. (1) and (2), which should be attributed to the simple assumption on the distribution of stress or strain along the boundary between the two phases in the mechanical models. However, the difference is not so large as to deny the above discussion on the definitive effect of the phase of the medium upon the mechanical properties of the mixed system.

Generalized Models and Distribution Functions of Volume Fraction Relating the Degree of Mixing to the Mechanical Behavior of the Mixed System

Two types of mechanical models which correspond to a mean radius sphere floating in unit cubic lattice are much simpler than the actual manner in which the force lines should run through media consisting of the two polymer phases coupled in series, in the sense of the parallel model in Figure 1b, with the volume fraction varying from zero to unity continuously. The mechanical models in Figures 1b and 1c may be generalized by models illustrated in Figures 4b and 4c, respectively.*

For the generalized parallel model in Figure 4b, when one assumes λ to be a function of φ , i.e.,

$$\lambda(\varphi)d\varphi = \sum_{\varphi < \varphi^i < \varphi + d\varphi} \lambda_i \quad (3)$$

* The volume fractions, φ_{iA} and φ_{iB} in the i th elements of the two types of mechanical models should be as follows; $\varphi_{iA} = \sum_{j=1}^l \varphi_{iA}^{(j)}$ and $\varphi_{iB} = \sum_{k=1}^m \varphi_{iB}^{(k)}$. Namely, the i th element of the model in Figure 4b consists of l and m phases of each component coupled in series and that in Figure 4c coupled in parallel.

and n to be infinite, then eq. (1) may be replaced by

$$E(t, T) = \int_0^1 E(t, T, \varphi_A) \lambda(\varphi_A) d\varphi_A \tag{4}$$

$$\int_0^1 \lambda(\varphi_A) d\varphi_A = 1 \tag{5}$$

$$\int_0^1 \lambda(\varphi_A) \varphi_A d\varphi_A = V_A$$

where

$$E(t, T, \varphi_A) = \{ \varphi_A/E_A(t, T) + (1 - \varphi_A)/E_B(t, T) \}^{-1} \tag{6}$$

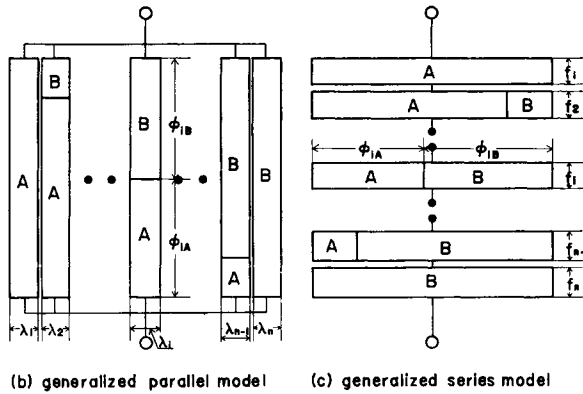


Fig. 4. Two types of generalized models relating the degree of mixing to the mechanical properties of the mixed system of two polymer components.

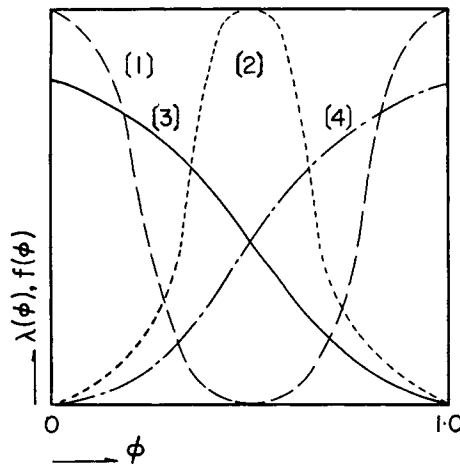


Fig. 5. Schematic representation of four types of distribution functions, $\lambda(\varphi)$ or $f(\varphi)$.

$E(t, T, \varphi_A)$ can be calculated from eq. (6) by substituting measurable function $E_A(t, T)$ and $E_B(t, T) \cdot E(t, T)$ is also a measurable function. This means that the function $\lambda(\varphi_A)$ can be decided by solving the integral eq. (4) under the additional conditions given by eq. (5).

$\lambda(\varphi_A)$ is a distribution function of volume fraction of the elements coupled in parallel with respect to the volume fraction of polymer phase A coupled in series in the elements and is a characteristic function representing a degree of mixing of the two phases in the mixed system.⁸

Similarly, for the generalized series model in Figure 4c, a distribution function of volume fraction of the elements coupled in series, $f(\varphi_A)$ can be defined by the following relations:

$$E(t, T) = \left[\int_0^1 f(\varphi_A) / E'(t, T, \varphi_A) d\varphi_A \right]^{-1} \quad (7)$$

$$\int_0^1 f(\varphi_A) d\varphi_A = 1 \quad (8)$$

$$\int_0^1 f(\varphi_A) \varphi_A d\varphi_A = V_A$$

where

$$E'(t, T, \varphi_A) = \varphi_A E_A(t, T) + (1 - \varphi_A) E_B(t, T) \quad (9)$$

Figure 5 shows four types of the distribution functions, schematically. Type (1) for $\lambda(\varphi_A)$ and type (2) for $f(\varphi_A)$ present a sort of "matrix-matrix" mixing of the two components, i.e., a mixture of independent network structures of each component through which the force lines run, and gives the mechanical properties resembling a simple parallel-couple of the two components. Type (2) for $\lambda(\varphi_A)$ and type (1) for $f(\varphi_A)$ present a sort of "island-island" mixing of the two components, i.e., a mixture of independent lamella structures of each component across which the force lines run, and gives the mechanical properties resembling a simple series-couple of the two components. Type (3) for $\lambda(\varphi_A)$ and $f(\varphi_A)$ presents "A-islands-in-B-matrix" mixing, and type (4) for $\lambda(\varphi_A)$ and $f(\varphi_A)$ presents "B-islands-in-A-matrix" mixing of the two components.

Determination of $\lambda(\varphi)$ or $f(\varphi)$

The determination of $\lambda(\varphi)$ and $f(\varphi)$ from the experimental data involves simply solving the integral eqs. (4) and (7) under the additional conditions of eqs. (5) and (8), respectively. However, in general, $E(t, T)$ is not necessarily given by an analytical function, and one can only solve the equations numerically. For example for eq. (4), the interval of φ_A from zero to unity is split into n small intervals, $\Delta\varphi_{Ai}$, where $i = 1, 2, 3, \dots, n$; this yields the set of equations of eq. (10) approximately,

$$\begin{bmatrix} 1 \\ V_A \\ E(T_1) \\ E(T_2) \\ \vdots \\ E(T_{n-2}) \end{bmatrix} = \begin{bmatrix} 1 & 1 & \cdots & 1 \\ \varphi_{A1} & \varphi_{A2} & \cdots & \varphi_{An} \\ E(\varphi_{A1}, T_1) & E(\varphi_{A2}, T_1) & \cdots & E(\varphi_{An}, T_1) \\ E(\varphi_{A1}, T_2) & E(\varphi_{A2}, T_2) & \cdots & E(\varphi_{An}, T_2) \\ \vdots & \vdots & \vdots & \vdots \\ E(\varphi_{A1}, T_{n-2}) & E(\varphi_{A2}, T_{n-2}) & \cdots & E(\varphi_{An}, T_{n-2}) \end{bmatrix} \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \lambda_3 \\ \lambda_4 \\ \vdots \\ \lambda_n \end{bmatrix} \quad (10)$$

where $T_1, T_2, T_3, \dots, T_{n-2}$ are $(n - 2)$ different temperatures, φ_{A_i} are arbitrary values of φ_A within the respective small intervals $\Delta\varphi_{A_i}$, and

$$\lambda_i = \lambda(\varphi_{A_i})\Delta\varphi_{A_i} \quad (11)$$

The eq. (10) is a system of linear equations with n unknowns of λ_i , primarily simple, but troublesome to solve when n becomes large.

EXPERIMENTAL RESULTS

Mixed Systems of Poly(methyl Methacrylate) (PMMA)-Poly(vinyl Acetate) (PVAc) and of Lightly Crosslinked PMMA-PVAc

For the PMMA-PVAc systems, PMMA ($\bar{M} = 3.5 \times 10^5$) and PVAc ($\bar{M} = 2.4 \times 10^6$) were mixed simultaneously in acetone (common solvent) by various volume fractions, and for crosslinked PMMA-PVAc systems, two kinds of lightly crosslinked fine particles of PMMA (about 100 m μ diameter) obtained from emulsion copolymerization of 0.5/99.5 and 3/97 mixtures of allyl methacrylate with methyl methacrylate were mixed with acetone solutions of the PVAc, respectively. The test specimen was cast from the solutions into thin films by vaporizing the solvent gradually, and was leached in running water so as to remove acetone as completely as possible. The test specimen thus prepared was dried at 100–120°C. in vacuum for 3 days and was annealed at 170°C. for 20 min. before the stress relaxation measurements were made.

Figure 6 shows the temperature dependence of the 500 sec. relaxation modulus of PMMA-PVAc mixed systems having various volume fractions of each component. Within 60% volume fraction of PMMA component the behavior resembles that of PVAc; beyond this critical volume fraction, the behavior suddenly approaches that of PMMA alone.

Figure 7 shows the temperature dependence of the 500 sec. relaxation modulus of mixed systems of the PVAc with the two kinds of lightly crosslinked PMMA by 50/50 volume fractions. Those of PVAc and 50/50 PMMA-PVAc, together with that of 0.5% crosslinked PMMA, which is easily cast in the swollen form from acetone, are also shown for comparison. It is noted that the behavior is considerably different from that of 50/50 PMMA-PVAc, and resembles that of 80/20 PMMA-PVAc.

Figure 8 shows the volume fraction dependence of the relaxation modulus at a given time t_0 and temperature T_0 . The closed circles were plotted from

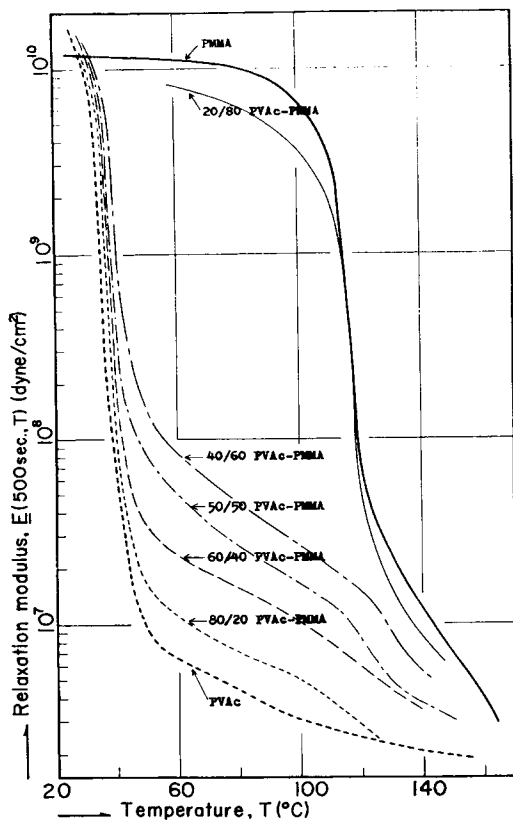


Fig. 6. Temperature dependence of 500 sec. relaxation moduli of mixtures of PVAc and PMMA.

the results of PMMA-PVAc mixed systems at 500 sec. and 80°C., and the thin solid lines are theoretical curves calculated by substituting the values of relaxation moduli of PMMA and PVAc alone into eq. (1) as in the case of Figure 2. Fairly good agreement is found between the experimental and calculated results, which show a remarkable increase of relaxation modulus with increase of volume fraction of PMMA at about 70%. This strongly suggests that a phase conversion from PMMA in PVAc to PVAc in PMMA occurs in the system at this critical volume fraction of PMMA. Actually the test specimens having a PMMA volume fraction less than 70% are easily extracted by hot ethanol (solvent for PVAc) but in those with more than 70% PMMA remains in the residue.

On the other hand, the relaxation moduli of the lightly crosslinked PMMA-PVAc systems are plotted as half filled circles in Figure 8. Their locations in the figure deviate considerably from thin broken lines which were calculated similarly from eq. (1) on assuming a phase conversion from PVAc in crosslinked PMMA to crosslinked PMMA in PVAc at 70 or 30% volume fraction of PVAc component. This may suggest that the systems

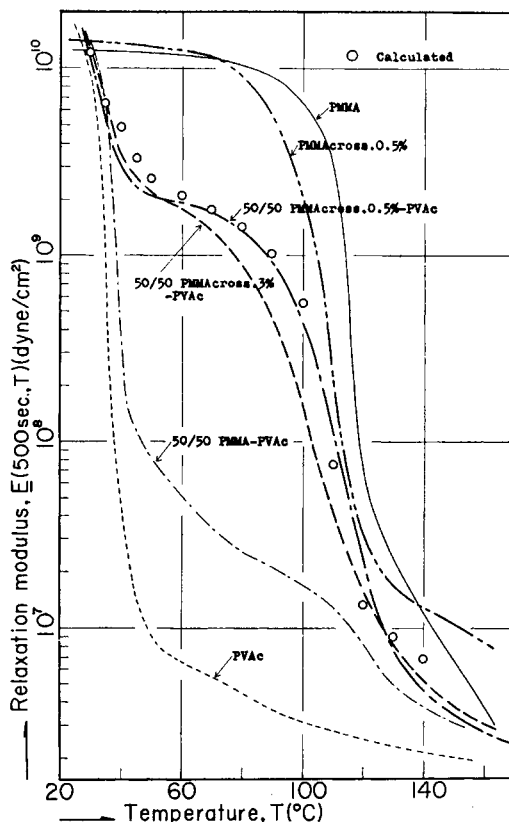


Fig. 7. Temperature dependence of 500 sec. relaxation moduli of the mixtures of PVAc with two kinds of lightly crosslinked PMMA particles and of the single component of lightly cross-linked PMMA: (O) calculated results for 50/50 0.5% crosslinked PMMA-PVAc on assuming matrix-matrix mixing.

differ from such a simple mixing as islands in matrix mixing. Actually, the test specimens can not be extracted by hot ethanol, suggesting, at least, that the PVAc component does not occupy the matrix phase.

From the temperature dependence of the 500 sec. relaxation moduli of PVAc, 0.5%-crosslinked PMMA, and 50/50 0.5% crosslinked PMMA-PVAc shown in Figure 7, the distribution function $f(\varphi)$ of the mixed system was determined by using a numerical method corresponding to eqs. (10) and (11) in which n was taken as 11. The results obtained are listed in Table I. It may be seen that $f(\varphi)$ is a type of Gaussian distribution around $\varphi = 0.5$ and belongs to type (2) of Figure 5. This suggests that the two components are mixed as matrix-matrix mixing in contrast to islands-in-matrix mixing for PMMA-PVAc. The open circles in Figure 7 along the experimental data of the thick chain line were plotted by a recalculation, with substitution of the values listed in Table I into eq. (10). The agreement between them is satisfactory.

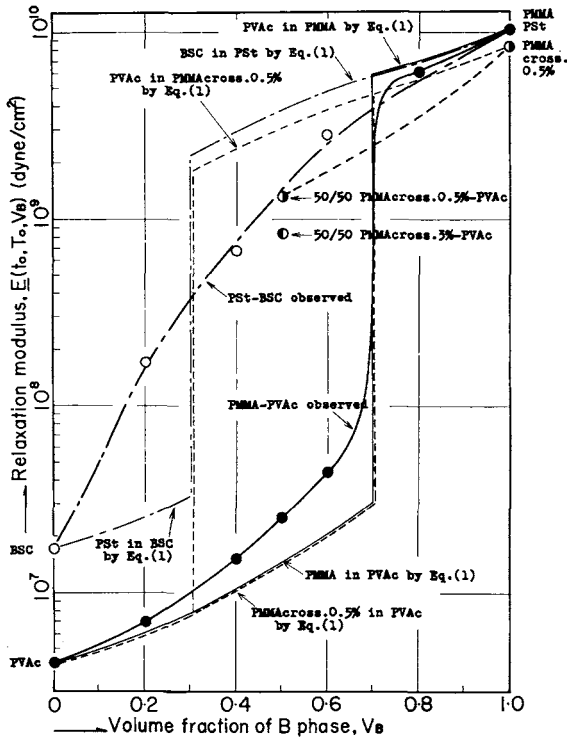


Fig. 8. Volume fraction dependence of relaxation moduli of the mixed systems of PVAc-PMMA, PVAc-lightly crosslinked PMMA particles, and PSt-BSC, in comparison with the calculated results on assuming a simple mechanical mixture, islands in matrix mixing.

TABLE I

Results of f_{Ai} and φ_{Ai} Obtained by the Numerical Integration Method for 50/50 0.5% Crosslinked PMMA-PVAc, Taking $n = 11$ and $V_A = 0.5$ (Where V_A is PVAc)

φ_{Ai}	f_i
$\varphi_1 = 0.05$	1.9×10^{-3}
$\varphi_2 = 0.1$	1.7×10^{-2}
$\varphi_3 = 0.2$	5.3×10^{-2}
$\varphi_4 = 0.3$	1.2×10^{-1}
$\varphi_5 = 0.4$	1.9×10^{-1}
$\varphi_6 = 0.5$	2.3×10^{-1}
$\varphi_7 = 0.6$	1.8×10^{-1}
$\varphi_8 = 0.7$	1.2×10^{-1}
$\varphi_9 = 0.8$	5.5×10^{-2}
$\varphi_{10} = 0.9$	1.8×10^{-2}
$\varphi_{11} = 0.95$	1.5×10^{-3}

Mixed Systems of Polystyrene (PSt)-30/70 Butadiene-Styrene Copolymer (BSC)

As the other example, the mixed systems of polystyrene-butadiene-styrene copolymer presented by Tobolsky⁹ were examined. Figure 9 shows the temperature dependence of the 10 sec. relaxation moduli of the systems varying in the weight fraction of each component. It is noted that the change of relaxation modulus with weight fraction of the component is more gradual than that of PMMA-PVAc systems in Figure 6.

The volume fraction dependence of relaxation modulus at a given temperature 80°C. was checked from Figure 9 and plotted in Figure 8 as open circles. It is also seen that the volume fraction dependence differs from the thin chain lines which are calculated from eq. (1) on assuming simple islands-in-matrix mixing and their phase conversion at about 30% volume fraction of polystyrene.

Again, from the temperature dependence of relaxation moduli of each component and of the mixed systems, the distribution function, $\lambda(\varphi)$ of the mixed systems was determined numerically by using eqs. (10) and (11). In this case, however, the procedure failed, especially for the systems of high polystyrene contents, due to more gradual changes of relaxation moduli of

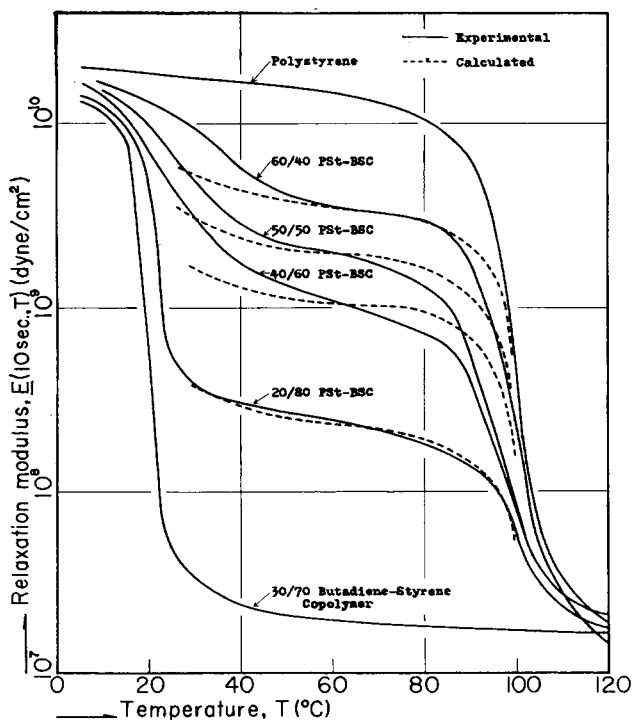


Fig. 9. Temperature dependence of 10 sec. relaxation moduli of the mixtures of PSt-30/70 butadiene-styrene copolymer after Tobolsky,⁹ in comparison with the calculated results on assuming matrix-matrix mixing.

the mixed systems at low and high temperatures than this theory demands. Thereby, the procedure was further tried by using the temperature dependence of relaxation modulus within relatively narrow temperature range of 30–100°C. The numerical integral method was used, n being taken as 6 in combination with a trial-and-error method.

The results obtained are listed in Table II for the four kinds of mixed systems. It may be suggested that the function should attain maxima at the extreme values of φ , i.e., $\lambda(\varphi)$ belongs to the type (1) of Figure 5. In other words, the mixed systems might be classified as matrix-matrix mixing, not of islands-in-matrix mixing.

TABLE II
Results of λ_{Ai} and φ_{Ai} Obtained by the Numerical Integration Method for Four Kinds of Blended Systems of Polystyrene and 30/70 Butadiene–Styrene Copolymer, Taking $n = 6$ and $V_A = 0.8, 0.6, 0.5,$ and 0.4 (Where V_A is Copolymer)

φ_{Ai}	λ_i			
	$V_A = 0.8$	$V_A = 0.6$	$V_A = 0.5$	$V_A = 0.4$
$\varphi_1 = 0.001$	2.3×10^{-2}	1.0×10^{-1}	2.1×10^{-1}	4.2×10^{-1}
$\varphi_2 = 0.01$	—	1.3×10^{-1}	1.8×10^{-1}	1.1×10^{-1}
$\varphi_3 = 0.1$	1.5×10^{-1}	1.2×10^{-1}	6.0×10^{-2}	5.0×10^{-2}
$\varphi_4 = 0.3$	5.0×10^{-2}	5.0×10^{-2}	4.0×10^{-2}	3.0×10^{-2}
$\varphi_5 = 0.6$	2.0×10^{-2}	4.2×10^{-2}	7.0×10^{-2}	1.0×10^{-2}
$\varphi_6 = 1.0$	7.6×10^{-1}	5.3×10^{-1}	4.4×10^{-1}	3.8×10^{-1}

The broken lines in Figure 9 were the results of recalculation with substitution of the values in Table II into eq. (10). The agreement between the experimental and recalculated results is still not so satisfactory as in the former case except for 20/80 polystyrene–butadiene–styrene copolymer. The discrepancies, especially for the systems of high polystyrene contents, at low and high temperatures are still conspicuous. This might be not only due to n being too small or the procedure being too crude to produce exact agreement, but rather due to a different nature of these blended systems from that represented by this type of mechanical mixture.

Actually, these blended systems have been called by Tobolsky as “poly-blends” and distinguished from merely mechanical mixtures.⁹ For the blended systems of high polystyrene contents, the glass–rubber transition corresponding to polystyrene and the copolymer appear in wider temperature ranges than those expected from merely mechanical mixing. This might suggest the existence of some chemical interaction between the two polymer components which modifies the manner of mixing of the systems from that anticipated here by a matrix-matrix mixing.

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Résumé

En admettant que les deux composants d'un polymère sont faiblement ou non compatibles et forment des systèmes sémi-micro-hétérogènes composés de phases homogènes de chaque composant, on propose deux types de modèles généralisés qui relient le degré d'interpénétration des deux phases, au comportement mécanique des systèmes. Dans cette théorie phénoménologique, on a négligé l'interaction chimique entre les deux composants polymériques et on a beaucoup simplifié les forces ou tensions de distributions existant au long des jonctions entre les deux phases. Ceci peut donner lieu à une erreur sérieuse lorsque les phases mêlées deviennent petites, l'effet de surface au lieu de l'effet de volume devenant important. Les mélanges mécaniques peuvent être classifiés par la manière de mêler les deux phases des composants A et B comme suit: mélanges "îlots A dans la matrice B" et "îlots A dans les îlots B." Les propriétés mécaniques des systèmes mélangés sont affectées non seulement par chacun des constituants et deux fractions de volume en bloc, mais d'une manière forte par la façon de mélanger. La terminologie qui est utilisée ici comme le degré de mélange, est une des représentations de la manière de mélanger rapportée à la fonction de distribution des fractions de volume partiel de chacun des constituants dans le système mélangé. L'analyse de quelques systèmes de mélanges est rapportée ci-dessous: les systèmes mêlés obtenus au départ de solutions acétoniques d'acétate de polyvinyle et de polyméthacrylate de méthyle, donnent des mélanges mécaniques du type "mélange d'îlots dans une matrice." Une conversion de phase "îlots de PMMA dans une matrice de PVAc en îlots de PVAc dans une matrice de PMMA" a lieu pour une fraction de volume égale à 70% en PMMA et est due à la formation de l'amas reserré hexagonal d'îlots de PMMA dans la matrice de PVAc avec augmentation de la fraction volumétrique en PMMA. D'autre part les systèmes obtenus au départ de mélanges de solutions acétoniques de PVAc et de fines particules de PMMA légèrement pontés, donne des mélanges mécaniques du type "matrice-matrice." Les systèmes mêlés de polystyrène et de copolymère butadiène-polystyrène 30/70, présentés et appelés "polyblends" par Tobolsky, peuvent être également une sorte de mélanges mécaniques classifiés dans les mélanges du type "matrice-matrice." La façon de mélanger pourrait cependant être fort modifiée par les interactions chimiques entre les deux composants.

Zusammenfassung

Unter der Annahme, dass die beiden Polymerkomponenten wenig oder nicht verträglich sind und halb-mikro-heterogene Systeme aus homogenen Phasen jeder Komponente bilden, werden zwei Typen allgemeiner Modelle angegeben, die den Mischungsgrad der beiden Phasen zum mechanischen Verhalten der Systeme in Beziehung bringen. In dieser phänomenologischen Theorie wurde die chemische Wechselwirkung zwischen den beiden Polymerkomponenten vernachlässigt und die Spannungs- oder Verformungsverteilung an den Grenzflächen zwischen den beiden Phasen stark vereinfacht. Das

kann zu grossen Fehlern führen, sobald die gemischten Phasen klein werden und der Oberflächeneinfluss den Volumseinfluss überwiegt. Die mechanische Mischung kann nach dem Mischungstyp der beiden Phasen der Komponenten A und B folgendermassen klassifiziert werden: "A-Inseln in B-Matrix," "B-Inseln in A-Matrix," "A-Matrix-B-Matrix" und "A-Inseln-B-Inseln." Die mechanischen Eigenschaften dieser Mischsysteme werden nicht nur durch diejenige jeder Komponente und ihren Volumbruchteil in der Probe, sondern auch sehr stark durch den Mischungstyp beeinflusst. Die hier für den Mischungstyp verwendete Terminologie bildet eine der Bezeichnungsmöglichkeiten für die Mischungsweise durch die Verteilungsfunktion der partiellen Volumbrüche jeder Komponente im Mischungssystem. Die Analyse einiger Mischsysteme aus den beiden Polymerkomponenten führte zu folgenden Feststellungen: Aus Acetonlösung von Polyvinylacetat und Polymethylmethacrylat gewonnene Mischsysteme bilden mechanische Mischungen vom Typ der Insel-Matrixmischung. Eine Phasenumwandlung von PMMA-Inseln in PVAc-Matrix zu PVAc-Inseln in PMMA-Matrix tritt bei 70 Vol% PMMA wegen der hexagonal-dichtesten Packung von PMMA-Inseln in PVAc-Matrix mit Zunahme des Volumsbruches an PMMA ein. Andererseits liefern die aus Mischung einer Acetonlösung von PVAc mit schwach vernetzten, feinen PMMA-Teilchen gewonnenen Systeme mechanische Mischungen vom Typ der Matrix-Matrixmischung. Die Mischsysteme aus Polyäthylen und 30/70-Butadien-Styrolcopolymerem, die von Tobolsky angegeben und als "Polyblends" bezeichnet wurden, könnten auch eine Art mechanischer Mischung und als Matrix-Matrixmischung zu klassifizieren sein. Der Mischungstyp könnte jedoch durch chemische Wechselwirkung zwischen den beiden Komponenten stark modifiziert werden.

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