Tensile Stress Relaxation Behavior of a Mechanical Mixture of Two Polymer Components*

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Synopsis

As one in a series of studies relating the rheological properties of mechanical mixtures of two polymer components to the degree of mixing, the temperature dependence of tensile stress relaxation behavior of two types of mixed systems, i.e., poly(methyl methacrylate)–poly(vinyl acetate) system and lightly crosslinked poly(methyl methacrylate–poly(vinyl acetate) system, was investigated over a temperature range covering the glass transition temperatures of both polymer components. The time–temperature superposition procedure was carried out for comparison of several parameters, such as fractional free volume and its thermal expansion coefficient, which were determined on the basis of the free volume concept from the viscosity in relation to the William-Landel-Ferry equation, with those of the individual polymer components. Although the fractional free volume and its thermal expansion coefficient thus determined for the mixed systems were apparent values, the results may, at least qualitatively, deny the simple additivity of the free volumes of the two-polymer mixed phases and suggest the existence of a sort of physical interaction between the phases, i.e., the internal pressure induced by one phase or the other due to a difference in thermal expansion coefficient between the phases.

Introduction

In a previous paper of this series,[1] two types of generalized models relating the degree of mixing to the rheological properties of a mechanical mixture of two polymer components were proposed. The theory proposed was based on the semimicro heterogeneity of the mixed system, neglected chemical interaction between the two polymers mixed, and simplified greatly the stress or strain distribution along the boundary of the mixed phases.

In this paper, the temperature dependence of tensile stress relaxation behavior of the mixed system in the range of linear viscoelasticity was investigated over a temperature range covering the glass transition tem-

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peratures of the two polymer components, and the time–temperature superposition procedure was carried out for comparison of several parameters, such as the fractional free volume and its thermal expansion coefficient which were determined on the basis of the free volume concept of the viscosity in relation to the Williams-Landel-Ferry equation,[2] with those of the individual polymer components.

The results obtained may be valid for modifying the previous model by adding a sort of physical interaction between the two polymer phases in terms of the internal pressure induced by one phase upon the other.

Test Specimens and Experimental Procedure

Two types of mixed systems, poly(methyl methacrylate) (PMMA)–poly(vinyl acetate) (PVAc) and lightly crosslinked PMMA(PMMA$_{cr}$)–PVAc, were prepared. For the PMMA–PVAc system PMMA($\bar{M}\eta = 3.5 \times 10^5$) and PVAc ($\bar{M}\eta = 2.4 \times 10^6$) were mixed simultaneously in acetone (common solvent) in various proportions (80/20, 60/40, 50/50, 40/60, and 20/80) and for the PMMA$_{cr}$–PVAc system lightly crosslinked, fine particles of PMMA (about 100 mμ diameter) obtained from emulsion copolymerization of a 0.5/99.5 mixture of allyl methacrylate with methyl methacrylate were mixed with acetone solutions of PVAc in various proportions (70/30, 50/50, 40/60, and 20/80).

The test specimens were cast from the solutions into thin films by vaporizing the solvent gradually and leached in running water so as to remove acetone as completely as possible. The test specimens thus prepared were dried at 100–120°C. in vacuum for 3 days and annealed at 170°C. for 20 min. before the stress relaxation measurements were made.

For the stress relaxation measurements, a chainomatic balance type autorecording relaxometer, described elsewhere,[3] was used, and the tensile stress relaxation of ribbon-shaped test specimens of about (1–5) $\times$ 50 $\times$ 0.2 mm. dimensions was measured over a period of 30–6000 sec. under given strains within the limit of linear viscoelasticity at various temperatures ranging from room temperature up to 170°C.

Experimental Results and Discussion

Figures 1–3 show the temperature dependence of relaxation moduli of the three kinds of amorphous polymers which were used as the individual components of this study. The behavior is typical of amorphous polymers.*

Figures 4 and 5 show also the temperature dependence of relaxation moduli of 50/50 PVAc–PMMA and 50/50 PVAc–PMMA$_{cr}$ as typical examples of the two types of mixed systems, respectively. When the two sets of results are compared, it may be seen that for the PVAc–PMMA system the glass–rubber transition of the PVAc at around 35°C. appears

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* The PMMA$_{cr}$ test specimen was cast into thin films by swelling the PMMA$_{cr}$ powder in acetone and then vaporizing the acetone gradually.
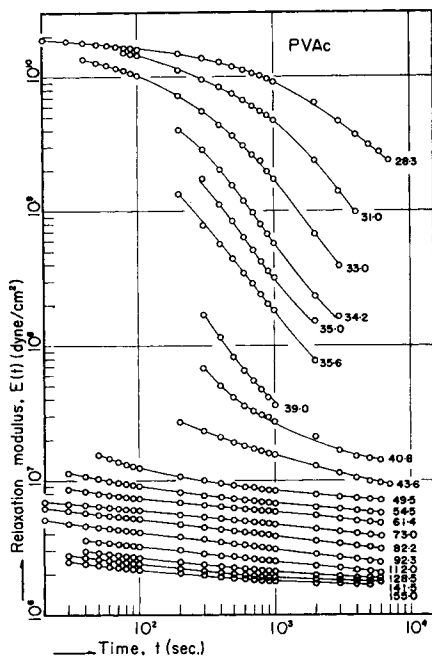
Fig. 1. Temperature dependence of relaxation modulus of poly(vinyl acetate), PVAc, used as a component of mixed system.

clearly but that of the PMMA at around 110°C. is indistinct; for the PVAc-PMMA$_{cr}$ system the glass–rubber transition of the PVAc is not clear, but that of the PMMA$_{cr}$ also at around 110°C. is clear. This remarkable reverse should be attributed to a difference in the mode of mixing of the two phases in the two systems.

Figures 6 and 7 show the temperature dependence of the relaxation modulus at 500 sec. as a function of volume fraction of the mixed components for the PVAc–PMMA and PVAc–PMMA$_{cr}$ systems, respectively, replotted from the two series of experimental results for the two systems for which typical examples are shown in Figures 4 and 5. This remarkable reverse of the effect of the volume fraction of each component upon the temperature dependence of the 500-sec. relaxation modulus is also seen for the two systems, i.e., for the PVAc–PMMA system the behavior resembles that of PVAc alone until the volume fraction of PMMA component reaches 60%, and suddenly approaches that of the PMMA alone beyond a critical volume fraction of around 70%, while for the PVAc–PMMA$_{cr}$ system the behavior is of reversal at a critical volume fraction of PMMA$_{cr}$ of around 30%.

In order to explain the reversal of the behavior between the two systems in terms of the mode of mixing, the volume fraction dependence of the 500-sec. relaxation moduli E of the two systems at a given temperature (80°C.), which was replotted again from Figures 6 and 7, was compared
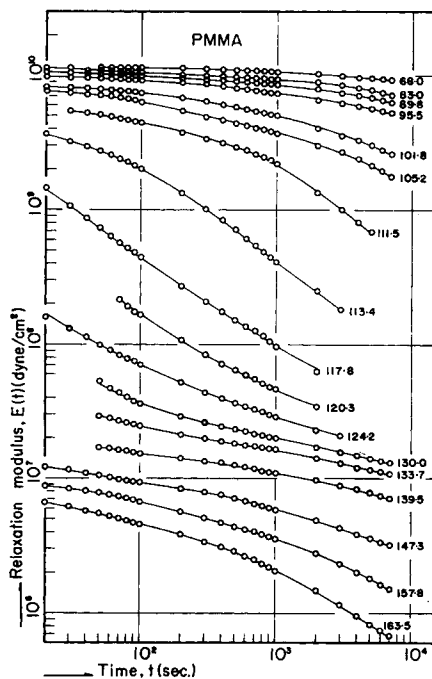
Fig. 2. Temperature dependence of relaxation modulus of poly(methyl methacrylate), PMMA, used as a component of mixed system.
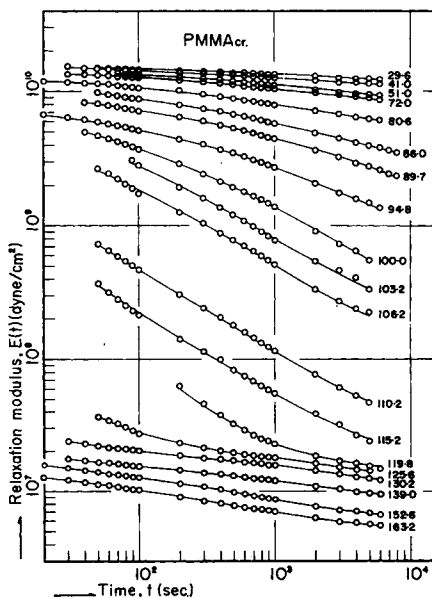

Fig. 3. Temperature dependence of relaxation modulus of lightly crosslinked poly-(methyl methacrylate), PMMA_cr, used as a component of mixed system.
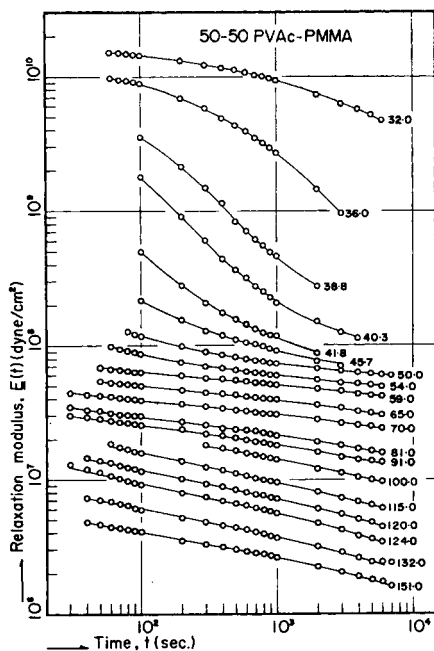
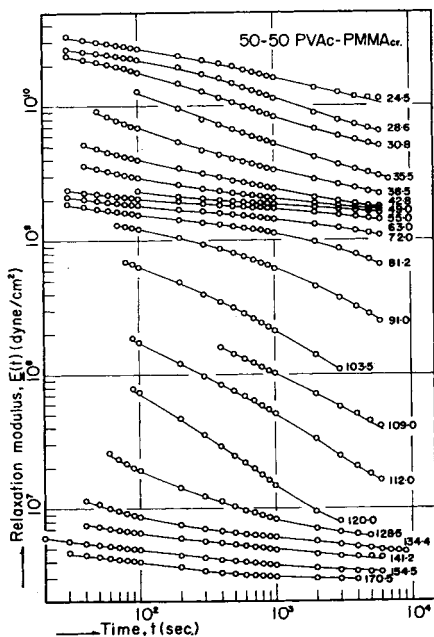Fig. 4. Temperature dependence of relaxation modulus of 50/50 PVAc–PMMA mixed system.

Fig. 5. Temperature dependence of relaxation modulus of 50/50 PVAc–PMMA$_{cr}$ mixed system.
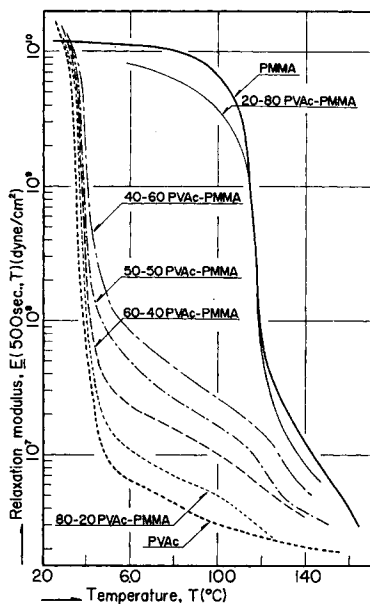
Fig. 6. Temperature dependence of 500 sec. relaxation modulus as a function of volume fraction of mixed components for the PVAc–PMMA mixed system.
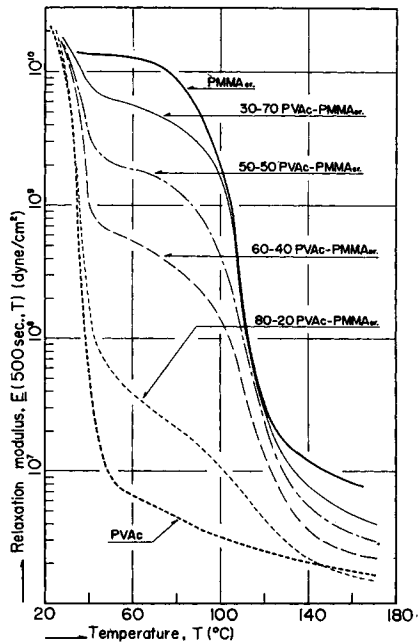

Fig. 7. Temperature dependence of 500 sec. relaxation modulus as a function of volume fraction of mixed components for the PVAc–PMMA$_{cr}$ mixed system.
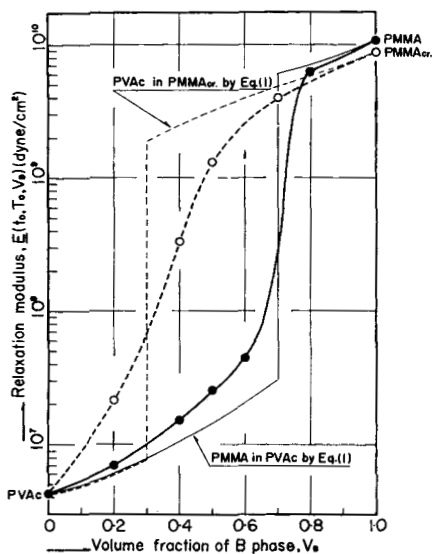
Fig. 8. Volume fraction dependence of 500 sec. relaxation modulus at 80°C. for the two types of mixed systems, PVAc–PMMA and PVAc–PMMA$_{cr}$, in comparison with the calculated results on assuming a simple mechanical mixture of a sphere of one component in a matrix of the other component and a phase conversion due to hexagonal close-packing of the sphere phase.

with the results calculated on the basis of a simple model of mechanical mixing as given by eq. (1), in which one assumes a sphere of component B floating in a unit cubic matrix of component A, approximates a sphere to a cube of the same volume and takes account of a phase conversion from B in A to A in B at 30 or 70% volume fraction of component B due to the hexagonal close-packing of the sphere phase of component A or B, respectively.[1]

$$E(t_0, T_0, V_B) = \lambda_1 E_A(t_0, T_0) + \lambda_2 [\phi_{2,A}/E_A(t_0, T_0) + \phi_{2,B}/E_B(t_0, T_0)]^{-1} \quad (1)$$

As seen in Figure 8, the experimental results given by the heavy solid line for the PVAc–PMMA system agree fairly well with those calculated (thin solid line) from the simple model of a PMMA sphere floating in a unit cubic PVAc matrix within a range of volume fraction of PMMA from 0 to 70%, beyond which the phase conversion from PMMA sphere in PVAc matrix to PVAc sphere in PMMA matrix occurs, while that (given by the heavy broken line) for the PVAc–PMMA$_{cr}$ system agrees roughly with the results (thin broken line) calculated from the simple model as above but assuming phase conversion from the PMMA$_{cr}$ sphere in PVAc matrix to PVAc sphere in PMMA$_{cr}$ matrix at a volume fraction of PMMA$_{cr}$ of 30% instead of 70% as above.

Although there exists a considerable discrepancy, especially for the PVAc–PMMA$_{cr}$ system, between the experimental and calculated results, the mode of mixing may be, at least qualitatively, given by the simple
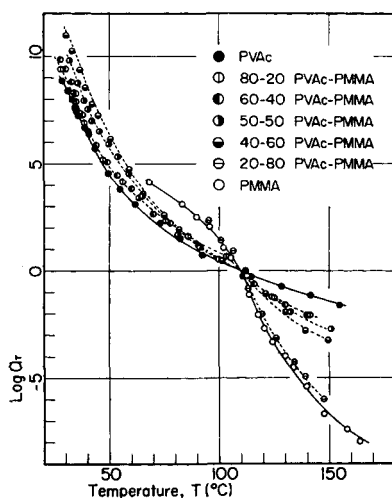
Fig. 9. Temperature dependence of shift factor a_T for the master relaxation curve of PVAc–PMMA mixed systems, taking the reference temperature as 110°C.
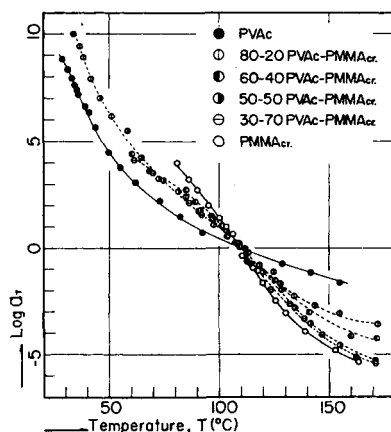

Fig. 10. Temperature dependence of shift factor a_T for the master relaxation curve of PVAc–PMMA$_{cr}$ mixed systems, taking the reference temperature as 112°C.

model above if the phase selectability of each component is taken into account. Actually, the test specimens of the PVAc–PMMA system containing less than 70% volume fraction of PMMA component can be easily extracted by hot ethanol (solvent only for PVAc) but those beyond 70% cannot, and the same situation as above occurs for the PVAc–PMMA$_{cr}$ system, except for the change of the critical volume fraction of the PMMA$_{cr}$ component from 70 to 30%.

In the previous paper[1] the discrepancy for the PVAc–PMMA$_{cr}$ system from the simple model was explained in terms of a sort of distribution function of volume fraction, $f(\phi)$ for the generalized series model, instead
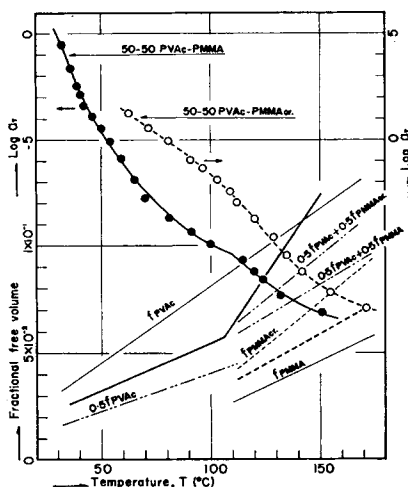
Fig. 11. Comparison of temperature dependence of apparent fractional free volume of the mixed systems determined experimentally with results calculated from simple additivity of free volume of each component.

of $\lambda(\phi)$ for the generalized parallel model, and the temperature dependence of the 500 sec. relaxation modulus for the 50/50 PVAc–PMMA$_{cr}$ was quantitatively explained in terms of a "matrix–matrix mixing" having a Gaussian type distribution $f(\phi)$ around $\phi_A = 0.5$.

As seen from Figures 4 and 5, which are typical of the temperature dependence of the relaxation modulus for the two systems, the procedure of time–temperature superposition for obtaining the so-called master relaxation curve, which is, of course, apparent in such multiple-phase system as these, can be performed, at least perfunctorily, without any difficulty. The temperature dependence of the shift factor $a_T{}^4$ thus determined by taking as the reference temperature 110°C. is illustrated in Figures 9 and 10 for the PVAc–PMMA and the PVAc–PMMA$_{cr}$ systems, respectively.

After examining the temperature dependence of the shift factor, it was revealed that the temperature dependence was well approximated by the WLF equation within the temperature range from 35°C. (the glass transition temperature of the PVAc) to 110°C. (the glass transition temperature of the PMMA and PMMA$_{cr}$) and beyond 110°C., separately, with some exceptions; i.e., the WLF equation did not hold in the temperature range between the two glass transition temperatures for the 20/80 PVAc–PMMA and for the 60/40, 50/50, and 30/70 PVAc–PMMA$_{cr}$, for which PMMA or PMMA$_{cr}$ was postulated to occupy the matrix phase in the mixed systems.

Table I lists the two constants, C_1 and C_2, in the WLF equation thus separately determined for the two temperature ranges by taking the reference temperatures as 110 and 35°C., respectively, from which the apparent fractional free volume and its thermal expansion coefficient for the mixed systems may be evaluated.

TABLE I
Values of Constants C_1 and C_2 in the WLF Equation Determined From the Temperature Dependence of the Shift Factor a_T for the Master Relaxation Curves for the Two Types of Mixed Systems

System	$T_0 = 383°K.$		$T_0 = 308°K.$	
	C_1	C_2	C_1	C_2
PVAc–PMMA				
0/100	16.1	55.6	—	—
20/80	15.4	53.0	—	—
40/60	7.18	43.7	16.8	52.2
50/50	6.71	43.8	16.7	60.7
60/40	5.24	43.1	12.4	45.6
80/20	4.87	39.0	11.7	42.7
100/0	4.88	123	12.4	48.9
PVAc–PMMA$_{cr}$				
0/100	10.2[a]	51.5[a]	—	—
30/70	14.6[a]	99.6[a]	—	—
50/50	11.6[a]	69.2[a]	—	—
60/40	11.5[a]	99.6[a]	—	—
80/20	6.23[a]	41.0[a]	18.3	67.8
100/0	4.88[a]	123[a]	12.4	48.9

[a] $T_0 = 385°K.$

In an extreme case where no physical interaction between the A and B phases exists, the total volume, V_{bl} may be given by simple additivity as follows:

$$V_{bl} = (V_{0A} + v_A) + (V_{0B} + v_B) \quad (2)$$

$$v_{bl} = v_A + v_B \quad (3)$$

and

$$f_{bl} \cong v_{bl}/(V_{0A} + V_{0B}) \cong \lambda_A f_A + \lambda_B f_B \quad (4)$$

where V_0, v, f, and λ are occupied volume, free volume, fractional free volume, and volume fraction in bulk of each phase, respectively. Therefore, the temperature dependence of the fractional free volume of the mixed system $f_{bl}(T)$ may be given by

$$f_{bl}(T) \cong \lambda_A[f_{gA} + \alpha_{fA}(T - T_{gA})] + \lambda_B[f_{gB} + \alpha_{fB}(T - T_{gB})] \quad (5)$$

where f_g and α_f are fractional free volume at glass transition temperature T_g and the difference of the thermal expansion coefficient of free volume below and beyond the glass transition temperature, respectively.

In the usual case, however, where some physical interaction between the two phases, such as internal pressure induced by one phase on the other due to the difference of thermal expansion coefficient between the two phases, exists, the total fractional free volume f_{bl} given by eq. (4) may be modified as follows:

$$f_{bl}(T) \cong \lambda_A\beta_A(p,T)f_A(T) + \lambda_B\beta_B(p,T)f_B(T)$$

$$= \lambda_A f_A(p,T) + \lambda_B f_B(p,T) \quad (6)$$

where β is an interaction parameter, and the functions of internal pressure and temperature $\beta(p,T)f(T)$ may be rewritten as $f(p,T)$. The $f(p,T)$ should be closely related to the shift factor $a_{p,T}$[5,6] in the procedure of time–temperature–pressure superposition of linear viscoelasticity through the Doolittle's equation,[7] in which the viscosity is interpreted in terms of the fractional free volume.

In Figure 11, f_{PVAc}, f_{PMMA}, and $f_{PMMA_{cr}}$, which were determined from C_1 and C_2 values listed in Table I by using the well-known relations of $C_1 = 1/(2.303\ f_g)$ and $C_2 = f_g/\alpha_f$,[2] represent the temperature dependence of the fractional free volume of the individual polymer components. The plots for $(0.5 f_{PVAc} + 0.5\ f_{PMMA})$ and $(0.5\ f_{PVAc} + 0.5\ f_{PMMA_{cr}})$, which were calculated from the above values of fractional free volume of the individual components by using eq. (5), represent the temperature dependence of the 50/50 PVAc–PMMA and 50/50 PVAc–PMMA$_{cr}$ systems having non-physical interaction between the two phases.

On the other hand, the heavy solid and broken lines in Figure 11, which were determined from the temperature dependence of the shift factor a_T as shown in the upper half of the figure and also in terms of the values of C_1 and C_2 in the WLF equation in Table I, represent the temperature dependence of the apparent fractional free volume of the 50/50 PVAc–PMMA and 50/50 PVAc–PMMA$_{cr}$. When one compares these experimental results with the results calculated for nonphysical interaction, it is evident that the experimental result is greater than the calculated one for the 50/50 PVAc–PMMA system, and the converse is true for the 50/50 PVAc–PMMA$_{cr}$ system.

Although the experimental results are only qualitative as discussed above, this may suggest an existence of the physical interaction between the two phases; i.e., in the case of 50/50 PVAc–PMMA system, the PVAc matrix surrounds the PMMA sphere and acts in such a way as to make β_{PMMA} in eq. (6) greater than unity while keeping β_{PVAc} near unity, and in the case of 50/50 PVAc–PMMA$_{cr}$, the PMMA matrix surrounds the PVAc sphere and acts in such a way as to make β_{PVAc} less than unity while keeping $\beta_{PMMA_{cr}}$ near unity. This type of explanation holds generally (at least qualitatively) for all of the experimental results of other volume fraction for the two systems which are not shown in the figure, and agrees well in the phase selectability with what is postulated (Fig. 8) in terms of the phase conversion of the simple model of mixing.

The interaction parameter, $\beta(p,T)$ should be determined experimentally from another source, such as the specific volume–temperature relation of the specimen, from which the rheological properties of the mixed system may be explained more quantitatively in combination with the degree of mixing.

References

1. Fujino, K., Y. Ogawa, and H. Kawai, *J. Appl. Polymer Sci.*, **8**, 2147 (1964).
2. Williams, M. L., R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
3. Fujino, K., T. Horino, K. Miyamoto, and H. Kawai, *J. Colloid Sci.*, **16**, 411 (1961).
4. Ferry, J. D., *J. Am. Chem. Soc.*, **72**, 3746 (1950).
5. McKinney, J. E., H. V. Belcher, and R. S. Marvin, *Trans. Soc. Rheol.*, **4**, 347 (1960); J. E. McKinney and H. V. Belcher, *J. Res. Natl. Bur. Std.*, **67A**, 43 (1963).
6. Ferry, J. D., and R. A. Stratton, *Kolloid-Z.*, **171**, 107 (1960).
7. Doolittle, A. K., *J. Appl. Phys.*, **22**, 1471 (1951).

Résumé

Suite à un article antérieur, relatif aux propriétés rhéologiques du mélange mécanique de deux polymères en fonction du degré de mélange, on a étudié la dépendance vis-à-vis de la température de la relaxation de la force de tension de deux types de systèmes en mélange, le système polyméthacrylate de méthyle–polyacétate de vinyle et le système faiblement ponté polyméthacrylate de méthyle–polyacétate de vinyle. Cette étude a été effectuée dans un domaine de température comprenant la température de transition vitreuse des deux systèmes de polymères. Le procédé, appelé superposition température–temps, a été employé pour comparer plusieurs paramètres tels que le volume libre partiel et son coefficient de dilatation thermique avec ceux des composés polymériques individuels. Ces paramètres ont été temporairement déterminés sur la base de l'influence du concept de volume libre sur la viscosité, en relation avec l'équation de William-Landel-Ferry. Bien que le volume libre partiel et son coefficient de dilatation thermique, déterminés pour les systèmes en mélange, soient des valeurs apparentes, les résultats peuvent, au moins qualitativement, démentir la simple additivité des volumes libres des deux phases polymériques en mélange et suggèrent l'existence d'une sorte d'interaction physique entre les phases, c'est-à-dire la pression interne induite par une phase sur l'autre et due à la différence dés coefficients d'expansion thermique entre les phases.

Zusammenfassung

Als Fortsetzung einer früheren Arbeit über die Beziehung der rheologischen Eigenschaften einer mechanischen Mischung aus zwei Polymerkomponenten zum Mischungsgrad wurde die Temperaturabhängigkeit des Zug-Spannungsrelaxationsverhaltens der beiden Mischungssystemtypen Poly(methylmethacrylat)-Poly(vinylacetat)- und schwach vernetztes Poly(methylmethacrylat)-Poly(vinylacetat)-System in einem Temperaturbereich, der die Glasumwandlungstemperatur der beiden Polymerkomponenten umfasst, untersucht. Die sogenannte "Zeit–Temperatursuperposition" wurde beim Vergleich mehrerer Parameter, wie Bruchteil an freiem Volumen und sein thermischer Expansionskoeffizient mit denjenigen der individuellen Polymerkomponenten durchgeführt. Diese Parameter wurden jeweils auf Grundlage der Beeinflussung der Viskosität nach dem Konzept des freien Volumens in Beziehung zur William-Landel-Ferry-Gleichung bestimmt. Obgleich der in dieser Weise für die Mischungssysteme bestimmte freie Volumsbruchteil und sein thermischer Expansionskoeffizient dem scheinbaren Wert entsprachen, lassen die Ergebnisse zumindest qualitativ doch die einfache Additivität des freien Volumens der beiden gemischten Polymerphasen als zweifelhaft erkennen und sprechen für das Bestehen einer Art von physikalischer Wechselwirkung zwischen den Phasen, d.h. für das Auftreten eines, durch eine Phase auf die andere infolge des Unterschieds der thermischen Expansionskoeffizienten zwischen den Phasen ausgeübten, inneren Drucks.