Comparison of Tensile Stress Relaxation Behavior of Graft Copolymer of Poly(vinyl Acetate) with Styrene and Mechanical Mixture of Poly(vinyl Acetate) with Polystyrene*

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Synopsis

As one in a series of studies relating the rheological behavior of mechanical mixtures of two polymer components to the degree of mixing, the tensile stress relaxation behavior of a graft copolymer of poly(vinyl acetate) with styrene, obtained by ^{60}Co γ-irradiation of poly(vinyl acetate) in styrene solution and extraction of homopolymers, was investigated as a function of the fraction of styrene component and compared with that of a mechanical mixture of poly(vinyl acetate) with polystyrene, one of the typical combinations of incompatible components. The results obtained may classify the graft copolymer as a sort of mechanical mixture giving stable mixing even for incompatible components.

INTRODUCTION

In the first paper of this series,[1] the tensile stress relaxation behavior of a random copolymer composed of methyl methacrylate and methyl acrylate was investigated as a function of monomer ratio. It was concluded that the behavior was typical of an amorphous polymer having a single glass transition temperature, which shifted with the monomer ratio in accordance with the equation of Gordon and Taylor.[2]

This behavior resembled that of a blended system of two completely compatible polymer components, which has been found only for a few examples, such as blended systems of poly(vinyl chloride) with butadiene–acrylonitrile rubber[3,4] and nitrocellulose with polyurethane[5] in the narrow composition range of components for which a shift of the single glass transition temperature with the fraction of one component was also found.

This suggests that the mode of mixing for such a blended system of complete compatibility is a type of homogeneous mixing in molecular order, i.e., a sort of solution.

In contrast to this, a mixed system of two incompatible or poorly compatible polymer components, which is more often the case, gives a sort of mechanical mixture, a heterogeneous mixing, rather than a solution. This common type of mixing usually shows the existence of two glass transition temperatures which correlate, more or less, with the original glass transition temperatures of each component; this suggests that the mechanical mixture leaves homogeneous phases of each component.[6,7]

In this study, the tensile stress relaxation behavior of poly(vinyl acetate) irradiated by ^{60}Co in styrene solution, which has been considered to give a graft copolymer of poly(vinyl acetate) with styrene after the extraction of homopolymers,[8] was investigated as a function of the fraction of styrene component. The results are compared with those for a mechanical mixture of poly(vinyl acetate) with polystyrene, a typical combination of incompatible components. The results obtained may be of use for characterizing the graft copolymer as a type of polymer blendings.

TEST SPECIMENS AND EXPERIMENTAL PROCEDURE

Graft Copolymers of Poly(vinyl Acetate) with Styrene

A fractionated poly(vinyl acetate) ($\bar{M}_v = 2.0 \times 10^6$) was dissolved in styrene monomer, sealed in a glass tube under a vacuum for removing oxygen, and subjected to irradiation with γ-rays from a ^{60}Co source under various conditions as shown in Table I. The irradiated polymers were

TABLE I
Conditions of Irradiation with γ-Rays from ^{60}Co onto Poly(vinyl Acetate)–Styrene Solutions and Chemical Analysis of Styrene Content of Poly(vinyl Acetate)–Styrene Graft Copolymer

Designation	PVAc/ styrene mole ratio	Dose rate, r/hr.	Irradiation time, hr.	Irradiation temp., °C.	Styrene content, mole-%[a]
A-1	1/1	1.70×10^5	2	15	—
A-2	1/1	1.70×10^5	4	15	1.6
A-3	1/1	1.70×10^5	6	15	1.9
A-4	1/1	1.70×10^5	8	15	4.3
A-5	1/1	1.70×10^5	10	15	—
A-6	1/1	1.70×10^5	15	15	12.4
A-7	1/1	1.70×10^5	20	15	82.5
B-1	1/4	3.65×10^3	15	30	4.1
B-2	1/1	3.65×10^3	15	30	37.1
B-3	7/3	3.65×10^3	15	30	84.6
B-4	4/1	3.65×10^3	15	40	65.3

[a] From results of elementary analysis.

further fractionated in the order as shown in Figure 1 to remove the poly-(vinyl acetate) and polystyrene homopolymers and to obtain the graft co-polymer of poly(vinyl acetate) with styrene from the irradiated mixture.

The styrene content in these fractionated graft copolymers was deter-mined from an ordinary chemical elemental analysis, and results are given in the last column in Table I, but the grafted density of polystyrene along the trunk polymer of poly(vinyl acetate) or the chain length of branched polymer of polystyrene are not known.

PVAc Solution in Styrene Monomer

↓ Irradiated by γ-ray from 60Co

Irradiated polymers

Dissolved in benzene and
precipitated with ligroin

Precipitation

Dissolved in benzene and
precipitated with cyclohexane

Precipitation   Solution

(homo-PVAc, PVAc–St)   (homo-PSty)

Dissolved in MEK and
precipitated with EtOH–H2O mixture

Precipitation   Solution
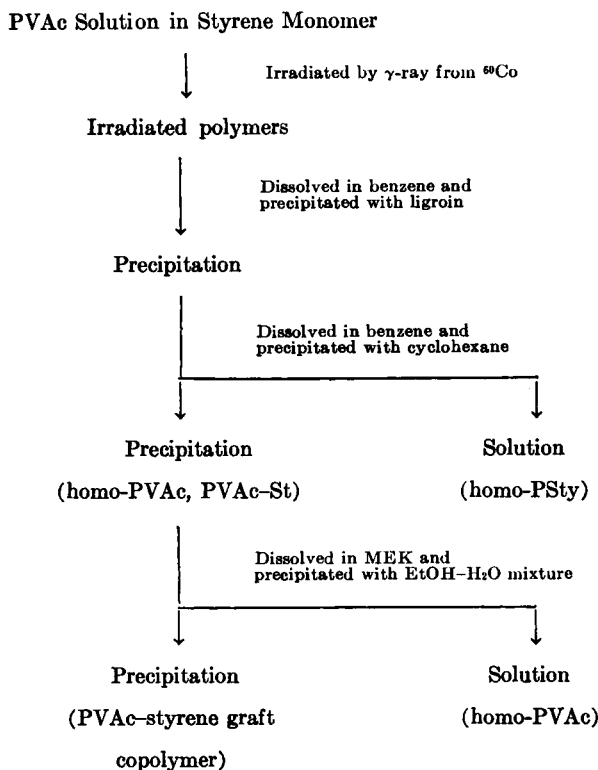
(PVAc–styrene graft   (homo-PVAc)

copolymer)

Fig. 1. Fractionating order at room temperature for removing poly(vinyl acetate) and polystyrene homopolymers from mixture with graft copolymer of styrene on poly(vinyl acetate).

The test specimen was cast from about 10% benzene solutions of these graft copolymers into thin films about 0.3 mm. thick by gradual evaporiza-tion of the solvent; the films were then leached in running water so as to remove benzene as completely as possible. The test specimen thus pre-pared was air-dried, cut into a ribbon about 1–6 mm. wide and 60 mm. long, further dried at about 60°C. in vacuum for 3 days, and annealed at the various conditions shown in Table II before the stress relaxation measurements were made.

TABLE II
Annealing Conditions and Volume Fraction of Each Component of Test Specimen Used

| | Annealing conditions | | Volume fraction |
Designation	Temp., °C.	Time, min.	(PVAc/PSty)[a]
Graft copolymers of styrene on poly(vinyl acetate)			
A-4	70	20	94.6/5.4
A-6	93	20	87.3/12.7
A-7	140	20	16.8/83.2
B-1	72	20	95.6/4.4
B-2	100	30	61.2/38.8
B-3	130	20	14.9/85.1
B-4	130	20	33.2/66.8
Mechanical mixtures of poly(vinyl acetate) with polystyrene			
100-0 PVAc-PSty	70	10	100/0
80-20 PVAc-PSty	80	45	78.2/21.8
60-40 PVAc-PSty	90	50	57.3/42.7
50-50 PVAc-PSty	95	50	45.9/54.1
40-60 PVAc-PSty	95	50	37.3/62.7
20-80 PVAc-PSty	95	50	18.2/81.8
0-100 PVAc-PSty	110	40	0/100

[a] Calculated by assuming the densities at 25°C. of poly(vinyl acetate) and polystyrene phases in the mixed systems to be identical to those of the homopolymers, i.e., 1.17 and 1.05 g./cc., respectively.

Mechanical Mixture of Poly(vinyl Acetate) with Polystyrene

Poly(vinyl acetate) is a typical polymer incompatible with polystyrene, and it is usually difficult to get a uniformly dispersed system of both phases from a solution casting by using a common solvent such as benzene. Therefore, a melt casting of fine precipitate, which was obtained by pouring continuously a small amount of relatively dilute solution of both polymers in a common solvent into a precipitant, was used. Polyvinyl acetate ($\bar{M}_v = 1.0 \times 10^5$) and polystyrene ($\bar{M}_v = 1.6 \times 10^5$) were dissolved in benzene in various ratios (80/20, 60/40, 50/50, 40/60, and 20/80) to make dilute solutions of about 1% concentration. A small amount of each solution was added continuously to an excess of n-hexane with vigorous stirring. The precipitates thus obtained were leached, dried, and cast into thin films about 0.3 mm. thick by using a laboratory press under the conditions of 150°C. and 300 kg./cm.[2] for 15 min.

The test specimen thus obtained was cut into ribbons about 1–6 mm. wide and 60 mm. long, and annealed at the various conditions shown in Table II before the stress relaxation measurements were made.

The tensile stress relaxation measurements were carried out by using a chainomatic balance-type autorecording relaxometer, which has been described elsewhere,[9] over a period of 30–6000 sec. under given tensile strains within the limit of linear viscoelasticity of the specimens at various temperatures ranging from room temperature up to a temperature at which the

relaxation moduli of the specimens decreased to 1×10^5 dyne/cm.^{2} within the time period.

EXPERIMENTAL RESULTS AND DISCUSSION

Figures 2–5 are typical results showing the change of tensile stress relaxation behavior of the graft copolymer with the increase of the fraction of polystyrene grafted.

When the fraction of polystyrene is less than several per cent, as shown in Figure 2 for A-4 (95-5 PVAc–Psty), the behavior is almost identical to that of the original poly(vinyl acetate), whose behavior was shown previously in Figure 1 of the previous paper,[10] except for the appearance of the flow region at relatively low temperatures (about 70°C.). This may be due to the disintegration of the poly(vinyl acetate) chain under the irradiation of high energy from ^{60}Co.

With increasing fraction of polystyrene grafted, the effects upon the relaxation behavior appear gradually, i.e., the relaxation modulus of the first rubbery plateau following the glass–rubber transition of poly(vinyl acetate) increases from 1×10^7 for the original poly(vinyl acetate) and A-4
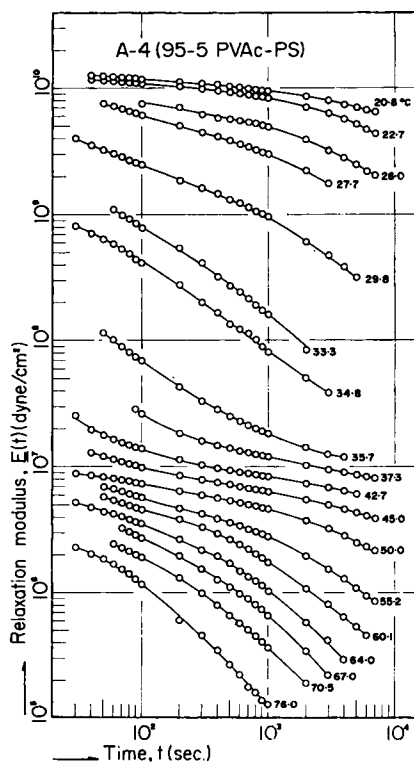

Fig. 2. Temperature dependence of relaxation modulus of 95-5 graft copolymer of styrene on poly(vinyl acetate).

(95-5 PVAc–PSty) up to more than 1×10^8 dyne/cm.² for B-4(35-65 PVAc–PSty) and makes the transition less distinctive, while the glass–rubber transition of polystyrene, which is not so clear for B-2 and B-4 because of the lack of the second rubbery plateau of polystyrene (probably due to the short chain length of polystyrene grafted), appears in a counterchanged fashion.

Figures 6–9 show the change of tensile stress relaxation behavior of the mechanical mixtures with the increase of the fraction of polystyrene.   Here
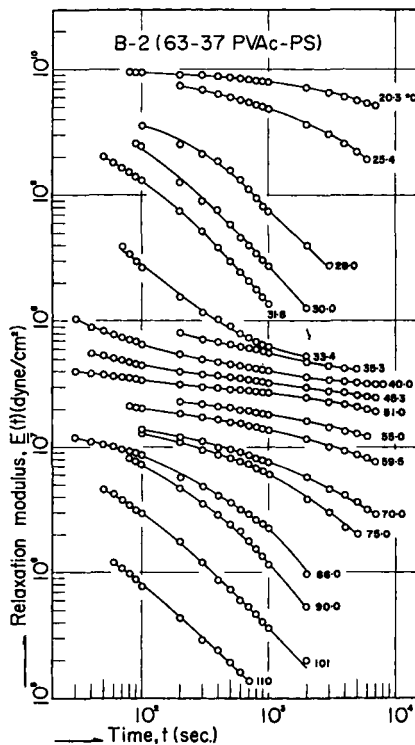
Fig. 3. Temperature dependence of relaxation modulus of 63-37 graft copolymer of styrene on poly(vinyl acetate).

again, the same counterchanged effects of the fraction of each component upon the tensile stress relaxation behavior as those of the graft copolymers are observed.

With increasing fraction of polystyrene mixed, more rapid increase of the relaxation modulus of the first rubbery plateau of poly(vinyl acetate) from 1×10^7 for 100-0 PVAc–PSty to 1×10^{10} dyne/cm.² for 40-60 PVAc–PSty and more distinct appearance of the second rubbery plateau of polystyrene for 40-60 PVAc–PSty are observed, compared to the case of the graft copolymers; i.e., the disappearance of the glass–rubber transition of the poly(vinyl acetate) phase and the counterchanged appearance of that of

polystyrene phase with increasing polystyrene content occur more rapidly than the case of the graft copolymers.

Figures 10 and 11 show the temperature dependence of relaxation modulus at a given time (500 sec.) as a function of the fraction of each component; these are replotted not only from the results above but also from the results of other fractions.

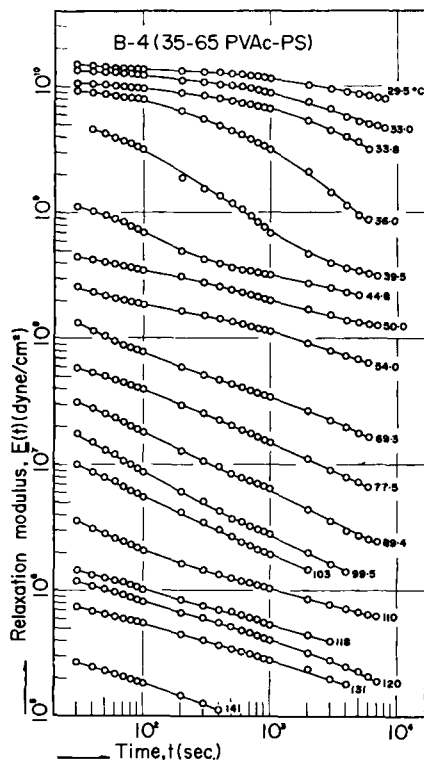The existence of two glass transition temperatures as well as a remarkable reverse of the effects of the fraction upon the temperature dependence

Fig. 4. Temperature dependence of relaxation modulus of 35-65 graft copolymer of styrene on poly(vinyl acetate).

of the 500 sec. relaxation modulus are seen for the two systems. The existence of two glass transitions at about 30 and 110°C., whose quantitative fraction dependence is uncertain except for a somewhat distinctive shift to higher temperature side for the low glass-transition temperature of B-4, suggests, that the graft copolymer may be a sort of heterogeneous mixture in which there remain homogeneous phases of each component. For the graft copolymer the behavior rather resembles that of PVAc alone until the fraction of polystyrene grafted reaches 65%, and suddenly approaches that of polystyrene alone beyond a critical fraction of around 70%,

while for the mechanical mixture the behavior shows a reversal at a critical fraction of polystyrene of around 30%.

A distinctive appearance of the second plateau of relaxation modulus seen in Figure 10 for A-7, whose polystyrene fraction is almost the same as that of B-3, may suggest the grafted chain to be longer than that for B-3. No concrete interpretation in terms of the difference of the irradiation conditions is, however, possible for such a direct radiation grafting as these.
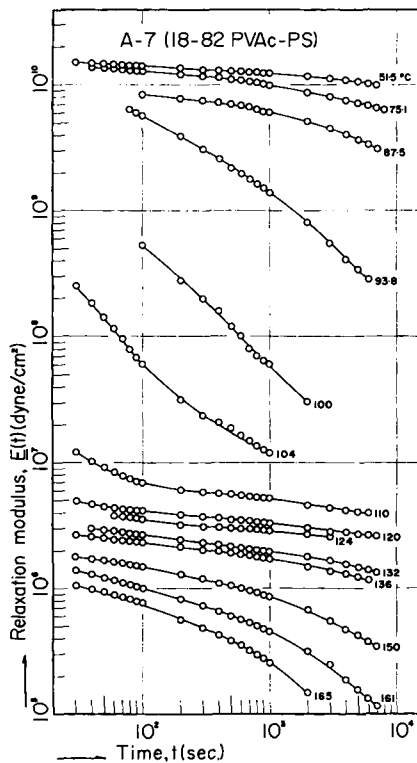

Fig. 5. Temperature dependence of relaxation modulus of 18-82 graft copolymer of styrene on poly(vinyl acetate).

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 of the two systems at a given temperature (70°C.), which was replotted again from Figures 10 and 11, was compared with the results calculated on the basis of a simple model of mechanical mixing, in which one assumes a sphere of component B floating in a unit cubic matrix of component A, approximates the 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 of component A or B, respectively.[11]
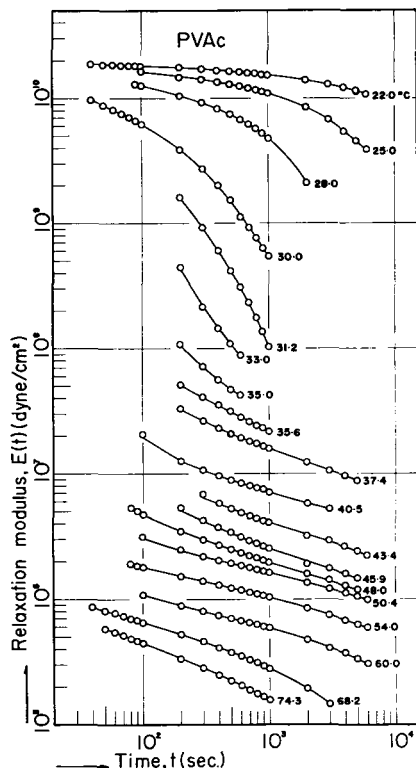
Fig. 6. Temperature dependence of relaxation modulus of poly(vinyl acetate) used in the mechanical mixture.

As seen in Figure 12, the experimental results given for the mechanical mixture (heavy solid line) agree roughly with those (thin solid line) calculated from the simple model of a polystyrene sphere floating in a unit cube of poly(vinyl acetate) matrix in a range of volume fraction of polystyrene from 0 to 30%, beyond which the phase conversion from polystyrene spheres in poly(vinyl acetate) matrix to poly(vinyl acetate) spheres in polystyrene matrix occurs.   On the other hand, the experimental results (heavy dotted line) for the graft copolymer also agree roughly with that calculated (thin dotted lines) from the simple model as above but assuming the phase conversion at a volume fraction of polystyrene of 70% instead of 30%.   Here, the upper dotted line was calculated by taking the relaxation modulus of the poly(vinyl acetate) phase as 4.6×10^6 dyne/cm.^{2} for the original unirradiated poly(vinyl acetate).

The rather close values of relaxation moduli for the graft copolymers of B-1 and A-4, much lower than that of the original poly(vinyl acetate), $(4.6 \times 10^6$ dyne/cm.$^2)$, to the other poly(vinyl acetate) used for the mechanical mixture $(3.1 \times 10^5$ dyne/cm.$^2)$, may be interpreted in terms of the chain scission as a result of the high-energy irradiation of the original
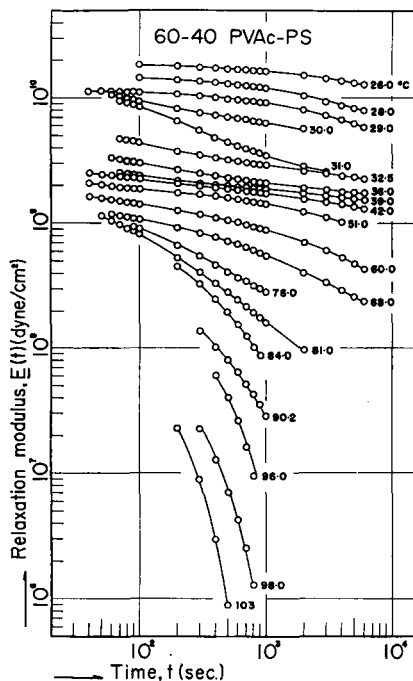
Fig. 7. Temperature dependence of relaxation modulus of 60-40 poly(vinyl acetate)-polystyrene mixed system.

poly(vinyl acetate) to the chain length of the other poly(vinyl acetate) as discussed above, while the rather close values of the relaxation moduli for the graft copolymers B-2 and B-4 to the upper dotted line may be just fortuitous and should not be interpreted in terms of the milder chain scission with the increasing of PVAc mole ratio, as shown in Table I, under irradiation. Any quantitative interpretation in terms of the rates of chain scission and graft copolymerization is quite uncertain for the direct radiation grafting system, except for the systematic increase of the grafted chain length of polystyrene with the increase of polystyrene fraction, which may be assured from the gradual appearance of the second plateau of relaxation modulus in Figures 2–5.

Although there exists a considerable discrepancy between the experimental and calculated results for the mechanical mixture and an uncertainty in the interpretation of the irradiation effects upon chain scission for the graft copolymer, the mode of mixing may be, at least qualitatively, given by the simple model above if the phase selectability of each component is taken into account.

As seen from Figures 2–9, the well-known procedure of time–temperature superposition for obtaining the so-called master relaxation curve, which is, of course, apparent in such multiple-phase systems as these, can be performed, at least perfunctorily, without any difficulty. The temperature

dependence of the shift factor a_T[12] thus determined by taking reference temperature as 70°C. (102°C. for the 40-60, 20-80, and 0-100 PVAc-PSty mechanical mixtures) is illustrated in Figures 13 and 14 for the graft copolymer and the mechanical mixture, respectively.

After examining the temperature dependence of the shift factor, it was revealed that the temperature dependence was well approximated by a WLF type equation[13] within the temperature range from 35°C. (the glass transition temperature of the PVAc) to 102°C. (the glass transition temperature of the PSty) and beyond 102°C., separately, with some exceptions,
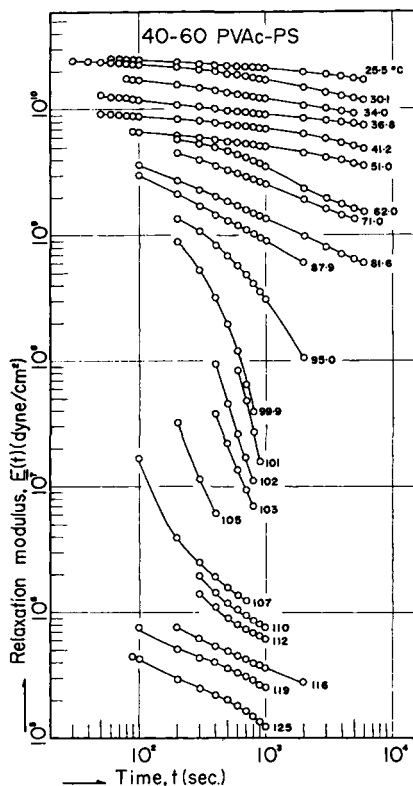
Fig. 8. Temperature dependence of relaxation modulus of 40-60 poly(vinyl acetate)–polystyrene mixed system.

i.e., the WLF equation did not hold in the temperature range between two glass transition temperatures for the graft copolymers of A-7 and B-3 and for the mechanical mixtures of 60-40, 50-50, 40-60, 20-80 PVAc–PSty, for which polystyrene was postulated to occupy the matrix phase in the mixed systems.

Table III lists the two constants, C_1^0 and C_2^0, in the WLF equation thus separately determined for the two temperature ranges by taking the reference temperatures as 70 and 140°C. (130°C. for the mechanical mix-

ture), respectively, from which the apparent fractional free volume and its thermal expansion coefficient for the mixed systems may be evaluated.

In an extreme case where no physical interaction between the A and B phases exists, the temperature dependence of the fractional free volume of the mixed system f_{b1} (T) may be given by a simple additivity as follows:

$$f_{b1}\ (T) \cong \phi_A f_A(T) + \phi_B f_B\ (T)$$

$$= \phi_A[f_{gA} + \alpha_{fA}\ (T - T_{gA})] + \phi_B[f_{gB} + \alpha_{fB}(T - T_{gB})] \qquad (1)$$
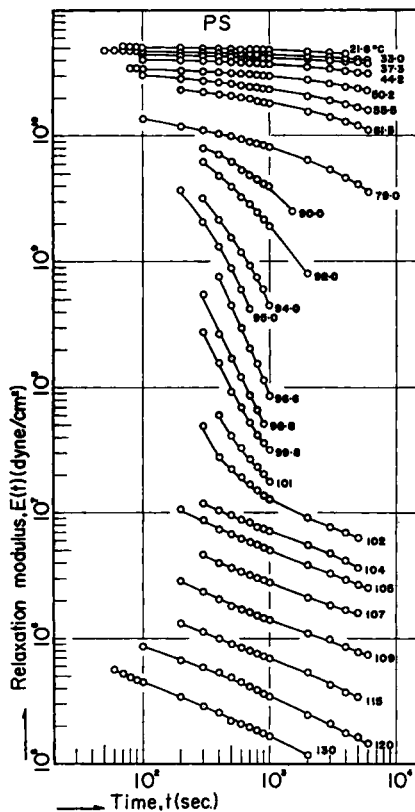
Fig. 9. Temperature dependence of relaxation modulus of polystyrene used in the mechanical mixture.

where ϕ, f_g, and α_f are volume fraction, 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 of each component, respectively.

In the usual case, however, where there is some physical interaction between the two phases, such as internal pressure induced by one phase or the other due to the difference of thermal expansion coefficient between the two

phases, the total fractional free volume f_{b1} given by eq. (1) may be modified by introducing the interaction parameter $\beta(p, T)$ as follows:

$$f_{b1}(T) \cong \phi_A \beta_A(p,T) f_A(T) + \phi_B \beta_B(p,T) f_B (T)$$

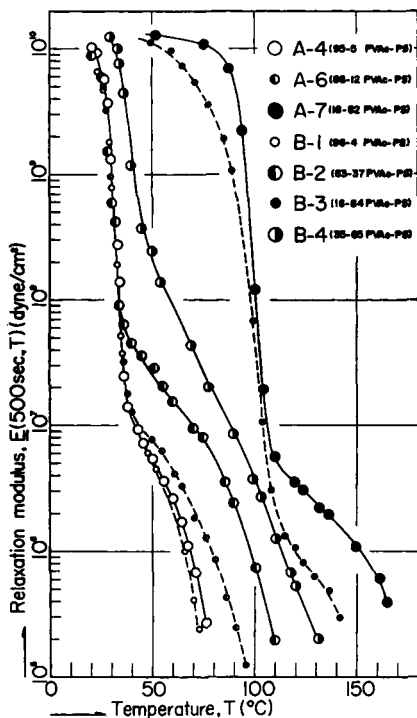$$= \phi_A f_A (p,T) + \phi_B f_B (p,T) \tag{2}$$

Fig. 10. Temperature dependence of 500-sec. relaxation modulus as a function of volume fraction of each component for the graft copolymers of styrene on poly(vinyl acetate).

where $f(p,T)$ should be closely related to the shift factor[14-16] $a_{p,T}$ in the procedure of time–temperature–pressure superposition of linear viscoelasticity through the Doolittle's equation,[17] in which the viscosity is interpreted in terms of the fractional free volume.

The temperature dependence of fractional free volume of the individual polymer component beyond the glass transition temperature can be determined from C_1^0 and C_2^0 values listed in Table III by using the well-known relations:[13]

$$C'_1 = 1/(2.303 f_g)$$

$$C'_2 = f_g/\alpha_f^2 \tag{3}$$

$$C'_1 = C_1^0 C_2^0/(C_2^0 + T_g - T_0)$$

$$C'_2 = C_2^0 + T_g - T_0$$

where C'_1 and C'_2 are constants of the WLF equation, the glass transition temperature being taken as the reference temperature. Therefore, the temperature dependence of the fractional free volume of a mixed system having no physical interaction can be calculated by putting the values of f_g and α_f of the individual components into eq. (1), provided that the fractional free volume of each component below the glass transition temperature is postulated to be identical to f_g.
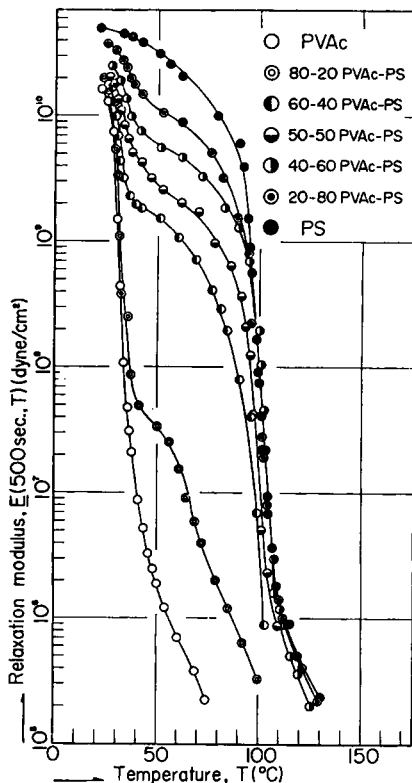

Fig. 11. Temperature dependence of 500-sec. relaxation modulus as a function of volume fraction of mixed components for the poly(vinyl acetate)–polystyrene mixed system.

On the other hand, the temperature dependence of the fractional free volume of the mixed system could be calculated directly from the apparent fractional free volume and its thermal expansion coefficient, which are determined by putting the values of C_1^0 and C_2^0 of the mixed systems in Table III into eq. 3. When one compares these experimental results with the results calculated for the case of no physical interaction, it is revealed that the experimental result is greater than the calculated one for the graft copolymers A-6, B-2, and B-4, as shown schematically in the middle of Figure 15, and the converse is true for the mechanical mixtures of the

50-50, 40-60, and 20-80 PVAc–PSty, as shown schematically in the top of Figure 15 beyond the upper glass transition temperature. This is also shown in Figure 16 at a temperature range between the two glass transition temperatures by the experimental fact that the specific volume of the mechanical mixture is always less than that calculated on a basis of the simple additivity.

Although the experimental results are simply qualitative as discussed above, this may suggest an existence of the physical interaction between the two phases; i.e., in the former case of the graft co-polymer, the PVAc
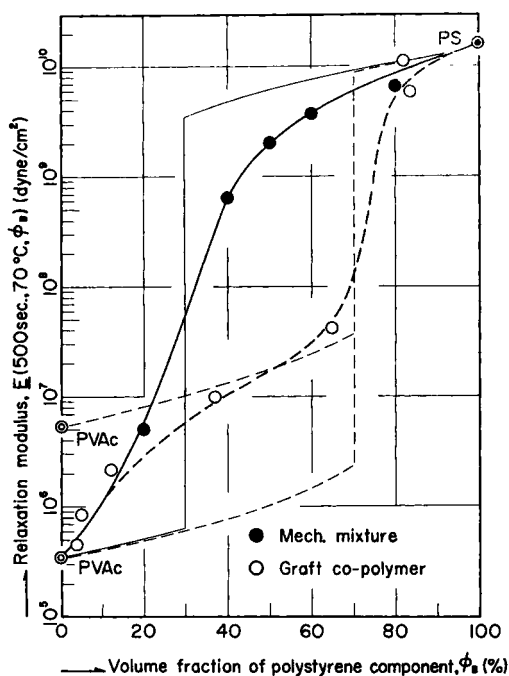

Fig. 12. Volume fraction dependence of 500-sec. relaxation modulus at 70°C. for the mechanical mixture of poly(vinyl acetate) with polystyrene and the graft copolymers of styrene on poly(vinyl acetate) in comparison with the results calculated on assuming a simple mode of mixing of a sphere of one component in a matrix of the other component and a phase conversion due to hexagonal close packing of spheres.

matrix surrounds the PSty sphere and acts in such a way as to make β_{PSty} in eq. (2) greater than unity while keeping β_{PVAc} near unity so that the slope of the thermal expansion of the fractional free volume beyond the upper glass transition temperature is much steeper than that in the case of no physical interaction as illustrated in Figure 15. In the latter case, for the mechanical mixture, the PSty matrix surrounds the PVAc sphere and acts in such a way as to make β_{PVAc} less than unity while keeping β_{PSty} near unity. This type of explanation agrees well in the phase selectability with
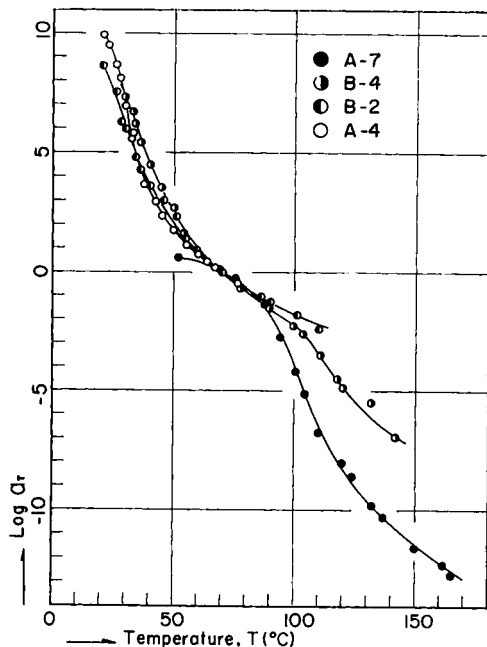
Fig. 13. Temperature dependence of shift factor a_t for composing the master relaxation curve of the graft copolymers of styrene on poly(vinyl acetate) for a reference temperature of 70°C.
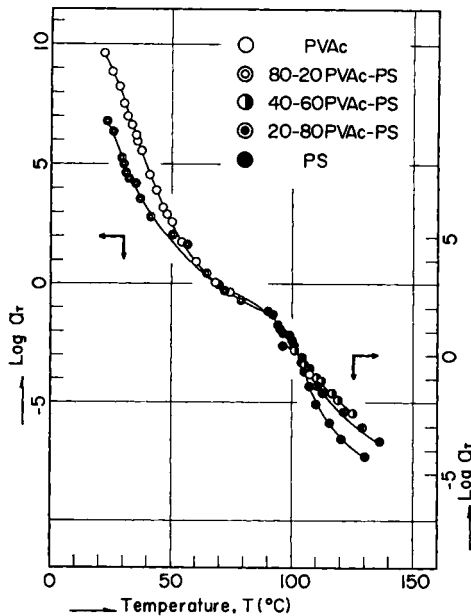

Fig. 14. Temperature dependence of shift factor a_T for composing the master relaxation curve of the mechanical mixture of poly(vinyl acetate) with polystyrene for reference temperatures of 70 and 102°C.
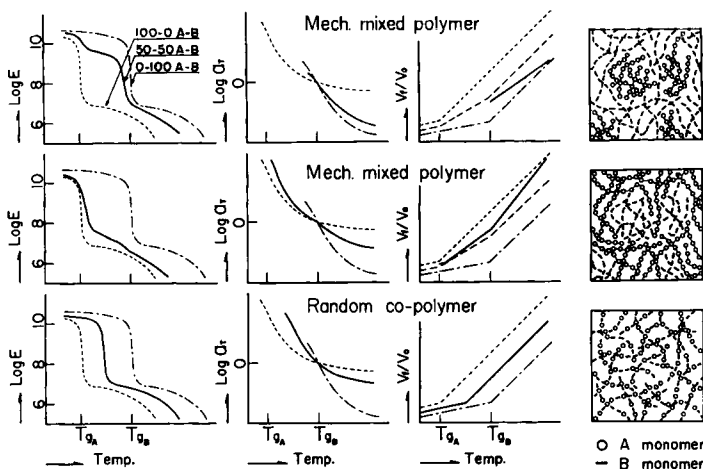
Fig. 15. Schematic illustration of the temperature dependences of relaxation modulus, $E(t_0, T)$, shift factor, $a_{T_0}(T)$, and fractional free volume, $f(T)$ of the two types of mechanical mixture and a random copolymer in relation to the mode of mixing and two glass transition temperatures of each component.
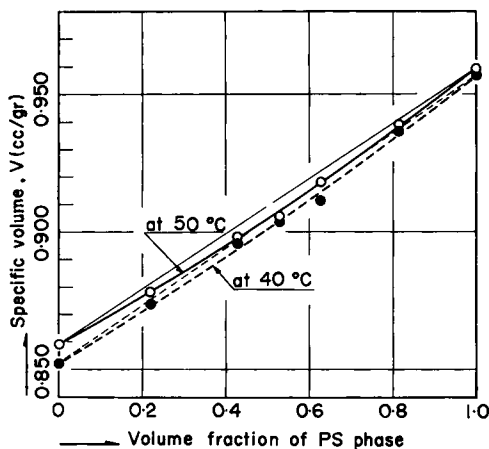

Fig. 16. Volume fraction dependence of specific volume of the mixed system of poly-(vinyl acetate) with polystyrene at 40 and 50°C.

what is postulated in terms of the phase conversion of the simple model of mixing.

Figure 15 is a schematic illustration in connection with the previous paper[10] for concluding the temperature dependences of the relaxation modulus, $E(t_0, T)$, the shift factor, $a_{T_0 = T_{gB}}(T)$, and the fractional free volume, $f(T)$ of two types of mechanical mixture and a random copolymer in relation to the mode of mixing and two glass transition temperatures of each component, where the broken lines correspond to the individual polymer components and the solid line to the mixed system. The graft copolymer

of poly(vinyl acetate) with styrene cast from a common solvent such as benzene may be classified as a mechanical mixture corresponding to the middle line rather than the top line in Figure 15, which depends upon the solvent power of the common solvent for the two components.   It is also

TABLE III

Values of Constants $C_1{}^\circ$ and $C_2{}^\circ$ in the WLF Equation Determined from the Temperature Dependence of the Shift Factor a_T for Composing the Master Relaxation Curves for the Mixed Systems at Reference Temperature T_0

Reference temperature T_0, °C.	PVAc–PSty systems	$C_1{}^\circ$	$C_2{}^\circ$
	Graft copolymers		
70	A-4 (95-5)	3.39	60.3
70	A-6 (87-13)	6.53	81.5
70	B-1 (96-4)	5.31	75.0
70	B-2 (63-37)	6.43	83.5
70	B-4 (35-65)	6.02	68.8
140	A-4 (95-5)	a	a
140	A-6 (87-13)	a	a
140	A-7 (18-82)	9.84	100.3
140	B-1 (96-4)	a	a
140	B-2 (63-37)	a	a
140	B-3 (15-85)	2.65	50.5
140	B-4 (35-65)	4.59	64.9
	Mechanical mixtures		
70	100-0	7.81	80.5
70	80-20	6.18	89.1
130	100-0	a	a
130	80-20	a	a
130	60-40	a	a
110	50-50	0.98	31.4
130	40-60	5.65	86.4
130	20-80	2.81	46.7
130	0-100	2.56	43.5

a Measuring temperature could not be extended high enough to determine the constants at a reference temperature of 140 or 130°C.

concluded that the graft copolymer gives a stable and uniformly dispersed system of two components, which are extremely incompatible with each other so as to give a definite phase separation when cast from the common solvent.

References

1. K. Fujino, K. Senshu, and H. Kawai, *J. Colloid Sci.*, **16**, 262 (1961).
2. M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **2**, 495 (1952).
3. M. Kawamata and Y. Inoue, *Kogyo Kagaku Zasshi*, **63**, 1831 (1960).
4. M. Takayanagi, H. Harima, and Y. Iwata, *J. Soc. Mat. Sci., Japan*, **12**, 389 (1961).
5. T. Soen, Y. Ogawa, T. Horino, and H. Kawai, *J. Appl. Polymer Sci.*, to be submitted.
6. E. Jenkel and H. U. Herwig, *Kolloid-Z.*, **148**, 57 (1956).
7. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, pp. 270–275.
8. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Wiley, New York, 1962, pp. 680–691.
9. K. Fujino, T. Horino, K. Miyamoto, and H. Kawai, *J. Colloid Sci.*, **16**, 411 (1961).
10. T. Horino, Y. Ogawa, T. Soen, and H. Kawai, *J. Appl. Polymer Sci.*, **9**, 2261 (1965).
11. K. Fujino, Y. Ogawa, and H. Kawai, *J. Appl. Polymer Sci.*, **8**, 2147 (1964).
12. J. D. Ferry, *J. Am. Chem. Soc.*, **72**, 3746 (1950).
13. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
14. J. E. McKinney, H. V. Belcher, and R. S. Marvin, *Trans. Soc. Rheol.*, **4**, 347 (1960).
15. J. E. McKinney and H. V. Belcher, *J. Res. Natl. Bur. Std.*, **67A**, 43 (1963).
16. J. D. Ferry and R. A. Stratton, *Kolloid-Z.*, **171**, 107 (1960).
17. A. K Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).

Résumé

On a effectué une série d'études pour relier le comportement rhéologique des mélanges mécaniques de deux polymères au degré de mélange. Ainsi on a étudié le comportement à la relaxation sous tension d'un acétate de polyvinyle irradié en présence de cobalt 60 en solution dans le styrène et qui était considéré comme étant un copolymère greffé d'acétate de polyvinyle avec le styrène après extraction des homopolymères. Le comportement a été étudié en fonction de la fraction de styrène incorporé et est comparé avec celui du mélange mécanique d'acétate de polyvinyle avec du polystyrène, exemple typique d'une combinaison de composants incompatibles. Les résultats obtenus permettent de classifier les copolymères greffés comme une sorte de mélange mécanique donnant un mélange stable même pour des composants incompatibles.

Zusammenfassung

In der Reihe der Untersuchungen über die Beziehung des rheologischen Verhaltens von mechanischen Mischungen zweier Polymerkomponenten zum Mischungsgrad wurde das Zugspannungs-Relaxationsverhalten von in Styrollösung mit Co⁶⁰ bestrahltem Polyvinylacetat als Funktion des Bruchteils der Styrolkomponente gemessen und mit demjenigen einer mechanischen Mischung von Polyvinylacetat und Polystyrol, einer typischen Kombination unverträglicher Komponenten, verglichen. Es wird angenommen, dass die Bestrahlung uach Extraktion der Homopolymeren ein Pfropfcopolymeres von Polyvinylacetat und Styrol liefert. Die erhaltenen Ergebnisse lassen das Pfropfcopolymere als eine Art mechanischer Mischung mit stabiler Mischung sogar der unverträglichen Komponenten erscheinen.