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WORKING PARTY ON STRUCTURE AND PROPERTIES OF COMMERCIAL POLYMERS*

VISCOELASTIC PROPERTIES OF RUBBER-MODIFIED POLYMERIC MATERIALS AT ELEVATED TEMPERATURES

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ABSTRACT: Viscoelastic properties of model systems for commercial rubber-modified polymeric materials such as HIPS and ABS resins were measured at relatively high temperatures in several laboratories. Rubber particles and the matrix polymers (polystyrenes and acrylonitrile-styrene copolymers) were separately prepared and mixed with each other. Viscoelastic parameters and related problems considered in this report are temperature and frequency dependences of storage shear modulus and loss modulus, relaxation spectrum, rubbery plateau modulus, characteristic relaxation time for entanglement couplings in the matrix phase, the second plateau modulus which typically appears in particle-dispersed systems, and the effects of dispersion of particles and composition of copolymers. These subjects are discussed in terms of the rubber particle content, the molecular weight and its distribution of matrix polymers and the relative stiffness of particles to the matrix phase. The dispersion of rubber particles and matching in composition of matrix copolymers and grafted ones on the surface of rubber particle were found to be most important to determine the rheological properties of the composite materials. The aims of the report are to establish the fundamental concepts for viscoelastic and related properties of rubber-modified polymeric materials and to contribute to improvements of processability and performance of the commercial polymeric materials.

1. INTRODUCTION

During the thirty years after rubber modified polymeric materials such as high-impact polystyrenes (HIPS) and ABS resins were invented, these materials have been used for various purposes. Because of their high impact strength and high ductility, the rubber-modified polymers have become important commercial materials. The studies on physical properties of these materials were first started by measurements of impact strength (1-5) and then spread out in other mechanical and viscoelastic properties of the solids (6-9). However, the number of investigations of rubber-modified polymeric materials is still small compared with that for the polymeric materials containing solid particles and fiber reinforced plastics (10).

Recently, a considerable number of rheological studies have been made on rubber-modified polymeric materials in the molten state or at elevated temperatures, in connection with the processability of the materials (11-23). Among these investigations, almost all are on steady state viscosity (11-13,15,16,18-20,23) and a few involve elastic properties (12,14,17,23), which certainly play an important role in the processing of these materials. Furthermore, the HIPS and ABS employed as samples in these studies were commercially available materials and were not necessarily characterized well with respect to particle size, molecular characteristics of the matrix polymers (molecular weight, molecular weight distribution and so on), molecular characteristics of grafted macromolecules on the rubber particles, the size and crosslinking density of the particles, the degree of dispersion of the particles in the matrix, and others. As is well known, these fundamental characteristics, especially the dispersion of particles in the polymeric matrix, strongly affect the rheological properties of the polyblends and it has sometimes happened that studies on similar samples have led to mutual contradictory conclusions.

Rheological studies on industrially important plastics emphasize non-linear viscoelasticity (21) and extensional flow behavior (23), which are directly related to the processability of the materials. On the other hand, it is also important that the rheological properties of only well characterized polymer-rubber particles systems are investigated so that general conclusions can be drawn on the viscoelastic properties of dispersed systems in molten states. To perform this kind of work, it is necessary to know the effects of molecular characteristics, such as molecular weight (24), molecular weight distribution (25,26), and branching (27-29) on the homogeneous polymer melts. With this information the universal effects of the mixing of the particles into the polymeric systems

can be determined by measuring the rheological or viscoelastic properties of the well characterized rubber-modified polymer systems.

The above method has been used for the past several years particularly in Japan (30-37) to study the viscoelastic properties of rubber-modified polymer systems. Although these studies have been limited to the region of linear viscoelastic properties, important and reliable results have been obtained on the viscoelastic properties of the rubber-modified polymeric materials at elevated temperatures. The Sub-Group of IUPAC Working Party on "Structure and properties of commercial polymers" (IV-2-1) which meets in Japan (IV-2-1-1) have collected available data on the rheological properties of rubber-modified polymeric systems and discussed these data to determine general conclusions on the effect of the rubber particles mixed into uniform polymeric systems. Some experiments have been added to fill a gap between the experimental results obtained by different laboratories. This report describes the more general and qualitative conclusions on the viscoelastic properties of the polymeric systems containing relatively soft particles and also the effects of the particles on the rheological properties of the rubber-modified polymeric materials.

The Sub-Group of the Working Party meeting in Japan believes that this report provides the essential fundamental guiding principle to consider the processability of the similar commercial polymers.

2. MATERIALS

Two series of rubber-modified polymeric materials, acrylonitrile-styrene copolymer(AS)-polybutadiene(PB) particle system, and polystyrene(PS)-polybutadiene particle systems are employed in this report. The matrix polymers and the particles were separately prepared, and then mixed by a Brabender Plastograph. Polybutadiene particles are crosslinked and AS copolymer and PS are grafted on the surface of particles for the model systems of HIPS and ABS resins, respectively, to get a good dispersion. Prior to the mixing, the particles have been well characterized in size, size distribution, grafting degree, and in molecular weight and acrylonitrile contents of grafted polymers and so on. The characteristics of particles used in this study are given in Table I. Particles A-E were used for AS-particle systems (model for ABS resins) and F-H for PS-particle systems (model for HIPS). Particle E represents five kinds of particles of different AN% in grafted copolymers, ranging from 21.4 to 29.7.

Table I. The particle size and the molecular characteristics of the grafted polymers on the surface of the particles.

particle	diameter(nm) (size distribution)	grafted polymer	GD* ¹	AN%* ²	M _{gw} * ³	MWD* ⁴
A	100-1000(av.250) (broad)	AS copolymer	0.37	26	6x10 ⁴	3
B	200 (narrow)	AS copolymer	0.85	unknown	6x10 ⁴	3
C	350 (narrow)	AS copolymer	0.20	26	6x10 ⁴	3
D	170 (narrow)	AS copolymer	0.41	26	6x10 ⁴	3
E	340 (narrow)	AS copolymer	0.28	21.4-29.7	8x10 ⁴	3
F	250 (narrow)	PS	0.20	--	1.26x10 ⁵	2.6
G	250 (narrow)	PS	0.22	--	1.40x10 ⁵	2.7
H	250 (narrow)	PS	0.40	--	2.21x10 ⁵	2.9

*¹ grafting degree defined as the ratio of the weight of the grafted polymer to that of the particles.

*² weight % of Acrylonitrile in the grafted AS polymers.

*³ weight average molecular weight of the grafted polymer.

*⁴ M_w/M_n for the grafted polymers.

Fig. 1 and 2 respectively show electron micrographs and histograms of the particle diameter of the particles C(a) and D(b). Each of the particles has a fairly narrow distribution in particle size. In Fig. 3, is shown an electron micrograph of the polybutadiene particles F, which also have a narrow distribution of sizes. The polybutadiene particles shown in Table I can form a film because of the grafted polymers on

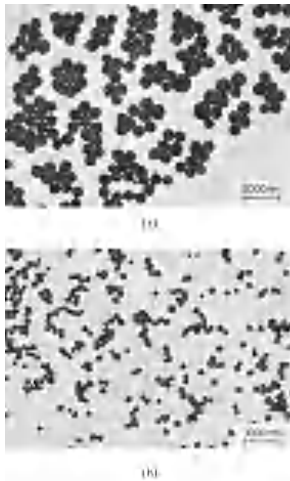


Fig. 1. Electron micrographs of rubber polybutadiene particles C(a) and D(b).

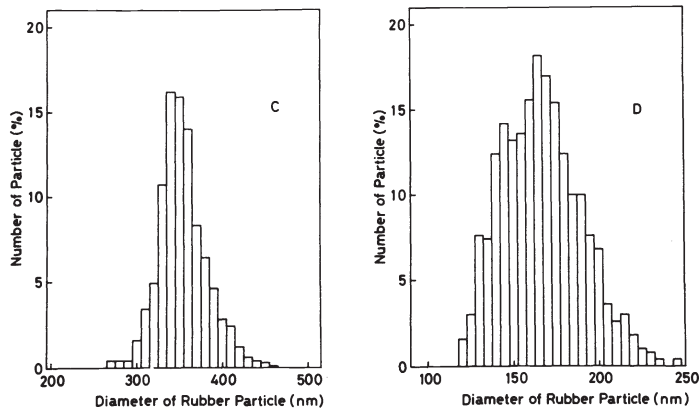


Fig. 2. Diameter of particles C(a) and D(b).

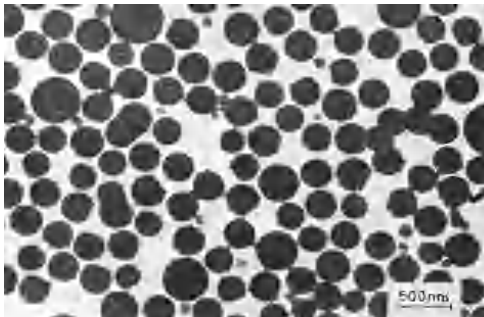


Fig. 3. Electron micrograph of polybutadiene particles F.

Table II. The weight-average molecular weight (M_w), the molecular weight distribution of the polymers used for the matrix phases of the rubber-modified polymers and AN% for AS copolymers.

polymer	M_w	M_w/M_n	AN%(wt%)
AS1	5.75×10^4	2.5	25
AS2	5.75×10^4	2.7	25.7
AS3	7.8×10^4	2.5	26.4
PS1	5.66×10^5	1.20	--
PS2	1.47×10^5	1.21	--
PS3	5.54×10^4	1.23	--
PS4	4.01×10^5	1.33	--
PS5	2.51×10^5	1.35	--
PS6	1.70×10^5	1.28	--
PS7	6.7×10^4	1.22	--

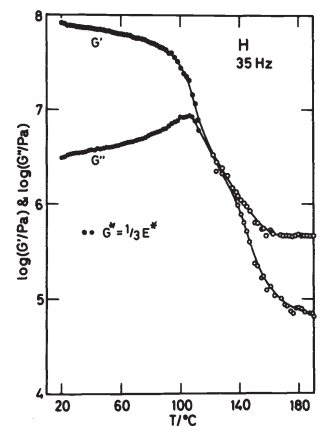


Fig. 4. Storage modulus G' and loss modulus G'' for polybutadiene particles (H) plotted against temperature at 35 Hz. The small and large closed circles represent data calculated by use of the relation; $G^* = E^*/3$.

the surface, and the measurements of dynamic moduli E' and E'' under extensional deformation were possible at temperatures below T_g of grafted polymers. Above T_g , the measurements of G' and G'' were made in shear deformation. The results for particle H are shown in Fig. 4, in which closed circles represents the data of G' and G'' calculated from E' and E'' . G' curve gives a constant value of 4.3×10^5 Pa at high temperatures, which might be the modulus of the polybutadiene particles G_p . Other particles in Table II gave a similar values of G_p , which are comparable with the rubbery plateau modulus of the matrix polymers in the rubber-modified systems.

Acrylonitrile-styrene copolymers(AS) and polystyrenes(PS) were used for the continuous phase of the polyblends. The weight average molecular weight and the molecular weight distribution of polymers and AN% of AS copolymers are shown in Table II. The molecular weight of AS copolymers were determined from viscosity measurements of the dilute solutions in *N,N*-dimethylformamide at 20°C, using the Lange-Baumann equation (38). M_w of PS samples and the polydispersity index M_w/M_n were determined by gel permeation chromatogram (GPC).

The rubber-modified polymeric systems were prepared by blending particles with matrix polymers using a Brabender Plastograph at 200°C for 10-20 mins. No degradation of polymer chains occurred by this procedure. To achieve a good dispersion of particles, the condition must be satisfied that the molecular weights of the matrix polymer and the grafted polymer should be similar. It will be shown that equality of composition in the copolymers is more important than matching molecular weights. As seen from Tables I and II, the combinations of the AS copolymers AS1 and particle A (AS1-A), and AS2-C and -D satisfy the condition of equality in composition and gave a very good dispersion; an example is shown in Fig. 5. The sample code used in this report is "matrix polymer-particle concentration in wt%", for example, AS1-A-10 implies the rubber-modified polymers consisting of AS1 as a matrix phase and particle A of 10 wt%. Fig. 6 shows electron micrographs of sample PS2-F-20 and a good dispersion of particles. For PS-systems, the equality in molecular weights of matrix PS and grafted PS is not a strict condition for good dispersions and PS1-3 were well mixed with particle F. Figs. 5 and 6 clearly demonstrate that the dispersion of particles does not become bad by a heat treatment for these systems.

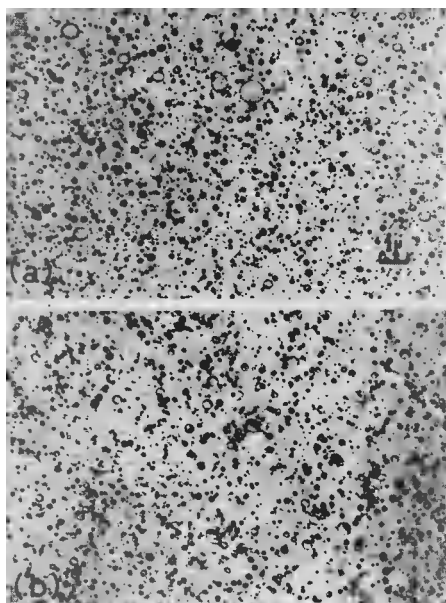


Fig. 5. Electron micrographs of sample AS1-A-10 before (a) and after (b) experiment at 245°C.

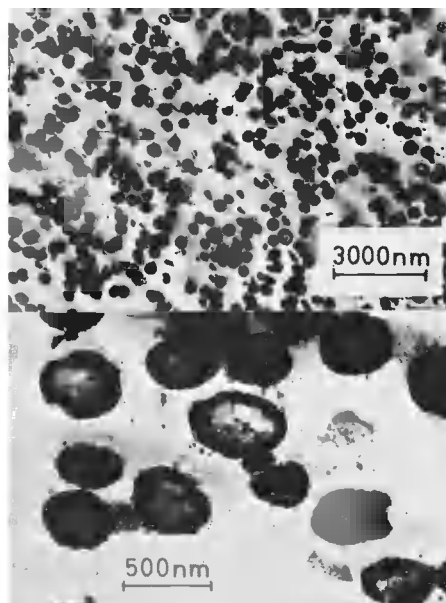


Fig. 6. Electron micrographs of sample PS2-F-20 after the heat treatment at 200°C for 1 hrs.

3. MEASUREMENTS

A concentric cylinder type rheometer was used for measurements of viscoelastic properties of the samples. The measuring temperatures were varied from 120°C to 245°C and the frequencies from 6.67×10^{-4} Hz to 1.0 Hz. The frequency dependence curves of the storage shear modulus G' and the loss modulus G'' at various temperatures were superposed into the master curves at 170°C (AS-series) and 160°C (PS-series) according to the time-temperature superposition. All samples showed the linear viscoelastic response to strain

amplitudes of about 10%. This behavior is in marked contrast to that of solid particle-containing polymeric systems, which show a non-linear viscoelastic behavior as low as 3% or less (39).

4. EFFECTS OF TEMPERATURE

In Figs. 7-10, are shown the frequency dependence curves of storage shear modulus G' and loss modulus G'' measured at various temperatures for ASI-A-20 and ASI-B-20.

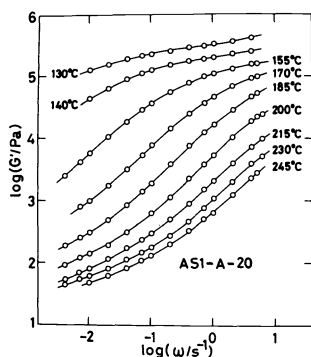


Fig. 7. Frequency dependence of the storage modulus G' for ASI-A-20 at various temperatures.

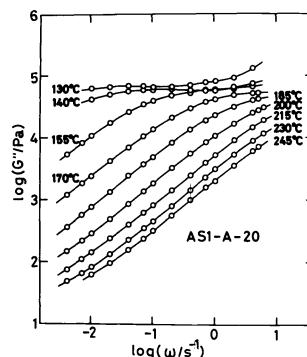


Fig. 8. Frequency dependence of the loss modulus G'' for ASI-A-20 at various temperatures.

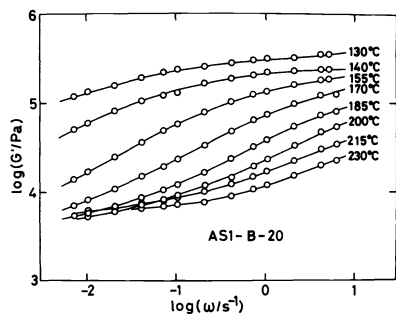


Fig. 9. Frequency dependence of the storage modulus G' for ASI-B-20 at various temperatures.

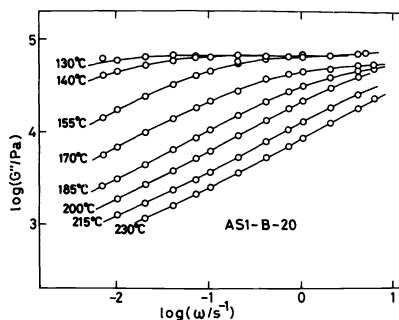


Fig. 10. Frequency dependence of the loss modulus G'' for ASI-B-20 at various temperatures.

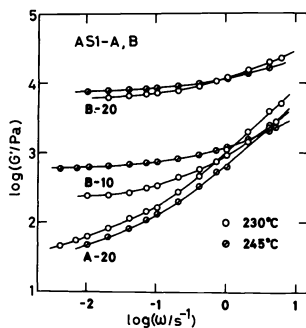


Fig. 11. Frequency dependence of the storage modulus G' for ASI-A-20, -B-10 and -B-20 at 230°C and 245°C.

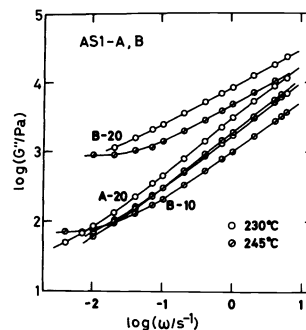


Fig. 12. Frequency dependence of the loss modulus G'' for ASI-A-20, -B-10 and -B-20 at 230°C and 245°C.

Viscoelastic functions G' and G'' of particle-containing systems show a peculiar behavior in low frequency regions and at high temperatures (flow region). The G' curve exhibits another plateau region at a lower magnitude of rigidity than the rubbery plateau of the polymer melt. This plateau in long time scales, the "second plateau" usually appears for heterogeneous systems, such as polyblends and particle-containing polymers, suggesting that the system has very long relaxation times (39). Similar results have been obtained for ABS resins (14,17) and have been attributed to rubber elasticity from the rubber particles (14). This discussion is probably incorrect because the modulus of the particle, 4.3×10^9 Pa, is much higher than the magnitude of the second plateau as seen from Fig. 9 and the second plateau modulus strongly depends on the degree of dispersion and the viscosity of the matrix phase, as discussed subsequently.

The second plateau regions of G' and G'' for AS1-A and AS1-B are compared with each other in Figs. 11 and 12. The plateau modulus of AS1-B is much higher than that of AS1-A (see Fig. 11). Abnormal behavior of AS1-B-10 and -B-20 is shown by the fact that the curves at 245°C are higher than those at 230°C. This suggests that the dispersion of particles has been changed by raising the temperature to 245°C, as confirmed by the electron micrographs shown in Fig. 13. This figure can be compared with that for AS1-A systems (see Fig. 5) which do not show any change of dispersion at 245°C. The unstable dispersion of AS1-B samples could be caused by the difference in composition of the AS copolymer (AN%) of the matrix polymer (AS1) and the grafted polymer on the particle, although the AN% for particle B was not measured. The second plateau phenomena have also been observed for PS1, 2, 3-F series and the magnitude G''_{pa} increases with increasing rubber particle content and the molecular weight of the matrix polystyrenes. Quantitative discussions will be given in section 9.

The frequency dependence curves of G' and G'' at various temperatures (Figs. 7-10) can be superposed into a master curve by shifting the curves along the frequency axis by a factor a_T . Figs. 14-16 show the temperature dependence of a_T for AS1-A, AS2-C and PS-F. Solid or broken lines drawn in each figure represent the WLF equation (40) written as

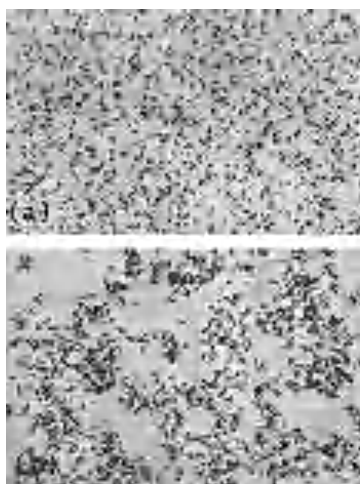


Fig. 13. Electron micrographs of AS1-B-10 before (a) and after (b) experiment at 245°C.

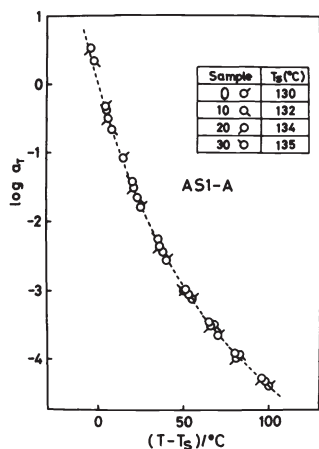


Fig. 14. The shift factor a_T for AS1 copolymer, AS1-A-10, -A-20 and -A-30 plotted against temperature difference $T - T_g$. The reference temperatures are indicated in the figure. The dotted line is for the WLF equation.

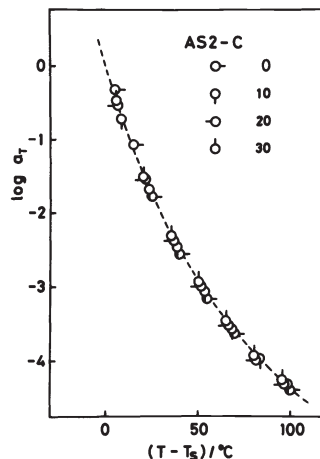


Fig. 15. The shift factor a_T for AS2-C-10, -C-20 and -C-30 plotted against temperature difference $T - T_g$. The dotted line represents the WLF equation.

$$\log a_T = -8.86(T - T_g)/(101.6 + T - T_g) \quad (1)$$

T_g is very slightly dependent on particle content for the AS-particle systems as shown in Fig. 14 and Table III, but is almost constant ($T_g = 139^\circ\text{C}$) for the PS-particle systems.

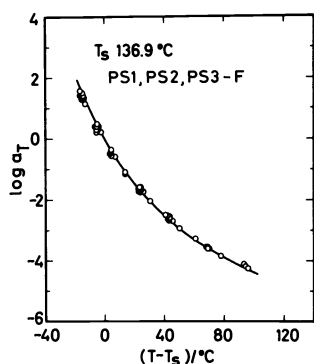


Fig. 16. The shift factor a_T plotted against temperature difference $T - T_g$. The reference temperature T_g is 136.9°C . The solid line is for the WLF equation.

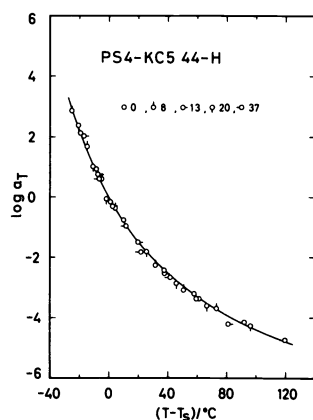


Fig. 17. The shift factor a_T for disperse systems of particle H in polystyrene (PS4) solution plotted against temperature difference $T - T_g$. The solid line is for the WLF equation. Numerical values in the figure indicate volume % of particle H in mixture.

concluded that the dependence of T_g on particle content is closely related to the change of free volume of the materials; polymer melt-rubber particle systems do not change much in volume by mixing of particles.

5. VISCOELASTIC FUNCTIONS

The master curves of the viscoelastic functions G' and G'' for the rubber-modified polymer samples as well as the matrix polymers are shown in Figs. 18-31. The curves were obtained by horizontal shifting the G' and G'' versus frequency curves measured at various temperatures. In these figures, the numbers (0, 10, 20, 30 etc) on the data lines indicate

Table III. Volume fraction of particle ϕ and reference temperature T_g in the WLF equation (40) for AS2-C and AS2-D series.

sample	ϕ	$T_g/^\circ\text{C}$
AS2	0	130
AS2-C-10	0.138	131
AS2-C-15	0.204	132
AS2-C-20	0.270	133
AS2-C-25	0.334	134
AS2-C-30	0.397	134
AS2-D-5	0.079	131
AS2-D-10	0.158	132
AS2-D-15	0.233	133
AS2-D-20	0.308	134

Table IV. Volume fraction of particle ϕ and reference temperature T_g of the disperse systems of the rubber particles H in 44.4 wt% solution of PS4 in partially chlorinated biphenyl KC5.

sample	ϕ	$T_g/^\circ\text{C}$
PS4-KC5	0.00	53
PS4-KC5-H	0.08	59
	0.13	61
	0.20	65
	0.37	69

Fig. 17 shows the temperature dependence of a_T for PS solution-particle systems, for reference, in which the WLF equation is also valid, but particle content dependence of T_g was observed for this solution-particle system as shown in Table IV. From these results, it is

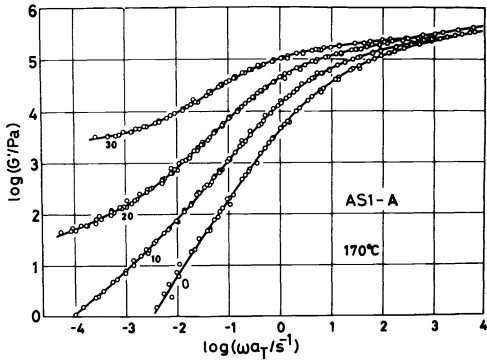


Fig. 18. Master curves of the storage modulus G' for AS1-A with different rubber particle contents at 170°C.

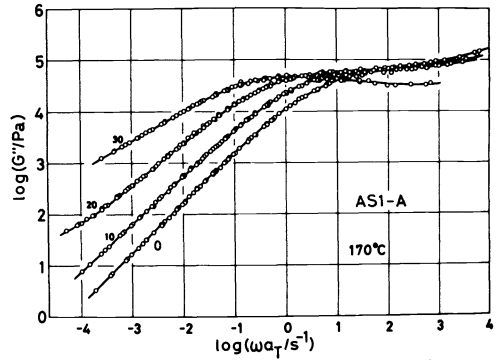


Fig. 19. Master curves of the loss modulus G'' for AS1-A with different rubber particle contents at 170°C.

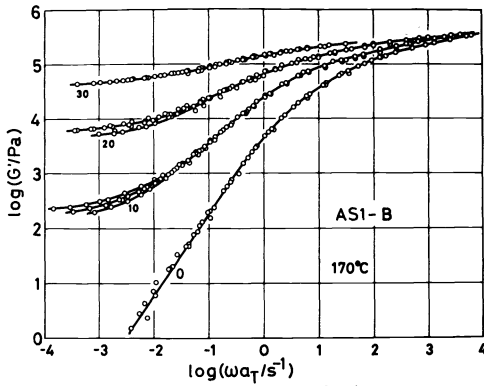


Fig. 20. Master curves of the storage modulus G' for AS1-B with different rubber particle contents at 170°C.

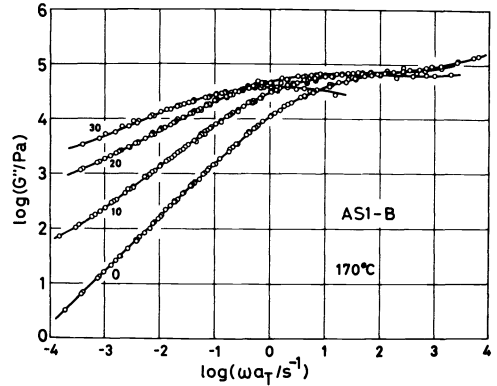


Fig. 21. Master curves of the loss modulus G'' for AS1-B with different rubber contents at 170°C.

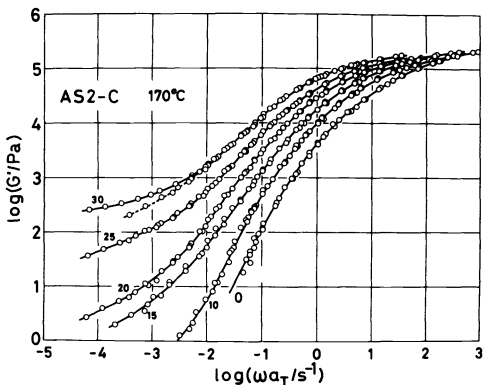


Fig. 22. Master curves of the storage modulus G' for AS2-C with different rubber contents at 170°C.

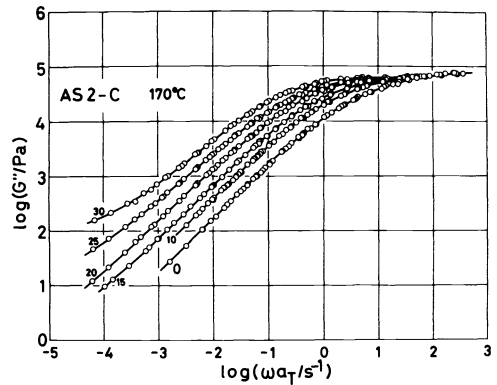


Fig. 23. Master curves of the loss modulus G'' for AS2-C with different rubber particle contents at 170°C.

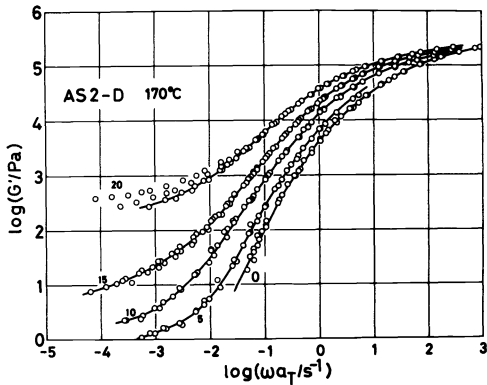


Fig. 24. Master curves of the storage modulus G' for AS2-D with different rubber particle contents at 170°C.

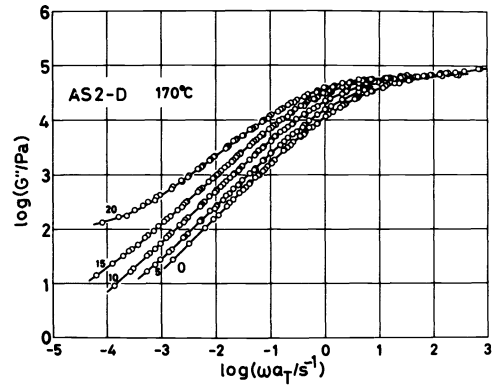


Fig. 25. Master curves of the loss modulus G'' for AS2-D with different rubber particle contents at 170°C.

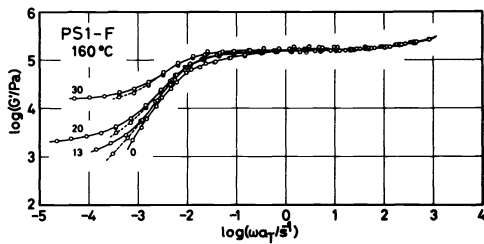


Fig. 26. Master curves of the storage modulus G' for PS1-F with different rubber particle contents at 160°C.

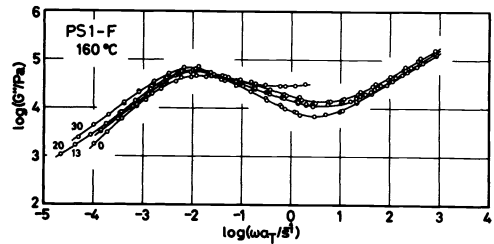


Fig. 27. Master curves of the loss modulus G'' for PS1-F with different rubber particle contents at 160°C.

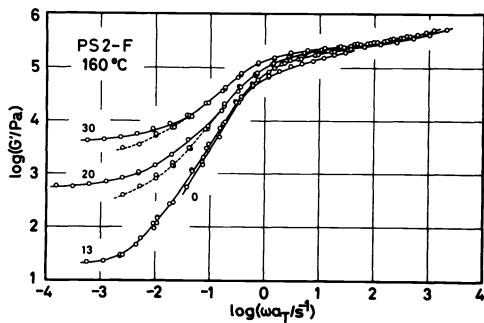


Fig. 28. Master curves of the storage modulus G' for PS2-F with different rubber particle contents at 160°C.

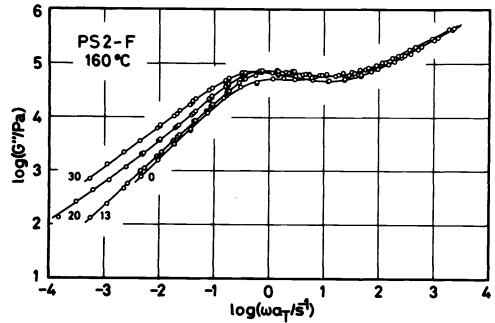


Fig. 29. Master curves of the loss modulus G'' for PS2-F with different rubber particle contents at 160°C.

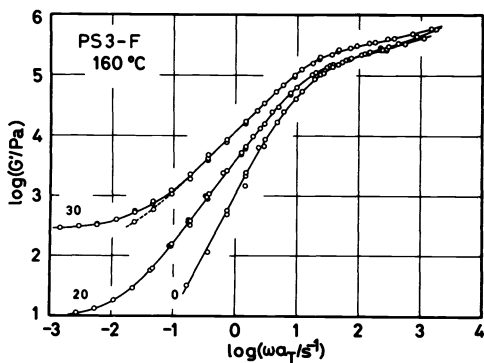


Fig. 30. Master curves of the storage modulus G' for PS3-F with different rubber particle contents at 160°C.

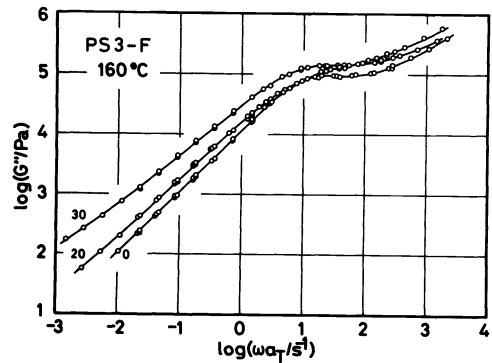


Fig. 31. Master curves of the loss modulus G'' for PS3-F with different rubber particle contents at 160°C.

the weight % of the rubber particles. The reference temperatures for the AS and PS series are 170°C and 160°C, respectively.

The general characteristic features of the viscoelastic functions for rubber-modified systems can be clearly seen from these figures. The rubbery plateau modulus, which can be estimated from the G' curves, does not depend much on the rubber particle content, because of the similarity in the rigidity of rubber particle and matrix polymer as will be discussed in section 7. The rubbery plateau regions of both G' and G'' extend to the lower frequency side (long time scales) with increasing particle content, suggesting the relaxation time becomes longer due to the presence of particles. The details will be discussed in section 8.

The most remarkable viscoelastic behavior of particle-containing systems is in the lower frequency region (the flow region). G' curves as well as G'' curves exhibit the "second plateau", which was first named for disperse systems of solid particles in polymer liquids (39). The second plateau becomes clear and the intensity becomes higher with increasing particle content, as seen from Figs. 18-31. A complete application of the time-temperature superposition principle on the G' function sometimes fails at low frequencies where the second plateau appears, as seen in Figs. 20, 22, 24, 26, 28 and 30. In this frequency region, the result measured at higher temperature gives a higher value of G' . This behavior was observed only for G' curves for the samples with relatively high contents of the particles. However, the sample after a heat treatment at 200°C for 1hr showed normal behavior and the data coincide with the uppermost curves in these figures, with good reproducibility. The materials still showed a good dispersion of particles after the heat treatment as seen from Fig. 6 and would be stabilized rheologically.

Master curves of G'' for the PS series shown in Figs. 27, 29 and 31, have maxima and the corresponding frequency becomes lower with increasing particle content. The appearance of the maximum is due to the narrow distribution of molecular weights of the polystyrenes employed for the PS series, and the shift of the frequency results from a change of the relaxation time for entanglements of polymer chains in the matrix phase with the coexistence of rubber particles. The effect of the particles on G'' at low frequencies is much less than that on G' . This behavior is quite different from that for solid particle-containing polymeric systems (39), which have a higher-order structure of the particles - so called agglomerated structure, skeleton structure or network structure. Another difference between the rubber-modified systems and solid particle-dispersed systems is that the former still shows a linear viscoelastic behavior for strain amplitudes of 10 % and higher, while the latter shows a remarkable non-linear viscoelasticity and a plastic flow (very flat G'' curves in the low frequency region) under a strain of less than 3 %.

The effects of particle size can be seen by comparing the results for AS2-C (Figs. 22 and 23) with those for AS2-D (Figs. 24 and 25). The smaller size of particles gives the higher value of the second plateau at low frequencies for the same contents. Comparing the G' curves of AS1-A-20 and -10 in Fig. 18 with those of AS2-C and AS2-D having the same contents (Fig. 22 and 24), it appears that the distribution of particle size makes the second plateau modulus high. The effects of the molecular weight of the matrix polymers on the viscoelastic functions can be seen from Figs. 26-31. The second plateau becomes higher and the maximum in the G'' curves becomes clear with increasing the molecular weight of the polystyrenes. This is due to the high viscosity and long relaxation time of high molecular weight polymers.

6. RELAXATION SPECTRA

The relaxation spectra $H(\tau)$ of the rubber-modified polymers were calculated using the second-order approximation equation proposed by Tschoegl (41). The results are shown in Figs. 32-38. The relaxation spectra calculated from G' and G'' master curves agree well

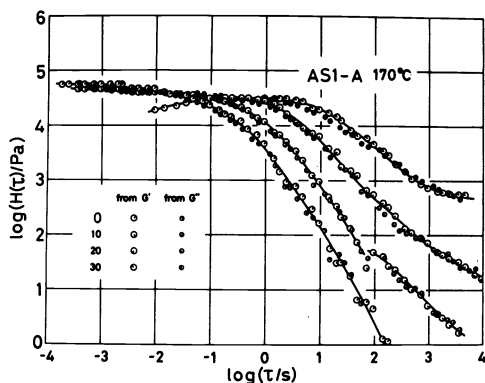


Fig. 32. Relaxation spectra for AS1-A with different rubber particle contents at 170°C.

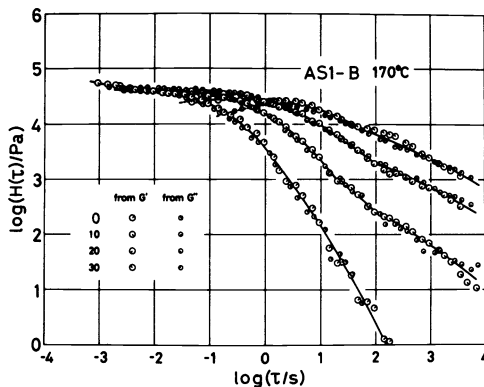


Fig. 33. Relaxation spectra for AS1-B with different rubber particle contents at 170°C.

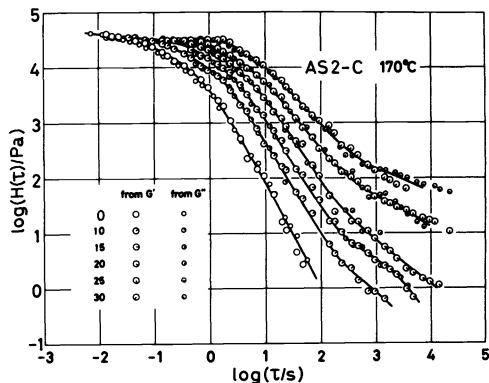


Fig. 34. Relaxation spectra for AS2-C with different rubber particle contents at 170°C.

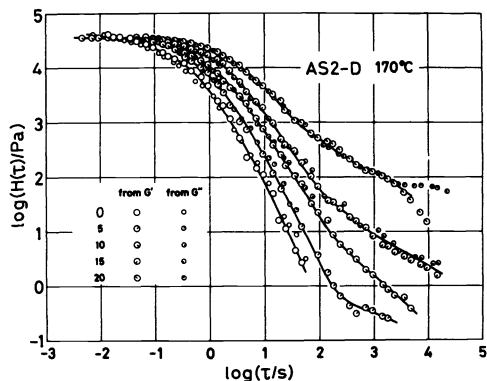


Fig. 35. Relaxation spectra for AS2-D with different rubber particle contents at 170°C.

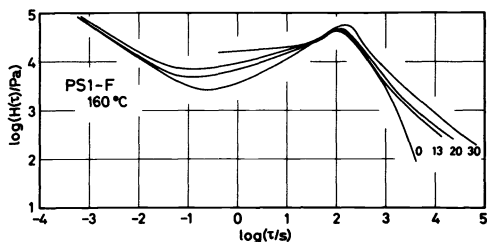


Fig. 36. Relaxation spectra for PS1-F with different rubber particle contents at 160°C.

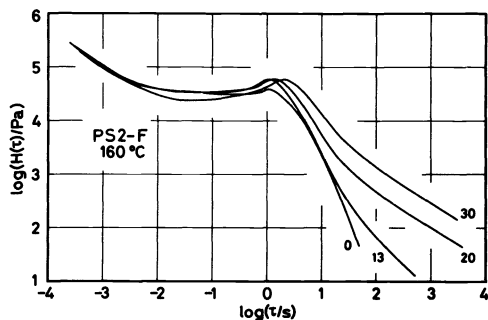


Fig. 37. Relaxation spectra for PS2-F with different rubber particle contents at 160°C.

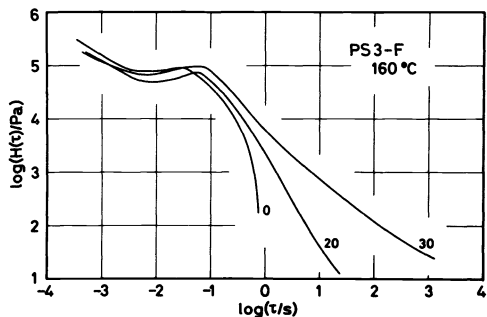


Fig. 38. Relaxation spectra for PS3-F with different rubber particle contents at 160°C.

with each other as shown in Figs. 32-35, suggesting that the viscoelastic properties measured here are linear. Although it is not shown in the figures, the same is true for PS series (Figs. 36-38). This is of marked contrast to the solid particle-polymer systems, whose viscoelastic behavior is strongly nonlinear and the G' and G'' functions give quite different relaxation spectra (40).

The relaxation spectrum of particle-free polymer melt gives a maximum, which is associated with the slippage of entanglement couplings between polymer chains, and then rapidly decreases in the longer time region. The maximum is not clear for the AS series as compared with the PS series. This difference can be attributed to the molecular weight distribution of the matrix polymers. On the other hand, $H(t)$ of the rubber-particle system shows an extra set of relaxation times at extremely long times. The spectrum becomes higher and flatter, and the relaxation time at the maximum becomes slightly longer with increasing particle contents.

7. RUBBERY PLATEAU MODULUS

We chose several equations as shown in Table V and applied them to the plateau modulus of the rubber-modified systems. In this table, G_R is the rigidity of the rubbery plateau of the rubber-modified system $G_e(\phi)$ normalized by that of the matrix polymer $G_e(0)$, where ϕ is the volume fraction of the particles.

$$G_R = G_e(\phi)/G_e(0) \quad (2)$$

Table V. Theoretical equations used for comparison with experimental data.*1

Author(s)	Equation	
Einstein(42)	$G_R = 1 + 2.5\phi$	(T1)
Guth-Gold(43)	$G_R = 1 + 2.5\phi + 14.1\phi^2$	(T2)
Mooney(44)	$G_R = \frac{2.5\phi}{1 - \phi/0.637}$	(T3)*2
Kerner(45)	$G_R = \frac{1 + 1.5\phi}{1 - \phi}$	(T4)
Okano(46)	$G_R = \frac{1 + 9[G_p - G_e(0)]/[6G_p - 9G_e(0)]}{1 - 6[G_p - G_e(0)]/[6G_p + 9G_e(0)]}$	(T5)

*1 each equation is expressed by a reduced shear modulus $G_R = G_e(\phi)/G_e(0)$ in terms of the volume fraction of the particles in the system, ϕ . $G_e(0)$ is the rubbery plateau modulus of the matrix phase.

*2 the maximum packing fraction for random close packing is taken.

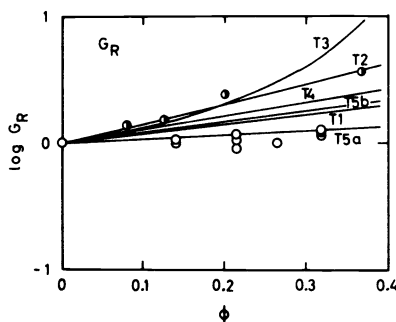


Fig. 39. The reduced plateau modulus $G_R = G_e(\phi)/G_e(0)$ plotted against the volume fraction of the particles, ϕ . The symbols put on the lines correspond to the numbers of equations in Table V. Open and half black circles denote the values for rubber modified systems in undiluted polystyrenes and polystyrene solutions, respectively.

T1: Einstein, T2: Guth-Gold, T3: Mooney, T4: Kerner, T5: Okano.

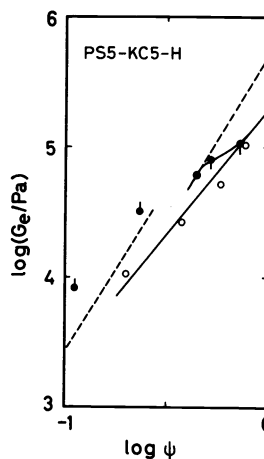


Fig. 40. The rubbery plateau modulus $G_e(\phi, \psi)$ plotted against the volume fraction of polymer in the matrix phase, ψ . Open and closed circles with pip denote the values for the polymer solutions and the rubber modified systems.

Among these equations, Okano's equation [eq.(T5)] is applicable to the soft-particle systems in which the rigidity of the particle is G_p . Okano's equation has the same form as Kerner's when G_p becomes very high.

The reduced rubbery plateau modulus $G_R = G_e(\phi)/G_e(0)$ for various particle systems dispersed in 44 wt% polystyrene solutions and undiluted polystyrenes, are plotted against the volume fraction of particle ϕ in Fig. 39. The predicted lines for the theoretical equations tabulated in Table V are also drawn in the same figure. The numbers put on the lines correspond to those of the equations in Table V. To determine the lines (T5a) and (T5b) in Fig. 39, the $G_e(0)$ values of 2.0×10^5 Pa for undiluted polystyrenes and of 3.5×10^4 Pa for 44 wt% solutions were used. The rigidity of the particles (G_p) has been measured to be 4.3×10^5 Pa. In the case in which the matrix is undiluted polystyrene and the relative stiffness of the particle and the matrix is small [$G_p/G_e(0) = 2.2$], the experimental results can be well expressed by Okano's equation (T5a).

For the polymer solution systems where $G_p/G_e(0) = 12.1$, however, the equation (T5a) can not express well the experimental results represented by the half-black circles in

Fig. 39. Mooney's equation is good for low but a deviation takes place in the high particle content region. The Guth-Gold equation can well express the experimental results for the system of higher relative stiffness. This equation was used for analysis of rubbery plateau modulus of styrene-butadiene-styrene block copolymers.

In Fig. 40, the rubbery plateau modulus $G_e(\phi, \psi)$ for the particle-containing systems is plotted against the volume fraction of polymer in the matrix phase ψ . $G_e(0, \psi)$ for polymer solutions is also plotted in this figure. The open circles are for polymer solutions and the closed circles for particle systems. Two broken lines drawn in this figure correspond to the calculated values from the following Guth-Gold equation employed by Kraus and Rollmann (47).

$$G_e(\phi, \psi) = \psi^2(\rho/M_e)RT(1 + 2.5\phi + 14.1\phi^2) \quad (3)$$

where ρ is the density and M_e is the average molecular weight between entanglement points of undiluted polystyrenes. As seen from this figure, G_e values of the particle system do not agree with eq. (3) but fall on the solid line for polymer solutions for $\psi > 0.71$. With decreasing ψ , the experimental data deviate from the line for polymer solutions and approach the broken line. At $\psi = 0.48$, the rubbery plateau modulus falls on the line expressed by eq. (3). The relative stiffnesses $G_p/G_e(0, \psi)$ at $\psi = 0.48$ and 0.71 are 9.0 and 4.2, respectively. This behavior is quite consistent with the discussions described for Fig. 39. It is very difficult to determine the plateau modulus for solutions of lower concentrations. This might be the reason why one point at the lowest concentration deviates from the theoretical broken line.

8. CHARACTERISTIC RELAXATION TIME

As pointed out in Section 6, the relaxation spectrum for rubber-modified polymeric materials can be separated in two parts; one is a set of relaxation times associated with the entanglement relaxations of matrix polymer chains and the other comes from the existence of particles. The dependences of the characteristic relaxation time for entanglement networks in the matrix phase on the molecular weight and the volume fraction of particles are discussed in this section. As seen from Figs. 32-38, the characteristic relaxation time τ_p can be determined by the time at the peak of $H(\tau)$ for the PS series, because of the narrow distributions of matrix polystyrenes. For the AS series, however, $H(\tau)$ does not show any peak and we can estimate only the ratio of the characteristic relaxation time of the rubber-modified sample to that of the matrix AS polymer τ/τ_{AS} , by shifting the $H(\tau)$ curves horizontally.

Figs. 41 and 42 show the volume fraction(ϕ) dependence of τ/τ_{AS} for the systems AS1-A, -B, and AS2-C, -D at a constant free-volume fraction of $f = 0.0658$. The comparison of the relaxation times in an iso-free-volume state is definitely important when the free volume or T_g in eq.(1) changes with particle content. AS2-C, -D and polystyrene solution-particle systems are such cases (see Table III and IV, respectively).

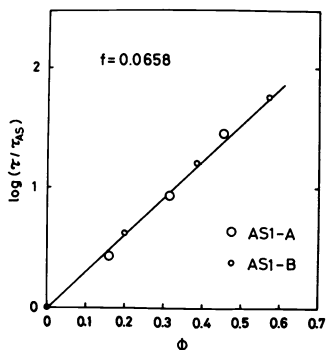


Fig. 41. Volume fraction dependence of τ/τ_{AS} for AS1-A and AS1-B at $f = 0.0658$.

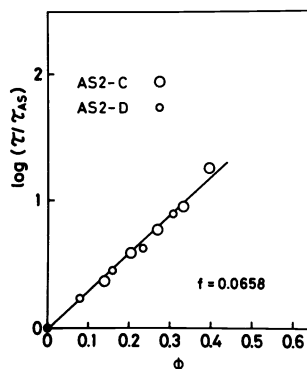


Fig. 42. Volume fraction dependence of τ/τ_{AS} for AS2-C and AS2-D at $f = 0.0658$.

The experimental results shown in Figs. 41 and 42 give the relation between τ/τ_{AS} and ϕ as

$$\tau = \tau_{AS} \exp(7.0\phi) \quad (4)$$

Molecular weight dependences of the characteristic relaxation time τ_p for rubber-

modified polystyrenes, PS-F, and the product of steady-state compliance and zero-shear viscosity, $J_e \eta_0$ for the polystyrene melts are plotted in Fig. 43. $J_e \eta_0$ is often used as a characteristic relaxation time for entanglement slippage in polymer liquids. The molecular weight dependence of τ_p for rubber-modified systems is the same as for polymer melt; τ_p is proportional to $M^{3.5}$. The volume fraction dependence of τ_p is shown in Fig. 44, which gives the relation

$$\tau_p = \text{const.} M^{3.5} \exp(1.87\phi) \tag{5}$$

considering the results from Fig. 43.

The weak dependence of the characteristic relaxation time τ_p for the AS series would be caused by the particle content dependence of free volume and T_g for this series. To check this idea, similar measurements have been made for polystyrene solution-particle systems. The results are shown in Figs. 45 and 46. The proportionality of τ_p to $M^{3.5}$ is true again, but τ_p has a strong dependence on the volume fraction of rubber particles for the solution systems. T_g for this system varies with the volume fraction of rubber particle (see Table IV). The molecular weight and dependence of τ_p for the solution system can be expressed as

$$\tau_p = \text{const.} M^{3.5} \exp(6.9\phi) \tag{6}$$

which gives a similar dependence to eq.(4).

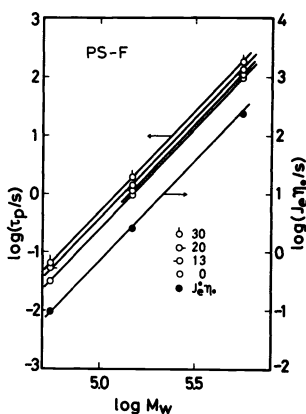


Fig. 43. Molecular weight dependence of the characteristic relaxation time τ_p for rubber modified systems (open circles) and the product of steady state compliance and zero-shear viscosity, $J_e \eta_0$ for polymer melts (closed circles) at 160°C.

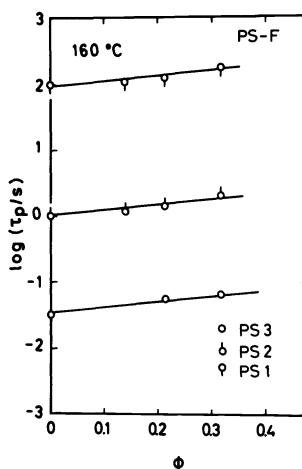


Fig. 44. Dependence of the characteristic relaxation time τ_p on volume fraction of particles ϕ for the rubber modified systems at 160°C.

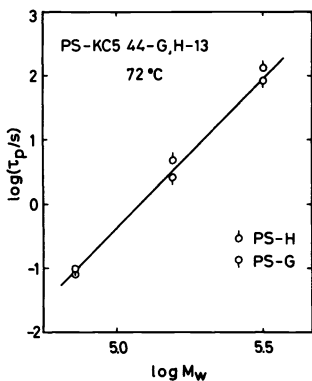


Fig. 45. Molecular weight dependence of characteristic relaxation time τ_p for rubber modified systems of particle A and B in polystyrene solutions at 72°C. Concentration of the solution is 44.4 wt% and particle content is 13 vol%.

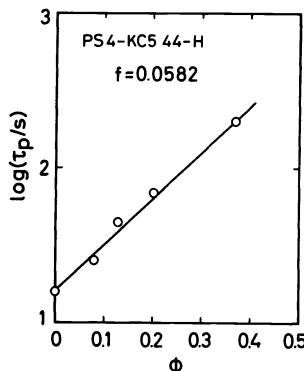


Fig. 46. Dependence of the characteristic relaxation time τ_p on volume fraction of particle, ϕ , for rubber modified systems of particle H in polystyrene (PS4) solutions in an iso-free-volume state ($f = 0.0582$). Concentration of the solution is 44.4 wt%.

9. SECOND PLATEAU MODULUS

The height of the second plateau which appears at long time scales (at low frequencies) of the storage modulus G' curves of particle-containing materials, depends on particle content and molecular weight of the matrix polymer as well as on the degree of dispersion, as shown in Section 5. The second plateau modulus G_{pa} estimated from frequency dependence curves of G' for the AS series of the samples (Figs. 18, 20, 22, and 24) are plotted against the surface distance between the neighboring particles r_s in Fig. 47. r_s was calculated using the particle content and assuming that the each particle locates on the body-centered cubic lattice. Data for the AS series, except for AS-B, can be expressed by a straight line having a slope of -7.7 . This result suggests that the dependence of the second plateau modulus of well dispersed particle systems of different particle content and particle size can be correlated with the surface distance between the neighboring particles. Deviation of the data for AS1-B is clearly due to the bad dispersion of the particles as was seen in Fig. 13. It should be emphasized that the degree of dispersion is the most important factor which affects on the second plateau modulus, the non-linear viscoelastic behavior and the yield stress. The upper limit of G_{pa} , of course, is the rigidity of the particles.

The second plateau modulus G_{pa} also depends on the molecular weight of the matrix

polymers as is shown in Fig. 48. The details of the mechanism of the influence of molecular weight on G_{pa} is unknown, but we believe that the viscosity of the matrix phase is important in determining the modulus. Fig. 49 shows similar plots for the PS series to Fig. 47. PS1-3 and PS7 are different in molecular weight and show different behavior, while AS1 and AS2 have the same molecular weight (Table II). The results of a trial to examine the effects of r_s and molecular weight of the matrix polymer are shown in Figs. 50 and 51. Three groups of data for PS1, PS2 and PS7 in Fig. 49 were shifted horizontally onto those for PS3 and a single master curve was constructed as shown in Fig. 50. The superposition works well and the slope of the line in the higher r_s region (low particle content) is -7.7 which is in good agreement with that for the AS series (Fig. 47). In Fig. 51, the reduced molecular weights M/M_0 (M_0 is 5.54×10^4 for PS3) are plotted against the shift factor, a , to obtain the master curve of Fig. 50. The

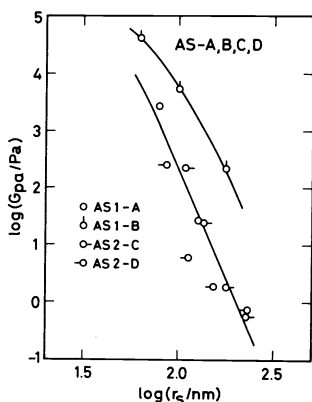


Fig. 47. Dependence of the height of the second plateau G_{pa} on surface distance between the neighboring particles for AS-Particle systems.

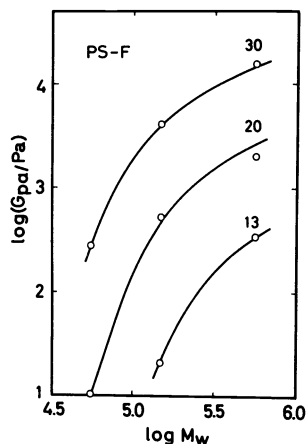


Fig. 48. Molecular weight dependence of the height of the second plateau G_{pa} for PS-F systems. Numerical value in the figure indicates weight percentage of particle.

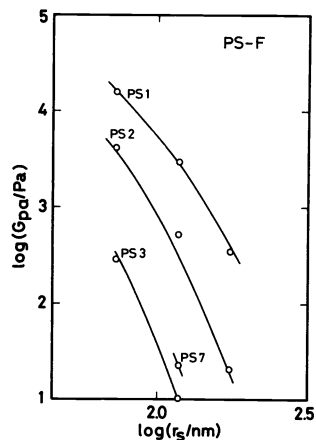


Fig. 49. Dependence of the height of the second plateau G_{pa} on surface distance between the neighboring particles for PS-F systems.

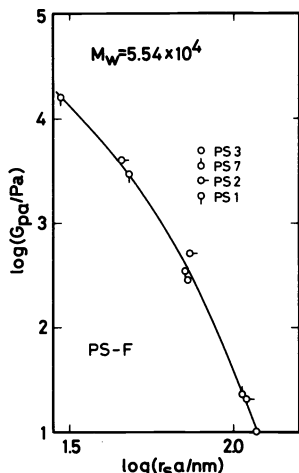


Fig. 50. Reduced curves of height of the second plateau, G_{pa} obtained by shifting the data in Fig. 49 along the horizontal axis.

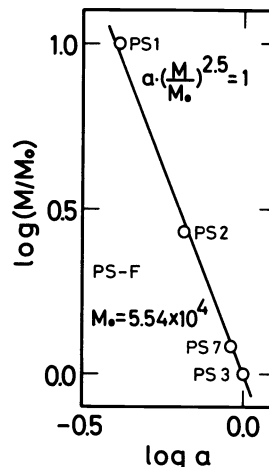


Fig. 51. Relaxation between the reduced molecular weight (M/M_o) and the horizontal shift factor a for r_s .

experimental points are well represented by a straight line of the slope -2.5 , indicating the relation $a(M/M_o)^{2.5} = 1$ or $M^{2.5}/r_s = \text{const}$. Accordingly, the increase of molecular weight of the matrix polymer and decrease of r_s work to increase the second plateau modulus.

10. EFFECTS OF COMPOSITION OF GRAFTED AS COPOLYMER

The viscoelastic functions and the second plateau modulus are significantly affected by the degree of dispersion of rubber particles in the matrix phase as was seen in Sections 5 and 9. On the other hand, it is also well known that a good combination of molecular weight and/or composition of grafted AS copolymer on the butadiene particles with matrix copolymers is very important to produce a high performance ABS resins. In this section, the effects of chemical composition of the grafted copolymers on the viscoelastic properties is investigated.

In Figs. 52 and 53, are shown the storage modulus G' and loss modulus G'' measured at 230°C for the sample AS3-E-15. The molecular weight and AN% of the AS3 copolymer are shown in Table II. The molecular weight of the grafted copolymer is almost same as the matrix phase (AS3) and AN% is varied from 21.4 to 29.7. The G' and G'' at low frequencies strongly

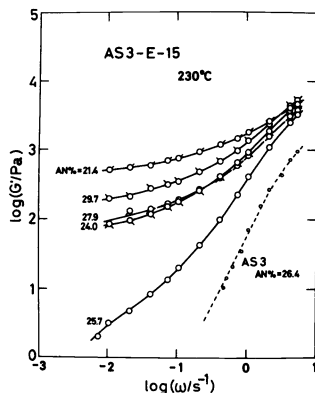


Fig. 52. Frequency dependence of the storage modulus G' for AS3-E-15 with different acrylonitrile content of grafted AS copolymer at 230°C . Small circles denote G' of matrix AS copolymer. AN% in the figure indicates acrylonitrile content of grafted AS copolymer for ABS polymer.

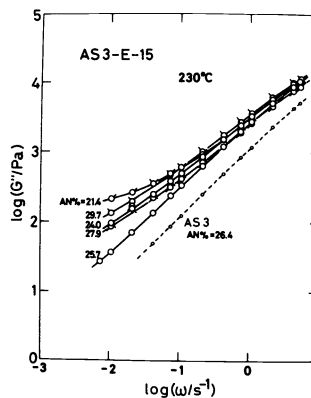


Fig. 53. Frequency dependence of the loss modulus G'' for AS3-E-15 with different acrylonitrile content of grafted AS copolymer at 230°C .

depend on the AN% of the grafted copolymer. The values of G' at $\omega = 1.05 \times 10^{-2} \text{ s}^{-1}$ are plotted against AN% of the grafted copolymer in Fig. 54. The arrow put in this figure indicates the position of AN% of the matrix copolymers of 26.4%. It is clear that the G' value takes a minimum when the AN% of the matrix polymer and of the grafted one are the same and a small deviation of AN% makes a great increase of G' . Fig. 55 shows the electron micrographs of the two samples with different AN% of grafted copolymers. When the AN% of matrix and grafted polymers are different, an agglomeration of particles is observed and a higher-order structure of particles produces a high value of the second plateau modulus.

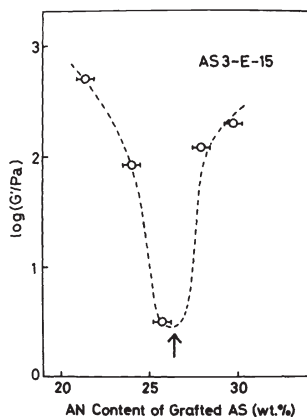


Fig. 54. Storage modulus G' at $\omega = 1.05 \times 10^{-2} \text{ sec}^{-1}$ plotted against acrylonitrile content of grafted AS copolymer. Arrow denotes acrylonitrile content of matrix AS copolymer.



Fig. 55. The electron micrographs of two AS3-E samples after experiment. A: acrylonitrile content of grafted AS copolymer is 35.7%. C: acrylonitrile content of grafted AS copolymer is 29.7%.

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