Macromolecules **1987**, *20*, 2208–2213

(16) Lebedev, B. V.; Mukhina, N. N.; Kulagina, T. G. *Vysokomol. Soedin., Ser. A.* **1978**, *20*, 1297–1303; *Polym. Sci. USSR (Engl. Transl.)* **1979**, *20*, 1458–1466.
(17) Godovskii, Y. K.; Levin, V. Y.; Slonimskii, G. L.; Zhdanov, A. A.; Andrianov, K. A. *Vysokomol. Soedin., Ser. A* **1969**, *11*, 2444–2451; *Polym. Sci. USSR (Engl. Transl.)* **1969**, *11*, 2778–2786.
(18) Gaur, W.; Lau, C.; Wunderlich, B. *J. Phys. Chem. Ref. Data* **1983**, *12*, 91–108.
(19) Godovskii, Y. K.; Dubovik, I. I.; Papkov, V. S.; Valetskii, P. M.; Dolgoplosk, S. B.; Slonimskii, G. L.; Vinogradova, S. V.; Korshak, V. V. *Dokl. Akad. Nauk SSSR* **1977**, *232*, 105–107; *Dokl. Phys. Chem. (Engl. Transl.)* **1977**, *232*, 4–6.
(20) Shimura, Y.; Hatakeyama, T. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 653–662.
(21) Wang, B. Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, NY, 1987.
(22) Wang, B.; Krause, S., manuscript in preparation.
(23) Anderson, J. E.; Davis, D. D.; Slichter, W. P. *Macromolecules* **1969**, *2*, 166–169.
(24) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 2nd ed.; Wiley: New York, 1980.
(25) Shih, H.; Flory, P. J. *Macromolecules* **1972**, *5*, 758–761.
(26) Weissler, A. *J. Am. Chem. Soc.* **1949**, *71*, 93–95.
(27) Valles, E. M.; Rost, E. J.; Macosko, G. W. *Rubber Chem. Technol.* **1984**, *57*, 55–62.

Dynamic Viscoelastic Properties of ABS Polymers in the Molten State. 5. Effect of Grafting Degree

Yuji Aoki

Yokkaichi Research and Development Department, Mitsubishi Monsanto Chemical Co., Ltd., Toho-cho, Yokkaichi, Mie 510, Japan. *Received January 23, 1987*

ABSTRACT: Dynamic viscoelastic and steady-flow properties of molten ABS polymers with different grafting degree were measured by using a concentric cylinder-type rheometer. It was found that the viscoelastic functions, in terms of storage shear modulus G' and loss shear modulus G'' as a function of angular frequency ω and shear stress τ as a function of shear rate $\dot{\gamma}$, depend strongly on grafting degree in the long-time region associated with particle–particle interactions. As the grafting degree increases, the viscoelastic functions first decrease and then increase. The minima in the functions occurred at the grafting degree of about 0.45 for ABS polymers having rubber particle size of 170 nm. When the grafting degree is below or above 0.45, second-plateau regions in G' and yield stresses in the flow curves were observed in the long-time region. Observation of the state of dispersion of rubber particles by transmission electron microscope revealed that the rubber particles of samples having the minima in the viscoelastic functions are finely dispersed but that those of the other samples exhibiting second plateaus or yield stresses form an agglomerated or a three-dimensional network structure of rubber particles. Relationship between grafting degree and colloidal stability of rubber particles is also discussed.

Introduction

Recently, many kinds of rubber-modified thermoplastic polymers have been developed and used in industrial fields. By blending of rubber component to rigid polymers, impact strength of the polymer is improved, while the other properties, for example, modulus and processability, are generally deteriorated. Therefore, it is very important for development of rubber-modified polymers to find how to improve the impact strength without deterioration of the other properties.

ABS (acrylonitrile–butadiene–styrene) polymers are one of the most typical rubber-modified polymers commercialized at about 3 decades ago. Manufacturing of ABS polymers first was made by blending of AS (acrylonitrile–styrene) copolymer and rubber. Nowadays, ABS polymers of graft type are made by copolymerizing styrene and acrylonitrile monomers in the presence of rubber. During the polymerization some of the AS copolymers become grafted to the rubber. These grafted AS copolymers act as a dispersing agent. Physical properties of ABS polymers are influenced by not only the rubber content, rubber particle size, and molecular weight of the matrix AS copolymer, but also the quantity, composition, and molecular weight of the grafted AS copolymer on the surface of rubber particles.

We have made model ABS polymers by emulsion polymerization and studied dynamic viscoelastic properties of the polymers in the molten state for several years.[1-6] We found that there are two kinds of ABS polymers, each having a different dynamic behavior.[1,2] One kind has the second-plateau region. In other words, it exhibits the pseudoequilibrium modulus (G_e) that storage shear modulus G' does not depend on frequency at a low frequency, as was previously found by Zosel[7] and Moroni and Casale;[8] the other does not have the second-plateau region and its G' decreases with a lowering of frequency. The former was found in the systems in which rubber particles agglomerate in the matrix phase (or form three-dimensional network structure), while the latter was found in finely dispersed systems without agglomerated structure. It was also found that the viscoelastic properties of ABS polymers are influenced by acrylonitrile content (AN%) in grafted AS copolymers[3] and by rubber particle size.[4,6] When the difference in AN% between grafted and matrix AS copolymers was small, the rubber particles were dispersed finely without agglomeration, and no G_e was found. The mismatching of AN% caused the agglomeration of particles and led to the observation of G_e in these ABS systems. We also reported that the long-time relaxation spectra of ABS polymers having good dispersion of particles are remarkably affected by the rubber particle size.[4,6]

Huguet and Paxton made some model ABS polymers in which the amount of graft is varied for several particle sizes of rubber and found that the melt viscosities of these polymers first decrease and then increase as the grafting degree increases.[9] Their measurement was made by a capillary rheometer and then was limited at high shear rate. Rheological properties of ABS polymers show anomalous behavior in the long-time region.[1-10] Therefore, it is of interest to study the relationship between the grafting degree and the rheological properties in the long-time region.

In this paper, we made model ABS polymers in which only the amount of grafted AS copolymers is varied, and

0024-9297/87/2220-2208$01.50/0 © 1987 American Chemical Society

Table I
Molecular Characteristics of the Matrix[a] and the Grafted AS Copolymers

sample	GD[b]	graft AN%	graft $M_w \times 10^{-4}$	graft $M_n \times 10^{-4}$
ABS-1	0.232	25.6	7.5	2.5
ABS-2	0.413	25.1	8.8	2.9
ABS-3	0.687	23.0	10.0	3.3
ABS-4	1.109	26.5	10.9	3.6

[a] In all samples, the matrix has AN% = 25.8, $M_w = 5.75 \times 10^4$, and $M_n = 2.1 \times 10^4$. [b] Grafting degree defined as the ratio of the weight of the grafted AS copolymer to that of the rubber particles.

the AN% and the particle size are constant. The influence of grafting degree on the rheological properties (dynamic viscoelastic and steady-state properties) was studied. The state of dispersion of rubber particles was observed by transmission electron micrograph. A relationship between the state of dispersion and the rheological properties was found. We also discuss colloidal stability of the rubber particles in ABS polymers.

Experimental Section

(1) Materials. Four kinds of ABS polymers with different grafting degree were mainly used in this work. Table I shows some characteristics of the ABS polymers. The number-average diameter of the rubber particles was 170 nm. These samples have very narrow distribution of rubber particle size (rubber latices used in this work were the same as ABS-D in ref 4). The amount of AS copolymers grafted on the particles was measured from the acetone-insoluble part of the ABS polymers. Grafting degree, defined as the ratio of the weight of the grafted AS copolymer to that of the rubber particles, is 0.232 (ABS-1), 0.413 (ABS-2), 0.687 (ABS-3) and 1.109 (ABS-4) (100 times grafting degree is sometimes designated % graft). The AN% and molecular weight of the grafted AS copolymers were measured after ozonolysis of the insoluble part of the ABS polymers. AN% was measured by elementary analysis (Yanaco, CHN Coder). The weight-average molecular weight (M_w) and the polydispersity index (M_w/M_n) were determined by GPC (Waters, 150C ALC/GPC) in tetrahydrofuran. The differences in AN% were very small, although the AN% of grafted AS copolymer is 2.5% lower than that of the matrix AS copolymer for ABS-3. The molecular weight of grafted AS copolymers increased with an increase in grafting degree and was 1.5 times to twice larger than that of the matrix AS copolymer.

ABS polymer samples with different rubber content were prepared by blending AS copolymer (M_w = 57000, AN% = 25.8%) with ABS polymers of high rubber content. Blending was performed at 200 °C for about 10 min by using a Brabender Plasticoder.

(2) Measurements. A concentric cylinder type rheometer was used for measurements of viscoelastic properties of the samples. The measuring temperatures were varied from 155 to 230 °C and the frequencies from 6.67×10^{-4} to 1.0 Hz. The frequency-dependence curves of the storage shear modulus G' and the loss modulus G'' at various temperatures were superimposed onto the master curves at 170 °C according to the time–temperature superposition. The measuring temperatures of steady-flow measurements were 170, 200, and 230 °C and the shear rates from 4.45×10^{-3} to 1.78 s^{-1}. Correction of non-Newtonian flow was performed by the method of Krieger and Maron.[11] All measurements were performed under nitrogen so as to minimize oxidative degradation at high temperature.

Results and Discussion

(1) Dynamic Properties. Figures 1 and 2 show the master curves of the storage shear modulus G' and loss shear modulus G'' for ABS-1 at 170 °C. Numbers (10%, 20%, 30%) indicate rubber content. Below 200 °C, both the G' and G'' could be superposed into a single master curve for each sample. However, at temperatures above 200 °C, the G' and G'' became high by raising the temperature and could not be superposed. As the G'' at higher frequency was able to be superposed, the master curves were obtained by using the shift factors of G'' at higher frequency. The G' of the sample of 10% rubber content decreases with a lowering of frequency, but those of 20% and 30% rubber content became independent of frequency and exhibited the pseudoequilibrium modulus (G_e) at a low frequency.

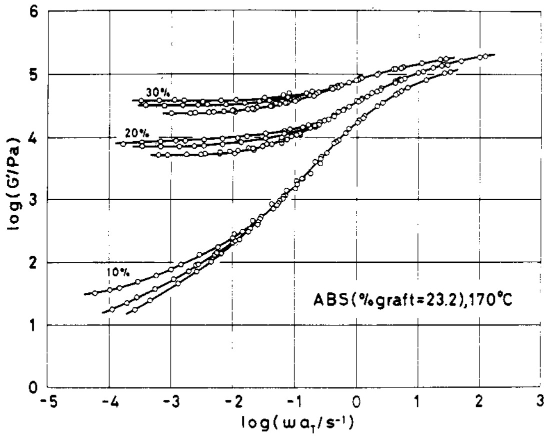

Figure 1. Master curves of the storage modulus G' for ABS-1 (% graft = 23.2) with different rubber contents at 170 °C.

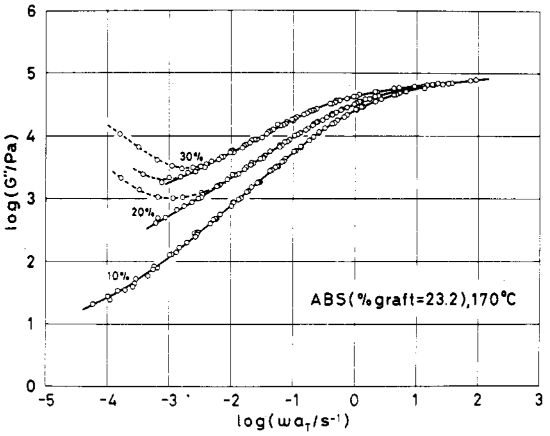

Figure 2. Master curves of the loss modulus G'' for ABS-1 with different rubber contents at 170 °C.

The G' and G'' may be nonsuperimposable for the following reasons. As the amount of the grafted copolymers is very small, the rubber particles in ABS-1 cannot form a stable colloid. When the temperature is raised, the viscosity of the matrix AS copolymer decreases. The formation of the three-dimensional network structure should be promoted by raising the temperature. Moreover, the distance between neighboring rubber particles becomes very short, when the rubber content becomes above 20%, as described in the previous papers.[4,5] Then the three-dimensional network structure can be formed more easily for the samples with 20% and 30% rubber contents.

Figures 3 and 4 show the master curves of G' and G'', respectively, for ABS-2, ABS-3, and ABS-4 with 10% rubber content. Numbers in these figures indicate % graft. Time–temperature superposition was satisfied in all the regions of temperature for three samples. The G' and G'' do not depend much on the grafting degree at high frequencies, but become higher with an increase in the grafting degree in low-frequency regions. For ABS-2 (% graft = 41.3), the G' and G'' decrease with a lowering of frequency, while for ABS-3 (% graft = 68.7) and ABS-4 (% graft = 1.109) the pseudoequilibrium modulus (G_e) is attained at a low frequency. The same tendency is seen

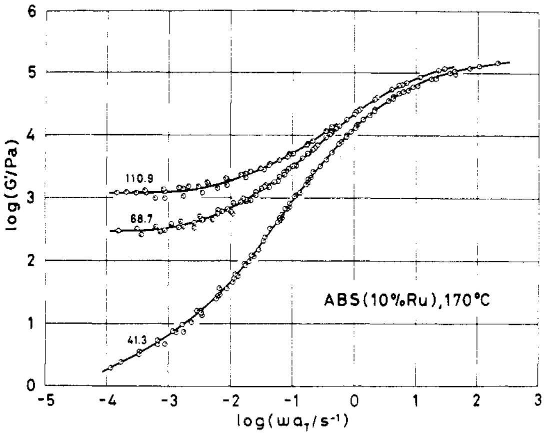

Figure 3. Master curves of the storage modulus G' for ABS-2 (% graft = 41.3), ABS-3 (% graft = 68.7), and ABS-4 (% graft = 110.9) with 10% rubber content at 170 °C.

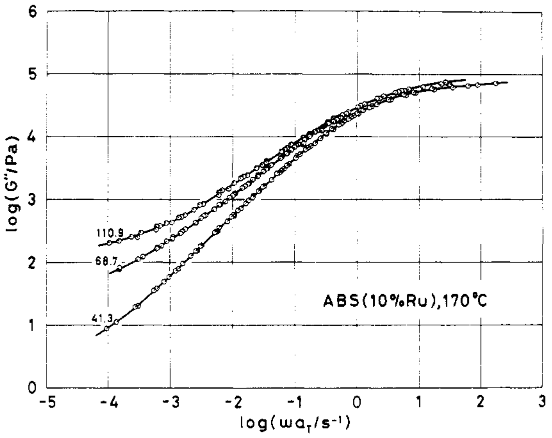

Figure 4. Master curves of the loss modulus G'' for ABS-2, ABS-3, and ABS-4 with 10% rubber content at 170 °C.

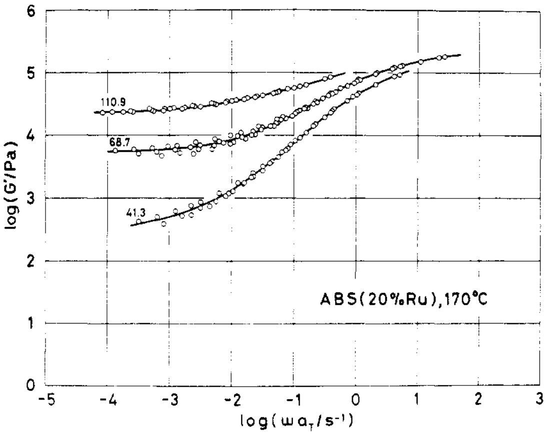

Figure 5. Master curves of the storage modulus G' for ABS-2, ABS-3, and ABS-4 with 20% rubber content at 170 °C.

for the samples with 20% rubber content shown in Figures 5 and 6.

In order to elucidate grafting degree dependence of the viscoelastic functions, the values of G' at $\omega a_T = 10^{-3}$ s^{-1} were plotted against grafting degree, as shown in Figure 7. In this figure, seven experimental values which were not given before were added. It is clear that the G' value takes a minimum when the grafting degree is about 0.45 and a deviation from the value makes a great increase of G'. The G'' value was also found to take a minimum at the same grafting degree.

In the previous paper,[3] we studied the effect of AN% of grafted AS copolymers on G' and G'' at low frequencies

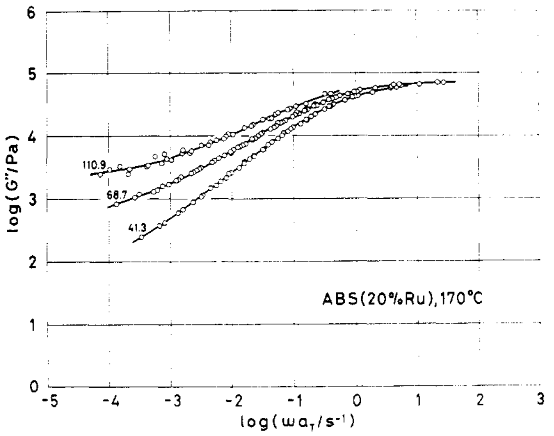

Figure 6. Master curves of the loss modulus G'' for ABS-2, ABS-3, and ABS-4 with 20% rubber content at 170 °C.

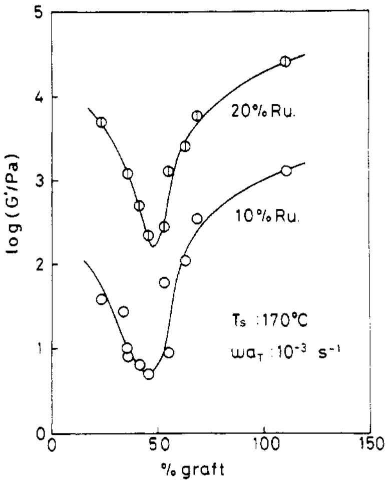

Figure 7. Storage modulus G' at $\omega = 10^{-3}$ s^{-1} plotted against % graft (= 100 × grafting degree).

and found that both G' and G'' have the smallest values when the difference between AN% of the grafted and matrix AS copolymers is within 1.5% and become higher with an increase in the difference of AN%. From this experiment, it was demonstrated that the viscoelastic properties of ABS polymers are influenced not only by the AN% but also by the amount of the grafted AS copolymers.

The minima in G' and G'' occur at the grafting degree of about 0.45 for ABS polymers having particle size of 170 nm. These minima, of course, should depend on the particle size. Because when the particle size becomes larger, the grafting degree at which G' and G'' have minimum values becomes smaller, as the surface area becomes smaller with an increase in the particle size.

(2) Steady-Flow Properties. When we measured the steady-state viscosity of ABS-1, the shear stress increased with time, and we could not observe the steady-state viscosity. But for the other samples steady-state viscosity could be obtained.

Figure 8 shows the experimental data of the steady-state and dynamic properties of ABS polymers with rubber content of 10% for ABS-2, ABS-3, and ABS-4 and the matrix AS copolymer (AS-1) at 200 °C. Open circles denote the steady-state viscosity η and closed circles the absolute value of complex viscosity defined as $|\eta^*| = (\eta'^2 + \eta''^2)^{1/2}$. In homophase polymer melt, the validity of the empirical equation by Cox and Merz[12] has been verified;

$$|\eta^*(\omega)| = \eta(\dot{\gamma}), \qquad \text{at } \omega = \dot{\gamma}$$

It can be seen from Figure 8 that the empirical equation

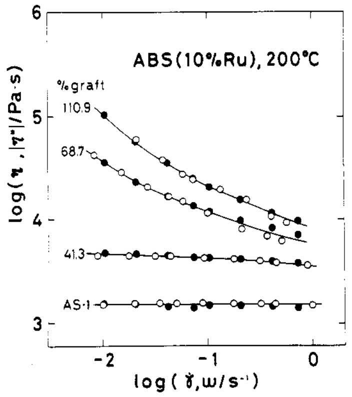

Figure 8. Shear-rate dependence of steady-state viscosity (○) and frequency dependence of absolute value of complex shear viscosity (●) for the matrix AS copolymer (AS-1), ABS-2, ABS-3, and ABS-4 with 10% rubber content at 200 °C.

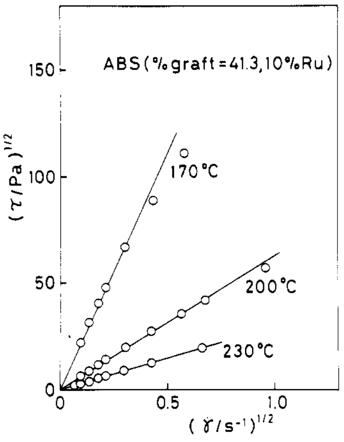

Figure 9. Casson plots of ABS-2 with 10% rubber content at various temperatures.

holds well also for rubber particle filled systems such as ABS polymers. An increase in the grafting degree leads to an obvious change of the shape of the viscosity functions. For the matrix AS copolymer and ABS-2, the viscosity functions reach to the zero-shear viscosity at low shear rates or frequencies. For ABS-3 and ABS-4, the zero-shear viscosities are not reached and the viscosity still increases at low shear rates or frequencies. This behavior becomes more pronounced at higher grafting degree.

In the rheology of suspensions and dispersions, the yield stress is usually determined according to a plot proposed by Casson:[13]

$$\tau^{1/2} = k_0 + k_1\dot{\gamma}^{1/2}$$

When $\tau^{1/2}$ is plotted against $\gamma^{1/2}$, the extrapolation of the linear part of the curve to $\dot{\gamma}^{1/2} = 0$ is claimed to give the square root of the yield stress. We checked whether Casson's equation holds well for ABS polymers. Casson plots of three kinds of ABS polymers are given in Figures 9–11. It was found that the Casson plot is applicable for the determination of the yield stress for ABS polymers. For ABS-2 with 10% rubber content, at which G' exhibits the lowest value, the k_0 is equal to zero and no yield stress exists. However, k_0 is nonzero for the other samples and the yield stress could be estimated. Table II shows yield stress τ_y obtained from Casson plot and pseudoequilibrium modulus G_e. These yield stresses are independent of temperature. The G' of samples having the yield stress becomes constant in the lower frequency region and exhibits a pseudoequilibrium modulus. As G_e is nearly equal to τ_y, it is concluded that G_e and τ_y are due to the same structure.

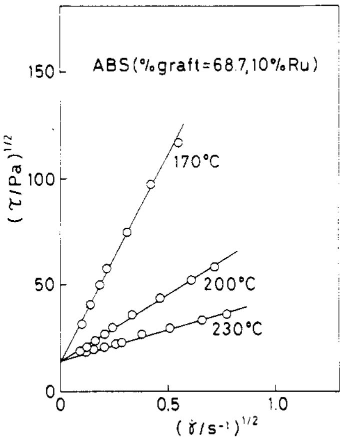

Figure 10. Casson plots of ABS-3 with 10% rubber content at various temperatures.

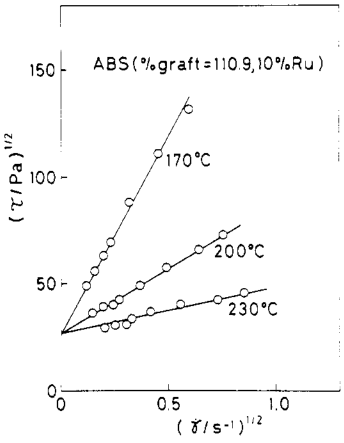

Figure 11. Casson plots of ABS-4 with 10% rubber content at various temperatures.

Table II
Pseudoequilibrium Modulus G_e and Yield Stress τ_y for ABS-2, ABS-3, and ABS-4

sample	Ru%	G_e/Pa	τ_y/Pa
ABS-2	10		0
ABS-3	10	2.7×10^2	2.0×10^2
ABS-4	10	1.1×10^3	7.3×10^2

(3) Electron Microscopic Observation. Transmission electron microscopic observation was made in order to elucidate the relationship between the viscoelastic properties and the dispersion of rubber particles in ABS polymers. According to the method developed by Kato,[14] ultrathin sections were prepared after rubber particles were stained by osmium tetraoxide. Figures 12 and 13 give the electron micrographs of four samples with 10% rubber content before (a) and after (b) measurements. Before viscoelastic measurements, the rubber particles disperse uniformly and an agglomeration cannot be observed for the four samples. The sample having grafting degree of 0.413 shows a good dispersion both before and after measurements. For the other samples the agglomeration of the rubber particles can be observed. The degree of agglomeration becomes remarkable for the samples having higher yield stress τ_y and pseudoequilibrium modulus G_e. It was also demonstrated from electron microscopic observation that G_e and τ_y are caused by agglomeration structure.

Next the agglomeration of rubber particles was examined. The electron micrographs of ABS-3 and ABS-4 having 10% rubber content were taken after measurements at 170, 200, and 230 °C. The agglomeration of the rubber

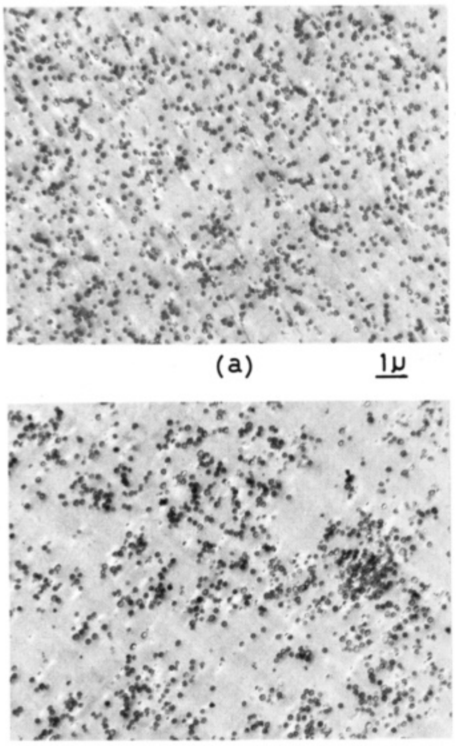

Figure 12. Electron micrographs of ABS-1 before (a) and after (b) experiment.

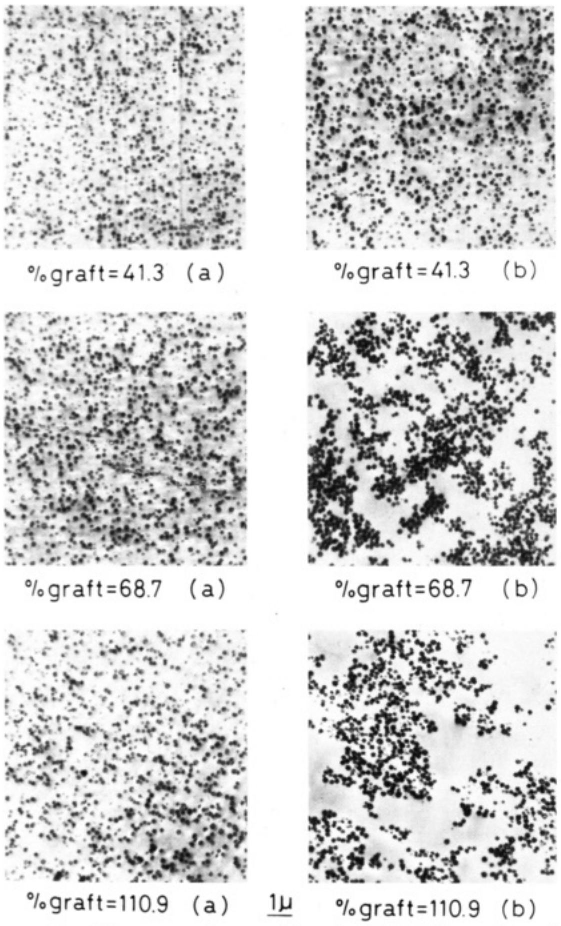

Figure 13. Electron micrographs of ABS-2 (% graft = 41.3), ABS-3 (% graft = 68.7), and ABS-4 (% graft = 110.9) before (a) and after (b) experiment.

Table III
Characteristics of the Grafted AS Copolymers on the Surface of the Particles

sample	L/nm[a]	D^2/nm^2[b]	L/D
ABS-1	5.2	21.0	1.1
ABS-2	8.8	14.0	2.4
ABS-3	13.9	9.4	4.5
ABS-4	20.9	6.4	8.4

[a] Grafted layer thickness (L) calculated by using core-shell structure. $L/R = (1 + \mathrm{GD}\rho_{\mathrm{Ru}}/\rho_{\mathrm{AS}})^{1/3} - 1$. ρ_{Ru} is the density of the rubber (0.90 g/cm^3), ρ_{AS} that of the AS copolymer (1.07 g/cm^3), and R the radius of the particle (85 nm). [b] Surface area (D^2) occupied by a single grafted AS copolymer. $D^2 = 3M_{\mathrm{w}}/R\rho_{\mathrm{Ru}}N_{\mathrm{A}}\mathrm{GD}$, N_{A} is Avogadro number.

particles was found for the samples and it scarcely depended on the measuring temperature. This is the reason that time-temperature superposition could be applied satisfactorily for the samples despite of existence of agglomeration. Before viscoelastic measurements, the sample was set into a cylinder at about 240 °C for 30 min, so as to insert a bob. The agglomeration structure should be formed at that time. In order to prove it, we examined the change in dispersion state of rubber particles by heat treatment. The agglomeration structure was observed after 30 min by annealing at 240 °C. As mentioned before, we found that the G' and G'' of ABS-1 could not be superimposed. This should be the reason for the agglomeration structure to change with time at higher temperature.

(4) Relationship between Grafting Degree and Rubber Agglomeration. We will discuss the reason why the formation of the agglomeration structure is influenced by the grafting degree. For samples with low grafting degree, the surface of the rubber particles cannot be covered perfectly with grafted AS copolymers. Then an agglomeration of the rubber particles should be caused, as the particles do not form a stable colloid. When the grafting degree becomes greater, the entropic repulsion between neighboring particles becomes stronger, resulting in the uniform dispersion of rubber particles in the AS copolymer, as seen for ABS-2. When the grafting degree is increased further, the grafted chains are stretched more and more. The matrix chains are progressively expelled from the grafted layers, as already discussed by de Gennes.[15] The expulsion should cause a formation of the agglomeration structure of grafted rubber particles.

We try to adopt this point of view to our experimental results. Grafted layer thickness (L) using a core–shell structure and surface area (D^2) occupied by a single grafted AS copolymer were calculated. The results are tabulated in Table III. For ABS-1, the distance between neighboring grafted points (D) is somewhat smaller than the linear dimension $R_0 = N^{1/2}a$, where N degree of polymerization is about 1000 and a a monomer size of 0.25 nm. Thus, the surface of the rubber particles seems to be covered perfectly with grafted AS copolymers even for ABS-1. However, an agglomeration structure was found for ABS-1. We consider that the reason is due to the distribution of grafting degree among each particle. In fact, the electron micrograph in Figure 12 revealed that many rubber particles are dispersed finely without agglomeration. We can suppose that the grafting degree of agglomerated rubbers is smaller than that of the average value and the particles cannot form a stable colloid.

For ABS-2, L/D is equal to 2.4. Therefore, the surface of the rubber particles should be covered perfectly with grafted AS copolymers, even if the rubber particles have the distribution of grafting degree among each particle. All the rubber particles are observed to be dispersed finely without agglomeration. As the entropic repulsion between neighboring rubber particles in ABS-2 becomes strong, the repulsion leads to a uniform dispersion of the particles. This repulsion arises from a decrease in the configurational entropy of the grafted chain due to the loss of possible configurations, as suggested by Clayfield[16] and Meier[17] and applied to ABS polymers by Moritani et al.[18]

For ABS-3 and ABS-4, the agglomeration of the rubber particles was observed. This is the first observation of agglomerated particles for ABS polymers having high grafting degree, as far as the author knows. It is very interesting to know the reason why the rubber particles are agglomerated at high grafting degree. We speculate as follows, although we can not explain the reason elaborately. For these ABS polymers, D is very much smaller than R_0, and L/D is large. The grafted chains must be stretched strongly. Then, the matrix AS copolymers are expelled from the grafted chains. Phase separation between the matrix and grafted chains is caused and the agglomeration of rubber particles is formed. We are now studying the formation of agglomeration structure at high grafting degree.

Concluding Remarks

In this paper, we reported the effect of grafting degree on the melt viscoelasticity of ABS polymers having particle size of 170 nm. We found that the viscoelastic functions depend strongly on grafting degree in the long-time region associated with particle–particle interactions. As the grafting degree increases, the viscoelastic functions first decrease and then increase. The minima in the functions occurred at the grafting degree of about 0.45. When the grafting degree is below or above 0.45, second-plateau regions in G' and yield stress in the flow curves were observed in long-time region. Transmission electron microscopic observation revealed that rubber particles are finely dispersed for samples having minima in the viscoelastic functions but that the other samples exhibiting second plateaus or yield stresses form an agglomerated or a three-dimensional network structure of rubber particles.

At low grafting degree, the rubber particles cannot form a stable colloid, because the particles are not covered perfectly with grafted chains. The rubber particles also cannot form a stable colloid at high grafting degree, as the matrix chains are expelled from the grafted chains. Only at intermediate grafting degree the particles form stable colloid by the repulsive force between neighboring particles.

Registry No. ABS (graft copolymer), 106677-58-1.

References and Notes

(1) Aoki, Y. *J. Soc. Rheol. Jpn.* **1979**, *7*, 20.
(2) Aoki, Y. *J. Rheol.* **1981**, *25*, 351.
(3) Aoki, Y.; Nakayama, K. *J. Soc. Rheol. Jpn.* **1981**, *9*, 39.
(4) Aoki, Y.; Nakayama, K. *Polym. J.* **1982**, *14*, 951.
(5) Masuda, T.; Nakajima, A.; Kitamura, M.; Aoki, Y.; Yamauchi, N.; Yoshioka, A. *Pure Appl. Chem.* **1984**, *56*, 1457.
(6) Aoki, Y. *J. Non-Newt. Fluid Mech.* **1986**, *2*, 91.
(7) Zosel, A. *Rheol. Acta* **1972**, *11*, 229.
(8) Moroni, A.; Casale, A. *Proc. Int. Rheol. Congr. 7th* **1976**, 339.
(9) Huguet, M. G.; Paxton, T. R. *Colloidal and Morphological Behavior of Block and Graft Copolymers*; Plenum: New York, 1971; p 183.
(10) Münstedt, H. *Polym. Eng. Sci.* **1981**, *21*, 259.
(11) Krieger, I. M.; Maron, S. H. *J. Appl. Phys.* **1952**, *23*, 147.
(12) Cox, W. P.; Merz, E. H. *J. Polym. Sci.* **1958**, *28*, 619.
(13) Casson, N. *Rheology of Disperse Systems*; Pergamon: New York, 1959.
(14) Kato, K. *J. Electron Microsc.* **1965**, *14*, 220.
(15) de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1075.
(16) Clayfield, E. J.; Lumb, E. C. *J. Colloid Interface Sci.* **1966**, *22*, 269.
(17) Meier, D. J. *J. Phys. Chem.* **1967**, *71*, 1861.
(18) Moritani, M.; Inoue, T.; Motegi, M.; Kawai, H. *Macromolecules* **1970**, *3*, 433.

Interactions in Mixtures of Poly(ethylene oxide) and Poly(methyl methacrylate)

H. Ito and T. P. Russell*
IBM Research, Almaden Research Center, San Jose, California 95120-6099

G. D. Wignall
Oak Ridge National Laboratory, Solid State Division, Oak Ridge, Tennessee 37830.
Received April 20, 1987

ABSTRACT: Small-angle neutron-scattering measurements have been performed on mixtures of poly(ethylene oxide), PEO, with protio- and deuteriopoly(methyl methacrylate), PMMAH and PMMAD, respectively, to evaluate the Flory–Huggins interaction parameter χ_{AB}. It has been found that χ_{AB} varies from -5×10^{-3} to -1×10^{-3} as the total PMMA concentration increases from 0.3 to 0.7. The temperature dependence of the scattering combined with other results indicates that entropic, rather than enthalpic, contributions dominate χ_{AB}. The magnitude of χ_{AB} is found to be on the same order of magnitude as that expected between PMMAH and PMMAD, particularly at high total concentrations of PMMA. Studies of PMMA at higher scattering vectors show that down to length scales of 25 Å no changes are observed in the conformation of PMMA in the mixtures in comparison to that of PMMA in the bulk.

Introduction

The binary interaction parameter in the free energy of mixing is critical for the evaluation of the miscibility between polymer pairs. In principle, the determination of the interaction parameter, χ, is possible by a variety of techniques. However, in practice, obtaining a precise value of χ is not trivial. Melting point depression studies have been used in the past to determine χ for semicrystalline/amorphous polymer pairs.[1] For some systems this method has been used with a fair degree of success. Use of the melting point depression technique requires the measurement of the equilibrium melting point, T_m^0 of the pure semicrystalline polymer and of the semicrystalline polymer in the mixture. By no means is this a simple and clear-cut measurement. Lamellar thickening during heating, modification of the crystal structure, and super-

0024-9297/87/2220-2213$01.50/0 © 1987 American Chemical Society