Application of the Theory of Elasticity and Viscosity of Two-Phase Systems to Polymer Blends

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Synopsis

An attempt was made to evaluate the apparent elastic constant of a two-phase system G from those of the components of the system. The modulus G is expressed as follows:

$$G = G_1 \frac{(7 - 5\nu_1)G_1 + (8 - 10\nu_1)G_2 - (7 - 5\nu_1)(G_1 - G_2)v}{(7 - 5\nu_1)G_1 + (8 - 10\nu_1)G_2 + (8 - 10\nu_1)(G_1 - G_2)v}$$

where G_1 and G_2 are the shear moduli of the suspending medium and the suspended particles, respectively, ν_1 is the Poisson ratio of the medium, and v is the volume fraction of the particles. The results for modulus were extended to dynamic viscoelasticity by the corresponding principle. Experimental verifications with dynamic viscoelasticity data were conducted for the system of styrene–acrylonitrile copolymer interpolymerized with polybutadiene particles. For shear viscosity comparisons with experiment were made for the system linear polyethylene–polybutene-1.

INTRODUCTION

Several formulas have been presented to calculate the elastic modulus or viscosity of a two-phase system from those of its components. Mackenzie[1] calculated the elastic constants of a solid containing spherical holes, and Smallwood[2] presented a formula for evaluating the Young's modulus of a system, such as a rubber, in which small rigid spheres were embedded. Their formulas are valid only when the ratio of elastic constant of one component to that of the other is infinitesimal or infinite. Kerner[3] presented the expression for the gross bulk and shear moduli of a composite system consisting of two components with arbitrary values of modulus. His method is based on the averaging procedure of Bruggeman[4] and an analysis of the effect of a uniform hydrostatic compression and of a uniform tension acting on a particle. Recently, Okano[5] reported the same results as that of Kerner, but the procedure of Okano is not described in detail in his short report.

In this paper, the general formulas for evaluating the apparent elastic constants of a two-phase system consisting of spherical particles and their suspending medium are presented, and the results are extended to dynamic viscoelasticity by the corresponding principle. The method of deduction

of the apparent elastic constants is different from that of Kerner. Although the result obtained was found to be the same as Kerner's in the case of shear modulus, Poisson's ratio was expressed in a different form. The formulas obtained were surveyed by their application to the dynamic viscoelasticity of the real system consisting of styrene–acrylonitrile copolymer in which the rubber particles of polybutadiene are homogeneously dispersed by interpolymerization.

Since the Navier-Stokes equation reduces to an expression similar to the differential equation of displacement under appropriate conditions, the gross shear viscosity of a two-phase system consisting of the dispersing spherical particles and their suspending medium was calculated from the viscosity of the components, and the results were compared with the experimental data obtained on the system of polyethylene and polybutene-1.

THEORETICAL

Consider a spherical isotropic elastic particle of radius a embedded in a continuous isotropic elastic medium with known elastic constants. When the medium is stretched by a simple tension T, the displacement and the stress in the vicinity of the particle are calculated. The differential equation of displacement in equilibrium are given by eqs. (1):

$$\Delta u + \frac{1}{1 - 2\nu} \frac{\partial e}{\partial x} = 0$$

$$\Delta v + \frac{1}{1 - 2\nu} \frac{\partial e}{\partial y} = 0 \tag{1}$$

$$\Delta w + \frac{1}{1 - 2\nu} \frac{\partial e}{\partial z} = 0$$

where x, y, z are the Cartesian coordinates and u, v, w are the vector components of displacement at the point x,y,z. ν is the Poisson's ratio of the medium, e is the volume dilatation, and Δ is the Laplacian operator.

The boundary condition first arises from the fact that the influence of the particle will extend only over a limited region of the medium. The displacement at a point far from the particle will correspond to that caused by the simple tension T. The next boundary condition is that the particle and the medium are completely bounded by each other at their intersurface. These boundary conditions are expressed by eqs. (2) and (3).

At $r = \infty$:

$$\left(\frac{du_{r1}}{dr}\right)_{\theta = 0} = 2G_1(1 + \nu_1)T$$

$$\left(\frac{du_{r1}}{dr}\right)_{\theta = \pi/2} = -2\nu_1 G_1(1 + \nu_1)T \tag{2}$$

or

$$(\sigma_{r1})_{\theta=0} = T$$

$$(\sigma_{r1})_{\theta=\pi/2} = 0 \tag{2'}$$

At $r = a$:

$$u_{r1} = u_{r2}$$

$$u_{\theta1} = u_{\theta2}$$

$$u_{\varphi1} = u_{\varphi2}$$

$$\sigma_{r1} = \sigma_{r2} \tag{3}$$

$$\tau_{r\theta1} = \tau_{r\theta2}$$

$$\tau_{\varphi r1} = \tau_{\varphi r2}$$

where r, θ, φ are the spherical coordinates. The origin of the coordinates is located at the center of the particle, and the polar axis is oriented parallel to the direction of stretching. u_r, u_θ, u_φ are the components of displacement in the spherical coordinates. σ and τ are the normal and the shear stress, respectively. The quantities designated by the subscript 1 are those for the medium, and the quantities designated by 2 are for the particle.

Under the boundary conditions mentioned above, the displacement and the stress are derived from eq. (1) as follows.

For the region of $r \geq a$:

$$u_{r1} = \frac{rT}{2G_1} \left\{ -\frac{\nu_1}{1+\nu_1} + \frac{A_1}{r^3} + (5-4\nu_1)\frac{B_1}{r^3} - \frac{C_1}{r^5} \right.$$

$$\left. + \cos^2\theta \left[1 - (5-4\nu_1)\frac{B_1}{r^3} + 3\frac{C_1}{r^5} \right] \right\} \tag{4}$$

$$u_{\theta1} = \frac{rT\sin\theta\cos\theta}{2G_1} \left[-1 + 2(1-2\nu_1)\frac{B_1}{r^3} + 2\frac{C_1}{r^5} \right] \tag{5}$$

$$u_{\varphi1} = 0 \tag{6}$$

$$\sigma_{r1} = T \left\{ -2\frac{A_1}{r^2} - 2(1-3\nu_1)\frac{B_1}{r^3} + 4\frac{C_1}{r^5} + \cos^2\theta \right.$$

$$\left. \times \left[1 + 2(1-5\nu_1)\frac{B_1}{r^3} - 12\frac{C_1}{r^5} \right] \right\} \tag{7}$$

$$\tau_{r\theta1} = T\sin\theta\cos\theta \left[-1 + 2(1+\nu_1)\frac{B_1}{r^3} - 8\frac{C_1}{r^5} \right] \tag{8}$$
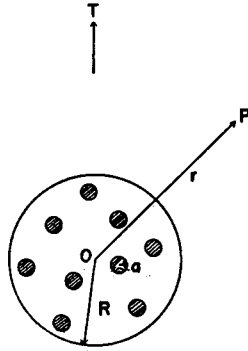
$$\tau_{\varphi r1} = 0 \tag{9}$$

Fig. 1. Model representation of two-composite system. The hatched portion represents the dispersed particles in the suspending medium.

For the region $r \leqq a$:

$$u_{r2} = \frac{rT}{2G_2} \left\{ A_2 + 2(1 - 2\nu_2)B_2 - \cos^2 \theta \left[3A_2 + 2(1 - 2\nu_2)B_2 \right] \right\} \quad (10)$$

$$u_{\theta 2} = \frac{rT \sin \theta \cos \theta}{2G_2} \left[3A_2 + 2(1 - 2\nu_2)B_2 \right] \quad (11)$$

$$u_{\varphi 2} = 0 \quad (12)$$

$$\sigma_{r2} = T \left\{ A_2 + 2B_2 - \cos^2 \theta \left[3A_2 + 2(1 - 2\nu_2)B_2 \right] \right\} \quad (13)$$

$$\tau_{r\theta 2} = T \sin \theta \cos \theta \left[3A_2 + 2(1 - 2\nu_2)B_2 \right] \quad (14)$$

$$\tau_{\varphi r2} = 0 \quad (15)$$

where A_1, A_2, B_1, B_2, and C_1 are the constants depending on the elastic constants and expressed as shown in eqs. (16)–(20).

$$A_1 = - \frac{a^3[(1 + \nu_1)(11 - 7\nu_1) + 2(4 - 2\nu_1 - 17\nu_2 - 8\nu_1\nu_2 + 15\nu_1{}^2\nu_2)\frac{G_1}{G_2} - (1 + \nu_1)(19 + 5\nu_1)(1 - 2\nu_2)]}{(1 + \nu_1)\left[2(4 - 5\nu_1) + (7 - 5\nu_1)\frac{G_1}{G_2} \right]\left[1 + \nu_2 + 2(1 - 2\nu_2)\frac{G_1}{G_2} \right]} \quad (16)$$

$$B_1 = \frac{5a^3[1 - (G_1/G_2)]}{2[2(4 - 5\nu_1) + (7 - 5\nu_1)(G_1/G_2)]} \quad (17)$$

$$C_1 = \frac{3a^5[1 - (G_1/G_2)]}{2[2(4 - 5\nu_1) + (7 - 5\nu_1)(G_1/G_2)]} \quad (18)$$

$$A_2 = \frac{\begin{array}{c} 46 - 30\nu_1 - 42\nu_1 - 20\nu_1\nu_2 + 30\nu_1{}^2\nu_2 - (1 - 2\nu_2) \\ \times (6 + 25\nu_1 - 15\nu_1{}^2)(G_1/G_2) \end{array}}{\begin{array}{c} 2(1 + \nu_1)[2(4 - 5\nu_1) + (7 - 5\nu_1)(G_1/G_2)] \\ \times [1 + \nu_2 + 2(1 - 2\nu_2)(G_1/G_2)] \end{array}} \quad (19)$$

$$B_2 = -\frac{3(1 - \nu_1)}{4(1 + \nu_1)[1 + \nu_2 + 2(1 - 2\nu_2)(G_1/G_2)]} \tag{20}$$

The terms of r^{-3} and r^{-5} in eqs. (4), (5), (7), and (8) come from the perturbation caused by the particle dispersed in the medium.

In order to find the elastic constants of the composite system, we now consider a spherical domain of radius R in medium 1, in which the particles of radius a are assumed to be homogeneously dispersed (Fig. 1). The radius of the spherical domain R is large enough compared with the radius of the particle a.

If the particles are not dispersed in the spherical domain, the field of displacement at a point P is uniform. The distance r of the point P from the origin O is very large compared to the radius of the spherical domain. However, the field at the point P is perturbed by the existence of n dispersed particles in the domain. The materials in the spherical domain with n dispersed particles is assumed to be an isotropic material having the apparent shear modulus G and Poisson's ratio ν. The perturbation is regarded as ΔU that is caused by spherical material of radius R located at the point O. On the other hand, if the interactions among the small particles in the domain are neglected, the perturbation is also n times as large as the effect Δu, which is independently caused by each small particle in the domain. These relations are expressed as follows:

$$\Delta U = n\Delta u \tag{21}$$

Since eq. (21) holds for any arbitrary distance r satisfying the condition that $r \gg R$, eq. (21) can be rewritten by the aid of eqs. (4), (5), and (6):

$$A = nA_1 \tag{22}$$

$$B = nB_1 \tag{23}$$

$$C = nC_1 \tag{24}$$

where A, B, and C are the quantities when G_2, ν_2, and r in eqs. (16) to (18) are replaced by G, ν, and R, respectively. Equations (22)–(24) do not simultaneously hold for any arbitrary n. Under the condition that $r \gg R$, the effect of the term of r^{-5} upon the displacement at the point P is very small and negligible compared with the effect of r^{-3}. Therefore, eq. (24) need not be considered. By putting eqs. (16) and (17) into eqs. (22) and (23) and arranging them, we obtain eqs. (25) and (26):

$$G = G_1 \frac{(7 - 5\nu_1)G_1 + (8 - 10\nu_1)G_2 - (7 - 5\nu_1)(G_1 - G_2)\nu}{(7 - 5\nu_1)G_1 + (8 - 10\nu_1)G_2 + (8 - 10\nu_1)(G_1 - G_2)\nu} \tag{25}$$

$$\nu = \left[-(1 - 7\nu_2 + 10\nu_1\nu_2)\frac{G_1}{G_2} + (1 + \nu_2)\frac{G_1}{G_2} + 2\nu_2(1 - 5\nu_1)\frac{G_1^2}{GG_2} \right.$$

$$\left. + (1 - 5\nu_1)(1 - 2\nu_2)\frac{G_1^2}{G_2^2} - (1 - 5\nu_1)(1 + \nu_2)\frac{G_1^2}{G^2} \right.$$

$$- (1 + 5\nu_1)(1 - 2\nu_2) \frac{G_1{}^3}{GG_2{}^2} + (1 + 5\nu_1 - 9\nu_2 - 5\nu_1\nu_2) \frac{G_1{}^3}{G^2 G_2} \Bigg] \Bigg/$$

$$\left[(1 - 7\nu_2 + 10\nu_1\nu_2) \frac{G_1}{G_2} + (7 - 10\nu_1)(1 + \nu_2) \frac{G_1}{G} + 2(1 - 5\nu_1) \right.$$

$$\times \frac{G_1{}^2}{GG_2} - (1 - 5\nu_1)(1 - 2\nu_2) \frac{G_1{}^2}{G_2{}^2} - 2(1 - 5\nu_1)(1 + \nu_2) \frac{G_1{}^2}{G^2}$$

$$\left. - (9 + 5\nu_1)(1 - 2\nu_2) \frac{G_1{}^3}{GG_2{}^2} + 2(1 + 5\nu_1 - 9\nu_2 - 5\nu_1\nu_2) \frac{G_1{}^3}{G_2 G^2} \right] \quad (26)$$

where the volume fraction of the dispersed particles to the total volume in the spherical domain is given by $v = na^3/R^3$. Equations (25) and (26) give the effective shear modulus and the Poisson's ratio of the composite system consisting of the dispersed particles and their suspending medium. When the media of composite system are noncompressible materials, that is $\nu_1 = \nu_2 = 0.5$, the tensile modulus of the system E is given by eq. (27):

$$E = E_1[3E_1 + 2E_2 - 3(E_1 - E_2)v]/[3E_1 + 2E_2 + 2(E_1 - E_2)v] \quad (27)$$

where E_1 and E_2 are the moduli of the medium and the particles, respectively.

APPROXIMATION

Since the interaction between the particles has been ignored in deriving eqs. (25) and (26), the volume fraction v should satisfy the condition that

$$v \ll 1 \quad (28)$$

If the terms of v^2 and higher powers in eqs. (25) and (26) are neglected, they reduce to eqs. (29) and (30), respectively.

$$G = G_1 \left[1 - \frac{15(1 - \nu_1)(G_1 - G_2)}{(7 - 5\nu_1)G_1 + (8 - 10\nu_1)G_2} v \right] \quad (29)$$

$$\nu = \nu_1 \left\{ 1 + 3(1 - \nu_1) \left[(1 - 2\nu_1)(1 - 5\nu_1)(1 + \nu_2) - 2(1 + 2\nu_1 - 8\nu_2 \right. \right.$$

$$\left. + 8\nu_1\nu_2 - 5\nu_1{}^2 + 10\nu_1{}^2\nu_2) \frac{G_1}{G_2} + (1 + \nu_1)(1 - 5\nu_1)(1 - 2\nu_2) \frac{G_1{}^2}{G_2{}^2} v \right] \Bigg/$$

$$\left. \nu_1 \left[(8 - 10\nu_1) + (7 - 5\nu_1) \frac{G_1}{G_2} \right] \left[1 + \nu_2 + 2(1 - 2\nu_2) \frac{G_1}{G_2} \right] \right\} \quad (30)$$

When the very hard particles are dispersed in the medium, that is $G_1 \ll G_2$, the apparent shear modulus and the Poisson's ratio of the system are given by eqs. (31) and (32) respectively.

$$G = G_1 \left[1 + \frac{15(1 - \nu_1)}{2(4 - 5\nu_1)} v \right] \quad (31)$$

$$\nu = \nu_1 \left[1 + \frac{3(1 - \nu_1)(1 - 2\nu_1)(1 - 5\nu_1)}{2\nu_1(4 - 5\nu_1)} \cdot v \right] \qquad (32)$$

Substituting 0.5 for ν_1 in eqs. (31) and (32), we obtain

$$G = G_1(1 + 2.5v) \qquad (33)$$

$$\nu = 0.5 \qquad (34)$$

The same relation as eq. (33) holds for the Young's modulus E, because of $\nu = 0.5$, that is

$$E = E_1(1 + 2.5v) \qquad (35)$$

Equation (35) agrees with the equation previously derived by Smallwood,[2] who discussed the filler effect of carbons on the modulus of rubber.

On the other hand, when the holes are dispersed in the medium, that is $G_1 \gg G_2$, eqs. (29) and (30) are reduced to the following forms:

$$G = G_1 \left\{ 1 - \frac{15(1 - \nu_1)}{7 - 5\nu_1} v \right\} \qquad (36)$$

$$\nu = \nu_1 \left\{ 1 + \frac{3(1 - 5\nu_1)(1 - \nu_1{}^2)}{2\nu_1(7 - 5\nu_1)} v \right\} \qquad (37)$$

Equations (36) and (37) agree with Mackenzie's equation[1] which gives the elastic constant of the system having small holes. Equations (25) and (26) are the general expression of the effective elastic constant of the two-phase system dispersed by the spherical particles and, as their limiting cases, accord with Mackenzie's and Smallwood's equations.

APPLICATION OF THE THEORY TO EXPERIMENTAL DATA
Dynamic Viscoelasticity

In deriving the foregoing equations, it is assumed that the medium and the dispersed particles are elastic. It will be allowed, however, to extend these equations to the viscoelastic cases by the corresponding principle. Moreover, if the frequency of the applied stress is small and the wave length in the media is sufficiently small compared with the size of dispersed particles, the foregoing expression for effective moduli of the elastic composite system may be transcribed to the dynamic viscoelastic cases. Then, the expression of eqs. (25) and (27) are transcribed as follows:

$$G^* = G_1{}^* \frac{(7 - 5\nu_1)G_1{}^* + (8 - 10\nu_1)G_2{}^* - (7 - 5\nu_1)(G_1{}^* - G_2{}^*)v}{(7 - 5\nu_1)G_1{}^* + (8 - 10\nu_1)G_2{}^* + (8 - 10\nu_1)(G_1{}^* - G_2{}^*)v} \qquad (38)$$

$$E^* = E_1{}^* \frac{3E_1{}^* + 2E_2{}^* - 3(E_1{}^* - E_2{}^*)v}{3E_1{}^* + 2E_2{}^* + 2(E_1{}^* - E_2{}^*)v} \qquad (39)$$

where the asterisk (*) refers to complex quantities. It should be noted that eq. (39) holds when the dispersed particles and the suspending medium
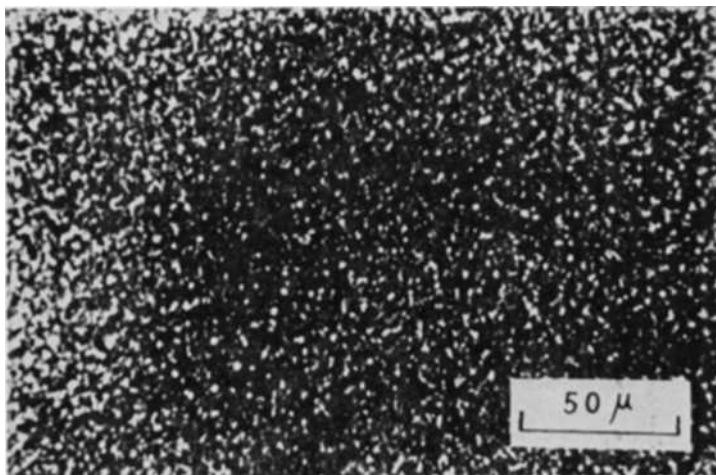
Fig. 2. Microphotograph of interpolymers of polybutadiene with styrene and acrylonitrile. White regions are polybutadiene rubber and black regions are styrene–acrylonitrile copolymer.

are noncompressible. Since the Poisson's ratio for polymer, however, is usually about 0.5, eq. (39) may be used for calculating the modulus of a system of two-component polymers.

The theory was verified by applying eq. (39) to the system of particles of polybutadiene rubber homogeneously dispersed in styrene–acrylonitrile copolymer. This system is widely known as ABS resin and manufactured commercially for use in high-impact plastics. This resin is a typical system and consists of hard medium and soft particles dispersed as separated phase. The reversal case, where the hard particles are homogeneously dispersed in the soft phase, corresponds to the rubber system dispersed by fillers, such as carbon black or silicate. Many detailed measurements have been made on the latter system. It is more appropriate to select plastics with dispersed butadiene rubber particles for verification of our theory, since no quantitative description has been reported on the mechanical properties of this system, and it will have some engineering significance to predict the properties of this system from those of the component polymers.

Interpolymers of polybutadiene (PBD) with styrene (ST) and acrylonitrile (AN) were prepared by Dr. E. Shiraki, by the following method. A 50-g. portion of PBD in the emulsion state, 160 g. of water, 18 g. of ST were polymerized in an emulsion state at 60°C. for 4 hr. by the use of redox catalyst. Blends with various composition of the interpolymers and the ST–AN copolymer were prepared by emulsion polymerization of 60 g. of ST and 36 g. of AN at 60°C. for 4 hr.; the nitrogen content on analysis of this polymer was 7.66%. The volume fraction of PBD in the blend was determined from the nitrogen content. The films for measurement of dynamic viscoelasticity were made by the hot-press at 180°C. Figure 2
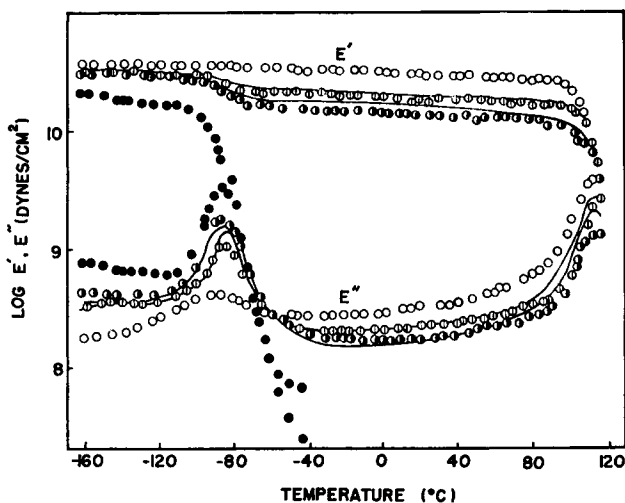
Fig. 3. Temperature dependence of dynamic modulus E' and loss modulus E'' for the interpolymers of PBD with ST-AN at 138 cycles/sec.: (———) calculated from the present theory; (O) experimental data for ST-AN copolymer; (●) PBD rubber; (◑), (◐) interpolymer of PBD and ST-AN for the volume fraction of PBD 0.23 and 0.34, respectively.

is a phase-contrast microphotograph of the blend of the interpolymer used in this paper. White regions are polybutadiene rubber and the black regions correspond to the ST–AN copolymer.

This differs clearly in appearance from the material obtained by simple roll-mixing of polybutadiene and ST–AN copolymer without any polymerization process, in which large globules are found in a more heterogeneous state. Absence of graft polymerization in the latter case is the reason for this difference.

To measure the dynamic tensile modulus E^* of a sample, the authors used a direct-reading dynamic viscoelastometer (Toyo Measuring Co., Ltd., Vibron Model DDV-1) which was constructed on the basis of a principle developed in the laboratory of the authors.[6] The value of loss tangent tan δ is directly read off on the meter by adjusting the electrically converted amplitude of stress s and strain γ to unity and subtracting the converted strain vector from the converted stress vector. The real part E' of the dynamic tensile modulus E^*, that is, dynamic modulus, is easily calculated by $(s/\gamma) \cos \delta$. The imaginary part E'' of E^*, is given by $E' \tan \delta$.

Figure 3 shows the temperature dependence of dynamic modulus E' and loss modulus E'' for the interpolymers of PBD with ST and AN monomers (with different compositions) at 138 cycles/sec. The solid curves of Figure 3 are calculated by eq. (39), using the volume fraction of PBD evaluated by the analytical method. The Poisson's ratios of the particle and the medium are assumed to be 0.5. E_1^* and E_2^* in eq. (39) are dynamic tensile moduli of styrene–acrylonitrile copolymer and polybutadiene, respectively. v is the volume fraction of polybutadiene. As
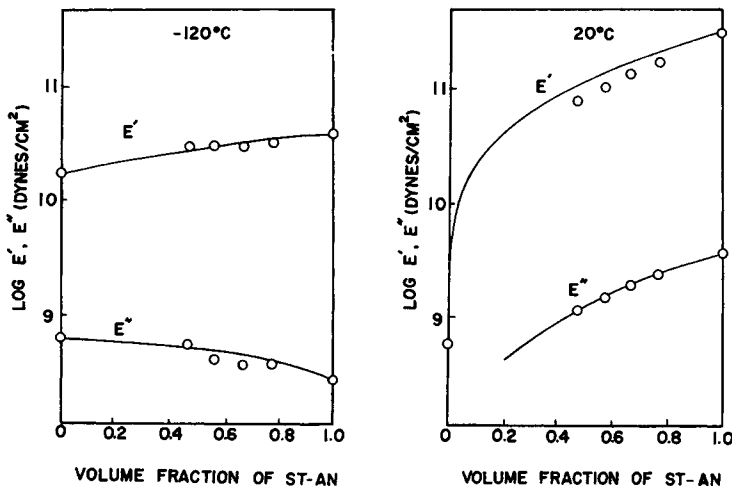
Fig. 4. Comparison of experiments with theory for dynamic modulus E' and loss modulus E'' of the interpolymer PBD with ST–AN at temperatures of -120 and $20°$C.: (———) calculated from the present theory; (O) experimental data.

there are no data available for polybutadiene at a temperature over $-45°$C., it is assumed that the dynamic modulus E' of polybutadiene at the temperature is 5×10^7 dynes/cm.^{2} and that the loss modulus E'' is negligibly small. Figure 3 shows that the theoretical prediction for the system with the volume fraction $v = 0.2$ agrees satisfactorily with the experimental results over a temperature range from -160 to $120°$C.

Figure 4 shows the relation between the modulus of the composite system and its composition at -120 and $20°$C. With increasing volume fraction of PBD, the disagreement between the experimental and the theoretical results increases. This disagreement is attributable to the fact that, in a process of deducing eqs. (25) and (27), we ignored the interactions among the dispersed particles and that the particles are in a perfect spherical shape. With increasing volume fraction of polybutadiene, its shape is not considered to be perfectly spherical and the interaction among the particles will become significant.

The equations of Mackenzie[1] and Smallwood[2] or Smallwood and Guth[7] have been applied to a system in which the modulus of the dispersed spherical particles is overwhelmingly low or high compared with that of the medium. It should be noticed that eqs. (25) and (26) hold independently of the moduli of the dispersed particles and the medium. The equations of Mackenzie and Smallwood can be deduced from eqs. (25) and (26) as the limiting cases.

Shear Viscosity

When a change of hydrostatic pressure in a fluid is absent and the force of inertia is negligible compared with the viscous force of the fluid, the Navier-Stokes equation for a fluid is reduced to the same form as that of the funda-

mental equation for elasticity. Therefore, the viscosity coefficient η of a composite system consisting of a viscous fluid of viscosity η_1 in which spherical particles of viscosity η_2 are homogeneously dispersed can be calculated by the analogous method as in elasticity. The formula obtained agrees with the equation for shear modulus, being different only in the point that the shear modulus G is replaced by the shear viscosity, that is,

$$\eta = \eta_1 \frac{(7 - 5\nu_1)\eta_1 + (8 - 10\nu_1)\eta_2 - (7 - 5\nu_1)(\eta_1 - \eta_2)v}{(7 - 5\nu_1)\eta_1 + (8 - 10\nu_1)\eta_2 + (8 - 10\nu_1)(\eta_1 - \eta_2)v} \tag{40}$$

Equation (40) also holds for the complex shear viscosity η^*, when the frequency of the applied shear stress is small enough for the inertia force and the wave length in the fluid is sufficiently small compared with the size of dispersed particles. This relation is entirely the same as that between elastic shear modulus G and complex shear modulus G^*. Equation (41) is obtained from eq. (40)

$$\eta^* = \eta_1^* \frac{(7 - 5\nu_1)\eta_1^* + (8 - 10\nu_1)\eta_2^* - (7 - 5\nu_1)(\eta_1^* - \eta_2^*)v}{(7 - 5\nu_1)\eta_1^* + (8 - 10\nu_1)\eta_2^* + (8 - 10\nu_1)(\eta_1^* - \eta_2^*)v} \tag{41}$$

Experimental verification was conducted on the composite system of linear polyethylene (PE) and polybutene-1 (PB-1). Pellets of PE and PB-1 were mixed by hot rolling at about 150°C. for 20 min. and pressed to form a sheet 2 mm. in thickness.

The viscosity of the specimen was measured by use of a parallel plate plastometer of the commercial type. After the sample was heated at the desired temperature, the load was applied to two parallel plates and the distance between the two parallel plates was read off as a function of time. The shear viscosity was determined by a standard method. The fact that the satisfactory linear relation between the square of reciprocal distance of the parallel plates and time was obtained shows that the viscosity determined corresponds with the Newtonian viscosity. Measurements were made by Dr. Yujiro Kosaka and Mr. Masatoshi Sato of Toyo Soda Co., Ltd.

Figure 5 shows the relation between the zero-shear viscosity and the composition at 161 and 182°C. The upper solid curves in Figure 5 were calculated by eq. (40), assuming that the particles of PE were embedded in the matrix of PB-1. The lower solid curves were calculated assuming that the particles of PB-1 were embedded in PE. The Poisson ratios of both PE and PB-1 were assumed to be 0.5 in the calculation. With increasing volume fraction of PE, the experimental values of viscosity gradually increase and deviate from the lower theoretical values. When the fraction increases by 20–30%, the experimental curves deviate remarkably from the lower theoretical and finally approach the upper theoretical curves. As a whole, the experimental curves assume an S shape. This is interpreted as follows. The viscosity of the two-phase system, which consists of PE in which a little of inclusion of PB-1 of high viscosity is embedded, is close to the viscosity of PE and may be determined theoretically by the
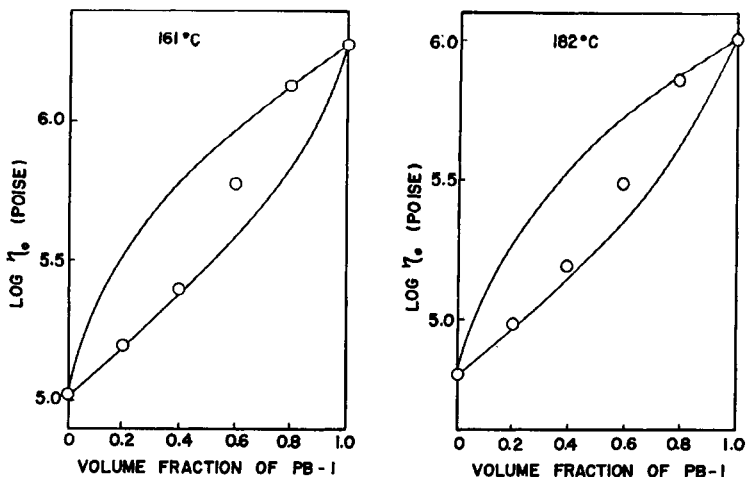
Fig. 5. Comparison of experiment with theory for zero-shear viscosity of composite system of polyethylene and polybutene-1 at temperatures of 161 and 182°C.: (O) experimental data; (———) theoretical curves (upper curves calculated on assumption that PB-1 particles are embedded in a PE matrix; lower curves calculated for PE embedded in a PB-1 matrix).

eq. (40) under the condition that inclusions of PB-1 are dispersed in a matrix of PE. For the system that consists of PB-1 in which a little PE is dispersed, the eq. (40) is also available, being different only in the point that the material of the matrix of the former system is the inclusion in this case. In the intermediate fraction, the inversion of material of a matrix is occurring, and it is impossible to classify inclusions from a matrix. Therefore, it is reasonable that the theoretical result disagrees with the experiment. Such an inversion generally occurs with increasing fraction of inclusions.

The curve of viscosity of the two-component system versus its composition generally assumes an S shape. Such a phenomenon also occurs with the modulus of polymer blends. Considering the inversion of the material of a two-phase matrix, the theory gives satisfactory results. However, the S-shape phenomenon cannot be expressed in detail by the theory.

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Résumé

Un essai d'évaluation de la constante élastique apparente d'un système à deux phases G au départ de celles des composants du système a été décrit. (L'expression du module G est donnée dans le résumé anglais); G_1 et G_2 sont les modules du milieu de suspension et des particules en suspens respectivement, ν_1 est le rapport de Poisson du milieu et ν la fraction de volume des particules. Le résultat concernant le module a été étendu à la viscosité dynamique par le principe de correspondante. Des vérifications expérimentales concernant la viscosité dynamique ont été effectuées sur le système du copolymère styrène–acrylonitrile avec des particules de polybutadiène. Des vérifications expérimentales concernant la viscosité de cisaillement ont été effectuées sur un système formé de polyéthylène linéaire et de polybutène-1.

Zusammenfassung

Ein Versuch zur Ermittlung des scheinbaren Elastizitätsmoduls eines Zweiphasensystems, G, aus den Moduln der Komponenten des Systems wurde unternommen. (Den Ausdruck für den Modül G siehe englische Zusammenfassung) Das Ergebnis für den Modül wurde in entsprechender Weise auf die dynamische Viskosität ausgedehnt. Eine experimentelle Bestätigung der Aussagen für die dynamische Viskosität wurde am System der Interpolymerisation des Styrol–Acrylnitrilkopolymeren mit Polybutadienteilchen gewonnen. Eine experimentelle Bestätigung bezüglich der Schubviskosität wurde an einem zusammengesetzten System aus linearem Polyäthylen und Polybutan-1 durchgeführt.