Blend Rules for Homogenous and Heterogenous Systems

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SYNOPSIS

Blend rules for (a) homogeneous and (b) heterogeneous systems are proposed in a form of $P = (\phi_1^m P_1 + \phi_2^m P_2)/(\phi_1^m + \phi_2^m)$, where P is the property, and ϕ, the volume fraction of component 1 or 2. For (a) $m > 1$ and for $P_2 > P_1$, an S-shaped relation occurs between P or ϕ_1. On the contrary, for (b) $m < 1$, an anti-S-shaped relation occurs. When the hard component forms particles in continuous soft media, P is larger than the arithmetic mean $\bar{P}$. When the interface slips, a mean of harmonic function holds so that $1/P = \phi_1/P_1 + \phi_2/P_2$ and $P < \bar{P}$. For special cases, i.e., the filler in the rubber and the rubber particles in the resin, the strength at break attains a maximum at 20 and 13% of particles, respectively. For rubber blended with a small amount of polypropylene by dynamic vulcanization, the latter forms a continuous phase, reinforcing rubber domains by the plastic force when the size of rubber particles becomes very small. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The multicomponent systems of polymers are the topics of the day,[1] because they often exhibit excellent properties. They are blends of polymers and are often called polymer alloys, similary to metallic alloys, although the definition is not simple and precise. Polymer blends are mostly heterogeneous mixtures except in some limited cases due to their poor miscibility and sometimes they are merely a mixture of polymers and other ingredients.

Various blend rules have been proposed. For example, the author[2] proposed the following equation of the viscosity η of the blend of components 1 and 2 whose viscosities are η_1 and η_2, respectively, and the volume or molar fractions are ϕ_1 and ϕ_2, respectively:

$$(\log \eta)^n = \phi_1 (\log \eta_1)^n + \phi_2 (\log \eta_2)^n$$

When n is larger than unity, $\log \eta$ is larger than the arithmetic mean, i.e., the case of n equal to 1. According to Park,[3] it implies a positive deviation. For n less than unity, it shows a negative deviation.

In general, property P is expressed as the n-order mean with respect to P:

$$P^m = \phi_1 P_1^m + \phi_2 P_2^m \qquad (1)$$

Equation (1) was proposed for the elasticity E where 1 is adopted for m.[4] As a special case of this type, there is the mean of the reciprocal property or the case of m of -1.[5]

However, for homogeneous blends of polymers, the mean with respect to the order of the fraction ϕ may be available, because the polymer coils entangle with each other and the number of entanglements or the pseudo-cross-link ν, the time τ for its relaxation, and the viscosity η are proportional to ϕ^2, ϕ^2, and ϕ^4, respectively.[6] For example, the elasticity E is expressed simply as

$$E = \phi_1^2 E_1 + \phi_2^2 E_2 + 2\phi_1 \phi_2 E_{12} \qquad (2)$$

Where E_{12} is concerned with a mutual entanglement of chains of each component.

On the contrary, in the heterogeneous blend, each component forms independent domains and its contribution to the mechanical property such as elasticity or viscosity is proportional to the concentration of each component locating in the cross section of the specimen and the contribution is mostly pro-

portional to the two-thirds power of each fractions, $\phi^{2/3}$. In other words, n in eq. (3) in the following paragraph is $\frac{2}{3}$ and the positive deviation is expected, but n is much affected by the mobility of the domain on its interface.

This article deals with blend rules in terms of the properties and the morphological states.

THEORY

Homogeneous System

According to the pseudo-cross-link theory, the entanglement of chains is proportional to a square of the concentration of the chains. Accordingly, property P is to be expressed as

$$P = \{\phi_1^m P_1 + \phi_2^m P_2 + 2(\phi_1^m \phi_2^m)^{1/2} P_{12}\}/$$
$$(\phi_1^{m/2} + \phi_2^{m/2})^2 \quad (3)$$

The third term is concerned with the mutual entanglement of components 1 and 2 and P_{12} is its property. Here, m is larger than unity. If P_{12} is taken to be the geometry mean or $(P_1 P_2)^{1/2}$, and the ratio P_2/P_1 is taken to be larger than unity, eq. (3) is transformed to

$$P = P_1\{(1 + x^{m/2} r^{1/2})/(1 + x^{m/2})\}^2 \quad (4)$$

where x is ϕ_2/ϕ_1 and r is P_2/P_1.

For the arithmetic mean $\bar{P}$, m is taken to be unity and the ratio $P/\bar{P}$ is given as

$$\left(\frac{P}{\bar{P}}\right)^{1/2} = \frac{1 + 1/(x^m r)^{1/2}}{1 + 1/(xr)^{1/2}} \cdot \frac{1 + 1/x^{1/2}}{1 + 1/x^{m/2}}$$
$$\cong 1 + (1/r^{1/2} - 1)(1/x^{m/2} - 1/x^{1/2}) \quad (5)$$

Equation (5) becomes

$$P/\bar{P} = 1 \quad \text{for } x = 1 \quad (6)$$

Thus, the region of $x > 1$ gives the positive deviation, whereas that of $x < 1$ gives the negative one. In other words, eq. (5) gives an S-shaped relation between P and ϕ_2, as shown in Figure 1.

Heterogeneous System

The polymer blend is formed mostly of the mutual dispersion or the particles-continuous phase. The property depends not only on the morphological structure but also on the property of the interface,
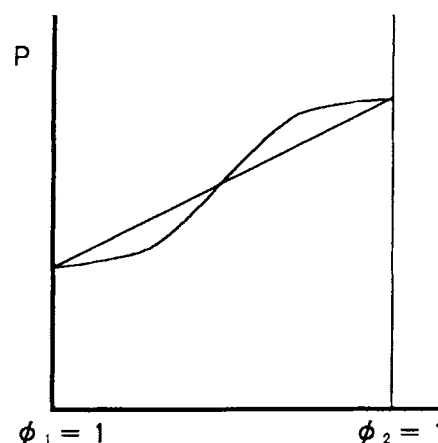

Figure 1 Homogeneous system.

mobile or immobile under deformation of the specimen. As model cases, the following types are proposed:

(a) Hard-particle dispersion in soft medium: Taking component 2 as the hard component and component 1 as the soft one and with the former forming the particles dispersed in the later continuous phase, the ratio of the properties $P_2/P_1 = r$ is larger than unity and the average property P becomes

$$P = (1 - \phi_2^m)P_1 + \phi_2^m P^2$$
$$= P_1 + (P_2 - P_1)\phi_2^m \quad (7)$$

The difference between P and the arithmetic mean $\bar{P}$ becomes

$$P - \bar{P} = (P_2 - P_1)(\phi_2^m - \phi_2) > 0 \quad (8)$$

because $m < 1$ and $\phi_2 < 1$. This means a positive deviation.

(b) Mutual dispersion: When both components form independent domains that disperse into each other, P is expressed as

$$P = (\phi_1^m P_1 + \phi_2^m P_2)/(\phi_1^m + \phi_2^m) \quad (9)$$

This is similar to eq. (3), but m is $\frac{2}{3}$ or less than unity. The equation is modified as

$$P = P_2(1 - x^m r)/(1 + x^m)$$

and is compared with the arithmetic mean, i.e.,

$$\bar{P} = P_2(1 + xr)/(1 + x)$$

and it follows that

$$P/\bar{P} \cong 1 - (r - 1)(x^m - x) \quad (10)$$

Equation (10) becomes larger than unity for the region of $x < 1$ and smaller for that of $x > 1$. This gives an anti-S-shaped relation between P and ϕ_1.

(c) Particle dispersion slipping in the interface: The slippage, if it occurs, allows formation of the different deformations of each domain and, e.g., the elastic force f becomes

$$f = \phi_1 E_1 \alpha_1 + \phi_2 E_2 \alpha_2 \quad (11)$$

where E_1 and E_2 are the elasticity, and α_1 and α_2, the deformation of each component. When the slippage is completely independent of each other and the force of each domain is balanced as

$$E_1 \alpha_1 = E_2 \alpha_2 = E\alpha \quad (12)$$

where α and E are the deformation and the elasticity of the specimen, respectively. Inserting eq. (12) into eq. (11), it follows that

$$1/E = \phi_1/E_1 + \phi_2/E_2 \quad (13)$$

Thus, the average is expressed as a harmonic function. A similar equation also holds for the viscosity η, because the viscous force f is proportional to η and the shear rate $\dot{\gamma}$ and the relation such as $\eta_1 \dot{\gamma}_1 = \eta_2 \dot{\gamma}_2$ is assumed.

In general, property P is expressed by an equation similar to eq. (13) or

$$P = (P_1/\phi_1)\{1/(1 + x/r)\} \quad (14)$$

The ratio $P/\bar{P}$ becomes

$$\frac{P}{\bar{P}} = \frac{P_1}{\phi_1^2} \frac{1}{(1 + x/r)(1 + x)} \quad (15)$$

For the region of $x < 1 < r$, $P/\bar{P}$ becomes less than unity, giving a negative deviation.

The schematic diagrams of the cases (a), (b), and (c) are shown in Figure 2.

Special Cases

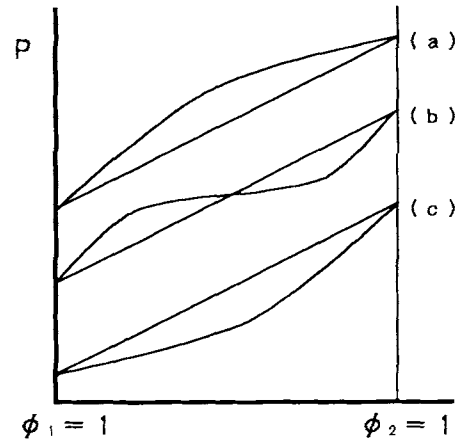As special cases, the reinforcement of rubber by active fillers and the improvement of the impact

Figure 2 Heterogeneous system.

strength of the resin with the dispersion of rubber particles were discussed in the preceding paper.[7] They are summarized as follows:

(a) Active filler: Filler is a solid particle and it does not deform but exerts the influence upon the matrix rubber. For the small deformation, no slip takes place and the deformation of the rubbery matrix is enhanced, and as a result, it gives rise to the increase of the stiffness as expressed by the Guth–Gold eq. (16):

$$E = E_1/(1 - a\phi_2)$$
$$= E_1\{1 + a\phi_2 + (a\phi)^2 + \cdots\} \quad (16)$$

where the coefficient "a" runs parallel to the thickness of the adsorbed layer on the filler particle and it is mostly 2.5. For the case of the large deformation or the case of rupture, the slip takes place, and instead of the elastic force, the viscous resistance of the interface is the main part. It is so large that it gives a larger reinforcement than that in the elastic rupture. In the preceding paper, E is proportional to $\phi^{2/3}$, the specific surface area equal to a reciprocal of the diameter of particle d, and the adsorption constant K:

$$E \propto \phi^{2/3} K/d \quad (17)$$

On the other hand, the relaxation time τ for the slippage is decreased with decreasing the portion of rubber due to the incorporation of filler as

$$\tau \propto (1 - a\phi)^{1/3} \quad (18)$$

Also, the elongation α and the force f for the

plastic rupture are expressed, respectively, as

$$\alpha = 2\dot{\alpha}\tau \propto (1 - a\phi)^{1/3} \qquad (19)$$

and

$$f = E\tau\dot{\alpha}\alpha \propto \phi^{2/3}(1 - a\phi)^{2/3} \qquad (20)$$

giving a maximum of f at the fraction ϕ equal to $\frac{1}{2}a$ or 0.2 for a of 2.5.

(b) Rubber dispersion in resin: The rubbery dispersion in the resin has little effect on the elasticity of the matrix but exerts a great improvement to the impact strength. This is due to the retardation of the propagation of craze. Since the propagation proceeds linearly, the force balance between (1) the rubbery particle and (2) the matrix resin is expressed with a one-third power of the volume fraction ϕ as

$$\phi_1^{1/3}\alpha_1 E_1 = \phi_2^{1/3}\alpha_2 E_2 \qquad (21)$$

Equation (21) leads to the increase of the impact energy W, which is given by $\phi E\alpha^2$ and the following relation:

$$\begin{aligned} W &= \phi_1 E_1 \alpha_1^2 + \phi_2 E_2 \alpha_2^2 \\ &= w_2 \{ \phi_2 + (E_2/E_1)(\phi_1\phi_2^2)^{1/3} \} \end{aligned} \qquad (22)$$

Equation (22) gives a maximum of W at ϕ_2 of $\frac{1}{3}a$ or 0.13 for a of 2.5 and 0.33 for a of 1.

(c) Rubber reinforced by the resin layer: A special rubbery material is prepared by mixing the latex and the vulcanized latex or by so-called dynamic vulcanization of ethylene–propylene–diene rubber (EPDM) mixed with a small amount of polypropylene. In these cases, the fraction of the rubbery domain is larger than that of the resinous one, but the former exists as the dispersion of small particles, and the latter, as a continuous thin film covering the rubbery domain. It shows the rubbery elasticity and also the high tensile strength of the resin.

The authors assumed that the polypropylene domain forms a thin film partly reacted with rubber and covers the rubbery particle. The elastic force of the specimen comes from the deformation of (1) the rubbery domain, which is balanced with the plastic force of (2) the resinous film and the interface tension. It was found to exhibit a

large hysteresis due to the plastic force and the following relation is proposed at break:

$$\begin{aligned} \phi_1^{2/3} E_1 \alpha &= \phi_2^{2/3} \eta_2 \dot{\alpha}\alpha \\ &+ \phi_1^{2/3}(6\gamma/d)(ds/d\alpha)\alpha \end{aligned} \qquad (23)$$

where the elongation ratio α is assumed to be same in each domain and also in the interface, and the rubbery particles deform from a sphere of diameter d to an ellipsoid, whose longitudinal length is αd and the diameter is $d/\sqrt{\alpha}$. Then, the surface tensional force is given by a product of the surface tension γ and the surface change $(ds/d\alpha)$, i.e., $\alpha^{1/2}$. It leads to equations for the elongation α and the strength f at break as

$$\alpha^{1/2} = \frac{(6/d)(\gamma/E_1)}{1 - (\phi_2/\phi_1)^{2/3}(\eta_2\dot{\alpha}/E_1)} \qquad (24)$$

and

$$f = \phi_2^{2/3}\eta_2\dot{\alpha}\alpha = \phi_2^{2/3}\eta_2\dot{\gamma}(6\gamma/E_1 d)^2 \qquad (25)$$

These equations indicate that both elongation ratio α and strength f at break increase with decreasing the particle diameter d and given an anti-S-shaped relation between f and the fraction ϕ_2 or ϕ_2/ϕ_1.

DISCUSSION

Blend rules mentioned above are so wide that the examination needs much time for a large number of experiments to be done and, at present, some examples are taken from the literature:

(a) As a homogeneous system, the so-called interpenetrating network (IPN) has been proposed in the literature. It is prepared by the polymerization of another monomer in the swollen polymer network.[9] However, in most cases, the monomer forms domains after polymerization due to poor solubility of the prepared polymer. The resulting material often exerted excellent mechanical properties that were believed to arise from the IPN structure, but the morphological study appearing in the literature shows that it is the systems of heterogeneous dispersions in most cases.[1] The improvement in the mechanical properties seems, rather, to be attributed to the heterogeneous dispersion.

(b) For the heterogeneous system, the experiment of Park[3] is interesting to note. It was concerned with the melt viscosity of a nylon-polypropylene blend prepared in the presence of the polypropylene grafted with maleic anhydride as a compatibilizer.

The diagram between the viscosity and composition indicated that it was very similar to Figure 2: It shows a diagram of a positive deviation type and it changes to the S-shape one with increasing rate of deformation and, finally, it attains a diagram of a negative deviation type.

The morphology in his report indicates a nylon dispersion existing in the continuous medium of polypropylene and it changes to a mutual dispersion system with increasing rate of deformation.

(c) The properties of the polypropylene–EPDM blend prepared by the dynamic vulcanization method were reported by Coran and Patel in detail.[10] The data show the great increase both in elongation and strength at break with decreasing the diameter of particle to less than 1 μm.

The stress–strain cycle diagram prepared by the author[11] with the commercial sample shows a large hysteresis and it was found to be arising from the viscous flow of the polypropylene domain. Details will be published in a separate paper.

CONCLUSION

As mentioned above, the properties of the polymer blend change with various factors and the application of blend rules should be done on the basis of knowledge of the morphology and rheology.

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