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## Abstract

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## PHYSICAL CHEMISTRY

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# ON THE ASSESSMENT OF POLYMER COMPATIBILITY

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The attainment of a specified degree of dispersion of compatible polymer components can, under certain conditions, be achieved spontaneously at a very low mixing rate. However, this process can be considerably accelerated by the method of forced dispersion. The high viscosity of polymers and the absence of transverse chemical bonds between macromolecules make it possible in most cases to carry out forced dispersion of both compatible and incompatible components. In this case two possibilities arise: (a) the process of mutual dissolution of high-molecular-weight components and (b) the forced formation of a mixture having a tendency toward separation of the components. In the first case the selected pair of polymers is "thermodynamically compatible" and therefore constitutes a thermodynamically stable system. In the second case dispersion can be forced and can be carried out down to the size of macromolecules, but with time in such a system separation in microregions and an increase in inhomogeneity will occur. The two indicated cases differ fundamentally chiefly in the direction of the processes by which equilibrium is attained.

Thermodynamically compatible polymers, even if only coarsely dispersed in one another, will subsequently gradually increase the degree of dispersion, ultimately forming a molecular mixture. Thermodynamically incompatible polymers, on the contrary, even under molecular forced dispersion, will tend with time to decrease the degree of dispersion. However, polymers may be thermodynamically compatible not at all ratios, but only within a certain interval of relative fractions of the components in the mixture.

A widely used method for assessing polymer compatibility is based on the magnitude of the deviation of property–composition curves for a mixture from additive dependence. But very many of the properties studied for mixtures may be additive quantities. In certain cases the presence of extrema on property–composition curves is characteristic even of highly homogeneous mixtures. Owing to their own large dimensions (of the order of the size of colloidal particles), each individual macromolecule of one polymer in the medium of another is a microinhomogeneity, which, for example, may be strongly reflected in the optical properties of the mixture. An assessment of the incompatibility of polymers

Fig. 1. Curves of the dependence of the specific viscosity of a mixture of two fractions of high-pressure polyethylene: 1 $-C = 0.224\%$, 2 $-C = 0.36\%$

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with one another by the degree of deviation from the additive dependence of the viscosity of their solutions cannot be made because the presence of a solvent may so strongly alter the character of intermolecular interaction that "incompatible" polymers may become "compatible," and conversely. Moreover, deviations from the additive law for the viscosity of solutions may occur not because of incompatibility, but for other reasons. For experimental proof of these propositions we used, as a model of compatible polymers, different fractions of high-density polyethylene isolated from a single sample.

A thoroughly purified polyethylene sample deposited on quartz sand was fractionated by elution with toluene in an argon atmosphere with a gradual increase in the extraction temperature. The fractions were isolated in an inert-gas atmosphere by the vacuum-freezing method. To study the dependence of specific viscosity on the composition of the mixture, fractions were selected that differed sufficiently strongly in molecular weight and degree of branching. As the first component, a low-molecular-weight fraction with characteristic viscosity $[\eta] = 0.054$ was taken; as the second, a high-molecular-weight fraction with characteristic viscosity 0.916. The ratio of the number of methyl groups in the low-molecular-weight and high-molecular-weight fractions, determined spectroscopically from the intensity of the absorption bands at 1378 and 1465 $\text{cm}^{-1}$, was about $2:1$. The viscosity measurements of the solutions were carried out at $75 \pm 0.1^\circ$ in a capillary viscometer with an outflow time for pure toluene of 220 sec. The total concentration of the mixture of components in the solutions was 0.224 and 0.360%. The solution of the high-molecular-weight fraction directly in the viscometer was diluted with a solution of the low-molecular-weight fraction in such a way that the total concentration was preserved and only the ratio of the components changed. The experimental results are given in Fig. 1.

**Fig. 1.** Curves of the dependence of the specific viscosity of a mixture of two fractions of high-pressure polyethylene: **1** $-C = 0.224\%$, **2** $-C = 0.36\%$

It is seen from the graph that the experimental curves for the dependence of specific viscosity on composition have deviations from the law of additivity both toward a minimum and toward a maximum (the maximum deviation from the additive dependence is 18-20%, which is an order of magnitude greater than the error of the viscometric measurements).

According to the equation*

$$\eta_{\text{sp}}^{\text{mix}} = L\omega_1^2 + N\omega_1 + P, \tag{1}$$

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

where

$$L = (A_2' + A_2'')C^2 - 2K[\eta_1][\eta_2]C^2;$$

$$N = (\eta_{\text{sp}}' - \eta_{\text{sp}}'') - L; \quad P = \eta_{\text{sp}}'';$$

$\eta_{\text{sp}}'$ and $\eta_{\text{sp}}''$ are the specific viscosities of the fractions; the theoretical dependence of viscosity on the composition of the mixture has been calculated (in Fig. 1 shown by the dotted line). The equation clearly shows the absence of an additive dependence between $\eta$ and the composition of the mixture. Thus, neither the experimental nor the theoretical dependence of the viscosity of solutions of mixtures of fractions of one and the same polymer—polyethylene—obeys the law of additivity. Nor can incompatibility of the polyethylene fractions with one another be assumed. The viscosity of solutions of polymer mixtures is determined by a complex of hydrodynamic factors depending, for example, on the degree of branching of the macromole-

* Equation (1) was derived on the basis of regularities adopted in viscometry: $[\eta] = kM^{\alpha}$; $\overline{M}_v = (\Sigma\omega_i M_i^{\alpha}/\Sigma\omega_i)^{1/\alpha}$; $\overline{M}^{\alpha} = M_1^{\alpha}\omega_1 + M_2^{\alpha}\omega_2$; $\eta_{\text{sp}}/C = [\eta] + A_2 C$; $A_2 = [\eta]^2 \cdot K$. $K$ is the Huggins constant, $\omega_1$ and $\omega_2$ are the weight fractions of the components.

cule. Compatibility is determined by the change in the internal energy and the entropy term of the system upon the transition from the separate existence of the components to the mixture. Viscosity is a kinetic characteristic, whereas the degree of compatibility is a thermodynamic one.

The degree of compatibility is determined by the ratio of the polymer components of the mixture at which the system loses thermodynamic stability. Systems that are stable at all ratios are absolutely compatible. Systems that are not stable at any ratios prove to be absolutely incompatible.

**Fig. 2.** Dependence of the optical density of films made from mixtures on heating time: **1** —mixture of polyethylene fractions; **2** —mixtures of polyethylene with polypropylene in a ratio of 1 : 2

**Fig. 3.** Distribution curves of the strength limit, calculated for the initial cross section of specimens of a mixture of polyethylene with polypropylene: **1**

–mixture before heating; **2, 3, 4** –heating at 100° for 15, 45, and 60 min, respectively

Incompatible polymers during technological processing may be forcibly brought to the desired degree of mixing. Such systems during service can sometimes change their properties so slowly that from the beginning of service to the end of the product' s depreciation period no impermissible changes in the properties of the mixture occur. In this case one may speak of operational compatibility (dependent on service conditions).

In the experiment cited, it was shown that, on the basis of deviations of the specific viscosity from the law of additivity, fractions of one and the same polymer (polyethylene) should be regarded as incompatible polymers. Using the thermodynamic criterion of system stability, namely the independence of the state characteristics from the path by which the given state has been reached, one can make sure that the investigated mixture of polyethylene fractions is thermodynamically stable. Figure 2 (curve **1**) shows the change in optical density with heating time for a film prepared from a mixture of polyethylene fractions in a ratio corresponding to the maximum deviation from the law of additivity on the curve of the dependence of $\eta_{\mathrm{sp}}$ on the composition of the mixture. The film was periodically heated in a thermostat at 100° for 15 min, followed by equilibration at room temperature. The optical density was determined on an SF-4 spectrophotometer at a wavelength of 435 mµ and a slit width of 0.035 mm. The independence of the optical density from the method of attaining the specified constants indicates that the system is thermodynamically stable and that its components are compatible. Curve **2** in Fig. 2 shows the change in optical density of a film made from a mixture of polyethylene and polypropylene in a ratio of 1 : 2, subjected to the same test. A certain decrease in optical density can be explained by blurring of the phase-boundary interfaces, i.e., by a decrease in microheterogeneities due to the occurrence of diffusion–

processes. During heating of the system, further spontaneous dispersion takes place, and then the system becomes an equilibrium one.

Figure 3 gives the distribution curves for the strength limit, calculated for the initial cross section of a specimen of a mixture of polyethylene with polypropylene, obtained under the indicated test conditions. The shape of curve 4, Fig. 3, is the most symmetrical and has a smaller dispersion value (a decrease in dispersion on average from 40 to 26 kg/cm$^2$), which may serve as an indication of the greater homogeneity of the system. The maxima on the curve $\dfrac{\Delta N}{N\Delta\sigma_p} = f(\sigma_p)$ show a decrease in strength as the test time increases.

To assess service compatibility, it is necessary to determine within what limits and for which specific characteristics changes during service are permissible. Knowing the conditions and duration of service, one can experimentally predict whether, during the service period, changes in certain characteristics that exceed the permissible limits can be expected. For this purpose, the change in characteristics is produced under more severe conditions (for example, at a higher temperature) than the service conditions. Then, by noting the time during which the change in the selected characteristics exceeds the permissible limits, and extrapolating the resulting time–test temperature dependence, it is possible to determine whether the necessary properties will be lost during service.

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*Note: Figure translations are in progress. See original paper for figures.*

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