

Anomalous Dependence of the Size of Droplets of Disperse Phase on Intensity of Mixing

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SYNOPSIS

The dependence of phase structure on the intensity of mixing was studied for two modified polyamide/[poly(phenylene oxide) + polystyrene] (50/50) blends with different viscosity ratios of components. In these blends, polyamide forms the matrix and the mixture of miscible polymers [poly(phenylene oxide) and polystyrene] forms the disperse phase at all rates of mixing. The average size of the droplets of the disperse phase grows with increasing rate of mixing. This (rather surprising) result is explained as a consequence of the dynamic equilibrium between breakup and coalescence of droplets in a highly concentrated system at the condition of steady mixing. Generally, the dependence of droplet size on rate of mixing is not necessarily a monotonic function for blends with a high content of the disperse phase. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Many properties of blends of immiscible polymers depend on fineness of phase structure of such blends.^{1,2} For this reason, it is of great importance to study the relations between conditions of preparation and phase structure of polymer blends. Formation of phase structure during melt mixing of polymer blends has been studied in many papers.³⁻¹⁴ Contradictory results were reported, which limits applicability for formulation of general rules. A gradual decrease in droplet size with increasing time of mixing,^{3,7} the size of droplets independent of time of mixing,¹⁰ and eventually inhomogeneous evolution of phase structure in the process of mixing^{8,11,14} were found. For many systems, a decrease in droplet size with increasing intensity of mixing was obtained.^{4-7,9,15} Droplet size independent of intensity of mixing (stress and rate of deformation in melt) was found in other systems.^{10,12} Recently, a minimum was observed in the dependence of the mean droplet size on mixing energy input.¹³

In our opinion, competition between breakup and

coalescence of droplets should be taken into account when analyzing the dependence of droplet size on intensity of mixing. In an internal mixer, breakup of droplets of disperse phase prevails over their coalescence in the first period of mixing of polymer blends. Dynamic equilibrium between breakup and coalescence of droplets is achieved after steady mixing for some period of time. The average size of droplets is time-independent for longer times of mixing. The time of mixing necessary to achieve a steady size of droplets depends on properties of the blend components and decreases with increasing intensity of mixing.^{3,7,8,11,14} So far, there is no theory describing the time evolution of the average size of droplets during mixing. Schreiber and Olguin's empirical rule⁷ stating that size of droplets decreases with increasing energy input during mixing does not appear to be generally valid.⁸ Several approximative relations have been derived for determining the droplet size under steady-state conditions.^{3,16-18} According to these relations, the effect of coalescence on droplet size increases with increasing concentration of the disperse phase. As the dependencies of the number of breakups and the number of fusions of droplets on mixing rate may differ from one another, the dependencies of droplet size on rate of mixing are not necessarily the same for all compositions of a blend.

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In this paper, the dependence of phase structure on a rate of mixing is studied for modified polyamide/[poly(phenylene oxide) + polystyrene] blends with a high content of the disperse phase. The obtained dependence of droplet size on rate of mixing is discussed on the basis of theoretical relations derived for droplet size in the steady state.¹⁷ An attempt is made to formulate general conclusions about the dependence of droplet size on rate of mixing in blends with a high content of the disperse phase.

EXPERIMENTAL

Material

Two grades of a modified polyamide MPA1 and MPA2, prepared at the Institute of Technology and Engineering Neratovice (Czechoslovakia), were used as the components of the studied blends. MPA1 and MPA2 were mixtures of polyamide with EPDM rubber that was modified by maleic anhydride. Rubber content (by weight) was 5% in MPA1 and 20% in MPA2. Melt flow index (MFI) was 3.79 g/10 min for MPA1 and 0.9 g/10 min for MPA2. Two mixtures of miscible polymers [poly(phenylene oxide) and polystyrene, PPS1 and PPS2] prepared at the Institute of Technology and Engineering Neratovice, were used as the second component of the blends under investigation. PPS1 with MFI = 0.40 g/10 min contains 40% by weight of poly(phenylene oxide). PPS2 with MFI = 0.47 g/10 min contains 20% by weight of poly(phenylene oxide).

Mixing

The blends MPA1/PPS1 and MPA2/PPS2, of composition 50/50 by weight, were mixed in the W50EH chamber of the Brabender Plasti-Corder PL 2000 at the temperature of 230°C for 10 min. The blends were mixed at 5, 10, 20, 40, 80, and 120 rpm. The samples were removed from the chamber of the Plasti-Corder and quenched in cold water immediately after cessation of mixing.

Morphology

The phase structure of the blends was studied using a scanning electron microscope JSM 35 in the secondary electron mode at the accelerating voltage of 25 kV. The samples were cut with a glass knife in a vessel filled with liquid nitrogen.^{8,14} To make the phase structure visible, PPS1 or PPS2 was etched off from the sample surface with toluene. The size

of disperse particles was evaluated from their micrographs using a MINI MOP image analyzer (Kontron Co., Germany) by which the perimeter and planar area of the particle image can be measured. The phase structure of the samples was characterized by the mean radius \bar{r} of circles having the same perimeter and by the mean square radius $(\bar{r}^2)^{1/2}$ of circles having the same area as the investigated particle images. The same method was used in a previous paper.⁸ Both \bar{r} and \bar{r}^2 were calculated using the relations

$$\bar{r} = p/(2\pi n) \quad (1)$$

$$\bar{r}^2 = A/(\pi n) \quad (2)$$

where n is the number ($200 < n < 2000$), p is the total perimeter, and A is the total area of the particle images in the micrograph used in the evaluation. We did not recalculate the size of the images into the size of the particles, since particles were not always spherical and since we were more interested in obtaining the shape of the curve of particle size vs. rate of mixing than in determining the absolute size of the particles. Polydispersity of particle size was characterized by a parameter, P , defined by the equation

$$P = (\bar{r}^2)^{1/2}/\bar{r} \quad (3)$$

A small number of large particles with a radius of an order of magnitude of tens of micrometers was found in the blends. The number of large particles in the blends was so small that their inclusion into the quantitative analysis of the phase structure would require evaluation of the size of tens of thousands of disperse particles for each sample. For this reason, only homogeneous places were evaluated quantitatively and the occurrence of large particles was described qualitatively.

RESULTS AND DISCUSSION

Modified polyamide formed the matrix, and a mixture of poly(phenylene oxide) with polystyrene formed disperse droplets in both MPA1/PPS1 and MPA2/PPS2 blends at all rates of mixing. Generally, a modified polyamide can have a heterogeneous structure. Therefore, we investigated the phase structure of the samples of modified polyamides kneaded and prepared by the same methods as the samples of the polymer blends studied. There was no indication of heterogeneous phase structure of the modified polyamides. For this reason, we assume

that MPA1/PPS1 (50/50) and MPA2/PPS2 (50/50) can be considered two-phase blends.

Particle size has strictly bimodal distribution for samples of MPA1/PPS1 (50/50) and MPA2/PPS2 (50/50) mixed at low speed. Further, sparsely distributed large particles having their radii of an order of tens micrometers were found in these samples (Figs. 1 and 2). Sparsely distributed large particles were found in polypropylene/ethylene-propylene elastomer (PP/EPM)^{8,11} and polypropylene/ethylene-propylene-diene terpolymer/polyethylene (PP/EPDM/PE)¹⁴ blends that were mixed at a low rate for a short time. The number and size of large particles in PP/EPM and PP/EPDM/PE blends decreased with increasing rate and time of mixing.^{8,14} As a very low number of large particles was found in all samples of both blends, we could not draw a decisive conclusion about the dependence of their number and size on rate of mixing.

Bimodal distribution of particle sizes persists but the average particle size increases with increasing rate of mixing in MPA1/PPS1 blends (Fig. 3). Table I contains the results of quantitative evaluation of particle size as a function of rate of mixing, ω . The average particle size increases with increasing rate of mixing in the interval $5 \text{ rpm} < \omega < 80 \text{ rpm}$. The mean particle radius starts decreasing at 120

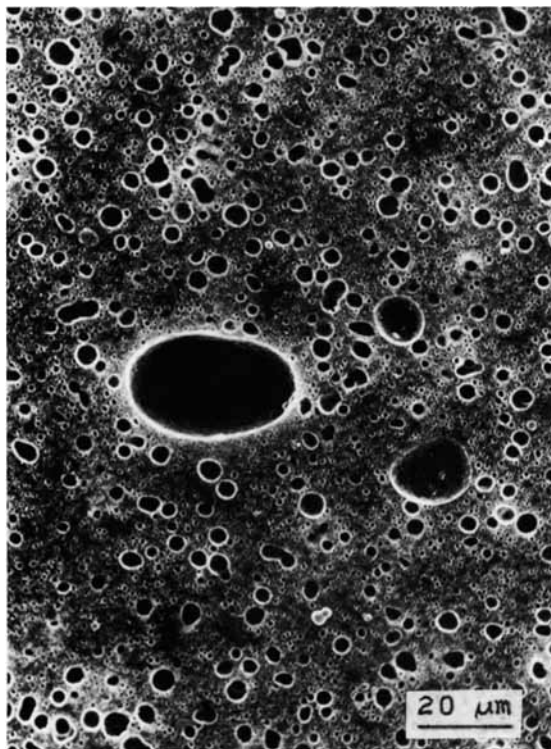


Figure 1 Morphology of the MPA1/PPS1 (50/50) blend mixed at 10 rpm.

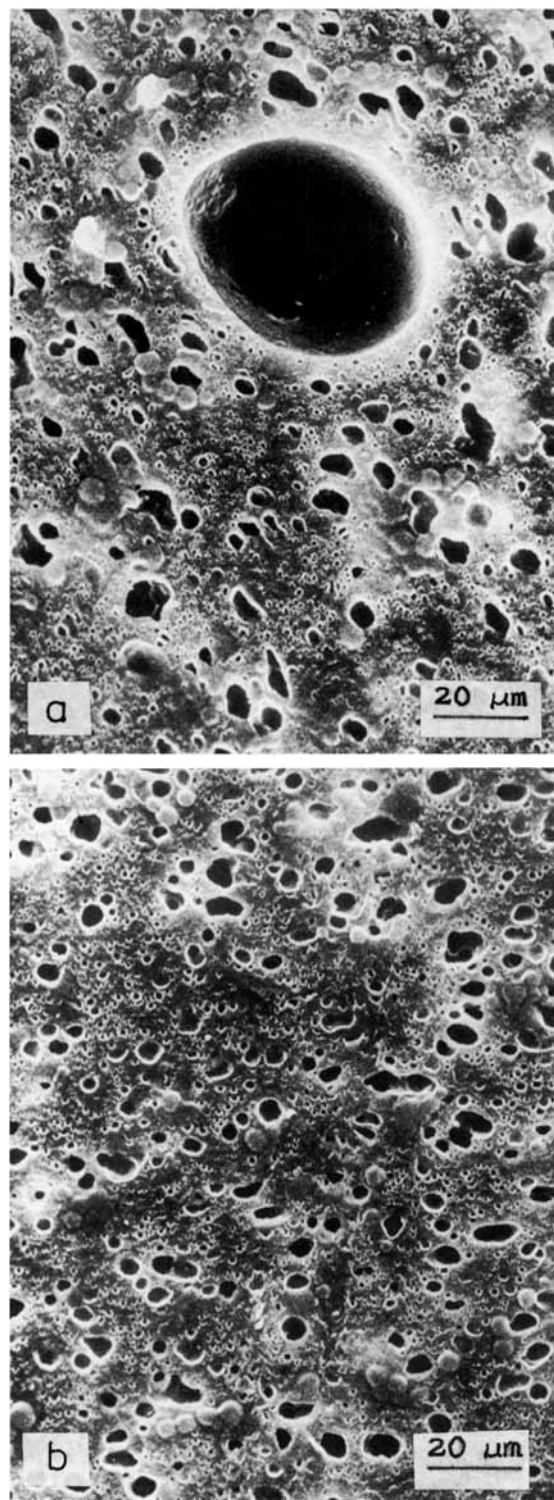


Figure 2 Morphology of the MPA2/PPS2 (50/50) blend mixed at 5 rpm: (a) large particle; (b) homogeneous area.

rpm. The polydispersity parameter, P , decreases with increasing particle size. P has the minimum value at 80 rpm. Generally, P increases with in-

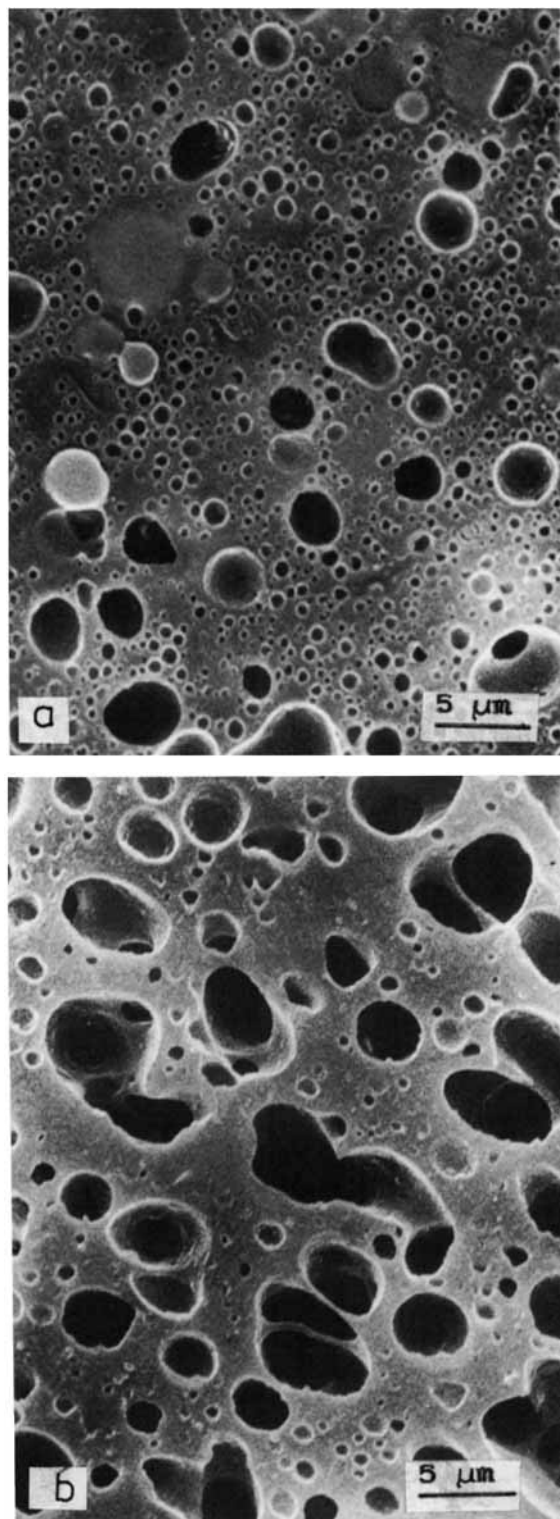


Figure 3 Morphology of the MPA1/PPS1 (50/50) blend mixed at (a) 10 rpm and (b) 80 rpm.

creasing polydispersity in the particle size.⁸ P decreases with an increasing difference between the shape of particle images from that of a circle. P is

lower than 1 for a set of monodisperse images having a shape differing from a circle.⁸ Figure 3 shows that the anisometry of particles increases with the increasing size of particles. This is why parameter P decreases with increasing particle size.

The number of small particles decreases and the average size of particles increases with increasing rate of mixing for the MPA2/PPS2 (50/50) blends (Fig. 4). From Table II we can see that the dependence of average particle size on rate of mixing is practically the same for the MPA2/PPS2 and MPA1/PPS1 blends. Both \bar{r} and $(\bar{r}^2)^{1/2}$ have a maximum at 80 rpm (the same rate as in the case of the MPA1/PPS1 blend). Only P has a minimum at 40 rpm. From the micrographs in Figure 4, it follows that the decrease of P may be attributed to the decreasing number of small particles and increasing anisometry of large particles simultaneously. With the samples quickly quenched immediately after removing them from a mixing chamber, particle shape is sensitive to their location in the mixing chamber in the moment of the flow cessation.

From Tables I and II we can see that \bar{r} and $(\bar{r}^2)^{1/2}$ are higher for MPA2/PPS2 (50/50) blends than for MPA1/PPS1 (50/50) blends at the same rates of mixing. This fact cannot be explained on the basis of rheological properties of the components, because the viscosities of MPA2 and PPS2 are (according to MFI) closer to one another than are the viscosities of MPA1 and PPS1. Therefore, finer dispersion should be expected in the MPA2/PPS2 (50/50) blends. The MPA1/PPS1 and MPA2/PPS2 blends probably have different interfacial tension between the components due to the different content of rubber in MPA1 and MPA2. Unfortunately, we have no evidence concerning the value of interfacial ten-

Table I Dependence of Particle Size on Rate of Mixing for the MPA1/PPS1 (50/50) Blend

ω^a (rpm)	M^b (Nm)	\bar{r}^c (μm)	$(\bar{r}^2)^{1/2 d}$ (μm)	P^e
5	4.5	0.38	0.53	1.38
10	7.0	0.51	0.63	1.24
20	5.5	0.68	0.78	1.15
40	11.0	0.92	1.08	1.18
80	12.3	1.62	1.79	1.10
120	12.5	1.02	1.28	1.26

^a ω = rate of mixing.

^b M = torque at the end of mixing.

^c \bar{r} = the average radius of particle image determined from eq.

(1). ^d $(\bar{r}^2)^{1/2}$ = the mean square radius of particle image determined from eq. (2).

^e P = polydispersity parameter determined from eq. (3).

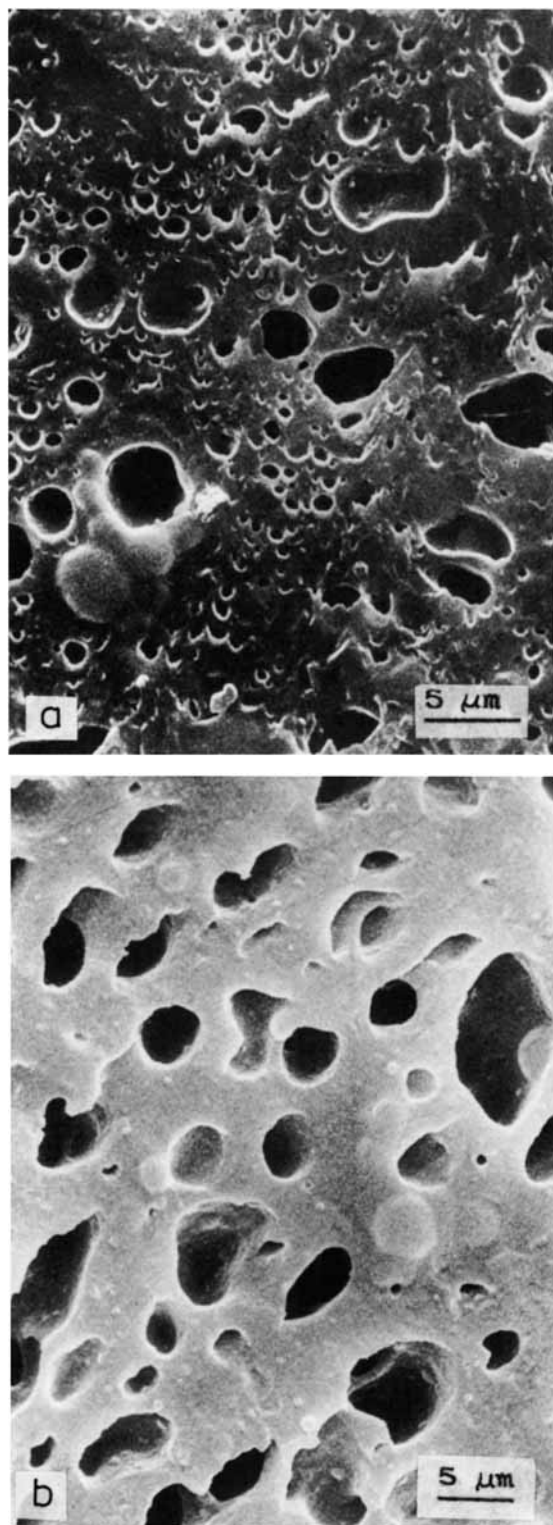


Figure 4 Morphology of the MPA2/PPS2 (50/50) blend mixed at (a) 5 rpm and (b) 120 rpm.

sion in the studied systems. For this reason, it is impossible to decide whether the coarser phase structure of the MPA2/PPS2 can be explained by

a higher interfacial tension between MPA2 and PPS2 than between MPA1 and PPS1.

The maximum on the dependence of \bar{r} on ω is rather surprising, and according to our knowledge, it has not been described in the literature as yet. Most authors have found a decrease in the size of disperse particles with an increasing rate of mixing.^{4-7,9} In many other cases, the size of disperse particles was found independent of rate of mixing.^{8,10,12} Very recently, a minimum has been discovered in the dependence of average particle size on energy input during mixing.¹³ Neither our results (cf. Tables I and II) nor the results from Ref. 13 can be explained by taking into account the particle breakup only. In both cases, blends with a high content of disperse phase were studied. In such systems, competition between breakup and coalescence of particles should be taken into consideration.

Relations derived for the average size of particles in the steady state¹⁷ will be used in the discussion of experimental results. It is possible that the steady state is not reached after 10 min for some rates of mixing. As the average particle size monotonically decreases with increasing time of mixing until a steady size is reached and the time necessary for attaining steady state decreases with increasing rate of mixing,^{3,8} the particle size in the steady state would be even smaller than that obtained experimentally at low rates of mixing. For this reason, the dependence of steady particle size on rate of mixing should be qualitatively the same as that of the experimental one. As a constant, i.e., the time-independent value of torque is reached for both systems after 2-3 min of mixing, it may be assumed that no chemical reactions, i.e., no changing rheological properties of the system, are taking place during mixing.

The following expression is valid for the droplet radius, r , in the steady state:¹⁷

$$r = r_c + (\sigma\alpha/\eta_m f_1)\phi \quad (4)$$

Table II Dependence of Particle Size on Rate of Mixing for the MPA2/PPS2 (50/50) Blend

ω (rpm)	M (Nm)	\bar{r} (μm)	$(\bar{r}^2)^{1/2}$ (μm)	P
5	6.0	0.56	0.77	1.38
10	9.0	0.92	1.25	1.36
20	11.0	1.39	1.56	1.12
40	12.3	1.58	1.63	1.03
80	12.4	1.95	2.37	1.21
120	13.5	0.96	1.30	1.35

The symbols used in Table II represent the same physical quantities as in Table I.

where

$$r_c = \sigma(We)_c / (\eta_m \dot{\gamma}) \quad (5)$$

and σ is the interfacial tension; α , the probability that droplets will coalesce after their collision; η_m , the viscosity of the matrix; ϕ , the volume fraction of the disperse phase; $\dot{\gamma}$, the shear rate; and f_1 , the slope of the function $F(We)$ describing the frequency of breakups of droplets at $(We)_c$. The number We is defined as

$$We = \eta_m \dot{\gamma} r / \sigma \quad (6)$$

$(We)_c$ is the critical value of the We number for the droplet breakup.¹⁹ $(We)_c$ is generally a function of the ratio, η_r , of viscosities of the disperse phase and matrix and of the ratio, λ_r , of elasticity parameters of both phases.^{20,21} For Newtonian droplets in a Newtonian matrix and $\eta_r < 1$, Taylor derived¹⁹⁻²¹ the following equation:

$$(We)_c = (1/2)(16\eta_r + 16)/(19\eta_r + 16) \quad (7)$$

In accordance with the theoretical analysis of the problem^{20,21} and experimental results for model systems^{20,21} and polymer blends,²² $(We)_c$ increases with increasing η_r for $\eta_r > 1$.

According to eq. (4), the radius of droplet, r , is equal to the critical radius, r_c , given by eq. (5), for an infinitely dilute system. Interfacial tension will be considered independent of rate of mixing, ω . $(We)_c$ depends on ω only through η_r and the ratio of elasticity parameters, λ_r . If $(We)_c$ is given by eq. (7), its dependence on η_r is only slight and its dependence on ω can be neglected. For the system of viscoelastic droplets in viscoelastic matrix, there is not available either a theoretical or a reliable empirical equation for $(We)_c$. However, we believe that, if dependence of η_r and λ_r on ω are not too strong, an assumption can be made that, in the first approximation, $(We)_c$ is independent of ω also in the case of viscoelastic liquids. In this case, the dependence of r_c on ω is determined by $\eta_m \dot{\gamma}$. During the mixing, $\eta_m \dot{\gamma} \sim M$, and according to eq. (5), r_c decreases with increasing torque, M . For highly dilute systems, a conclusion can be drawn that the radius of disperse droplets usually decreases with increasing rate of mixing. The only exception are systems where the torque does not increase (due to a strong decrease in viscosity of the matrix caused by its non-Newtonian behavior and/or temperature growth) and/or η_r sharply increases with increasing rate of mixing.

The value of the second term in eq. (4) increases with increasing concentration of the disperse phase. This term determines the dependence of r on ω for

systems with a high content of the disperse phase. f_1 , defined in Ref. 17, is a function of $(We)_c$ and rheological properties of the components. It is not an explicit function of $\dot{\gamma}$, i.e., of the rate of mixing. There is only very limited knowledge concerning the dependence of f_1 on the properties of the system. We believe that, in the first approximation, f_1 can be considered independent of ω at the same conditions as can $(We)_c$. η_m is a decreasing function of shear rate, and for the process of mixing, we can take $\eta_m \sim M/\omega$. A more complicated question is the dependence of the probability of fusion of droplets after their collision, α , on ω . According to Elmen-dorp's calculation,^{16,21} α is constant for small $\dot{\gamma}$. Above a certain value of $\dot{\gamma}$, α decreases with increasing $\dot{\gamma}$. For smaller droplets, α is constant up to a higher $\dot{\gamma}$ and the following decrease in α is steeper than that for larger droplets (Fig. 8-5 in Ref. 21). η_m and α are decreasing functions of shear rate, but, in general, their dependencies on $\dot{\gamma}$ are different. The second term in eq. (4) increases with increasing ω in the range of rates of mixing where α is independent of ω . When, starting from a certain rate of mixing, α begins to decrease with increasing ω more quickly than does η_m , a maximum will appear in the dependence of the second term in eq. (4) on ω . In concentrated systems, where the second term in eq. (4) exceeds r_c , a maximum also appears in the dependence of r on ω .

The preceding discussion was based on eq. (4). This equation was derived for simple shear flow under some approximations.¹⁷ In our opinion, this theory can describe substantial features of droplet formation correctly so that the conclusions of the preceding discussion are generally valid. Only in the blends with a very low content of the disperse phase is the droplet size predominantly determined by their breakup. In concentrated systems, the droplet size results from the dynamic equilibrium between breakup and coalescence of droplets. In general, the frequency of collisions in flow is proportional to the rate of deformation, whereas the frequency of breakups is a growing function of the stress. As stress increases more slowly than the rate of deformation in viscoelastic liquids, the droplet size may increase with increasing rate of mixing in concentrated systems. As the probability of droplet fusion after collision decreases with increasing rate of mixing (in a different way compared to the apparent viscosity), the dependence of droplet size on rate of mixing can generally be nonmonotonic. Dependence of α on the size of coalescing droplets results in a reduction of the interval of a possible droplet radius^{16,21} and, in some systems, probably leads to the weak dependence of droplet size on the rate of mixing.⁸

The preceding discussion can satisfactorily explain the measured anomalous dependence of droplet size on rate of mixing in modified polyamide/[poly(phenylene oxide) + polystyrene] (50/50) blends. Present theories can quantitatively predict neither the dependence of mean particle size nor the distribution of particle sizes on rate of mixing. A minimum in the dependence of average particle size on energy input during mixing obtained by Plochocki et al.¹³ can be explained as a consequence of unsteady particle size for a low input of energy. Particle size decreases with increasing energy input during the initial period of mixing. In the steady state, however, the particle size can increase with increasing rate of mixing in the concentrated blends studied. For this reason, a growth of particle size with increasing energy input is possible for higher energy input during mixing. Another reason for growth of the particle size can be seen in a degradation of the matrix during mixing.¹¹

From the thermodynamic point of view, fineness of the phase structure of polymer blends during steady mixing is controlled by entropy production.²³ For this reason, mixing cannot be described as a purely energetic process and particle size need not monotonically decrease with increasing rate of energy input.

CONCLUSIONS

Anomalous dependence of the average size of disperse particles on rate of mixing was obtained for modified polyamide/[poly(phenylene oxide) + polystyrene] (50/50) blends. Average particle size increases with increasing rate of mixing up to 80 rpm, where it reaches a maximum value, and then decreases with the further increase in the rate of mixing.

Dependencies of the size of disperse particles on rate of mixing are different for various concentrations of the disperse phase in the blend. A decrease in the steady particle size can be expected for blends with a low content of the disperse phase. Decreasing, increasing, or nonmonotonic dependence of the size of disperse particles on rate of mixing can be obtained for blends with a high content of the disperse phase. The character of the dependence is deter-

mined by the concentration of the disperse phase, interfacial tension, and rheological properties of the components of the blend.

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