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Non-uniform phase structure in immiscible polymer blends — reasons and consequences

Summary — Uniformity of the phase structure in binary and ternary polystyrene, polyamide and polyethylene blends was studied. It was found that areas containing particles with strongly different average size coexisted in quenched and compression molded samples of all blends under study. It was shown that neglecting of this effect could cause erroneous determination of the particle size dependence on the mixing conditions and properties of the blend components. An analysis of the competition between the droplet break-up and coalescence showed that non-uniformity of the phase structure was apparently caused by non-uniform flow field in a mixing device.

Key words: polymer blends, non-uniform phase structure, averaging particle size.

NIEJEDNORODNA STRUKTURA FAZOWA W MIESZANINACH POLIMERÓW WZAJEMNIE NIE-MIESZALNYCH — PRZYCZYNY I KONSEKWENCJE

Streszczenie — Badano jednorodność struktury fazowej dwu- i trójskładnikowych mieszanin polistyrenu, poliamidu i polietylenu różniących się stężeniem poszczególnych składników (tabela 1). Stwierdzono, że w badanych próbkach wytwarzanych metodą szybkiego schładzania i wytłaczania współistnieją obszary zawierające cząstki znacznie różniące się średnimi rozmiarami (tabela 2, rys. 1—4). Wykazano, że zaniedbanie tego efektu może prowadzić do otrzymania błędnych wyników podczas badań zależności rozmiarów cząstek od warunków mieszania i od właściwości składników mieszanin. Analiza konkurujących ze sobą, podczas procesu wytwarzania mieszanek, zjawisk rozdrabniania kropeł oraz koalescencji pokazała, że niejednorodność struktury fazowej jest spowodowana istnieniem obszarów nierównomiernego przepływu w urządzeniu mieszającym.

Słowa kluczowe: mieszanki polimerów, niejednorodna struktura fazowa, uśrednione rozmiary cząstek.

Polymer blends are very important materials. Control of their phase structure during their preparation is necessary for their efficient use and, therefore, it is a subject of intensive investigations [1—4]. It is generally accepted that the phase structure of immiscible polymers blend is mostly formed in the course of first 1 or 2 minutes of mixing of components in batch mixer [5—8]. It is assumed that this phase structure is stable during subsequent steady mixing if the temperature in melt is kept constant and chemical reactions changing properties of the blend components are suppressed. Exceptions are only the blends show low interfacial tension and high viscosity ratio of the dispersed phase and a matrix [9—11], and some blends with co-continuous structure [12, 13], where changes in morphology were observed

also after quite long and intensive mixing. In evaluation of the morphology of blends, it is generally considered that the phase structure of quenched or compression molded samples is uniform and an area containing from several hundreds to several thousands of dispersed particles can be used for quantitative characterization of the sample morphology. However, quite large areas containing hundreds to thousands particles and clearly differing in the average particle size were detected in quenched and compression molded samples of polypropylene/polystyrene (PP/PS) blends. Strongly non-uniform phase structure was observed also in the samples mixed intensively for a long time in a chamber of the Brabender Plasticorder or miniextruder [14—17]. Non-uniformity of the phase structure was not suppressed by changes in viscosity of the components, by an increase in time and rate of mixing or by the addition of a compatibilizer. Only enhancement of mixing temperature reduced non-uniformity of the phase structure remarkably. Recently, less pronounced non-uniformity of the

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phase structure was found also in polystyrene/low-density polyethylene (PS/PE-LD) blends without a compatibilizer and also with it [18, 19]. So far, this effect was neither satisfactorily explained nor described.

The aims of this study are to show that non-uniformity of the phase structure is not specific for polystyrene/polyolefin blends only and that neglect of it can lead to substantial errors in determination of average particle size. These errors can cause that the determined dependence of the average particle size on various parameters of the system may be quite unreliable. The further aim of the study is a discussion of the reasons of differences in the average particle size in various domains of the sample.

EXPERIMENTAL

Materials

Atactic polystyrene (PS) trade name Krasten 171 was commercial product of Kaučuk Co. (Kralupy, Czech Republic). It was characterized by molecular weight $\overline{M}_w = 300\,000$, polydispersity $\overline{M}_w/\overline{M}_n = 4.6$, melt flow rate $MFR = 5.2$ g/10 min (according to ISO 1133, 190 °C, 2.16 kg) and density 1.05 g · cm⁻³.

Polyamide 6 (PA) trade name Ultramid 4, delivered by BASF (Germany), has number-average molecular weight $\overline{M}_n = 33\,000$.

High-density polyethylenes named by supplier ExxonMobil (Saudi Arabia) as ExxonMobil HDPE HYA 600 (PE-HD1) and ExxonMobil HDPE HMA 018 (PE-HD2) were specified by MFR equal to 0.35 and 30 g/10 min, respectively (according to ASTM D 1238, 190 °C, 2.16 kg). Densities of both PE-HD were equal to 954 kg · m⁻³.

Sample preparation

The samples were mixed in the chamber B 50 EHT of a Brabender Plasticorder. Three binary blends PS/PA, PS/PE-HD1 and PS/PE-HD2 and eight ternary blends

PS/PA/PE-HD1 and PS/PA/PE-HD2 were prepared. The compositions of all samples are listed in Table 1. Components were mixed at 240 °C and at 60 rpm for 10 min (medium rate and time of mixing) or at 90 rpm for 20 min (long and intensive mixing). Quenched samples were prepared from small pieces of the blend and put to the cold water. Compression molded samples were prepared in a Fontijne laboratory press at 240 °C and pressure between the press plates 1.505 MPa for 2 min and 3.1 MPa for further 2 min. After that, the samples were transferred into another cold press cooled with water.

Morphology determination

Samples of ternary blends and binary blends were cut with a saw in selected places. From those cut surfaces, the layers were cut off using further cutting at the liquid nitrogen temperature with a glass knife, angle of which was 90°. We call this technique as "cryogenic smoothing". PA fraction was removed from the sample surface by dissolution in formic acid (20 min), then PS phase was stained in RuO₄ vapors for 1 h. Surfaces obtained these ways were mounted on a substrate (cut to a proper size, fixed onto a microscope stub), surface-coated with carbon to observe material contrast. Scanning electron micrographs (SEM) were obtained using a scanning electron microscope (Vega, Tescan, Czech Republic).

RESULTS AND DISCUSSION

The domains containing particles with strongly different average size were detected in all compression molded samples of binary and ternary blends. Examples of SEM micrographs are shown in Figs. 1 and 2.

Less pronounced but still detectable non-uniformity was also found in the quenched samples of the blends. For comparison with previous figures, the SEM micrographs of such way prepared samples 1 and 7 are shown in Figure 3 and 4. These results together with the results of previous investigations for PP/PS [14–17], PE-LD/PS [18, 19] and recent results for linear low-density polyethylene/polycycloolefin blends [20] show that non-uniformity of the phase structure appears for many polymer blends.

For illustration of danger, following from neglect of the non-uniformity of the phase structure when evaluating the dependence of the average particle size on parameters of the system, the average equivalent diameter $\langle d \rangle$ of PA particles was determined for four different areas in the micrograph of sample 9. The histograms were unsymmetrical and the median could better characterize the particle size. The results are summarized in Table 2. It is clearly visible that differences between $\langle d \rangle$ in areas containing small (Areas 1 and 2) and large (Areas

Table 1. Compositions of binary and tertiary blends prepared

Symbol of sample	Content of component, wt. %			
	PS	PA	PE-HD1	PE-HD2
1	80	20	—	—
2	80	—	20	—
3	80	—	—	20
4	79	1	20	—
5	75	5	20	—
6	79	1	—	20
7	75	5	—	20
8	79	20	1	—
9	75	20	5	—
10	79	20	—	1
11	75	20	—	5

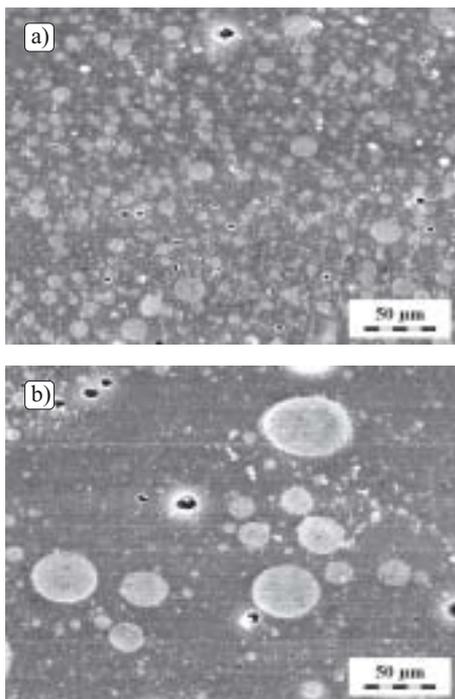


Fig. 1. SEM micrographs of compression molded sample 7 showing PA particles (dark) and different areas containing small (a) and large (b) PE-HD2 particles

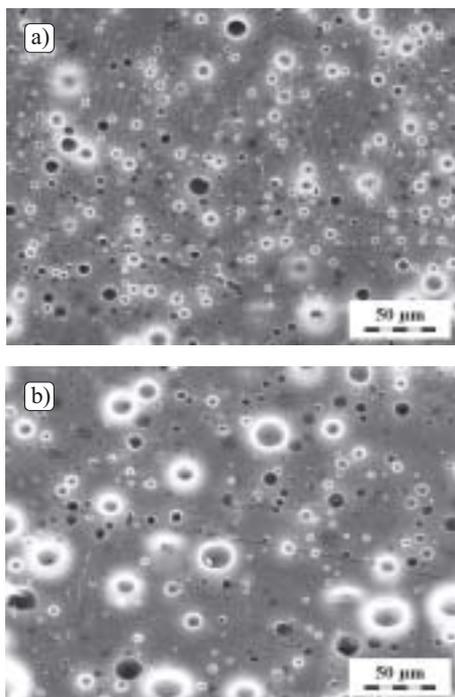


Fig. 2. SEM micrographs of compression molded sample 1 showing the areas containing smaller (a) and larger (b) particles

3, and 4) particles are substantially larger than it is considered as a significant difference when studying the dependence of $\langle d \rangle$ on the blend composition, properties of the components, and mixing conditions. This example clearly shows that erroneous conclusions can be a conse-

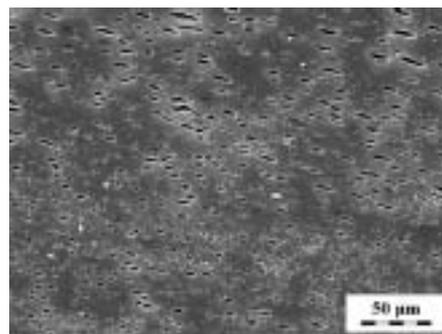


Fig. 3. SEM micrographs of quenched sample 1 showing non-uniform distribution of PA particles (dark)

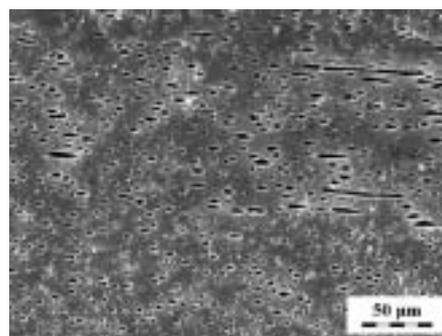


Fig. 4. SEM micrographs of quenched sample 7 showing areas with non-uniform phase structure

quence of inconvenient selection of the area of $\langle d \rangle$ determination.

Table 2. Comparison of the average diameter $\langle d \rangle$ and median of polyamide particles in various areas of compression molded sample 9

	Area 1	Area 2	Area 3	Area 4
No. of particles	456	263	161	210
$\langle d \rangle$, μm	3.24	3.95	5.50	5.13
median, μm	2.69	2.69	3.26	3.26

For the explanation of observed non-uniformity of the phase structure, it is necessary to consider the phase structure formation during mixing. It is well known that the particles sizes in the blends with dispersed structure are controlled by the competition between their break-up and coalescence [8]. The shape of a molten dispersed particle in flow is given by the competition between the flow stress, which tends to deform the particle, and the interfacial stress, which has the tendency to minimize the interfacial area [21–23]. This competition can be expressed with dimensionless capillary number (Ca). For a shear flow, Ca is defined as:

$$Ca = \frac{\eta_m \dot{\gamma} R}{\sigma} \quad (1)$$

where: η_m — viscosity of the matrix, $\dot{\gamma}$ — the shear rate, R — particle radius, σ — interfacial tension.

The break-up occurs when Ca is higher than a certain critical capillary number (Ca_c) where the particle deformation exceeds a certain value. Ca_c is a function of the viscosity ratio (p) and elasticity parameters of the dispersed phase and a matrix. Two main mechanisms of the droplet break-up (stepwise and transient) were recognized [24]. The stepwise mechanism consists in repeated break-up of the droplets into two halves (small satellite droplets can be formed at some viscosity ratios) [21]. If the transient break-up applies, the droplet stretches into a slender fibril, which subsequently breaks up by capillary-wave instability into a chain of small droplets. The stepwise mechanism prevails if Ca is only a little higher than Ca_c . For $Ca \gg Ca_c$ the transient break-up mechanism is operative [21]. However, to know which mechanism is operative for a certain system is a difficult task, especially for the complex flow fields [23].

Dependence of Ca_c on p in steady shear and extensional flows is understood quite well. For shear flow, Ca_c reaches a minimum for p between 0.1 and 1, steeply increases with increasing p for $p > 1$, and goes to infinity for $p \approx 4$. For $p < 0.1$, it somewhat increases with decreasing p . For extensional flow, a minimum for Ca_c was found at about $p = 1$. A very slight increase in Ca_c with increasing or decreasing p was found for $p > 1$ or $p < 1$, respectively. It seems that the increase in elasticity of droplets leads to an increase in Ca_c . On the other hand, an increase in elasticity of the matrix causes a decrease in Ca_c [23]. The dependence of the break-up frequency, *i.e.* the number of droplets formed from a certain droplet per time unit is substantially less understood. Recent results [23] seem to show that the break-up frequency increases slower than linearly with $R - R_c$ for Ca not much larger than Ca_c . R_c is defined as:

$$R_c = \frac{\sigma}{\eta_m \dot{\gamma}} Ca_c \quad (2)$$

For the transient mechanism, the break-up time of an extended fiber increases with increasing viscosity of the dispersed phase and matrix and decreases with increasing interfacial tension. On the other hand, increasing interfacial tension diminishes the deformation of a droplet to the extended fiber. Generally, the break-up time of the fiber increases and the sizes of fragments decrease in flow with respect to the quiescent state. Therefore, the break-up of fibers can appear after stop of the mixing. It should be mentioned that the sizes of fragments obtained according to the transient mechanism can be smaller than the sizes of smallest fragments (related to Ca_c) reached for stepwise mechanism. Break-up frequency for flow in mixing device is very difficult to estimate and strongly differing expressions were used in various theories describing evolution of the particle size [23].

Flow-induced coalescence is caused by the collisions of droplets having different velocities, *e.g.* due to the distance of their centers of inertia among 0 and $2R$ in the

direction of velocity gradient in the shear flow [8, 21, 23, 24]. It should be mentioned that, in first approximation, coalescence frequency increases with the square volume fraction of the dispersed phase in contrast to the break-up frequency, which is proportional to the first power of this volume fraction. For the simple shear and extensional flows, the dependence of coalescence frequency on the droplet radius seems to be qualitatively understood but its quantitative determination is a difficult task [23, 25]. In the quiescent state, the coalescence induced by collisions caused by attractive van der Waals forces and/or Brownian motion should be considered [23, 26, 27]. It should be mentioned that collision frequency induced by van der Waals forces and/or Brownian motion is much lower than that induced by flow at typical conditions of mixing or rheological measurements.

In homogeneous steady flow, dynamic equilibrium between the break-up and coalescence is stabilized after a certain time. The dynamic equilibrium means that the formation and disappearance of droplets with a certain sizes and shapes due to their break-up are balanced by their disappearance and formation due to their coalescence. As a consequence, steady, time independent, distribution of the droplet size and shape is established. Shape distribution of the droplets in steady state is determined by their average size and related break-up mechanism. If the average droplet radius is not much larger than R_c , droplets should break-up by the stepwise mechanism. If, due to pronounced coalescence increasing with volume fraction of the dispersed phase, the average droplet radius is substantially larger than R_c , a transient break-up mechanism can be operative also in the steady state (dynamic equilibrium) and highly anisometric particles can exist in steady morphology.

Flow field in a mixer is not homogeneous and stresses in various points differ substantially [22]. To explain the observed effect, it is necessary to consider the behavior of volume elements with linear dimension from tens to hundreds micrometers. If such volume elements spend the time needed to reach the steady particle size distribution in places with almost constant flow characteristics, the particle size distribution in a mixer will be position dependent. On the other hand, if the volume elements pass among the places with strongly different flow characteristic very quickly, the particle size distribution will depend on the average flow characteristic in a mixer. Therefore, the particle size distribution in the mixer will be position independent, *i.e.* uniform. The latter case has been assumed at determination of the particle size distributions in the blends prepared by melt mixing in batch mixers.

Unfortunately, it is very difficult to compare the rate of throughput of volume elements through a mixer with the time necessary to reach the dynamic equilibrium between the particle break-up and coalescence in this element. Break-up and coalescence frequencies must be known for determination of time required to reach the

steady particle size. The present knowledge of the break-up and coalescence frequency in simple shear or extensional flow is incomplete and it is very limited for more complex flow fields [23]. Generally, the break-up of a particle is possible only if the particle radius R is larger than the critical radius R_c . R_c is a function of the deformation rate and, therefore, it depends on the position in a mixer. For the particles with radius R not much larger than R_c , break-up frequency is an increasing function of R . For even larger R , situation is less clear [23]. In a region of small particle radii, the coalescence frequency is a constant or slowly decreasing function of R . This region is followed by a steep decrease in coalescence frequency to a very low value and, after that, by the asymptotic approach to zero [23]. Also the radius R_s , for which coalescence frequency falls to very low, practically negligible, value, depends on the position of the particle in a mixer. For $R_c < R_s$, the dynamic equilibrium between the particle break-up and coalescence can level off. For $R_c > R_s$, particles with $R > R_c$ undergo break-up while the particles with $R < R_s$ undergo coalescence. Coalescence of the particles with R between R_s and R_c is very slow (probability of coalescence of colliding particles is very low) and their size can be considered as a constant during their throughput through the related areas.

So far, rather small attention has been given to study of the time necessary to reach the dynamic equilibrium between the break-up and coalescence. The approximate theory for the shear flow [28] predicts that the order of magnitude of the time needed to reach the steady state (for $R_c < R_s$) is given by inversion of shear rate. It is known that the average shear rate in mixers in s^{-1} has the same order of magnitude as a number of kneader revolutions per minute [29]. It is practically impossible to predict relations between R_c and R_s in individual places in a mixer on the base of present knowledge about the particle break-up and coalescence. On the other hand, it can be estimated that the time necessary to reach the local steady state is substantially shorter than the time related to the path of a volume element during one revolution of a kneader. Therefore, it is reasonable to assume that the full local dynamic equilibrium is not established in individual places of a mixer but the average particle size in a volume element can change during its path through a mixer. This assumption agrees very well with the experimental results observed.

It follows from comparison of quenched and compression molded samples that non-uniformity of the phase structure in compression molded samples is substantially more pronounced than that in quenched ones. It is visible that particles in compression molded samples are larger and substantially less anisometric than those in quenched samples (cf. Figs. 1 and 2 with 3 and 4). It is caused by shape relaxation and coalescence in quiescent state during compression molding. Coalescence can cause differences in particle sizes in the places differing in their thermal histories. In compression

molded samples, the differences among average particle sizes in various places should continuously change from edges to the centre of a plate. It was not observed in the samples under study. The coalescence can cause also differences among average particle sizes in places differing in particles' concentrations. Also concentration fluctuations can result from inhomogeneous flow field in a mixer. We believe that the most probable explanation of the higher non-uniformity of compression molded samples lies in the fact that in these samples, volume elements distant in a mixer appear in the neighborhood during the sample removal from a mixer and compression molding.

It should be mentioned that an increase in the rate of mixing does not suppress non-uniformity of the phase structure automatically as a consequence of the enhancement of the throughput velocity but simultaneously it leads (*via* an increase in the average shear rate) to a decrease in time needed to reach the local steady state.

CONCLUSIONS

The areas containing particles with strongly different size distributions were detected in quenched and compression molded samples of various binary and ternary polymer blends. It was shown that neglect of non-uniformity of the phase structure can lead to erroneous determination of the phase structure dependence on the polymer blend composition, properties of the components and mixing conditions.

Observed non-uniformity of the phase structure was explained as a consequence of non-uniform flow fields in the mixers.

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