



Akademie věd České republiky

Teze doktorské disertační práce
k získání vědeckého titulu „doktor věd“
ve skupině věd chemických

**Phase structure formation and evolution in
polymer blends**

Komise pro obhajoby doktorských disertací
v oboru makromolekulární chemie

doc. RNDr. Ivan Fortelný, CSc.

ÚMCH AV ČR

Praha, březen 2006

Introduction

Mixing of two or more different polymers together makes it possible to achieve various property combinations of the final material – usually in a more cost-effective way than in the case of synthesis of new polymers. Therefore, polymer blends are substantial and growing part of polymeric materials. Recently, polymer blends also become the results of material recycling of mixed plastic scrap. Due to high molecular weight, mixing entropy of polymers is low in comparison with low-molecular-weight liquids. Therefore, most polymer pairs are immiscible. As a consequence, polymer blends are not formed spontaneously. At service temperatures, immiscible polymer blends have frozen non-equilibrium phase structure which depends on the process of their preparation.

Melt mixing is the most widespread method of polymer blend preparation in practice. Products from blends of plastics and plastics with uncrosslinked elastomers are prepared by the blends processing in molten state with the methods typical of thermoplastics. Because the phase structure of immiscible polymer blends determines, besides their composition and properties of the components, their properties, its control during mixing and processing is crucial. The phase structure formed in flowing molten polymer blends depends on their composition, viscosity and elastic properties of the components, interfacial tension and thermomechanical history. Because the phase structure is a function of as many factors which effects frequently cannot be separated, formulation of general rules for prediction of the phase structure is very difficult. The first possible approach is formulation of empirical rules based on experimentally determined correlations. However, all empirical rules, so far formulated using experimental results for some systems, totally failed for some other systems. The second possibility is microrheological description of the phase structure development, i.e. to study flow of individual domains in polymer blends and to describe individual events during phase structure development. Polymer melts are viscoelastic substances displaying complicated rheological behavior; flow fields in mixing and processing equipment are complex; and thermomechanical history is complicated by substantial heat production. Instantaneous morphology of a polymer blend affects the flow fields during mixing and processing, and the amount of dissipated energy and, consequently, temperature profile in the sample. Thus, morphology and thermomechanical history are interdependent. It is not surprising that ultimate aim of microrheological theory, a detailed prediction of the phase structure from the blend composition, properties of the components, and thermomechanical

history during blend preparation and processing, is still far from completion. It seems that combination of gradual improvement of approximate microrheological theory with experimental study of microrheological events as the droplet breakup and coalescence in model systems and with experimental study of the effects of a blend composition, individual properties of its components and mixing conditions on the blend morphology is a proper way to improvement of our knowledge. It should be mentioned that for practice, also qualitative but certain knowledge of the dependence of some parameters of the phase structure, e.g. average particle size, on properties of the components, e.g. viscosity, is of a great importance because it can make development of a new blend much more efficient.

The thesis was aimed to the contribution to improvement of understanding and description of the phase structure formation and evolution in molten immiscible polymer blends in flow and quiescent state. For achievement of this aim, we developed theoretical description of microrheological events in immiscible polymer blends and experimentally studied the effects of various parameters on the phase structure of polymer blends with well characterized components. We focused on the understanding and description of coalescence in molten quiescent polymer blends, on the description of flow induced coalescence and analysis of the competition between the droplet breakup and coalescence, on experimental study of the effect of a blend composition, rheological properties of the components and mixing conditions on the phase structure and on theoretical and experimental studies of the effect of a compatibilizer on the phase structure development. Results obtained at these studies we tried to utilize at development of efficient recycling methods for municipal plastic waste.

Results

Theory of coalescence in quiescent polymer blends

Remarkable growth of dispersed particles in molten quiescent polymer blends during their annealing has been observed from seventies [1,2]. It was found that the Smoluchowski theory of Brownian motion-induced coalescence [3] predicts only negligible effect for highly viscous polymer blends [1]. Therefore, applicability of the Smoluchowski theory to polymer blends was studied with respect to the approximations used at its derivation [A2]. It was found that the Smoluchowski theory contains approximations for diffusion flux of particles which are not applicable to polymer blends. The revised theory, using approximations appropriate for polymer blends, was derived. The theory predicts the rate of coalescence for systems with a high viscosity of the matrix somewhat higher than original Smoluchowski theory but

substantially lower than that detected experimentally for blends with a high content of the dispersed phase. The assumption of van Gisbergen and Meijer [4], that the rate of coalescence is controlled by the time of drainage of the matrix trapped between neighboring flattened droplets, was adopted in the paper [A15]. In contrast to [4], the effect of the volume fraction of the dispersed phase was included (using the assumption that only particles with distance smaller than the half of their radius can coalesce) in the theory [A15]. The time dependence of the average droplet radius was calculated for the case that the gravity, van der Waals forces or Brownian motion is driving force of the coalescence. Fully mobile, partially mobile and immobile interface were considered at description of the matrix drainage between the flattened droplets. The theory predicts the dependence of the coalescence rate on the content of the dispersed phase in qualitative agreement with experiment. Analysis of the results showed that the driving force of the coalescence and mobility of the interface cannot be determined from the shape of the time dependence of the average droplet radius. The weakest point of the theory is rapid increase of the coalescence rate with decreasing driving force of the coalescence for small driving forces which is a consequence of using of the model of highly flattened droplets. The model realistically describing coalescence in quiescent polymer blends was developed in [A21]. The coalescence is induced by combination of molecular forces and Brownian motion and the droplets keep spherical shape during the whole coalescence process. It was shown that the coalescence in blends with viscoelastic matrix is faster than that with Newtonian matrix with the same viscosity. The theory, derived with the assumption that molecular forces are the main driving force of the coalescence, predicts dependences of the average droplet radius on system parameters (viscosity of the components, interfacial tension, temperature) in qualitative agreement with experimental data. It also provides reliable magnitude of the coalescence rate. Generally, besides of the coalescence also Ostwald ripening can cause the droplet growth in molten quiescent polymer blends [8-12]. For this reason, dependences of the rate of growth of the average droplet radius on the system parameters, following from the above theory of coalescence [A21], theory of Ostwald ripening [8] and experimental data [2,4-6,8-12] were compared [A24]. Analysis of the theories showed that the rate of coalescence increases but the rate of the Ostwald ripening decreases with increasing interfacial tension. It undoubtedly follows from experimental data collected in the paper that the average droplet size of dispersed particles during annealing grows faster in blends with a higher interfacial tension. Therefore, the analysis led to the conclusion that the droplet growth in molten polymer blends with medium and high interfacial tension is caused by the coalescence. For polymer blends with a low interfacial tension, both

the coalescence and Ostwald ripening should be considered. Assumptions and results of existing theories were summarized and limits of their applicability on real molten polymer blends were discussed in [A30].

Description of flow induced coalescence and its competition with droplet breakup

It is broadly accepted that the size of dispersed droplets in flowing polymer blends is controlled by the competition between the droplet breakup and coalescence [18-22]. Both events are complex phenomena especially for blends with viscoelastic properties and a moderate or high content of the dispersed phase. Therefore, their theoretical study started with dilute systems containing Newtonian liquids. Only gradually, the studies have been generalized to systems better matching to real polymer blends.

Flow-induced coalescence is a complex event also in a mixture of Newtonian fluids with a low content of droplets. Generally, the approach of the droplets is affected by their mutual hydrodynamic interaction and their hydrodynamic interaction with other droplets. The approach of the droplets proceeds together with their rotation around their common center of inertia. During drainage of the matrix trapped between the droplets, flattening of the droplets appears which extent, depending on the system parameters, affects the drainage course. Shape relaxation of a coalesced droplet is affected by the stress in flow which has tendency to deform (and eventually burst) the droplet during latter stage of its rotation around center of inertia of the former droplet pair. Due to these complications, only theories restricted to individual stages of coalescence and/or valid for a restricted range of parameters are so far available.

The theory of flow induced coalescence of Newtonian droplets in Newtonian matrix, considering that the droplets keep spherical shape through the whole process till touching, was derived by Wang et al. [23]. However, the assumptions and approximations used in this theory are adequate only for systems at very low shear rates, e.g. at some rheological measurements. Only recently, the theory was generalized by Rother and Davis [32], by consideration of the droplet flattening as a small but singular perturbation. Approximate theories, assuming that the droplet flattening at coalescence is large, were derived by Elmendorp [25-27] and Janssen [21,29,30]. In the paper [A30], the assumptions and approximations used in Elmendorp's and Janssen's theories were analyzed and two new approximate methods of calculation of the probability, P_c , that the droplet collision will be followed by their fusion, were proposed. It was found that the shapes of the dependence of P_c

on the droplet radius, R , are similar for all compared theories but values of P_c for the same sets of parameters differ substantially. The theory of extensional flow induced coalescence was derived in [A38]. P_c was calculated using Elmendorp's and Janssen's methods and the method considering a change in the droplet flattening during coalescence with the same description mobility of the interface and system parameters. It was shown that, in the method considering a change in the droplet flattening, the condition that the approach of flattened droplets cannot be faster than that of the same droplets with spherical shapes must be taken into account. Using the last condition, the method considering a change in the droplet flattening leads to the conclusion that for small R , P_c is smaller than 1 and, in agreement with the Wang et al. theory [23], it depends on the viscosity ratio of the dispersed phase and matrix. A decrease of P_c at a high R can be qualitatively described with Janssen's theory. Analysis of the results and assumptions of existing theories and available experimental results showed [A40] that P_c can be successfully approximated by a product of the expressions for spherical droplets and for flattened droplets according to Janssen's theory.

The competition between droplet breakup and coalescence leads to the time development of the distribution of droplet sizes which can be obtained as a solution of the generalized Smoluchowski (balance population) equation [31,A13]. Its form depends on breakup mechanism (number and size of a drop fragments) and a number of droplets for which simultaneous coalescence is considered. Both a discrete model, where the volume of a dispersed droplet is a product of an integer and the elementary volume, and a continuous model, where such restriction does not apply, are used in the literature. Breakup of droplets in flow has been intensively studied. The results are summarized in several reviews [18-22,32]. Generally, a droplet can burst only when the flow stress, which has tendency to deform the droplets, prevails the interfacial stress (equal to the Laplace pressure), which has the tendency to minimize the interfacial area. The dimensionless capillary number, Ca , defined as

$$Ca = \frac{\tau R}{\sigma} \quad (1)$$

where τ is the flow stress, is used as a measure of the stress ratio. Breakup can occur only if Ca is larger than the critical capillary number, Ca_c , which is a function of rheological properties (ratio of viscosities of the droplet and matrix only for both Newtonian components). Various breakup mechanisms can appear in dependence on the system parameters. At present, the dependence of Ca_c on the system parameters is established quite

well, especially for simple (shear, extensional, etc.) flows. Substantially less explored is the breakup frequency, i.e. the time needed for deformation and breakup and a number of fragment formed by the breakup, as a function of the system parameters.

Many studies, using various approximations in formulating and solving the equation for the evolution of the droplet population and/or in determining coalescence and breakup frequency, deal with systems where dynamic equilibrium between breakup and coalescence is established [26,31,34-37]. In other papers, the path of a droplet through an extruder was modeled and breakup and/or coalescence in individual zones were considered [29,36,38,39]. All mentioned theories are focused on prediction of average droplet size, eventually droplet size distribution, as a function of the volume fraction of the dispersed phase, properties of the blend components and flow characteristics. The equation for average droplet radius in steady flow was derived in [A5] using the assumption that the dynamic equilibrium between the droplet breakup and coalescence is established. Simplified model, where the system is still monodispersed and the breakup leads to a decrease and coalescence to an increase in average droplet size, was treated. It was assumed at construction of the expression for frequency of droplet breakup that average droplet radius is not much larger than the critical radius for droplet breakup and that P_c is independent of the droplet radius. This theory predicts that the average droplet radius is equal to the critical one for droplet breakup in infinitely diluted system and it increases linearly with increasing volume fraction of the dispersed phase. In the following paper [A13], distribution of droplet sizes was considered at description of the competition between the droplet breakup and coalescence. Scaling rule, based on the assumption that breakup and coalescence frequencies are homogeneous with respect to the droplet sizes, was used. For the breakup frequency, expression similar to that used in [A5] was applied. It was assumed that P_c decrease with a power of the droplet radii. Equations for time of the system transition in the steady state and for the average droplet size in the steady state were derived. It was found that neither of them is sensitive on the size of fragments after droplet breakup. The time of the system transition decreases with the shear rate and volume fraction of the dispersed phase. If simultaneous collisions of three and more droplets are neglected, the theory predicts slower than linear growth of the droplet size with their volume fraction in a blend.

The effect of dependence of the breakup frequency on the droplet size on the description of the competition between the droplet breakup and coalescence for simplified model of polymer blend containing monodispersed droplets was analyzed [A32]. Graphic solution of the kinetic equation describing dynamic equilibrium between the droplet breakup and coalescence was

used for the analysis. It was shown that the dependence of the breakup frequency on the droplet radius, which shapes strongly differ in previous papers dealing with the competition between the droplet breakup and coalescence, has a fundamental effect on the steady droplet size. Unique solution of the kinetic equation and monotonic increase of the droplet radius with volume fraction of the dispersed phase are obvious only for monotonic increase of the breakup frequency with droplet radius. On the other hand, a volume fraction range where the droplet size is constant appears if the breakup frequency has a step character as a function of droplet radius. The kinetic equation has more than one solution if the breakup frequency is decreasing or is a nonmonotonic function of droplet radius.

Rules for prediction of the phase structure in immiscible polymer blends from the knowledge of their composition, component properties and the flow field in mixing or processing device are discussed in [A33]. The reliability of qualitative prediction of the dependence of phase structure on system parameters, important for industrial practice, was used as a criterion of plausibility of the rules. It was shown that no general rule for prediction of the phase structure type is available in the literature. Better description of dependence of the droplet breakup frequency on its size, contribution of simultaneous collisions of three or more droplets to coalescence and the effect of complex flow field on breakup and coalescence are needed for a reliable qualitative prediction of the dependence of the droplet size on the system parameters.

Experimental study of the phase structure development

Formation of the phase structure at the initial stage of the mixing was intensively studied by Macosko's group [40-44]. It was found that sheets of minor phase are formed after the start of mixing. Quite rapidly, holes are formed in these sheets that coalesce. Further, the sheets transform to fiber or co-continuous structures, which can pass (depending on blend composition and properties of the components) to a dispersed structure. If the softening or melting transition temperature of the minor phase is lower than that of the major phase, switching of phase continuity occurs at this stage of mixing [43]. It was found that the reduction of characteristic size of phase domains from millimeters (characteristic size of polymer pellets) to micrometers is rapid. This reduction has been achieved during the first 2 min in batch mixers and in first mixing zones in extruders.

For application of polymer blends, type and fineness of their phase structure are important. In blends of immiscible polymers 1 and 2 with low content of 2, particles of component 2 are

dispersed in the matrix of component 1. With rising fraction of 2, partially continuous structure of 2 appears. With further increase in the amount of 2, fully co-continuous structure is formed. After that, phase inversion occurs, where 2 forms the matrix and 1 the dispersed phase [18,45]. Intervals of the blend composition related to individual types of the phase structure depend on rheological properties of the components, interfacial tension, and mixing conditions. Moreover, continuity of a component increases with its volume fraction only gradually [45,46]. Several theories and empirical rules have been formulated for prediction the composition at which full or partial continuity of individual components appears. So far, no of them predicts conditions for continuity of the components quite satisfactorily [45,46].

Fineness of the phase structure was studied mostly for blends with droplets in matrix morphology. As it is shown above, the droplet size is controlled by the competition between the droplet breakup and coalescence. Experimental studies of the droplet size should serve for verification of ability of various theories to describe the phase structure development in polymer blends at real mixing conditions. Further studies are focused on the investigation of time development of the droplet size for which adequate theory is not available so far, on the study of the phase structure development in ternary polymer blends, where the effect of the third component to the droplet size is not included in any theory and on the study of blends, where the phase structure development is complicated by changes of the components by chemical reactions, e.g. at chemical degradation of the components and dynamic vulcanization.

Similar dependences of the morphology on composition were found for PE/EPDM and PP/EPDM blends [A1]. The crystallinity of both PE and PP considerably decreases with increasing content of EPDM in the blend. Dependence of the particle size and the impact strength on concentration of ethylene-propylene elastomer (EP(D)M) in PP/EP(D)M blends was studied using three grades of PP and four grades of EP(D)M differing in rheological properties [A3]. It was shown that an increase in viscosity of the polypropylene matrix leads to a finer phase structure at all concentrations of EP(D)M under study (5 – 30%). At a constant viscosity of PP, an increase in viscosity of EP(D)M caused coarsening of the phase structure at low contents of EP(D)M and a slower decrease of the reduced interfacial area (growth of the droplet size) with concentration of EP(D)M. This dependence was explained as a consequence of the growth of critical radius for droplet breakup and a decrease of the value of coalescence probability P_c with increasing viscosity of the dispersed phase. The effect of the content and grade of linear polyethylene, of the type of EPDM rubber and of the mixing procedure on the structure and mechanical properties of PP/EPDM/PE blends was studied

[A4]. Particles with PE core and more-less continuous (in dependence on EPDM/PE ratio) EPDM shell were dispersed in PP matrix. Substitution less than 50% of EPDM with PE led to an enhancement of the impact strength. PP/EPDM/PE blends prepared by two-stage mixing (batch EPDM/PE was prepared at first) showed a higher impact strength than those prepared by one-stage mixing.

The papers [A6-A8,A11] dealt with experimental study and interpretation of the phase structure formation during mixing of PP/EP(D)M and PP/EP(D)M/PE blends. It was found that places with fine phase structure coexist with places containing large elastomeric particles surrounded with neat PP in PP/EP(D)M blends after short times of mixing in the chamber of a Brabender Plasticorder [A6]. A number and size of large elastomeric particles decreased with increasing time of mixing. After a certain time of mixing, large particles fully disappeared and blends achieved limit value of the impact strength. The mixing time, necessary for achievement of uniform structure and limit value of the impact strength, decreased with increasing rate of mixing and viscosity of the matrix and decreasing viscosity of the dispersed phase. The phase structure in PP/EP(D)M/PE blends develops by the same manner as in binary PP/EP(D)M blends [A7]. If a part of EP(D)M is substituted with polyethylene having a lower viscosity, uniform phase structure and limit value of the impact strength are achieved at a shorter time and lower speed of mixing. At substitution of a part of EP(D)M with PE having practically the same viscosity, the same mixing conditions as for the binary blend are necessary for achievement of the uniform phase structure. Study of the dependence of average particle size on time of mixing in PP/EP(D)M blend showed [A8] that, after the start of mixing, the average particle size decreased till its minimum value. After that, it started to growth with further increasing time of mixing. During initial period of mixing, the phase structure developed by the manner described in [A6]. The phase structure was uniform for a long time of mixing. Evaluation of the torque during mixing and measurements of intrinsic viscosity of the samples let to the conclusion that polypropylene matrix degrades at long times of mixing. A decrease in viscosity of PP matrix due to its degradation induces growth of the particle size, because it enhances the critical radius for droplet breakup and probability of coalescence. It was found that, for a certain system, the uniform phase structure is achieved at a constant product of the time and rate of mixing which is proportional to the whole sample deformation [A11]. For a certain matrix, value of this limit product increases with viscosity of EP(D)M. Value of the limit product correlates with viscosity measured at low shear rates, not at shear rates related to the mixing conditions. This effect was interpreted as a consequence of

the fundamental role of extensional component of the flow at the droplet breakup – extensional viscosity correlates with the shear viscosity measured at low shear rates.

The dependence of phase structure on a blend composition was investigated for two types of PP/EPM blends differing in rheological properties of the components in [A9]. It was found that the blend with similar viscosities of the components showed co-continuous structure for substantially broader range of composition than the blend where viscosity of EPM was substantially higher than that of PP. Surprisingly, the phase inversion point, defined as the centre of the composition range related to the co-continuous morphology, was determined for a lower content of EPM for the blend with a higher EPM/PP viscosity ratio in contrast with rules formulated for prediction of the phase inversion composition from viscosity of the blend components [18,45,46]. This result cannot be explained either by the Van Oene theory considering elasticity of the blend components [45,46]. The results of the paper clearly demonstrate the fact that no predictive rule, formulated so far, for determination of the phase inversion in polymer blends has general validity.

Development of the phase structure in polypropylene/polyisobutylene (PP/PIB) blends was inhomogeneous [A10], similar to the PP/EP(D)M blends [A6,A8,A11]. The size of PIB particles gradually increases with PIB content in a blend but slope of the increase depends on molecular weight of PIB in agreement with imagination that the effects of viscosity of the dispersed phase on the droplet breakup and coalescence are different. In ternary PP/PIB/PE blends with PP matrix, PIB and PE particles are neither independently dispersed in PP matrix nor form core-shell structure. PIB and PE are mostly in mutual contact and form small clusters. Finer PIB particles than that in the related PP/PIB blends were found in PP/PIB/glass fibers composites, probably due to an increase in stress during mixing which was caused by the addition of glass fibers. The dependence of phase structure on intensity of mixing was studied for two modified polyamide/[poly(phenylene oxide)+polystyrene] (MPA/PPOS) (50/50) blends with different viscosity ratios of components in [A12]. In these blends, MPA forms the matrix and the mixture of miscible polymers (PPOS) forms the dispersed phase at all rates of mixing. It was found that the average size of the PPOS droplets grows with increasing rate of mixing till a maximum and after that starts to decrease. This surprising result was analyzed using models considering dynamic equilibrium between the droplet breakup and coalescence at steady mixing. The analysis showed that, for systems where coalescence is nonnegligible, the dependence of the droplet size on rate of mixing can be decreasing, increasing or nonmonotonic in dependence on the system parameters.

The study of dynamic curing of PP/EPDM blends showed [A14] that the rate of curing must be optimized by the choice of the curing system composition and mixing protocol for achievement of the blend with fine phase structure and high impact strength. Large EPDM particles, appearing after short times of mixing [A6,A8], are crosslinked and, therefore, fixed if curing is too rapid. Their existence in a final blend is detrimental for impact strength of the blend. The using of a curing inhibitor in the system and a one-step method of dynamic curing leads to an increase in the impact strength of blends. From comparison of dependences of the impact strength for dynamically cured and uncured PP/EPDM blends on the absolute value of complex shear modulus, it followed that dynamically cured blends have substantially higher impact strength at the same level of stiffness.

Systematic study of the phase structure development in polypropylene/polystyrene (PP/PS) blends [A16,A19,A23,A25] showed that nonuniform phase structure is formed. It was found that regions, containing several hundreds of particles, with strongly different average size of PS particles coexist in all studied blends. Nonuniform phase structure appeared at all compositions of the blends and properties of the blend components and surprisingly persisted also after long and intensive mixing. A decrease of the average particle size with the growing rate of mixing was found for PP/PS (95/5) blends [A16]. On the other hand, systematic dependence of the average particle size on the rate of mixing was not found for PP/PS (75/25) blends. This difference in behavior of PP/PS (95/5) and (75/25) blends was explained using the assumption that the coalescence is not pronounced in (95/5) and a decrease in particle size is caused by their breakup into smaller parts at more intensive mixing. On the other hand, coalescence is important for PP/PS (75/25) blends and the dependence of the particle size on the rate of mixing can be weak or nonmonotonic from the reasons discussed in [A12]. The addition of a compatibilizer (styrene-butadiene block copolymer (SB)) led to a finer phase structure but did not suppress its nonuniformity [A19,A23]. Nonuniform phase structure was formed in both the mixers used at the study – a chamber of the Brabender Plasticorder and microextruder. The only way how to enhance uniformity of the phase structure was an increase in the mixing temperature [A23,A25] – uniform phase structure was detected in the blend mixed at 250 °C.

It was found that the particle sizes of the dispersed component in polycarbonate/poly(styrene-*co*-acrylonitrile)/poly(ethylene-*co*-propylene) (PC/SAN/EPM) blend immediately after mixing were larger than those for the related binary blends [A17]. On the other hand, the coarsening of the phase structure during annealing was slower for the ternary than for the binary PC/SAN and PC/EPM blends. In the ternary blends containing

only 40% PC, polycarbonate still formed a continuous matrix with SAN and EPM inclusions in contrast to the cocontinuous structure of a PC/PSAN (60/40) blend. These results confirm the generally positive influence of the presence of dispersed, mutually immiscible minority components in ternary blends on a lowering of the concentration needed for the matrix phase continuity. It was found for low-density polyethylene/isotactic polypropylene (LDPE/PP) blends [A18] that EPDM is localized at the interface between LDPE and PP phases in the whole range of LDPE/PP ratios. The admixture of 5% EPDM substantially enhanced impact strength of LDPE/PP blends at all the compositions. Higher intensity and longer mixing time had a positive effect on the impact strength of blends with a higher content of LDPE. For blends with a high content of polypropylene, positive effect of long and intensive mixing is manifested only when the blend degradation is prevented by additional stabilization.

Dynamic mechanical properties of molten uncrosslinked and dynamically crosslinked polypropylene/ethylene-propylene-diene elastomer blends (PP/EPDM) were compared in [A20]. It was found for uncrosslinked blends that the dependence of dynamic viscosity and storage modulus on frequency reflects the type of their phase structure. Dynamically crosslinked blends with the content of elastomer above 20% showed remarkable increase in viscosity and storage modulus in the region of small frequencies – rheological properties typical of systems where physical network of dispersed particles exists (e.g. polymers filled with very fine mineral fillers). Rheological properties of dynamically crosslinked blends at low frequencies and low shear rates were explained as a consequence of long-lived entanglements among touching crosslinked elastomer particles in blends with elastomer particles having concentration above the percolation threshold or among crosslinked domains if the elastomer phase is continuous.

Effect of a compatibilizer on the phase structure development

The presence of compatibilizers (block or graft copolymer, pre-made or formed in flow) at the interface has fundamental effect on the phase structure development in polymer blends. So far, no quantitative theory describing the effect of a compatibilizer on the type of the phase structure has been proposed. The effect of a compatibilizer on the size of dispersed droplets in a matrix can be predicted if the compatibilizer effect on the droplet breakup and coalescence and its distribution between the interface and bulk phases are known. The effect of copolymers on the droplet breakup and coalescence shares features with the related effect of surfactants in water-oil mixtures, broadly studied in the literature. The approach to the

description of the both types of systems is similar but plausibility of various approximations and importance of various contributions to the effects can differ strongly due to the different molecular nature of the components and many orders difference in the values of rheological functions. Summary and discussion of the results of the studies of compatibilizer effects on the morphology of polymer blends can be found in [68].

Analysis of the effect of a compatibilizer on the breakup and coalescence of droplets in flowing polymer blends [A26] is based on theories developed in the literature for low molecular weight emulsions containing a surfactant. The effect of a compatibilizer on the stepwise and transient breakup mechanisms is qualitatively different. For the stepwise mechanism, the presence of a compatibilizer causes a larger deformation and easier breakup of the droplet due to a decrease in interfacial tension. Inhomogeneous distribution of a compatibilizer on the interface due to its convection in flow supports and the dilution of a compatibilizer in the droplet deformation suppress the droplet breakup with respect to the neat system with the same equilibrium interfacial tension. Inhomogeneous distribution of a compatibilizer can also change a mode of the breakup, e.g. breakup into two halves to tip-streaming. Contributions of the individual effects are dependent on the rates of compatibilizer migration on the droplet surface and between the interface and bulk phases. In the transient mechanism, the presence of a compatibilizer causes an easier elongation of the droplet. On the other hand, it leads to its longer breakup time. The presence of a compatibilizer suppresses coalescence of droplets due to an increase in the capillary number, a decrease in mobility of the interface, and slowing of the shape relaxation of the droplets. The effect of a compatibilizer to the probability of coalescence increases with decreasing ratio of the viscosities of the droplets and matrix.

It was showed [A28] that in description of the effect of a compatibilizer on the phase structure development in molten polymer blends, the following three processes must be considered: (i) a decrease in the interfacial tension, (ii) the effect of a compatibilizer on the course of droplet breakup and coalescence, and (iii) the effect of the competition between the droplet breakup and coalescence on the interfacial area. The last effect cannot be neglected if establishment of the steady state is considered. A theory describing the dependence of the size of dispersed droplets on the composition of compatibilized polymer blends in steady shear flow was derived [A29]. Dynamic equilibrium between the droplet breakup and coalescence and steady distribution of a compatibilizer between the interface and bulk phases were assumed. The effect of droplets breakup and coalescence on the interfacial area available for molecules of a compatibilizer and, hence, on interfacial tension was considered. Dependences

of the droplets size on the volume fraction of the dispersed phase were determined using different assumptions about rules controlling distribution of a compatibilizer between the interface and bulk phases. Remarkable effect of the chosen rule on the dependence was found. The results of the theory show that the dependences of the average droplet size on the volume fraction of the dispersed phase are qualitatively different for cases where: (i) the ratio of the amounts of a copolymer and dispersed phase or (ii) the total amount of the copolymer in the blend is a constant.

The expression for probability of flow-induced coalescence, P_c , of deformable droplets, proposed in the form: a decreasing function of viscosity ratio of the dispersed phase and matrix multiplied by P_c from Janssen's and Meijer's theory [29,30], was used for analysis of the origin of coalescence suppression in compatibilized polymer blends [A40]. It was shown that a strong negative correlation exists between the mechanisms of coalescence suppression considered so far: the Marangoni force and steric repulsion between layers of a copolymer on the surface of droplets. The analysis led to the conclusion that the decisive mechanism of the coalescence suppression cannot be determined from the dependence of the coalescence frequency on the flow deformation rate. The steric repulsion can manifest itself only if the Marangoni effect is negligible. However, for prediction of the magnitude of the Marangoni effect, the knowledge of the rate of copolymer diffusion along the interface, which is not available for molten polymer blends, is necessary.

The effect of molecular structure of styrene-butadiene (SB) block copolymers on their compatibilization efficiency, i.e. their effect on fineness of the phase structure and mechanical properties of compatibilized blends, was studied for blends of atactic polystyrene (PS) or high-impact polystyrene (HIPS) with various sorts of polyolefins [A31,A34,A36,A37,A39,A42,A45]. It was found that the type of the phase structure in HDPE/HIPS and LDPE/HIPS blends was not affected by the addition of SB compatibilizer for both the blends. The localization and supermolecular structure of the SB compatibilizer in the blends depended on the type of PE (HDPE or LDPE) and, surprisingly, also on the PE/HIPS ratio. Addition of the SB compatibilizer improved the impact strength of both HDPE/HIPS and LDPE/HIPS blends in the whole concentration range, especially of blends with a low content of the minor phase. For blends with PE/HIPS ratio of about 1/1, the SB copolymer is a better compatibilizer (from the point of view of the impact strength improvement) for HDPE/HIPS than for LDPE/HIPS blends. Compatibilization of PS/PP, PS/HDPE, PS/LDPE and polystyrene/polybutadiene (PS/PB) blends with model set of SB copolymers with various number of blocks and lengths of styrene blocks showed that the

length of styrene blocks have a fundamental effect on the distribution of SB copolymers between the interface and bulk phases and on their supermolecular structure in blends [A34,A36,A37,A39,A42,A45]. It was found that SB copolymers with long styrene blocks are more efficient compatibilizers for PS/PB than SB with short styrene blocks. On the other hand, SB copolymers with short styrene blocks were more efficient compatibilizers in PS/PP blends [A34]. Kinetics of the morphology development in PS/HDPE (4/1) blends compatibilized with styrene-butadiene diblock copolymer with short styrene block and pentablock copolymer with long styrene blocks was studied [A36]. It was found that a substantial part of SB diblock was localized at the interface of the blends. Surprisingly, the shape of diblock domains was strongly dependent on the rate of mixing. The mixing rate had also a nonnegligible effect on the viscoelastic properties of the blends compatibilized with the diblock. On the other hand, the pentablock copolymer was mostly localized as particles in PS matrix and its localization was not sensitive to the mixing rate. The copolymers with short styrene blocks were preferentially localized at the interface, the copolymers having long styrene blocks were mostly localized in the PS matrix [A37]. It was found that enhancement of the viscosity and storage modulus of molten blends was higher for blends compatibilized with SB having short styrene blocks than for those with SB having long styrene blocks. The enhancement decreased with increasing number of blocks in the SB copolymer. Addition of SB copolymers with short styrene blocks led also to a higher tensile impact strength than that of those with long styrene blocks. In contrast to viscoelastic properties, addition of triblock with short styrene blocks caused the highest improvement of tensile impact strength. The effect of SB triblock copolymers with a short (SB1) and long (SB2) styrene blocks on morphology and properties of PS/PP (1/4), (1/1) and (4/1) blends was studied [A39]. It was found that a substantial part of SB1 copolymer maintained the ordered supermolecular structure of the neat copolymer, and its particles were mostly attached to the PS-PP interface, regardless of the PS/PP blends composition. A small part of SB1 formed a thin interfacial layer on the PS-PP interface, thus improving the interfacial tension. The SB2 copolymer was mostly localized in PS phase in the form of micelles. In blends with low contents of PS, a part of this copolymer covered the interface. In compression molded blends with PS matrix, coverage of the interface with SB2 copolymer was much less complete than in preceding case. Despite differences in the location and structure of block copolymers, the related blends with PS/PP ratio 4/1 and 1/4 compatibilized with both the copolymers showed practically the same increase in the impact strength when compared with uncompatibilized blends. The addition of SB2 led to a greater improvement in the impact strength than that of SB1 in PS/PP blends

with 1/1 composition. The most surprising result was a pronounced migration of SB1 and SB2 copolymers in the molten quiescent PS/PP (4/1) blends which was detected by comparison of the morphology of quickly quenched, compression molded and annealed blends. Coalescence of SB1 particles was detected in molten PS/PP/SB1 blends which led to a worsening of the interface coverage. On the other hand, a pronounced migration of SB2 copolymers to the interface was found in the molten quiescent PS/PP/SB2 blends. These changes in the structure were strongly reflected by a decrease in the impact strength of PS/PP/SB1 and by an increase in that of PS/PP/SB2 when annealed and conventionally compression molded samples were compared.

Nonuniform phase structure similar to that found in PP/PS blends [A16,A19,A23,A25] was observed in PS/LDPE (4/1) blends compatibilized with SB copolymers having short or long styrene blocks [A42]. Nevertheless, careful image analysis, performed in three different ways, yielded reasonable and reproducible results and enabled to detect differences in the particle sizes in the blends, caused by various SB copolymers. It was shown that the dependence of the LDPE particle size on the amount of added SB and localization of SB compatibilizers in blends is predominantly controlled by the length of their styrene blocks. The effect of SB copolymers with short styrene blocks on the size of LDPE particles and on the tensile impact strength of blends achieved its limit values at 5% of SB copolymers. A pronounced decrease in the LDPE particle size and an increase in the tensile impact strength were found when the concentration of SB copolymers with long styrene blocks increased from 5 to 10%. Pronounced changes in the localization of SB copolymers during annealing, similar to those found in PS/PP/SB blends [A39], were detected. The length of styrene blocks in SB copolymers is important also for their localization in PS/LDPE (1/4) blends [A45]. Surprisingly, distribution of SB copolymers between the interface and bulk phases and their supermolecular structure strongly differed in blends with 1/4 and 4/1 PS/LDPE ratios, prepared at the same conditions (cf. [A42]). It was found that the addition of triblock and pentablock SB copolymers with long styrene blocks led to a decrease in the blend impact strength in spite of the fact that these SB improved the toughness of the both blend components. This effect was explained by the phase structure of these blends where the whole amount of SB copolymers was localized into brittle SB particles. Negative effect of an increase of the effective volume of PS particles apparently was not compensated by an increase in the particle toughness. In contrast to blends with PS/LDPE 4/1, annealing of PS/LDPE (1/4) blends compatibilized with SB having long styrene blocks did not lead to the migration of SB copolymer at the interface and an improvement of the impact strength. The

results obtained for polystyrene/polyolefin blends clearly illustrate the fact that, besides of molecular structure of SB copolymers and polyolefins, also the composition of polystyrene/polyolefin blends has fundamental effect on the compatibilization efficiency of various SB copolymers. The order of compatibilization efficiency of various SB changes with their concentration in blends and distribution of SB copolymers between the interface and bulk phases in steady state depends on the rate of mixing and it is not the same as in thermodynamic equilibrium (at rest).

Recycling of mixed plastic waste

With increasing amount of consumed plastics, their efficient recycling is still more important task. There are four main methods of plastic waste recycling [93]: energy recovery (incineration), feedstock recycling (pyrolysis, hydrogenation, gasification), chemical (de-polymerization) and material recycling. Of the mentioned processes the material ones, i.e. those reprocessing the waste into a new material, use the largest part of the stored energy. Therefore, material recycling should be preferred when degradation damage of consumed plastics is not too strong. At present, it is successfully applied to a single-sort industrial plastic waste. A more difficult task is recycling of post-consumer, in particular municipal, plastic waste. Municipal plastic waste is a mixture of several commodity polymers, frequently used for packaging, with various degrees of damage. At present, only a small part of municipal plastic waste is reprocessed by down-cycling: a molten mixture of plastic is extruded into a final form. Articles obtained by this method can be bulky but they show mediocre mechanical properties. This fact strongly limits their applicability.

The main reason for unsatisfactory mechanical properties of recycled mixed plastic waste is incompatibility of most polymer pairs, discussed in the above section. For most pairs of virgin polymers, more-less efficient compatibilization procedure was found [94] and many compatibilized polymer blends have been commercialized [95]. Compatibilization of mixed plastic waste is a more difficult task, because simultaneous compatibilization of several damaged polymers is needed. Moreover, for successful application in practice, the chosen compatibilizers should not be expensive and recycling technology should not be complicated. Besides of compatibilization, also protection of recyclates against their damage during processing and using should be achieved [96,97].

It was found that reactive liquid polybutadiene/organic peroxide compatibilization system and SB block copolymers substantially enhanced the impact strength of

LDPE/HDPE/PP/HIPS blends which can serve as a model of municipal plastic waste after separation of PET bottles [A27]. An analysis of the samples of mixed plastic waste after separation of PET bottles, recycled in Transform Bohdaneč, showed that the samples contained substantial amounts of LDPE, HDPE, PP and styrenic plastics and an admixture of PET and other plastics [A35]. It was shown that a mixture of commercial styrene-butadiene block copolymers SB and ethylene-propylene elastomers (EP(D)M) is very efficient compatibilizer for model LDPE/HDPE/PP/PS and LDPE/HDPE/PP/HIPS blends and also for real plastic waste [A35,A41]. In both cases, the addition of SB/EP(D)M mixture improved the impact strength of the blend several times and it was substantially more efficient than SB or EP(D)M alone. Surprisingly, it was found that SB/EP(D)M mixture is more efficient compatibilizer (from the point of view of the impact strength of compatibilized blends) than neat SB copolymer also for some binary polyethylene/polystyrene (or HIPS) blends [A41]. Superiority of SB/EP(D)M compared with neat SB for some binary polyolefin/polystyrene (PO/PS) blends was explained as a consequence of the effect of EP(D)M on localization of SB in PO/PS blends – a part of SB which has a tendency to be localized in the PS phase is “pulled” onto the interface due to the attraction with EP(D)M. Due to admixtures of plastic with a high melting or glass temperature, especially PET, in real samples of mixed plastic waste, the samples should be mixed at a high temperature (higher than about 240 °C). Because at high mixing temperatures main components of the waste (PE, PP and PS), especially when pre-aged, can be damaged, stabilizers were added for protection of the recycle components. Unexpected cooperative effect of SB/EP(D)M compatibilizers and stabilizers, especially those based on substituted diamines, on impact strength of the recycles was detected [A41]. It was found that application of cooperative compatibilization system in 5% concentration enhanced the impact strength of the recycles 4 – 6 times to the value comparable with virgin polyethylene. Synergism between the effects of SB/EP(D)M compatibilizers and substituted diamine stabilizers (PD) was detected also in simplified model system: pre-aged low-density polyethylene/polystyrene blends [A41,A43,A44]. Analysis of the results for the model system led us to the conclusion that the synergism between SB/EP(D)M was caused by the formation of graft SB-polyolefin copolymers which are better compatibilizers than SB copolymers alone. Formation of the graft copolymers is induced or at least strongly enhanced by the presence of substituted diamines. Detailed analysis of chemical reactions which can proceed during mixing of pre-aged LDPE/HIPS/(SB/EP(D)M) blends at presence of PD showed that pre-oxidation of LDPE and the presence PD-based antidegradants increase probability of chemical reactions leading to the grafting of LDPE chains to butadiene

blocks of SB. The rate of these reactions increased with increasing mixing temperature. Due to less regularity and presence of long LDPE blocks, formed graft polymers are more efficient compatibilizers for LDPE/HIPS blends than the SB copolymers alone.

Conclusions

Theory of coalescence of dispersed droplets in molten quiescent polymer blends was derived. It was shown that molecular forces between the droplets and their Brownian motion are main driving forces of the coalescence. The theory considers that typical polymer blends are concentrated systems where the rate of coalescence is determined by the drainage of the matrix film between neighbor droplets. Due to week driving forces of the coalescence, the droplets keep spherical shape. The theory of molecular forces induced coalescence predicts an increase in the coalescence rate with: increasing volume fraction of the dispersed phase, increasing interfacial tension and decreasing viscosity of the dispersed phase and matrix. This prediction is in qualitative agreement with experimental results. The coalescence is faster in blends with viscoelastic than Newtonian matrix with the same viscosity of the components and interfacial tension. In polymer blends with a very low content of the dispersed phase, the coalescence rate is controlled by free diffusion of droplets. At its description, approximations valid for systems with a low viscosity in the original Smoluchowski theory must be substituted by approximations applicable in highly viscous systems. The coalescence in latter systems is slow and practically undetectable by available experimental methods. An analysis of experimental data and theories of the coalescence and Ostwald ripening showed that coarsening of the phase structure in molten blends with dispersed structure and a high or moderate interfacial tension is caused by coalescence. Both the coalescence and Ostwald ripening contribute to the phase structure coarsening in molten blends with a low interfacial tension.

The theory of extensional flow induced coalescence was derived which showed that probability, P_c , that the collision of droplets will be followed by their fusion, for droplets with a small radius is lower than 1 and it is a function of the viscosity ratio of the dispersed phase and matrix. As a result of the effects of various factors in available theories of flow induced coalescence and experimental data, the expression for P_c was suggested in the form of the product of P_c for coalescence of spherical droplets and of P_c from Janssen's theory of the coalescence of highly flattened droplets. Two theories predicting the average droplet size in

steady flow were derived using the assumption that dynamic equilibrium between the droplet breakup and coalescence is established. The theories differ in the expressions for breakup frequency and the dependence of coalescence probability on droplet radius. It was demonstrated that graphic solution of the equation describing dynamic equilibrium between the droplet breakup and coalescence for simplified monodispersed system gives good insight into the problem of achievement of the steady state and dependence of the average droplet size on the system parameters. It was shown that the dependence of average droplet radius on the volume fraction of the dispersed phase is controlled by the breakup frequency of the droplets.

It was found by study of the dependence of average size of EP(D)M particles on their concentration in PP/EP(D)M blends that the effect viscosity of the components on this dependence matches to the assumption that the average size of EP(D)M particles is controlled by the competition between the particle breakup by stepwise mechanism and their coalescence. Measurements on polyamide/poly(phenylene oxide) blends demonstrated that the dependence of the average droplet size on intensity of mixing (stress in flow) in blends with moderate or high content of the dispersed phase can be nonmonotonic due to different shapes of dependences of the breakup and coalescence frequencies on stress in flow. Nonuniform phase structure (large particles surrounded areas with fine phase structure) was observed in PP/EP(D)M blends mixed at conditions commonly accepted as satisfactory for blends with uniform phase structure. The effect gradually disappears with increasing time and intensity of mixing. The product of the time and rate of mixing needed for the achievement of uniform phase structure increased with viscosity ratio of the dispersed phase and matrix. Different type of nonuniformity (rather large domains with strongly different average particle sizes) was observed in PP/PS blends. In contrast with PP/EP(D)M blends, nonuniformity of the phase structure in PP/PS blends was not suppressed by an increase in the rate and/or time of mixing but only strong enhancement of mixing temperature. The phase structure and toughness of dynamically vulcanized PP/EP(D)M blends were optimized by proper choice of vulcanization system and mixing conditions. Rheological properties of molten dynamically vulcanized PP/EP(D)M blends was plausibly explained as a consequence of long-living entanglements among partially crosslinked EP(D)M domains.

An analysis of the effect of a compatibilizer on the droplet breakup and coalescence in polymer blends showed that the effect can be estimated if available theories for low-molecular-weight emulsion are recalculated using relations and parameters for polymer melts. Quantification of contributions of individual events is impossible due to the lack of

knowledge about the rate of migration of a copolymer along the interface and between the interface and bulk phases. The first theory of the average droplet size in flowing compatibilized polymer blends, considering not only compatibilizer effect on the droplet breakup and coalescence but also changes in available interfacial area, was derived. Systematic study of the effect of SB copolymers on the phase structure and mechanical properties polystyrene/polyolefin (PS/PO) blends showed that molecular structure SB, PS and PO are not only parameters which affect compatibilization efficiency (measured by a decrease of particle size and improvement of mechanical properties) of SB copolymers in PS/PO blends. In contrast with common expectation, compatibilization efficiency of SB copolymers depended on PS/PO ratio in blends and mixing and processing conditions. The order of SB copolymers according to the effect on the phase structure and mechanical properties of a blend changed with SB concentration in the blend. Pronounced migration of SB copolymers during annealing of PS/PO/SB blends clearly demonstrated that localization of SB copolymers at steady mixing and in thermodynamic equilibrium are not the same. Therefore, the localization of compatibilizers in polymer blends generally cannot be predicted from the rules of equilibrium thermodynamics only.

It was found that a mixture of SB/EP(D)M copolymers is a very efficient compatibilizer for binary PO/PS blends, LDPE/HDPE/PP/PS blends and municipal plastic waste. The effect of SB/EP(D)M compatibilizer is further enhanced with the addition of substituted diamine based stabilizers, especially if compatibilized blends contain pre-oxidized polyolefins and high mixing temperature is used. The superiority of SB/EP(D)M mixture over neat SB in some PO/PS blends can be explained by correlation between localization of SB and EP(D)M particles in blends. The cooperative effect of SB/EP(D)M and substituted diamine based stabilizers is a consequence of grafting of polyolefin chains to butadiene blocks in SB copolymers during mixing which is enhanced by the presence of substituted diamines. Formed polymers have higher compatibilization ability than neat SB.

Generally, the results presented in the thesis substantially contributed to the present level of knowledge of the phase structure formation and evolution in polymer blends.

References

Literature

1. B. Z. Jang, D. R. Uhlmann, J. B. Vander Sande, *Rubber Chem. Technol.* **57**, 291 (1978)
2. C. C. Chen, J. L. White, *Polym. Eng. Sci.* **33**, 923 (1993)
3. J. T. G. Overbeek, Kinetics of flocculation, in *Colloid Science*, Vol. I, H. K. Kruyt, Ed., Elsevier, Amsterdam, 1952, pp. 278-301
4. J. G. M. van Gisbergen, H. E. H. Meijer, *J. Rheol.* **35**, 63 (1991)
5. Y. Liu, R. W. Truss, *J. Appl. Polym. Sci.* **60**, 1461 (1996)
6. W. R. White, P. Wiltzius, *Phys. Rev. Letters* **75**, 3012 (1995)
7. R. C. Willemse, E. J. J. Ramaker, J. Van Dam, A. Posthuma de Boer, *Polym. Eng. Sci.* **39**, 1717 (1999)
8. B. Crist, A. R. Nesarikar, *Macromolecules* **28**, 890 (1995)
9. F. M. Mirabella, *J. Polym. Sci., Part B: Polym. Phys.* **32**, 1205 (1994)
10. M. J. Hill, P. J. Barham, *Polymer* **36**, 3369 (1995)
11. F. M. Mirabella, J. S. Barley, *J. Polym. Sci.: Part B: Polym. Phys.* **32**, 2187 (1994)
12. F. M. Mirabella, J. S. Barley, *J. Polym. Sci.: Part B: Polym. Phys.* **33**, 2281 (1995)
13. A. K. Chesters, *Trans. Inst. Chem. Eng. (A)* **69**, 259 (1991)
14. W. Yu, C. Zhou, T. Inoue, *J. Polym. Sci.: Part B: Polym. Phys.* **38**, 2378 (2000)
15. W. Yu, C. Zhou, T. Inoue, *J. Polym. Sci.: Part B: Polym. Phys.* **38**, 2390 (2000)
16. H. Tanaka, *J. Chem. Phys.* **105**, 10099 (1996)
17. K. Wallheinke, P. Pötschke, C. W. Macosko, H. Stutz, *Polym. Eng. Sci.* **39**, 1022 (1999)
18. B. D. Favis, in D. R. Paul and C. B. Bucknall, eds., *Polymer Blends Vol. 1: Formulations*, John Wiley & Sons, Inc., New York, 2000, Chap. 16
19. J. Lyngaae-Jørgensen, in M. J. Folkes and P. S. Hope, eds., *Polymer Blends and Alloys*, Blackie Academic & Professional, London, 1993, Chap. 4
20. L. A. Utracki, Z. H. Shi, *Polym. Eng. Sci.* **32**, 1824 (1992)
21. J. M. H. Janssen, in H. E. H. Meijer, ed., *Materials Science and Technology, Vol. 8: Processing of Polymers*, Wiley-VCH, Weinheim, 1997, Chap. 3
22. C. L. Tucker, P. Moldenaers, *Annu. Rev. Fluid Mech.* **37**, 177 (2002)
23. H. Wang, A. K. Zinchenko, R. H. Davis, *J. Fluid Mech.* **265**, 161 (1994)
24. S. A. K. Jeelani, S. Hartland, *J. Colloid Interface Sci.* **164**, 296 (1994)
25. J. J. Elmendorp, *A Study on Polymer Blending Microrheology*, PhD. thesis, Tech. University Delft, The Netherland, 1986
26. J. J. Elmendorp, A. K. Van der Vegt, *Polym. Eng. Sci.* **26**, 1332 (1986)
27. J. J. Elmendorp, in C. Rauwendaal, ed., *Mixing in Polymer Processing*, Marcel Dekker, New York, 1991, Chap. 2
28. X. Zhang, R. H. Davis, *J. Fluid Mech.* **230**, 479 (1991)
29. J. M. H. Janssen, H. E. H. Meijer, *Polym. Eng. Sci.* **35**, 1766 (1995)
30. H. E. H. Meijer, J. M. H. Janssen, in I. Manas-Zloczower and Z. Tadmor, eds., *Mixing and Compounding of Polymers*, Hanser Publishers, Munich, 1994, Chap. 4
31. S. A. Patlazhan, J. T. Lindt, *J. Rheol.* **40**, 1095 (1996)
32. M. A. Rother, R. H. Davis, *Phys. Fluids* **13**, 1178 (2001)
33. H. A. Stone, *Annu. Rev. Fluid Mech.* **26**, 65 (1994)
34. N. Tokita, *Rubber Chem. Technol.* **50**, 292 (1977)
35. J. Lyngaae-Jørgensen, A. Valenza, *Makromol. Chem., Macromol. Symp.* **38**, 43 (1990)
36. M. A. Huneault, Z. H. Shi, L. A. Utracki, *Polym. Eng. Sci.* **35**, 115 (1995)

37. T. Milner, H. Xi, *J. Rheol.* **40**, 663 (1996)
38. L. Delamare, B. Vergnes, *Polym. Eng. Sci.* **36**, 1685 (1996)
39. H. Potente, M. Bastian, *Polym. Eng. Sci.* **40**, 727 (2000)
40. C. E. Scott, C. W. Macosko, *Polym. Bull.* **26**, 341 (1991)
41. C. E. Scott, C. W. Macosko, *Polymer* **36**, 461 (1995)
42. U. Sundararaj, C. W. Macosko, A. Nakayama, T. Inoue, *Polym. Eng. Sci.* **35**, 100 (1995)
43. U. Sundararaj, C. W. Macosko, Chi-Kai Shih, *Polym. Eng. Sci.* **36**, 1769 (1996)
44. C. W. Macosko, *Macromol. Symp.* **149**, 171 (2000)
45. P. Pötschke, D. R. Paul, *J. Macromol. Sci.* **C43**, 87 (2003)
46. C. Harrats, N. Mekhilef, in C. Harrats, S. Thomas, G. Groeninckx, eds., *Micro- and Nanostructured Multiphase Polymer Blend Systems*, Taylor & Francis, Boca Raton, 2006, Chap. 3
47. B. D. Favis, J. M. Willis, *J. Polym. Sci., Part B: Polym. Phys.* **28**, 2259 (1990)
48. B. D. Favis, J. P. Chalifoux, *Polym. Eng. Sci.* **27**, 1591 (1987)
49. S. Wu, *Polym. Eng. Sci.* **27**, 335 (1987)
50. V. Evaraert, L. Aerts, G. Groninckx, *Polymer* **40**, 6627 (1999)
51. P. G. Ghondgaonkar, U. Sundararaj, *Polym. Eng. Sci.* **36**, 1656 (1996)
52. W. Lerdwijitjarud, A. Sirivat, R. G. Larson, *Polym. Eng. Sci.* **42**, 798 (2002)
53. U. Sundararaj, in C. Harrats, S. Thomas, G. Groeninckx, eds., *Micro- and Nanostructured Multiphase Polymer Blend Systems*, Taylor & Francis, Boca Raton, 2006, Chap. 4
54. B. D. Favis, *J. Appl. Polym. Sci.* **39**, 285 (1990)
55. K. Min, J. L. White, J. F. Fellers, *Polym. Eng. Sci.* **24**, 1327
56. Z. K. Walczak, *J. Appl. Polym. Sci.* **17**, 169 (1973)
57. A. P. Plochocki, S. S. Dagli, R. D. Andrews, *Polym. Eng. Sci.* **30**, 741 (1990)
58. O. Franzheim, T. Rische, M. Stephan, W. J. MacKnight, *Polym. Eng. Sci.* **40**, 1143 (2000)
59. H. Potente, S. Krawinkel, M. Bastian, M. Stephan, P. Pötschke, *J. Appl. Polym. Sci.* **82**, 1986 (2001)
60. M. A. Huneault, F. Mighri, G. H. Ko, F. Watanabe, *Polym. Eng. Sci.* **41**, 672 (2001)
61. J. K. Lee, C. D. Han, *Polymer* **40**, 6277 (1999)
62. C. Z. Chuai, K. Almdal, J. Lyngaae-Jørgensen, *Polymer* **44**, 481 (2003)
63. S. Thomas, G. Groeninckx, *J. Appl. Polym. Sci.* **71**, 1405 (1999)
64. H.-J. Radusch, in C. Harrats, S. Thomas, G. Groeninckx, eds., *Micro- and Nanostructured Multiphase Polymer Blend Systems*, Taylor & Francis, Boca Raton, 2006, Chap. 9
65. Yu. P. Miroshnikov, G. S. Kozlova, Yu. N. Voloshina, *Vysokomol. Soed.* **31**, 767 (1989)
66. Yu. P. Miroshnikov, Yu. N. Voloshina, J. Ster, *Mech. Kompoz. Mater.* **2**, 341 (1991)
67. Yu. P. Miroshnikov, M. A. Letuchii, P. J. Lemstra, A. B. Govaert-Spoelstra, Y. M. T. Engelen, *Vysokomol. Soed.* **42**, 1200 (2000)
68. P. Van Puyvelde, S. Velankar, P. Moldenaers, *Curr. Opin. Colloid Interface Sci.* **6**, 457 (2001)
69. S. D. Hudson, A. M. Jamieson, in *Polymer Blends, Vol. I: Formulations*, D. R. Paul, C. B. Bucknall, eds., J. Wiley&Sons, New York, 2000, Chap. 15
70. J. F. Palieme, F. Lequeux, *J. Non-Newtonian Fluid. Mech.* **40**, 289 (1991)
71. P. Van Puyvelde, S. Velankar, J. Mewis, P. Moldenaers, *Polym. Eng. Sci.* **42**, 1956 (2002)
72. U. Sundararaj, C. W. Macosko, *Macromolecules* **28**, 2647 (1995)

73. S.-P. Lyu, T. D. Jones, F. S. Bates, C. W. Macosko, *Macromolecules* **35**, 7845 (2002)
74. S.-P. Lyu, *Macromolecules* **36**, 10052 (2003)
75. R. Fayt, R. Jerome, Ph. Teyssie, *J. Polym. Sci., Polym. Phys.* **27**, 775 (1989)
76. G. Xu, S. Lin, *Polymer* **37**, 421 (1996)
77. M. Taha, J. Frerejean, *J. Appl. Polym. Sci.* **61**, 969 (1996)
78. M. Wagner, B. A. Wolf, *Polymer* **34**, 1460 (1993)
79. T. Appleby, F. Czer, G. Moad, E. Rizzardo, G. Stavropoulos, *Polym. Bull.* **32**, 479 (1994)
80. Z. Horák, V. Fořt, D. Hlavatá, F. Lednický, F. Večerka, *Polymer* **37**, 66 (1996)
81. T. Li, V. A. Topolkaev, A. Hiltner, E. Baer, X. Y. Ji, R. P. Quirk, *J. Polym. Sci., Part B: Polym. Phys.* **33**, 667 (1995)
82. E. Kroeze, G. ten Brinke, G. Hadziioannou, *Polym. Bull.* **38**, 210 (1997)
83. D. Hlavatá, Z. Horák, F. Lednický, Z. Tuzar, *Polym. Network Blends* **7**, 195 (1997)
84. D. Hlavatá, Z. Horák, J. Hromádková, F. Lednický, A. Pleska, *J. Polym. Sci., Part B: Polym. Phys.* **37**, 1647 (1999)
85. T. J. Cavanaugh, K. Buttle, J. N. Turner, E. B. Nauman, *Polymer* **39**, 4191 (1998)
86. M. Maric, C. W. Macosko, *J. Polym. Sci., Part B: Polym. Phys.* **40**, 346 (2002)
87. Z. Horák, D. Hlavatá, J. Hromádková, J. Kotek, V. Hašová, J. Mikešová, A. Pleska, *J. Polym. Sci., Part B: Polym. Phys.* **40**, 2612 (2002)
88. J. W. Barlow, D. R. Paul, *Polym. Eng. Sci.* **24**, 525 (1984)
89. S. C. Tjong, S. A. Xu, *J. Appl. Polym. Sci.* **68**, 1099(1998)
90. P. Cigana, B. D. Favis, C. Albert, T. Vu-Khan, *Macromolecules* **30**, 4163 (1997)
91. B. D. Favis, P. Cigana, M. Matos, A. Tremblay, *Canad. J. Chem. Eng.* **75**, 273 (1997)
92. J. Li, B. D. Favis, *Polymer* **43**, 4935 (2002)
93. J. Schiers, *Polymer Recycling*, Wiley, Chichester, 1998
94. C. Konig, M. Van Duin, C. Pagnouille, R. Jerome, *Prog. Polym. Sci.* **23**, 707 (1998)
95. S. Datta, D. J. Lohse, *Polymeric compatibilizers*, Hanser, Munich, 1996
96. J. Pospíšil, S. Nešpůrek, R. Pfaender, H. Zweifel, *Trends Polym. Sci.* **5**, 294 (1997)
97. J. Pospíšil, S. Nešpůrek, Z. Horák, F. P. LaMantia, in *Handbook of Plastics Recycling*, F. P. LaMantia, ed., Rapra Technology, Shawbury, 2002, pp. 221 - 246

Author's papers relevant to the Thesis

- A1) Fortelný I., Kovář J., Sikora A., Hlavatá D., Kruliš Z., Nováková Z., Pelzbauer Z., Čefelín P.: The Structure of Blends of Polyethylene and Polypropylene with EPDM Elastomer.
Angew. Makromol. Chem. 132 (1985), s. 111-122
- A2) Fortelný I., Kovář J.: Theory of Coalescence in Immiscible Polymer Blends.
Polymer Composites 9 (1988), s. 119-124
- A3) Fortelný I., Kamenická D., Kovář J.: Effect of the Viscosity of Components on the Phase Structure and Impact Strength of Polypropylene/Ethylene-Propylene Elastomer Blends.
Angew. Makromol. Chem. 164 (1988), s. 125-141
- A4) Kruliš Z., Kolařík J., Fortelný I., Čefelín P., Kovář J.: The Effect of Composition, Processing and Morphology on Mechanical Properties of Polypropylene/Ethylene-Propylene Rubber/Polyethylene Blends.
Acta Polymerica 40 (1989), s. 80-86
- A5) Fortelný I., Kovář J.: Droplet Size of the Minority Component in the Mixing of Melts of Immiscible Polymers.
European Polym. J. 25 (1989), s. 317-319
- A6) Fortelný I., Michálková D., Koplíková J., Navrátilová E., Kovář J.: The Effect of Conditions of Mixing of Polypropylene/Ethylene-Propylene Elastomer Blends on Their Morphological Structure and Impact Strength.
Angew. Makromol. Chem. 179 (1990), s. 185-201
- A7) Fortelný I., Navrátilová E., Kovář J.: The Effect of Viscosity of Polyethylene on the Evolution of Phase Structure During Mixing of Polypropylene/EPDM Elastomer/Polyethylene Blends.
Angew. Makromol. Chem. 188 (1991), s. 195-204
- A8) Pukánszky B., Fortelný I., Kovář J., Tudos F.: Particle Break-up and Coalescence in Heterogeneous PP/EPDM Blends; Effect of Particle Size on Some Mechanical Properties.
Plast. Rubber Proc. Appl. 15 (1991), s. 31-38
- A9) Fortelný I., Kovář J.: Effect of the Composition and Properties of Components on the Phase Structure of Polymer Blends.
European Polym. J. 28 (1992), s. 85-90
- A10) Kelnar I., Fortelný I., Baldrian J.: The Effect of the Molar Mass of Polyisobutylene on the Morphology and Mechanical Properties of its Blends and Composites with the Polypropylene Matrix.
Plast. Rubber Proc. Appl. 18 (1992), s. 109-119
- A11) Fortelný I., Rosenberg R., Kovář J.: Effect of Rheological Properties of Minor Component on its Dispersion in Polymer Blends.
Polymer Networks and Blends 3 (1993), s. 35-37

- A12) Fortelný I., Černá Z., Binko J., Kovář J.: Anomalous Dependence of the Size of Droplets of Disperse Phase on Intensity of Mixing.
J. Appl. Polym. Sci. 48 (1993), s. 1731-1737
- A13) Fortelný I., Živný A.: Theory of Competition between Break-up and Coalescence of Droplets in Flowing Polymer Blends.
Polym. Eng. Sci. 35 (1995), s. 1872-1877
- A14) Kruliš Z., Fortelný I., Kovář J.: Effect of Dynamic Crosslinking on Mechanical Properties of PP/EPDM Blends.
Collection Czech. Chem. Commun. 58 (1993), s. 2642-2650
- A15) Fortelný I., Živný A.: Coalescence in Molten Quiescent Polymer Blends.
Polymer 36 (1995), s. 4113-4118
- A16) Fortelný I., Michálková D., Mikešová J.: Effect of the Mixing Conditions on the Phase Structure of PP/PS Blends.
J. Appl. Polym. Sci., 59 (1996), s. 155-164
- A17) Kelnar I., Fortelný I.: Effect of Melt Annealing on the Structure and Properties of Polycarbonate/ Poly(styrene-co-acrylonitrile)/ Poly(ethylene-co-propylene) Blend.
J. Polym. Eng. 14 (1995), s. 269-282
- A18) Fortelný I., Kruliš Z., Michálková D., Horák Z.: Effect of EPDM Admixture and Mixing Conditions on Morphology and Mechanical Properties of LDPE/PP Blends.
Angew. Makromol. Chem., 238 (1996), s. 97-104
- A19) Navrátilová E., Fortelný I.: The Effect of Compatibilization and Rheological Properties of Polypropylene on Morphology of Polypropylene/ Polystyrene Blends.
Polym. Networks Blends, 6 (1996), s. 127 – 133
- A20) Kruliš Z., Fortelný I.: Effect of Dynamic Crosslinking on Rheological Properties of Molten Polypropylene/Ethylene-Propylene Elastomer Blends.
Europ. Polym. J., 33 (1997), s. 513 – 518
- A21) Fortelný I., Živný A.: Film Drainage between Droplets During their Coalescence in Quiescent Polymer Blends.
Polymer, 39 (1998), s. 2669 - 2675
- A22) Horák Z., Kruliš Z., Baldrian J., Fortelný I., Konečný D.: Compatibilization of Polyamide/Acrylonitrile-Butadiene-Styrene Polymer Blends.
Polym. Networks Blends, 7 (1997), s. 43 – 49
- A23) Fortelný I., Michálková D.: Effect of Compatibilizer Admixture, Mixing Conditions and Temperature on the Development of the Phase Structure in Polypropylene/Polystyrene Blends.
Polym. Networks Blends, 7 (1997), s. 125 – 131

- A24) Fortelný I., Živný A., Jůza J.: Coarsening of the Phase Structure in Immiscible Polymer Blends. Coalescence or Ostwald Ripening?
J. Polym. Sci. B: Polym. Phys., 37 (1999), s. 181 - 187
- A25) Fortelný I., Michálková D.: Effect of Mixing Device and Temperature on the Phase Structure in Neat and Compatibilized Polypropylene/Polystyrene Blends.
Plastics Rubber Composites Process. Appl., 27 (1998), s. 53 - 57.
- A26) Fortelný I.: Breakup and Coalescence of Dispersed Droplets in Compatibilized Polymer Blends.
J. Macromol. Sci. – Phys., B39 (2000), s. 67 - 78
- A27) Fortelný I., Kruliš Z., Michálková D., Horák Z.: Compatibilization of Polyethylene/Polypropylene/Polystyrene Blends.
Angew. Makromol. Chem., 270 (1999), s. 28 - 32
- A28) Fortelný I., Živný A.: Competition between Breakup and Coalescence of Droplets in Polymer Blends Containing a Compatibilizer.
Macromolecular Symposia, 149 (2000), s. 157 - 163
- A29) Fortelný I., Živný A.: Theoretical Description of Steady Droplet Size in Polymer Blends Containing a Compatibilizer.
Polymer, 41 (2000), s. 6865 - 6873
- A30) Fortelný I.: Coalescence in Polymer Blends: Solved and Open Problems.
Macromolecular Symposia, 158 (2000), s. 137 - 147
- A31) Fortelný I., Michálková D., Hromádková J., Lednický F.: Effect of a Styrene-Butadiene Copolymer on the Phase Structure and Impact Strength of Polyethylene/High-Impact Polystyrene Blends.
J. Appl. Polym. Sci., 81 (2001), s. 570 - 580
- A32) Fortelný I.: Analysis of the Effect of Breakup Frequency on the Steady Droplet Size in Flowing Polymer Blends.
Rheol. Acta, 40 (2001), s. 485 - 490
- A33) Fortelný I.: Prediction of the Phase Structure in Polymer Blends: What is Needed for Success?
Macromol. Symposia, 170 (2001), s. 99 - 103
- A34) Horák Z., Hlavatá D., Fortelný I., Lednický F.: Effect of Styrene-Butadiene Block Copolymers Architecture on their Compatibilization Efficiency in PS/PB and PS/Polyolefin Blends.
Polym. Eng. Sci., 42 (2002), s. 2042 - 2047
- A35) Fortelný I., Kruliš Z., Michálková D.: Using of Additive Compatibilization for Recycling of Municipal Plastic Waste.
Polimery, 47 (2002), s. 534 - 537

- A36) Fortelný I., Hlavatá D., Mikešová J., Michálková D., Potroková I., Šloufová I.: The Effect of Mixing Conditions on the Morphology and Properties of Polystyrene/Polyethylene Blends Compatibilized with Styrene-Butadiene Block Copolymers.
J. Polym. Sci. B: Polym. Phys. 41 (2003), s. 609 - 622
- A37) Fortelný I., Mikešová J., Hromádková J., Hašová V., Horák Z.: Effect of Molecular Structure of Styrene-Butadiene Block Copolymers on Morphology, Rheological Properties and Impact Strength of Polystyrene/Polyethylene Blends.
J. Appl. Polym. Sci. 90 (2003), s. 2303 - 2309
- A38) Fortelný I., Živný A.: Extensional Flow Induced Coalescence in Polymer Blends.
Rheol. Acta 42 (2003), s. 454 - 461
- A39) Hlavatá D., Hromádková J., Fortelný I., Hašová V., Pulda: Compatibilization Efficiency of Styrene-Butadiene Triblock Copolymers in PS/PP Blends with Varying Composition.
J. Appl. Polym. Sci. 92 (2004), s. 2431 - 2441
- A40) Fortelný I.: An Analysis of the Origin of Coalescence Suppression in Compatibilized Polymer Blends.
Europ. Polym. J. 40 (2004), s. 2161 - 2166
- A41) Fortelný I., Michálková D., Kruliš Z.: An Efficient Method of Material Recycling of Municipal Plastic Waste.
Polym. Degrad. Stab. 85 (3) (2004), s. 975 - 979
- A42) Fortelný I., Šlouf M., Sikora A., Hlavatá D., Hašová V., Mikešová J., Jacob C.: The Effect of the Architecture and Concentration of Styrene-Butadiene compatibilizers on the Morphology of Polystyrene/Low-Density Polyethylene Blends.
J. Appl. Polym. Sci., in press
- A43) Pospíšil J., Fortelný I., Michálková D., Kruliš Z., Šlouf M.: Mechanism of Reactive Compatibilization of a Blend of Recycled LDPE/HIPS Using a Co-additive System EPDM/SB/Aromatic Diamine.
Polym. Degrad. Stab. 90 (2005), s. 244 - 249
- A44) Pospíšil J., Michálková D., Fortelný I., Kruliš Z., Šlouf M.: Aromatic Diamines as Cooperative Compatibilizers and Impact Modifiers in LDPE/HIPS Blends.
Polym. Polym. Compos. 13 (2005), s. 313 - 320
- A45) Fortelný I., Šlouf M., Hlavatá D., Sikora A.: Interfacial Activity of Styrene-Butadiene Block Copolymers in Low-Density Polyethylene/Polystyrene Blends.
Composite Interfaces, in press

Summary

Polymer blends represent a very important part of polymer materials. Most polymer pairs are immiscible and, therefore, the phase structure of their blends at service temperature is frozen in non-equilibrium state and depends on their preparation and processing. Because the phase structure affects most of blend properties very strongly, its control during the blend mixing and processing is essential for successful utilization of polymer blends in practice. The thesis is focused on the improvement of understanding and description of the phase structure formation and evolution in molten immiscible polymer blends. For this aim, development of microrheological description of individual steps of the phase structure evolution was combined with experimental studies of polymer blends with well characterized components.

Realistic model of the coalescence of droplets of a minor component in molten quiescent polymer blends, considering molecular forces among droplets and their Brownian motion, was found. Approximate theory of the coalescence, reliably describing the dependence of the coalescence rate on rheological properties of the components and interfacial tension, was derived. An analysis of the theories of coalescence and Ostwald ripening and experimental data showed that the coalescence is decisive mechanism of the droplet growth in molten polymer blends with high and moderate interfacial tension.

Approximations used for calculation of the probability, P_c , that the flow-induced collision of droplets will be followed by their fusion, were analyzed. The theory of P_c considering strong changes in droplet flattening during extensional flow-induced coalescence was derived. It was shown that P_c can be approximated as a product of expressions for spherical and strongly flattened droplets. Approximate equations for the average droplet size in steady flow were derived using various assumptions about dependences of breakup and coalescence frequencies on the droplet size. Graphic solution of the equation, describing dynamic equilibrium between the droplet breakup and coalescence, showed which parameters control establishment of the steady state or existence of hysteresis. It demonstrated that the breakup frequency has decisive effect on the dependence of the average droplet size on volume fraction of the dispersed phase.

Experimental studies showed that the dependence of the droplet size on the blend composition and viscosities of the components matches to the assumption that the size of droplets in steady flow is controlled by dynamic equilibrium between their breakup and coalescence. The same assumption allowed us to explain nonmonotonic dependence of the

average droplet size on the rate of mixing for blends with a high concentration of the dispersed phase. Nonuniform development of the phase structure (coexistence of large elastomer particles surrounded by neat matrix with areas showing fine phase structure at low rates and/or short times of mixing) was found in polypropylene/ethylene-propylene elastomer (PP/EPR) blends. Coexistence of areas substantially differing in the average droplet size was detected in polypropylene/polystyrene blends. In contrast with PP/EPR blends, nonuniformity of the phase structure did not disappear at enhancement of the rate and/or time of mixing. The phase structure of PP/EPR blends was modified and their impact strength was enhanced by dynamic vulcanization. Rheological properties of these blends were explained as a consequence of extremely long-living entanglements between crosslinked domains of elastomers.

Applicability of available theories for the breakup and coalescence of dispersed droplets in polymer blends containing a compatibilizer was analyzed. Solution of the equation describing dynamic equilibrium between the droplet breakup and coalescence showed that the shape of the dependence of the droplet size on the blend composition is affected by the compatibilizer distribution between the interface and bulk phases. The effect of styrene-butadiene block (SB) copolymers on their compatibilization efficiency in polystyrene/polyolefin blends was studied experimentally. It was found that the compatibilization efficiency of SB copolymers is not only a function of their molecular structure and a polyolefin type, as it was assumed, but it depends also on the composition of compatibilized blends and on the condition of mixing and processing of the blends. The order of SB copolymers from the point of view of their compatibilization efficiency can change in dependence on their content in a blend.

Knowledge obtained at the studies of the phase structure development and compatibilization was utilized at material recycling of mixed plastic waste. It was found that a mixture of SB and EPR copolymers is a very efficient compatibilizer for municipal plastic waste. It was verified for model blends of low- and high-density polyethylenes, polypropylene and polystyrene and for real samples of municipal plastic waste. A small addition of a substituted diamine-based stabilizer led to further enhancement of the impact strength to the values 4-5 times higher than for blends without a compatibilizer. The addition of 5% of this compatibilization system led to recyclates with mechanical properties comparable with virgin polyolefins.