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Prediction of the Phase Structure in Polymer Blends: What is Needed for Success?

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Summary: Rules for prediction of the phase structure in immiscible polymer blends from the knowledge of their composition, component properties and the flow field in a mixing or processing device are discussed. The reliability of qualitative prediction of the dependence of phase structure on system parameters is used as a criterion of plausibility of the rules. No general reliable rule for prediction of the phase structure type (continuity of phases) is available in the literature. Dependence of the droplet break-up frequency on its size, contribution of simultaneous collisions of three or more droplets to coalescence and the effect of complex flow field on coalescence must be better described for a reliable qualitative prediction of the dependence of the droplet size on the system parameters.

Introduction

A necessary condition for tailoring properties of polymer blends is a control of their phase structure in mixing and processing. The phase structure of polymer blends is a complex function of blend composition, properties of the components and mixing conditions. For this reason, empirical rules for prediction of the phase structure have only limited validity$^{1)}$. Understanding the phase structure evolution on the microrheological level seems to be necessary. Microrheological events in the phase structure development are very complex and their correct quantitative description and the following quantitative prediction of the phase structure is a distant target. In many cases, reliable knowledge of qualitative dependence of the phase structure on parameters of a system is sufficient for practice. As an example a question can be raised whether a finer phase structure will be achieved by the increase or decrease of viscosity of a certain component. The objective of the contribution is to analyse problems of reliable qualitative prediction of the droplet size in polymer blends with dispersed structure.

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Type of the Phase Structure

The most important feature of the phase structure is its type. The type determines whether the phase structure is dispersed, stratified or co-continuous. The knowledge which component forms the matrix or the dispersed phase and the important features of the shape of dispersed particles are necessary for determination of the dispersed structure type. It is well known that in binary blends of immiscible components A and B, particles of A in the matrix of B, are formed at a low content of component A in the blend. With increasing content of component A, co-continuous structure occurs. Finally, particles of component B dispersed in the matrix of A are characteristic for blends with high contents of A. The width of the composition regions related to individual types of the phase structure for various systems is strongly different. Several relations for prediction of the blend composition at the phase inversion point from viscosities of the components have been proposed. These relations are qualitatively correct for some systems but fail for the others. Moreover, they do not predict the width of the composition region with co-continuous structure[2,3)]. Lyngaae-Jørgensen and Utracki[4)] assumed that the formation of a co-continuous structure starts at the blend composition related to the percolation threshold for particles of the minor phase. However, the percolation threshold is strongly dependent on the shape of particles, which is unknown. Utracki[5)] assumed that the phase inversion occurs at the composition for which dispersion of A in the matrix of B and dispersion of B in the matrix of A have the same viscosity. A combination of the results from Refs.[4,5)] does not give a satisfactory qualitative prediction of the dependence of the phase continuity on the blend composition. Willemse et al.[3)] assumed that full co-continuity appears when a maximum packing density is achieved for randomly oriented rod-like particles. They assumed that elongated rod-like particles are stable if the capillary number, Ca, calculated using the rod diameter, is higher than unity. The expression for volume fraction of the minor phase, at which fully co-continuous structure is formed, is a function of the size of dispersed droplets, which cannot be predicted[3)]. It follows from the above discussion that at present there is no theory or empirical relation enabling qualitative prediction of the dependence of the phase structure type on the blend composition, properties of the components and mixing conditions.

Fineness of the Phase Structure

Degree of dispersion of the phase structure has been intensively studied for blends with dispersed structure. It is well known that the size of droplets in a flow is determined by the competition between their break-up and coalescence. For a prediction of the droplet size, it is necessary to characterize the flow field in a mixing or processing device, to describe break-up and coalescence of droplets in this field and to solve a kinetic equation describing droplet formation and decay. Due to the rapid development of computer methods in last years, quite satisfactory description of the flow fields in mixing and processing devices is available. A problem consists in an appropriate selection of a simplified model, applicable for a description of droplet break-up and coalescence. Great attention has been also paid to solution of kinetic equations describing competition between aggregation and break-up of particles. In spite of complexity of the problem, the solution of kinetic equation is not a limiting factor in reliable qualitative prediction of the droplet size. Instead, reliability of the description of droplet break-up and coalescence are decisive factors.

For solution of kinetic equations, the frequency of break-up and coalescence of droplets must be known as a function of parameters of the system. The droplet break-up occurs if the capillary number, $Ca = \tau R/\sigma$ (where τ is the stress in flow, R is the droplet radius and σ is the interfacial tension), is larger than critical value Ca_c. For $Ca >> Ca_c$, the break-up by a transient mechanism (the break-up of the highly elongated drop into a number of small droplets) is operative. For Ca only a little higher than Ca_c, the drop bursts into halves (stepwise mechanism)1,6,7). Somewhat different values of Ca, used as boundaries between the transient and stepwise mechanisms, appear in the literature6,7).

The dependence of Ca_c on parameters of the system, especially on viscosities of the components, is quite well known1,8,9). However, our knowledge of the breakup frequency, F, as a function of Ca is unsatisfactory. No conclusive experimental results are available in the literature. Therefore, it is not surprising that different expressions for F are used in various theories dealing with solution of the kinetic equation. For $Ca > Ca_c$, F is proportional to $Ca - Ca_c$1,10); F independent of Ca6) and F decreasing with increasing Ca7,11) were also used. It was shown12) that the dependence of the break-up frequency on Ca (R for a certain system and flow field) affects in a fundamental way the average droplet size in the steady state and its dependence on the amount of the dispersed phase. Several steady-state solutions of the kinetic equation may exist if the break-up frequency is not a monotonously increasing function of R.

The course of coalescence is satisfactorily described for a pair of undeformed droplets[13)]. However, this model is adequate only for a part of rheological measurements. Average forces between droplets in mixing and processing the polymer blends are so strong that droplet flattening cannot be neglected in description of coalescence[14)]. All theories of coalescence of flattened droplets contain rough approximations. Strong differences exist between results of various theories, but all of them predict similar dependencies of the coalescence frequency on the droplet radius[14)]: a high value, almost independent of R for small R, a steep decrease in the coalescence frequency with R in a certain range of R and a low but nonzero value asymptotically approaching to zero for high R. The nonzero value of coalescence frequency at high R is not an artefact, but it has a clear physical reason. When the region of low values of the coalescence frequency starts at $R < R_c$ (where R_c is related to Ca_c), the system can pass to the pseudosteady state. Transition between the pseudo-steady and steady state is a time-consuming process. The dependence of the coalescence frequency on viscosities of the components is controlled by a model of mobility of the interface[14)]. It seems that the Jeelani-Hartland model[15)] is the most realistic. Knowledge of the effect of elasticity parameters of components is very limited. Theories of coalescence of flattened droplets do not include the effect of difference in droplet size on the probability that collisions of droplets will be followed by their fusion. Little attention has been paid to the fact that anisometric, nonspherical droplets collide in flow. All theories applied so far to polymer blends have been derived for shear flow. According to the results for undeformed droplets[13)] and our preliminary analysis, the probability of droplet fusion after collision substantially differs for elongational and shear flows. This fact is very important for coalescence modeling in mixing and processing devices. A fundamental limit of all theories of coalescence consists in a fact that the effect of all other droplets on coalescence of a certain pair is neglected. Neglecting the simultaneous collisions of three or more droplets apparently strongly affects, e.g., the dependence of the average droplet size on the amount of dispersed phase[14)].

Conclusions

Reliable qualitative predictions of the dependence of the phase structure of polymer blends on their composition, properties of the components and mixing conditions are needed for practice.

No reliable theory or empirical rule describing dependence of the type of the phase structure (continuity of phases) on parameters of a system has been derived so far. All existing rules have only limited validity.

A reliable qualitative prediction of the dependence of steady droplet size in flowing polymer blends on the blend composition and properties of the components requires:

(a) Establishing a reliable dependence of the droplet break-up frequency on its size.

(b) Elucidation of the contribution of simultaneous collisions of three or more droplets to coalescence.

(c) Proposal of a proper model of coalescence in complex flow fields.

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