Macromol. Symp. ***158,*** *137–147 (2000)*

Coalescence in Polymer Blends: Solved and Open Problems

Ivan Fortelný

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského nám. 2, 162 06 Praha 6, Czech Republic

SUMMARY: Problems with microrheological description of the coalescence of dispersed droplets in polymer blends are discussed. Apparently, the coalescence in quiescent polymer blends is caused by molecular forces and Brownian motion. The coalescence rate is controlled by drainage of the matrix film between undeformed droplets. For further development of the theory: description of the coalescence induced by the Brownian motion should be improved, mutual influence of the Brownian and molecular forces should be considered and simultaneous interaction of three and more droplets should be investigated.

Probability, P_C, that the collision of droplets in a shear flow is followed by their fusion, is controlled by the competition between their approach and rotation around their common centre of inertia. The velocity of the droplet approach is controlled by drainage of the matrix between flattened droplets. The dependence of P_C on properties of the components is determined by the model of interface mobility, the magnitude of P_C depends on the description of the competition between approach and rotation of the droplets. The main shortcoming of the present theories of blends with a high content of the dispersed phase is neglecting any effect of other droplets on the collision of a certain pair of droplets.

Introduction

Microrheological description of the individual events at mixing and processing of immiscible polymer blends is a necessary condition for the control of the blend structure and properties. One of the most important microrheological events is the coalescence of dispersed droplets which follows their collision. The coalescence is a complex phenomenon which description is, in spite of its intensive study during recent years, still far from completion. Usually, the course of the coalescence is divided into four steps (Refs. 1,2):

1) approach of the droplets;
2) deformation of the droplets due to the axial force and removal of the continuous phase trapped between the droplets;

CCC 1022-1360/00/$ 17.50+.50/0

3) rupture of the remainder of the continuous phase, usually by the formation of a „hole“ on the thinnest spot;
4) evolution of the „neck“ to form a coalesced droplet.

Usually, it is assumed (Refs. 1,3) that the course of the coalescence is controlled by the steps 1 and 2. The third step is considered as much quicker than the preceding ones (Ref. 1). As it will be discussed bellow, the fourth step does not substantially affect the coalescence in quiescent state but it can affect flow induced coalescence. It should be mentioned that the hydrodynamic interaction should be considered also during approach of the droplets and splitting of the first and second steps is approximation. Description of the coalescence is somewhat simpler if droplet flattening is negligible and spherical shape of the droplets can be considered during the whole coalescence. For radius of the flattened part of the droplet, r_f, the following equation is valid

$$r_f = \left(\frac{RF}{2\pi\sigma} \right)^{1/2} \tag{1}$$

where R is the droplet radius, F is the driving force of the coalescence and σ is the interfacial tension.

In immiscible polymer blends with dispersed structure, the coalescence is important in both quiescent state and in flow. Coalescence in quiescent state is the main mechanism of coarsening of the phase structure (Ref. 4). Flow induced coalescence decides (with the droplet break-up) about the droplet size at mixing, processing and rheological measurements (Ref. 5). So far, discussion about mechanism controlling the coalescence in quiescent state has not been closed. Driving force of the flow-induced coalescence is well known, however serious problems with description of the second step of coalescence still persist. Therefore, the coalescence in quiescent state and in flow will be discussed separately. The main aim of the contribution is to summarise the most important results and problems, which must be solved prior derivation of satisfactory theory of the coalescence.

Coalescence in Quiescent State

It was found, about twenty years ago, that quite strong increase in the droplet size appeared in molten polymer blends at rest (Ref. 6). For low-molecular-weight emulsions, this effect was successfully described by the Smoluchowski theory (Ref. 7) of the coalescence induced by the

Brownian motion and its modifications (Ref. 8). However, the theory predicts immeasurable coalescence for polymer blends due to their high viscosity. We found (Ref. 9) that, at derivation of the Smoluchowski theory, the approximation for droplet flux was used, which is fully justified for systems with low viscosity of the matrix but it is inapplicable on polymer blends. The theory modified for polymer blends (Ref. 9) predicts somewhat quicker but still negligible coalescence. Besides the Brownian motion, coalescence in quiescent state can be induced by the gravity force, and molecular forces between dispersed droplets. The gravity force is weak (Ref. 1). Moreover, the first order effect for the gravity force is common motion of droplets to the top or bottom of the sample. Molecular forces between droplets decrease rapidly with inter-droplet distance. Therefore, their importance for coalescence is controlled by the average distance of a droplet from its nearest neighbour.

The average distance of a certain sphere from its nearest neighbour was calculated for a system of monodispersed randomly distributed spheres (Ref. 10). This distance is smaller than 0.5 R already at volume fraction of the spheres $\varphi = 0.1$ and it rapidly decreases with growing φ (Refs. 11,12). It is clear that molecular forces between droplets must be considered at description of the coalescence in typical polymer blends. Moreover, strong hydrodynamic interaction between droplets is operative through the whole coalescence process. It is apparent that the basic assumptions of the Smoluchowski theory (Ref. 7,8), which assumes that the coalescence is controlled by free diffusion of the droplets, are not fulfilled for polymer blends. If it is assumed that the coalescence is caused by van der Waals forces or the Brownian motion, it follows from Eq. (1) that $r_f << R$ always valid for polymer blends (Ref. 12). Therefore, undeformable droplets can be considered at description of the coalescence.

The theory of coalescence, induced by van der Waals forces or Brownian motion, in quiescent state was derived (Ref. 11). Driving force of the coalescence, F, for van der Waals force was

$$F = AR/(12h^2) \tag{2}$$

where A is the effective Hamaker constant and h is the distance between droplets. The force relating to the Brownian motion was estimated as

$$F = kT/(2h) \tag{3}$$

where k is the Boltzman constant and T is the absolute temperature. The theory of Zhang and Davis (Ref. 12) was used for description of the drainage of the matrix between droplets. For time dependence of the droplet radius, the following equation was derived (Ref. 11)

$$R^3 = R_0^3 + \frac{A}{18\pi\eta_m H_V} t \tag{4}$$

where t is the time, R_0 is the droplet radius at $t = 0$, η_m is viscosity of the matrix and H_V is a function defined by

$$H_V = \frac{1}{R}\int_0^{Rf} \frac{2h^2 + 0.402\sqrt{2}pR^{1/2}h^{3/2}}{2h + 1.711\sqrt{2}pR^{1/2} + 0.461p^2 R}\,\mathrm{d}h \tag{5}$$

where p is the ratio of the viscosities of the matrix and dispersed phase and f is given by the equation

$$f = \frac{(1-\varphi)^3}{6\varphi(2-\varphi)} \tag{6}$$

For coalescence induced by the Brownian motion, the following equation was derived

$$R^3 = R_0^3 + \frac{kT}{3\pi\eta_m H_B} t \tag{7}$$

with

$$H_B = \frac{1}{R}\int_0^{Rf} \frac{2h + 0.402\sqrt{2}pR^{1/2}h^{1/2}}{2h + 1.711\sqrt{2}pR^{1/2}h^{1/2} + 0.461p^2 R}\,\mathrm{d}h \tag{8}$$

It can be seen from Fig. 1 that the theory predicts, in difference with the previous ones, strong growth in the drop radius during several tens minutes of the annealing.

The theory was generalized on systems with viscoelastic matrix described by the Maxwell model (Ref.12). In this case Eqs. (5) and (7) pass to

$$R^3 - \frac{A\tau_m}{6\pi\eta_m H_V}\ln^2\frac{fR}{h_c} = R_0^3 - \frac{A\tau_m}{6\pi\eta_m H_V}\ln^2\frac{fR_0}{h_c} + \frac{A}{18\pi\eta_m H_V} t \tag{9}$$

$$R^3 - \frac{kT\tau_m}{2\pi\eta_m H_B}\ln^2\frac{fR}{h_c} = R_0^3 - \frac{kT\tau_m}{2\pi\eta_m H_B}\ln^2\frac{fR_0}{h_c} + \frac{kT}{3\pi\eta_m H_B} t \tag{10}$$

where τ_m is the relaxation time of the Maxwell model of the matrix and h_c is the critical distance between droplets at which film of the matrix bursts. The rate of the coalescence is higher in viscoelastic than in viscous matrix with the same viscosity and it increases with τ_m.

I believe that the model (Ref. 11), which was used at derivation of the theory, is realistic. The theory predicts qualitatively correctly the dependences of the rate of coalescence on parameters of the system and reasonable magnitude of the effect (Ref. 4). On the other hand, the theory contains several parameters, which have not been determined for polymer blends, and a number of approximations which effects should be investigated.

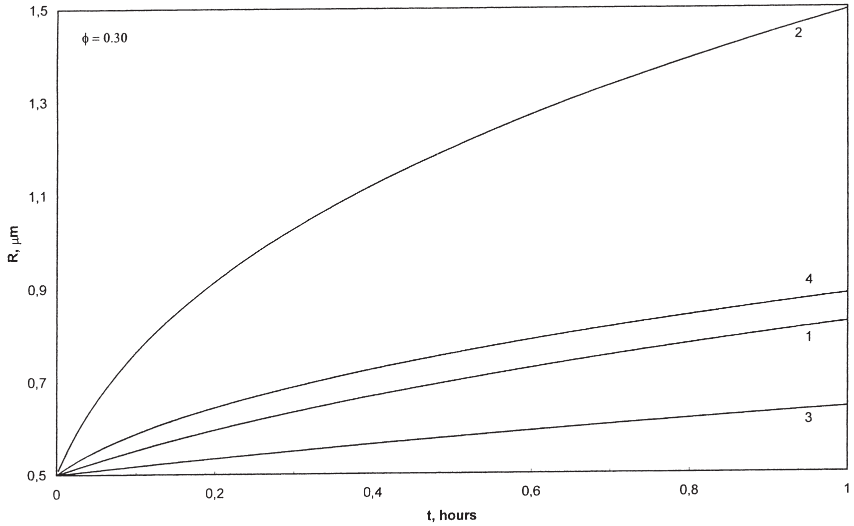

Fig. 1. The effect of the relaxation time, τ_m, and the ratio of viscosities, $p = \eta_m/\eta_d$, on the time dependence of the droplet radius, $R(t)$, for coalescence induced by van der Waals forces. Common parameters: $A = 10^{-20}$ J, $\eta_m = 1000$ Pa.s, $R_0 = 0.5$ μm, $h_c = 5.10^{-9}$ m, $\varphi = 0.30$. Curves: (1) and (4) $p = 1$, (2) $p = 10$, (3) $p = 0.1$; (1), (2) and (3) $\tau_m = 0$, (4) $\tau_m = 120$ s.

Quantitative verification of the theory needs knowledge of the effective Hamaker constant for polymer blends. *A* should be determined also for blends containing a compatibilizer. The theory was derived with the assumption that the system is monodispersed during coalescence and real distances between droplets at the origin of coalescence were substituted by their average value. However, the first (Ref. 9) and the second (Ref. 13) approximations do not lead to the substantial error in the average *R*. The description of the Brownian motion is very rough approximation. Moreover, the theory should described simultaneous effect of the Brownian motion and molecular forces. Also the effect of elastic properties of the matrix and dispersed phase needs further investigation.

Important shortcoming of the theory is the fact that the interaction of a certain droplet with its nearest neighbor is considered. Therefore, two effects, important for molecular forces induced coalescence, are neglected. Other droplets from the neighborhood are attracted to the coalescing droplet pair. On the other hand, motion of a droplet in a certain direction is suppressed by the attractive forces of the droplets from the opposite direction. The first effect leads to the higher and the second one to the lower rate of coalescence. I believe that the first effect prevails in blends with a low content and the second one in blends with a high content of the dispersed phase.

The above discussion considered the first and second steps of the coalescence. The assumption that the third step is much quicker than the first and second ones is apparently realistic. Some uncertainty exists only at determination of the critical distance h_c. The shape relaxation of the coalescing droplets can be quite long and the following collision can occur between anisometric droplets (Ref. 14). However, any forces, which can cause droplets breakup during this step, apparently does not exist in quiescent blends.

Flow Induced Coalescence

The coalescence is mostly studied in shear flow, where droplets with different coordinates in the direction of the velocity gradient collide. The force between the droplets is not radial and, generally, it leads to their complex trajectory. In first approximation, the trajectory can be split to the approach of the droplets and to their rotation around their common center of inertia. For a model considering the effect of hydrodynamic interaction and flattening of the droplets on their trajectory, the description of the first and second steps of the coalescence is very complicated (Refs. 15-17). Description of the coalescence of undeformable droplets is quite well elaborated (Ref. 17). Coalescence of deformable droplets in polymer blends has been studied mostly with the help of „ballistic„ approximation. Hydrodynamic interaction has been neglected at the description of the droplet approach. At description of the second step of coalescence, the competition between the drainage of the matrix between flattened droplets and the droplets rotation around their common center of inertia has been considered (Refs. 1,18).

For adequate description of the coalescence, the knowledge of the magnitude of the droplet flattening is very important. If driving force of the coalescence is estimated as (Ref. 18)

$$F = 6\pi\eta_m\dot{\gamma}R^2 \qquad (11)$$

where γ is the shear rate, it follows form Eq. (1)

$$r_f = (3Ca/\pi)^{1/2}R \qquad (12)$$

where $Ca = \eta_m\dot{\gamma}R / \sigma$ is the capillary number. It follows from Eq. (12) that $r_f < 0.1\ R$ is valid for $Ca < 0.01$. It is clear that the flattening of the droplets can be neglected only at the conditions relating to the rheological measurements at very low shear rates but not in other cases (mixing, processing, rheometry at high shear rates). It strictly limits applicability of the Milner and Xi theory (Ref. 19) of the droplet size in flow which uses relations for coalescence of undeformable droplets.

On Fig. 2, coalescence of two droplets with the same z-coordinates of their centers in the shear flow with velocity $\mathbf{v} = (\dot{\gamma}y, 0, 0)$ is shown. It is apparent from Fig. 2 that the force ***F*** between droplets can be split into component F_c, which causes approach of the droplets and component F_R leading to their rotation around their center of inertia. F_c can be expressed as

$$F_c = 6\pi\eta_m\dot{\gamma}R(R'+h/2)\sin\phi\cos\phi \qquad (13)$$

where $R' + h/2$ is the distance of a droplet center from the center of inertia and ϕ is the angle between the straight line connecting centers of the droplets and flow direction. It follows from Eq. (13) that driving force of the coalescence and, therefore, also flattening of the droplets change during rotation. The relations for drainage of the matrix trapped between droplets were derived for constant driving force (Refs. 3,20). For polymer blends, the equations for mobile, partially mobile and immobile interfaces are commonly used (Refs. 1,3,18).Their

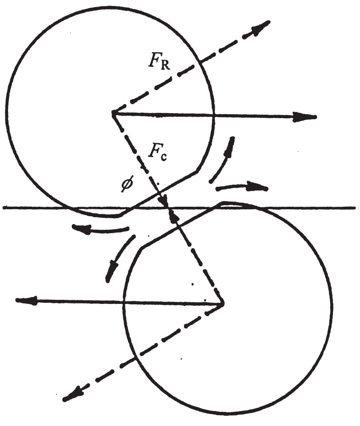

Fig. 2. Shear flow induced coalescence of two droplets with the same co-ordinate in neutral direction. ϕ is the angle between direction of flow and connection of the centers of the droplets.

disadvantage is the fact that they have different dependences on viscosity of the components and transition between them does not exist. From this point of view, the Jeelani's and Hartland's theory (Ref. 20) seems to be more advantageous. The theory describes systems with broad range of the ratios of viscosity of the dispersed phase and matrix and for high magnitude of this ratio pass to the relation for systems with immobile interface. Moreover, it describes also systems containing a compatibilizer.

Besides of the theories, describing coalescence between undeformed droplets (Ref. 21), mostly Janssen's (Ref. 20) and Elmendorp's (Ref. 1) approaches were applied on polymer blends. Janssen (Ref. 20) assumed that the probability, P_c, that the droplets collision (in „ballistic„ approximation) will be followed by their fusion, is given by

$$P_c = \exp\{-t_c/t_i\} \tag{14}$$

where t_c is the time of the droplets approach from the initial distance h_0 to the critical distance h_c and t_i is the interaction time defined as

$$t_i = \dot{\gamma}^{-1} \tag{15}$$

t_c was calculated with the assumption that the driving force of the coalescence is constant and given by Eq. (11).

For simplicity, Elmendorp's approach will be discussed for droplet pairs with the same z-coordinate (see Fig. 2). Elmendorp assumed (Ref. 1) that the droplets fusion occurs if t_c is shorter than t_R (relating to the rotation from the initial angle $\phi = \phi_0$ to the angle $\phi = \pi/2$). He used Eq. (13) for F_c and he assumed that the equations derived for constant F_c are valid also for variable F_c. For flattened droplets, t_c decreases with decreasing F_c (Ref. 3). Therefore, using Eq. (13) leads to the conclusion that fusion always occurs. Elmendorp solved this paradox by the assumption that the resistance of the matrix is the addition of the resistance against film drainage between planes and between rigid spheres. The physical reason of this asssumption was not explained. Moreover, using of the model of rigid spheres is justified only for systems with very high ratio of the viscosity of the dispersed phase and matrix.

We calculated P_c by two methods (Ref. 21). At both, we compared t_c with t_R. In the first case, we assumed that F_c is constant and it is given by

$$F_c = 6\pi\eta_m\dot{\gamma}R^2 \sin\phi_0 \cos\phi_0 \tag{16}$$

For the rate of drainage of the matrix film between droplets, the Jeelani and Hartland equation (Ref. 22) was used

$$-\frac{\mathrm{d}h}{\mathrm{d}t}=\frac{8\pi\sigma^2 h^3}{3\eta_m R^2 F_c}\left(1+3C\frac{\eta_m}{\eta_d}\right) \tag{17}$$

where η_d is the viscosity of the dispersed phase and parameter C is the ratio of circulation length and droplets distance.

In the second case, we considered variable force, given by Eq. (13), with approximation $R' + h/2 \approx R$. The ratio r_f/R was calculated from Eq. (1). We fixed limited value L for the ratio. For $r_f/R > \mathrm{L}$, approach of the droplets was described by Eq. (17). For $r_f/R \leq \mathrm{L}$, the equation for undeformed spheres (Ref. 13) was used

$$-\frac{\mathrm{d}h}{\mathrm{d}t}=\frac{2F_c h}{3\pi\eta_m R^2 g(m)} \tag{18}$$

where

$$g(m)=\frac{1+0.402m}{1+1.711m+0.461m^2} \tag{19}$$

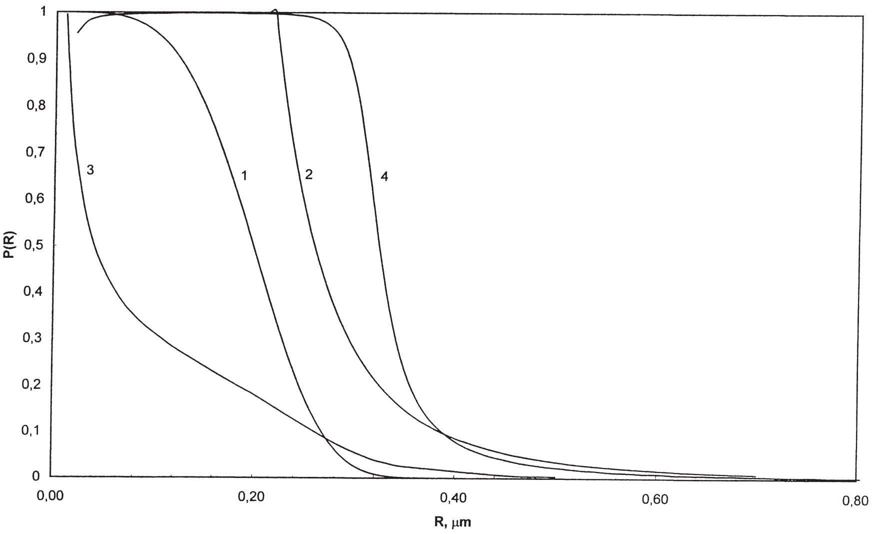

Fig. 3. Dependence of probability, P_C, on the droplet radius, R. Curves: (1) Calculation according to Janssen (Ref. 20). (2) Calculation for flattened droplets with F_c given by Eq. (16). (3) Elmendorp's procedure (Ref. 1). (4) Method taking into account a change of flattening due to changes of F_c. L = 0.05 is used. Common parameters: $\eta_m = \eta_d = 1000$ Pa.s, $\sigma = 0.005$N/m, $\dot{\gamma} = 1\ \mathrm{s}^{-1}$.

with m defined as

$$m = \frac{\eta_m}{\eta_d}\left(\frac{R}{2h}\right)^{1/2} \tag{20}$$

The results of calculation of P_c with the above methods and the Janssen and Elmendorp procedures (with using the Jeelani and Hartland theory) are compared on Fig. 3.

It seems that the qualitative dependence of P_c on parameters of the system is mostly determined by the choice of the theory for calculation t_c (the Jeelani and Hartland theory, system with mobile, partially mobile or immobile interface). The magnitude of P_c is strongly affected by chosen procedure of calculation (Elmendorp's, Janssen's or our procedure).

Besides of the above discussed problems, further serious problems exist. The values of P_c are strongly dependent on h_c which determination is not simple (Ref. 22). Because the driving force of the droplets approach is variable, elastic properties of the matrix affect (similarly to the coalescence in quiescent state) course of the coalescence. This problem has not been studied so far. Most theories describe coalescence between spherical droplets. However, droplets in flow are mostly anisometric. Patlazhan and Lindt (Ref. 23) found that P_c is higher for ellipsoidal than for spherical droplets. This problem needs further investigation. It is apparent from Fig. 2 that the repulsive force between droplets appears for $\phi > \pi/2$. If droplets are jointed only by thin neck (the fourth step of the coalescence is slow), the droplets can break away. This effect is not considered in present theories of the coalescence.

The most serious shortcoming of all theories of the flow induced coalescence published so far is the fact that they deal with collisions of a pair of droplets only and they neglect the effect of other droplets. For the number of fusion of droplets with radii R_i and R_j in a time unit, $N(i,j)$, the following equation is used

$$N(i,j) = \frac{4}{3}\dot{\gamma}(R_i + R_j)^3 P_c(R_i, R_j) n_i n_j \tag{21}$$

where n_i, n_j are numbers of droplets with radii R_i, R_j. Change in the droplet number in a time unit is, therefore, proportional to the second power of concentration of the dispersed phase. Due to a very short distance between a droplet and its neighbour in typical polymer blends, discussed above, it is apparent that simultaneous collisions of three and more droplets must be considered. In the relation for a change in the droplet number, terms containing the third and higher power of the concentration of the dispersed phase appear. We believe that the neglecting of multiple collisions is the main reason of disagreement of the solutions of equations, describing dynamic equilibrium between break-up and coalescence of the droplets, with experiment (Ref. 5). Also neglecting of the hydrodynamic interaction with near droplets, which do not take part in a collision, is rough approximation for blends with a high content of the dispersed phase.

Acknowledgement

The author thanks Dr. A. Živný for numerical calculations and Grant Agency of the Czech Republic for support by grant No. 106/99/0555.

References

(1) J. J. Elmendorp, in: *Mixing in Polymer Processing* (C. Rauwendaal, Ed.), Marcel Dekker, New York 1991

(2) I. Fortelný, A. Živný, *Polymer* **36**, 4113 (1995)

(3) R. K. Chesters, *Trans. Inst. Chem. Eng.* (A) **69**, 259 (1971)

(4) I. Fortelný, A. Živný, J. Jůza, *J. Polym. Sci. B: Polym. Phys.* **37**, 181 (1999)

(5) I. Fortelný, J. Kovář, M. Stephan, *J. Elastomers Plast.* **28**, 106 (1996)

(6) B. Z. Jang, D. R. Uhlman, J. B. Van der Sande, *Rubber Chem. Technol.* **57**, 291 (1984)

(7) M. Smoluchowski, *Phys. Z.* **17**, 557, 585 (1916)

(8) J. T. G. Overbeek, in: *Colloid Science,* Vol. I (H. K. Kruyt, Ed.), Elsevier, Amsterdam 1952

(9) I. Fortelný, J. Kovář, *Polym. Composites* **9**, 119 (1988)

(10)S. Torquato, B. Lu, J. Rubinstein, *Phys. Rev. A* **41**, 2059 (1990)

(11)I. Fortelný, A. Živný, *Polymer* **39**, 2669 (1998)

(12)X. Zhang, R. H. Davis, *J. Fluid Mech.* **230**, 479 (1991)

(13)I. Fortelný, M. Zápotocký, A. Živný, unpublished results

(14)K. Wallheinke, P. Pötschke, C. W. Macosko, H. Stutz, Polyblends'97, SPE RETEC, Boucherville 1997, Book of Proceedings, p. 510

(15)M. Manga, H. A. Stone, *J. Fluid Mech.* **300**, 231 (1995)

(16)M. A. Rother, A, Z. Zinchenko, R. H. Davis, *J. Fluid. Mech.* **346**, 117 (1997)

(17)H. Wang, A. Z. Zinchenko, R. H. Davis, *J. Fluid. Mech.* **265**, 161 (1994)

(18)J. M. H. Janssen, H. E. H. Meijer, *Polym. Eng. Sci.* **35**, 1766 (1995)

(19)S. T. Milner, H. Xi, *J. Rheol.* **40**, 663 (1996)

(20)S. A. K. Jeelani, S. Hartland, *J. Colloid Interface Sci.* **164**, 296 (1994)

(21)I. Fortelný, A. Živný, to be published

(22)G. E. Schoolenberg, F. During. G. Ingenbleek, *Polymer* **39**, 765 (1998)

(23)S. A. Patlazhan, J. T. Lindt, *J. Rheol.* **40**, 1095 (1996)