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FLOW INDUCED COALESCENCE IN POLYMER BLENDS

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Abstract. A modified theory of coalescence induced by extensional flow in polymer blends with Newtonian droplets in viscoelastic matrix has been derived. Results of this theory are compared with results of the theory of shear flow induced coalescence. Elasticity of the matrix leads to a decrease in the coalescence probability.

Keywords: coalescence, polymer blends, extensional flow, viscoelasticity.

1. Introduction

The competition between droplet breakup and coalescence controls the phase structure evolution during mixing and processing of immiscible polymer blends. Therefore, a correct description of flow induced coalescence is a necessary condition for reliable prediction of the particle size achieved in polymer blends with dispersed structure. As it is well known, the size of dispersed particles is crucial for many mechanical properties of polymer blends, *e.g.* their impact strength.

Coalescence in flowing polymer blends is a complex process still not satisfactorily described in spite of extensive theoretical and experimental studies [1-21]. Hydrodynamic interaction between coalescing droplets is of a long range type. Moreover, in typical polymer blends containing several tens of volume percent of the dispersed phase, coalescing droplets interact with other droplets in the system. After the approach to a short distance, the droplets can be deformed. The shape and size of the deformed parts of droplets have a crucial effect on the drainage of the matrix film trapped between them during the final stage of their approach. The state of the description art of the matrix drainage between coalescing droplets has been recently summarized by Janssen and Anderson [22]. Before collision, most droplets in polymer blends are not spherical; matrixes and droplets in polymer blends are viscoelastic substances. A flow field in mixing and processing equipments is complex and its proper modelling is a difficult task.

Due to difficulty of modelling and experimental determination of the coalescence in complex flow fields, theoretical and experimental studies of the flow induced coalescence have been focused on simple linear flows: shear and extensional [23]. The shear flow in rotational and capillary rheometers is most frequently used for determination of flow properties of molten polymer materials. In Cartesian coordinates, the shear flow can be described as a flow with the velocity in x direction having gradient in y direction; z is a neutral axis. In this coalescence model, it is assumed that the velocity gradient, *i.e.* shear rate, is constant. Measurements of molten polymer materials in the extensional flow are important for practice because extensional deformation plays a significant role in important processing operations, such as fiber spinning, thermoforming, blow molding, and foam production. Principles of the measurement and construction of rheometers are described in ref. [23]. In Cartesian coordinates, the velocity u, of steady uniaxial extension can be expressed as $u = \dot{\varepsilon}(-x, -y, 2z)$, where the rate of extension $\dot{\varepsilon}$, is constant.

The theory of coalescence in a dilute system of Newtonian droplets in a Newtonian matrix induced by linear flow fields was derived by Wang *et al.* [24] with the assumption that the droplets kept spherical shape until their fusion. Theories considering possible flattening of droplets are based on "ballistic" approximation [25], *i.e.* inter-droplet interactions are neglected until their approach to very short distances. Then, the coalescence is controlled by the competition between the rates of droplet approach, slowed down by drainage of the matrix film trapped between deformed droplets, and of their rotation around their common center of inertia. It is assumed that the matrix film between droplets bursts rapidly when they approach the critical distance h_c and that droplets fuse immediately thereafter [1-5, 26]. The probability P_c that the collision of droplets (calculated for non-interacting droplets) is followed by their fusion is used for characterization of the effect of the matrix drainage on coalescence.

The equations for the rate of droplets approach were derived for Newtonian droplets in a Newtonian matrix with the assumption that the flattened parts of the droplets were planes with a characteristic dimension much larger than inter-droplet distance. These equations were derived with various assumptions for the stress transfer at the interface. They depend on mobility of the interface, *i.e.* on the viscosity ratio p of the droplets and matrix for blends without a compatibilizer [1-5, 26]. Theories for fully mobile interface (FMI) partially mobile interface (PMI) and immobile interface (IMI) relate to low, medium and high p, respectively. Unfortunately, these expressions show different dependences on system parameters and limits of applicability of individual expressions are unclear. The systematic experimental study of the effect of p on P_c of Gabriele *et al.* [21] shows that in the limit of low and high p experimental results agree with theoretical predictions for fully mobile and immobile conditions. In the intermediate range of p, a smooth transition between the limiting fully mobile and immobile states was found.

The Elmendorp theory [1, 2] is based on the assumption that the resistance for the droplet approach can be expressed as a sum of resistances calculated for flattened droplets with FMI, PMI or IMI and for hard spherical droplets. This assumption leads to overestimation of the matrix resistance against the droplet approach. Therefore, this theory agrees with the experiment only if the FMI model for flatted droplets and unreliable large critical distance h_c are considered. The Janssen theory [4, 5] has frequently been used for description of the shear flow induced coalescence in polymer blends as it provides explicit expression for P_c, for systems related to the FMI, PMI and IMI models. The theory is based on the assumption that

$$P_c = \exp\{-t_c/t_i\} \tag{1}$$

where t_c is the coalescence time for the droplet approach from the original distance, h_0, to h_c and t_i is the interaction time equal to inversion value of the shear rate, $\dot{\gamma}$. A weak point of the theory is prediction of a higher P_c than that calculated for spherical droplets with the same other parameters for small droplet radius, R, and/or $\dot{\gamma}$. However, this result is unphysical because the resistance of the matrix against approach of flattened droplets cannot be smaller than that for the related spherical ones.

Rother and Davis [27] generalized the theory of Wang *et al.* [24] for deformable droplets considering the droplet deformation as a small but singular perturbation. They found that P_c for small R and/or $\dot{\gamma}$ was the same as for the related spherical droplets. At a certain R and $\dot{\gamma}$, P_c steeply decreases to a very low value similarly to the Janssen theory. Similar dependence of P_c on system parameters was obtained for uniaxial extensional flow by Fortelny and Zivny [28]. They considered that the formula for the matrix resistance between spherical droplets could be used if the ratio of radii of flattened part and undeformed droplet was smaller than a certain value; the formula for highly flattened droplet was used in the opposite case.

So far, only few studies have been devoted to the effect of elastic properties of the blend components on the flow induced coalescence. Yu and Zhou [29] modelled the shear flow induced coalescence by the diffuse interface method. They found that the matrix elasticity postponed the coalescence process but the effect was significant only if the matrix elasticity exceeded a certain critical value. The study deals with coalescence between droplets placed on the same streamlines at the coalescence origin, and it does not provide P_c as a function of system parameters. Recently, Fortelny and Juza [30] have derived the theory of the shear flow induced coalescence considering that viscoelastic properties of the matrix can be described by the Maxwell model. In describing the matrix drainage, the switch between the chosen formula for highly flattened droplets and the formula for spherical droplets is used; *i.e.* the formula predicting larger resistance for a certain set of system parameters is applied.

The aim of this study is to derive a theory describing the effect of matrix elasticity on the extensional flow induced coalescence and to compare its results with the theory of the shear flow induced coalescence. Further aim of this study is to contribute to understanding the effect of the model choice of interface mobility on P_c by comparing the results of the PMI model with the Jeelani-Hartland (JH) model [31] which passes to the IMI model for $p \to \infty$.

2. Theoretical Background

For simplicity, coalescence of two Newtonian droplets with the same radius R, in a viscoelastic matrix described by the Maxwell model is considered. For drag force $\boldsymbol{F}$ on the droplet moving with velocity $\boldsymbol{u}$ against this matrix, the following equation was derived [32, 33]:

$$\boldsymbol{F} = \varsigma \boldsymbol{u} - \tau_m \frac{d\boldsymbol{F}}{dt} \tag{2}$$

where z is the frictional resistance of the particle and t_m is the relaxation time of the matrix.

It leads us to the conclusion that the approach of droplets in this system can be described if F in the equations for the rate of the droplet approach in the Newtonian matrix is substituted by $F + t_m dF/dt$ [30, 34]. For close spherical droplets [26, 35], this substitution leads to:

$$-\left(\frac{dh}{dt}\right)_{Sp} = \frac{2h\left(F + t_m \frac{dF}{dt}\right)}{3\pi h_m R^2 g(m)} \tag{3}$$

where h is an inter-droplet distance and $g(m)$ is given by:

$$g(m) = \frac{1+0.402m}{1+1.711m+0.461m^2} \quad (4)$$

with m defined as:

$$m = \frac{h_m}{h_d}\left(\frac{R}{2h}\right)^{1/2} \quad (5)$$

where h_m and h_d are viscosities of the matrix and the droplets, respectively. For highly flattened droplets with partially mobile interface [3-5, 26], the following equation is valid for the droplet approach:

$$-\left(\frac{dh}{dt}\right)_{PMI} = \frac{4(2p)^{1/2}s^{3/2}h^2}{h_d R^{3/2}\left(F + t_m\frac{dF}{dt}\right)^{1/2}} \quad (6)$$

where s is an interfacial tension. The Jeelani-Hartland model [26, 31] for highly flattened droplets leads to:

$$-\left(\frac{dh}{dt}\right)_{JH} = \frac{8ps^2h^3}{3h_m R^2\left(F + t_m\frac{dF}{dt}\right)}\left(1+3C\frac{h_m}{h_d}\right) \quad (7)$$

where C is the dimensionless circulation length of the order of 1 [31].

2.1. Shear Flow

For shear flow with unperturbed velocity $\boldsymbol{u_0} = (\dot{\gamma}y, 0, 0)$, rotation of the spheres is described by the equations [24, 30]

$$\frac{df}{dt} = \dot{\gamma}D(f) = \dot{\gamma}\left[\left(1-\frac{b}{2}\right)\sin^2 f + \frac{b}{2}\cos^2 f\right] \quad (8)$$

$$\frac{dq}{dt} = \dot{\gamma}(1-b)\sin q\cdot\cos q\cdot\sin f\cdot\cos f \quad (9)$$

where q is polar angle, f is azimuth and b is a function of distances between spheres centers and $2R$ [24].

It is assumed that Eqs. (8) and (9) are also applicable in the case of droplet flattening and for a viscoelastic matrix. F can be expressed as:

$$F = (K/2)\pi h_m\dot{\gamma}R^2\sin^2 q\,\sin 2f \quad (10)$$

where K is a function of p [30].

Droplet collision is followed by their fusion if they approach the distance shorter than the critical distance h_c, for breakup of the matrix film earlier than the azimuth $f = \pi/2$ is achieved. Combination of Eqs. (3) and (6)-(10) leads to the following equations for the dependence of the inter-droplet distance on the azimuth [30].

For spherical droplets:

$$-\left(\frac{dh}{df}\right)_{Sp} = G_{Sp}\frac{h}{g(m)}\frac{Q(q,f)+t_m\dot{\gamma}S(q,f)}{D(f)} \quad (11)$$

where

$$G_{Sp} = \frac{2}{3}K \quad (12)$$

$$Q(q,f) = \frac{1}{2}\sin^2 q\,\sin 2f \quad (13)$$

and

$$S(q,f) = \frac{1-b}{8}(\sin 2q\,\sin 2f)^2 + D(f)\sin^2 q\,\cos 2f \quad (14)$$

For flattened droplets with partially mobile interface [30]:

$$-\left(\frac{dh}{df}\right)_{PMI} = G_{PMI}\frac{h^2}{D(f)\left[Q(q,f)+t_m\dot{\gamma}S(q,f)\right]^{1/2}} \quad (15)$$

where

$$G_{PMI} = \frac{4\sqrt{2}s^{3/2}}{K^{1/2}h_d h_m^{1/2}\dot{\gamma}^{3/2}R^{5/2}} \quad (16)$$

For flattened droplets with interface described by the JH model [30]:

$$-\left(\frac{dh}{df}\right)_{JH} = G_{JH}\frac{h^3}{D(f)\left[Q(q,f)+t_m\dot{\gamma}S(q,f)\right]} \quad (17)$$

where

$$G_{JH} = \frac{8}{3K(\mathrm{Ca}\,R)^2}\left(1+3C\frac{h_m}{h_d}\right) \quad (18)$$

and Ca is a capillary number defined as:

$$\mathrm{Ca} = \frac{h_m\dot{\gamma}R}{s} \quad (19)$$

The polar angle can be expressed as [30]:

$$q = \mathrm{arctg}\left(\mathrm{tg}\,q_0\left[\frac{(1-b)\sin^2 f + b/2}{(1-b)\sin^2 f_0 + b/2}\right]^{1/2}\right) \quad (20)$$

where q_0 and f_0 are polar angle and azimuth at the beginning of coalescence.

In calculating $h(\pi/2)$, Eq. (11) is combined with Eq. (15) or (17). Smaller of the values $-(dh/df)$ for the spherical or the chosen model of flattened droplets is used in the calculation.

2.2. Extensional Flow

For extensional flow with unperturbed velocity $\boldsymbol{u}_0 = \dot{\varepsilon}(-x, -y, 2z)$, rotation of the spheres is described by the following equation [24, 28]:

$$\frac{dq}{dt} = -3(1-b)\dot{\varepsilon}\sin q\,\cos q \quad (21)$$

and for driving force of the coalescence F, the following equation is valid [28]:

$$F = K\pi\dot{e}h_m R^2(1-3\cos^2 q) \quad (22)$$

Combination of Eqs. (21) and (22) with Eqs. (3), (6) or (7) leads to the equations describing the dependence of inter-droplet distance on the polar angle. Analogically to Eq. (11), we obtain for spherical droplets

$$\left(\frac{dh}{dq}\right)_{Sp} = G_{Sp}\frac{h}{g(m)}\frac{Q_e(q)+t_m\dot{\varepsilon}S_e(q)}{D_e(q)} \quad (23)$$

where

$$Q_e(q) = 1 - 3(\cos q)^2 \quad (24)$$

$$S_e(q) = -\frac{9}{2}(1-b)(\sin(2q))^2 \quad (25)$$

$$D_e(q) = \frac{3}{2}(1-b)\sin(2q) \quad (26)$$

For flattened droplets with partially mobile interface:

$$\left(\frac{dh}{dq}\right)_{PMI} = G_{PMI}\frac{h^2}{D_e(q)\left[Q_e(q) + t_m S_e(q)\right]^{1/2}} \quad (27)$$

analogically to Eq. (15); functions Q_e, S_e and D_e are defined in Eqs. (24)-(26).

For flattened droplets described by the JH model

$$\left(\frac{dh}{dq}\right)_{JH} = G_{JH}\frac{h^3}{D_e(q)\left[Q_e(q) + t_m S_e(q)\right]} \quad (28)$$

analogically to Eq. (17).

Collision of the droplets in extensional flow is followed their fusion if their distance h decreases bellow h_c until the polar angle q^* is achieved. Eq. (24) or (25) for flattened droplets is combined with Eq. (23) for spherical droplets in calculating of $h(q^*)$. Smaller of the dh/dq values for spherical or flattened droplets is used in the calculation. q^* is given by the condition $dh/dq = 0$.

$$q^* = \operatorname{arctg}\left(\sqrt{9t_m(1-b) + \frac{1}{2} + \sqrt{(9t_m(1-b))^2 + 9t_m(1-b) + \frac{9}{4}}}\right) \quad (29)$$

For t_m=0 is $q^* = \operatorname{arctg}(\sqrt{2})$.

2.3. Calculation of P_c

The rate at which the droplets collide with the following fusion is equal to the flux J_c, of pairs into the contact surface. J_c can be expressed as:

$$J_c = -n^2 \int_{A_c} \boldsymbol{u}\cdot\boldsymbol{n}\,dS \quad (30)$$

where n is the droplet number in the unit volume, $\boldsymbol{n}$ is the outward unit normal to the spherical contact surface, A_c is the upstream interception area, and dS is the surface element. P_c can be determined as:

$$P_c = J_c/J_0 \quad (31)$$

where J_0 is the flux of particles which do not interact until collision. For shear flow, P_c can be calculated as [30]:

$$P_c = 3\int_0^{\pi/2}\int_0^{\varphi_M} \sin\varphi_0 \cos\varphi_0 \sin^3\theta_0 \, d\varphi_0 \, d\theta_0 \quad (32)$$

where f_0 and q_0 are azimuth and polar angle at the beginning of coalescence and f_M is the maximum azimuth angle for a certain initial polar angle q_0 at which the droplets fuse. For extensional flow, the following equation is valid for P_c [28]:

$$P_c = \frac{3\sqrt{3}}{2}\left(\cos\theta_0^{(m)} - \cos^3\theta_0^{(m)}\right) \quad (33)$$

where $q_0^{(m)}$ is the minimum initial angle q at which the droplets fuse.

Values of P_c were determined by the numerical calculation as described in the recent paper [30] or, analogically:

1. The course of mutual position of the drop pairs from its initial value given by distance h_0 and angle q_0 for the extensional flow or angles f_0 and q_0 for the shear flow has been calculated by integration of Eqs. (11), (15) and (17) or (23), (27) and (28) until the distance decreases below its critical value h_c or starts increasing (azimuth reaches the right angle for shear flow or angle reaches q^* for extensional flow). Integration was performed by the Cash-Karp embedded Runge Kutta method [36].

In the calculations, the following parameters have been used: b = 0.075, K = 12.24, C = 1, initial integration step size is 10^{-5}, δ of the embedded Runge Kutta method is 10^{-12}.

2. For extensional flow, drop pairs coalesce for initial angles in the range from the limit angle $q_0^{(m)}$ to the right angle; $q_0^{(m)}$ is higher than q^*. For shear flow, drop pairs coalesce (if ever) at a given initial polar angle q_0 from zero azimuth to some limit value. Therefore, coalescence for $f_0 = 0$ and $f_0 = \pi/2$ is first tested using the procedure on level 1 for each q_0; the pairs not coalescing at $f_0 = 0$ have $f_M = 0$, while the pairs coalescing even for $f_0 = \pi/2$ have $f_M = \pi/2$. Otherwise, the limit angle f_M (or $q_0^{(m)}$) was determined by the bisection method combined with the regula falsi method applied to a function expressing the final distance of drops: positive value $h - h_c$ at $f = \pi/2$ for not coalesced drop pairs, negative number proportional to $f_c - \pi/2$ for coalesced drop pairs, where f_c is f for that drops approached h_c distance. The final step size of the method has been modified between 10^{-5} and 10^{-9} to get sufficiently precise results within reasonable time.

For extensional flow, steps 1–2 can be simply replaced by integration from q^* and supposed distance h_c back to distance h_0. However, sometimes this procedure leads to inappropriate results.

3. For extensional flow, P_c is obtained using Eq. (33). For shear flow, Eq. (32) can be expressed as:

$$P_c = \int_0^{p/2} P(q_0)\sin^3 q_0 \, dq_0 = \int_0^{p/2}\left[1 - \cos(2f_M(q_0))\right]\sin^3 q_0 \, dq_0 \quad (34)$$

This equation is solved again numerically, when each f_M is determined as described above. In fact, the range of polar angles with nonzero f_M is determined and the integration is carried out only over this range.

The initial integration step size was 0.1, δ of the embedded Runge Kutta method was 10^{-5}. These relatively large values cause imprecise results to be considered

semiquantitative only; however, since each integration point represents solving of an implicit equation of the function resulted from another numeric integration, results of better precision could not be obtained within reasonable time.

3. Results and Discussion

Fig. 1 shows that P_c for spherical drops somewhat decreases with increasing R. It should be mentioned that this decrease is a consequence of the choice of constant nonzero h_c [30]. P_c independent of R is obtained for spherical drops at $t_m = 0$ in accordance with Wang *et al.* [24] if $h_c = 0$ is considered. The same effect of h_c is also demonstrated for systems where flattening of drops is considered. Besides this effect, the shapes of P_c *vs.* R dependences for flattening drops in Newtonian blends for shear and extensional flows are also similar to those calculated by Rother and Davis [27], *i.e.* P_c is a constant relating to spherical drops for small R and starts decreasing steeply to a very low value for a certain critical R_c. For a set of parameters used in Fig. 1, the JH model leads to steeper decrease at smaller R than the PMI model. Fig. 1 shows that, if $\dot{\gamma}$ = $\dot{\varepsilon}$ is considered and other parameters are the same, P_c is lower and R_c is smaller for the extensional than for the shear flow.

Elasticity of the matrix does not change the shape of dependence of P_c on R. Longer relaxation time t_m reduces the probability of coalescence P_c as well as R_c described above. Both decreases are more rapid for the extensional than for the shear flow. The effect is not significant for $t_m < 1$ s, but it is pronounced for t_m of the order of seconds. It should be mentioned that a substantial part of commercial thermoplastics has $t_m < 1$ s [37, 38]. Therefore, the effect of elasticity on flow induced coalescence seems to be important only for systems with a high-molecular-weight matrix.

It can be seen from Fig. 2 that, while coalescence probabilities P_c are independent of elongation and shear rates for spherical particles in Newtonian systems, longer relaxation time leads to a decrease of P_c with increasing elongation and shear rates. The decrease is again more profound for the extensional flow induced coalescence. The P_c decrease is nearly linear for short relaxation times. For longer relaxation times, the decrease is not uniform in the whole range of shear or elongation rates: P_c decreases substantially for smaller rates; further rate growth brings only slight decrease or even increase in P_c. The models taking into account drops flattening (PMI and JH) do not differ from the spherical drops model for very low shear and elongation rates and later they provide P_c decreasing to zero, more steeply for longer relaxation time. For the chosen set of parameters, the JH model predicts steeper decrease of P_c starting at lower $\dot{\gamma}$ or $\dot{\varepsilon}$ than the PMI model.

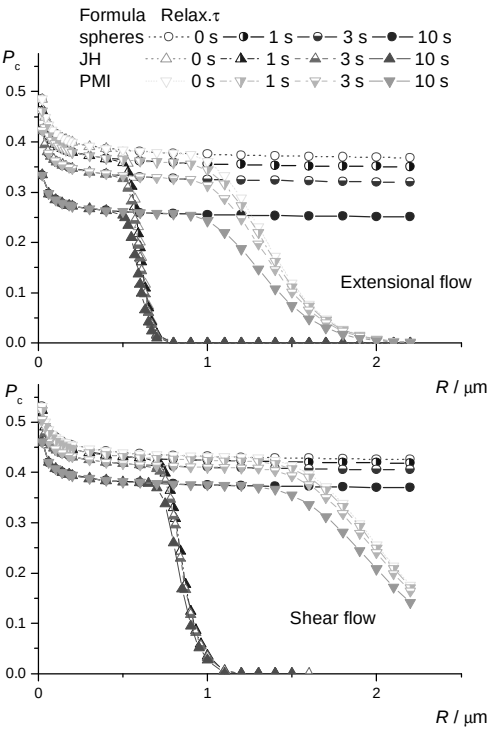

Fig. 1. Dependence of coalescence probability P_c on drop radius R, for different relaxation times for spherical particles and for flattening particles described by the partially mobile interface (PMI) model or the Jeelani and Hartland (JH) model: extensional flow (upper plot) and shear flow (lower plot). Parameters used: viscosities of drops h_d and of matrix h_m = 1 kPa·s; shear or elongation rate is 0.02 s^{-1}; interfacial tension is 1 mN/m, relative initial distance h_0/R = 10, critical distance h_c = 5 nm

Simple test of viscosity influence on coalescence induced by the extensional flow for Newtonian systems is presented in Fig. 3. P_c for spherical drops depends only on viscosity ratio p. If the matrix is more viscous than drops, P_c is higher, and vice versa. P_c is controlled only by p also for flattening drops in the range of small droplet radii. The critical drop radius R_c, at which P_c starts decreasing steeply, decreases with rising values of viscosities at a constant p. Steep decrease in P_c is more pronounced for systems with higher viscosities if the same p is considered. For partially mobile interface, R_c increases with decreasing viscosity of any phase. R_c is affected slightly stronger by the change in drop viscosity than the by change in matrix viscosity.

Fig. 4 shows what happens when the drop viscosity decreases at a constant h_m. For extensional flow induced coalescence, the Jeelani and Hartland model provides lower coalescence probabilities P_c than partially mobile interfaces for systems with equal viscosity of both phases. P_c approaches a limit value for immobile interface with increasing drop viscosity for the Jeelani and Hartland model, while it continues to decrease for the partially

mobile interface and therefore becomes lower than for the former model. The same result was obtained for the shear flow induced coalescence [30]. It is clear that the JH model is more reasonable than the PMI one for $h_d >> h_m$ but reliability of these models for $h_d \approx h_m$ should be the subject of further investigation.

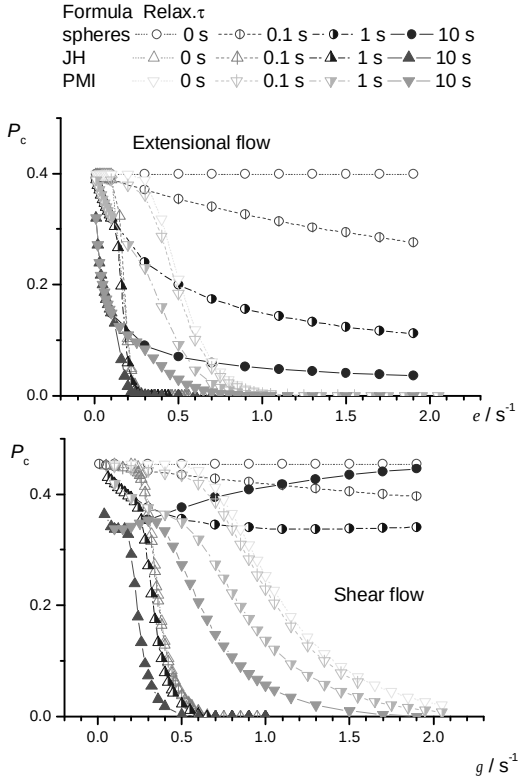

Fig. 2. Dependence of coalescence probability P_c on elongation rate (extensional flow – upper plot) or shear rate (shear flow – lower plot) for the spherical particles model and for the calculations switching between this model and formulae of the partially mobile interface model (PMI) or the Jeelani and Hartland (JH) model and for different relaxation times. Drop size R = 0.2 μm, other parameters are the same as in Fig. 1

Generally, the calculation of P_c based on the switch between equations for drainage of the matrix trapped between spherical or highly flattened droplets leads to the same type of its dependence on system parameter both for the shear and the extensional flow induced coalescence. This method leads to the same P_c as the calculation for spherical drops at small R. At a certain droplet radius R_c, P_c starts decreasing steeply to a negligibly small value. The value of R_c depends, besides the values of system parameters, on the model of interface mobility used for flattened droplets. The same type of the dependence of P_c on system parameters comes from the Rother and Davis theory [27] based on the assumption that flattening of the droplets is small but singular perturbation. It seems that both our theories and the Rother and Davis ones overestimate the steepest of the decreases of P_c with R because flattening of droplets increases gradually from zero to a high value with a rising driving force of the coalescence. Therefore, the value of R_c and the rate of decrease of P_c should be the subject of further investigation together with attempts to establish a reliable model of the interfacial mobility for flattened droplets. P_c decreases with increasing relaxation time, *i.e.* elasticity, of the matrix at any parameters of the system. It has been found that this decrease is not pronounced for t_m smaller than 1 s^{-1}, especially for shear flow induced coalescence. Therefore, using the theory of flow induced coalescence derived for Newtonian systems for polymer blends with matrixes of low to medium molecular weight does not cause substantial error. It should be mentioned that this theory has been derived for drops with the same radius. As a decrease in P_c has been found with the increasing ratio of radii of larger and smaller spherical droplets [24], P_c in blends with droplets polydisperse in size is smaller than that predicted by this theory.

Generally, the above approach to the description of the flow induced coalescence can also be applied to aggregation of solid particles in suspensions described, *e.g.* in [39]. It should be mentioned, however, that the resistance against matrix drainage between solid spheres is substantially stronger than that between liquid droplets. Zero P_c is predicted for solid spheres, *i.e.* $p \rightarrow \infty$, if molecular forces between them are not considered [24]. Therefore, non-negligible P_c can only be found in systems with strong attractive molecular forces. In this case, molecular forces should be specified in detail and explicitly added to the driving force of the coalescence (Eq. (10) or (22)) instead of their consideration by the

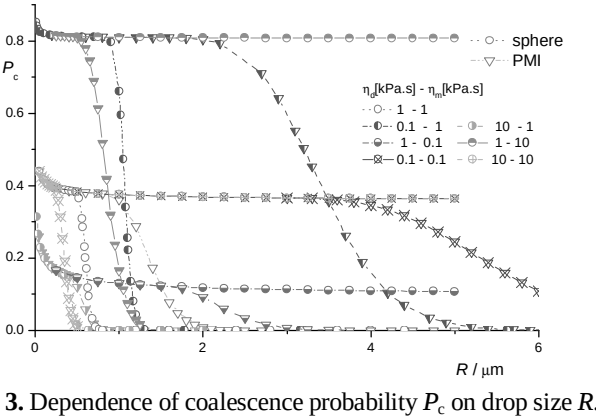

Fig. 3. Dependence of coalescence probability P_c on drop size R. Influence of changes of matrix and drop viscosities for spherical drops and for flattening drops in extensional flow described by the partially mobile interface model (PMI). Zero relaxation time (Newtonian system). The basic system with drop viscosity h_d = 1 kPa·s and matrix viscosity h_m = 1 kPa·s is compared with systems where one or both of h_d and h_m are 0.1 kPa·s or 10 kPa·s. Other parameters are the same as in Fig. 1.

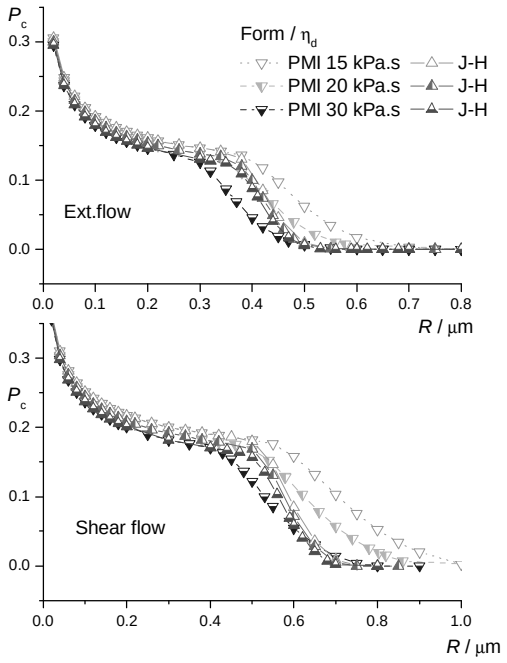

Fig. 4. Dependence of coalescence probability P_c on drop size R. Influence of drop viscosity change for the partially mobile interface (PMI) and for the Jeelani and Hartland (JH) model. Upper plot – extensional flow, lower plot – shear flow. Zero relaxation time (Newtonian system), other parameters are the same as in Fig. 1

choice of non-zero h_c only. In the case of anisometric solid particles, their rotation before collision should be considered, which substantially complicates modelling of their coalescence.

4. Conclusions

The coalescence probability, P_c, in the shear and extensional flows has been calculated using the switch between equations for drainage of the matrix trapped between spherical or highly flattened droplets. For Newtonian systems, the theory provides the same shape of the dependences of P_c on the droplet size and shear or elongation rates as the theory of Rother and Davis [27]. Drop radius R_c, for which flattening markedly reduces the coalescence probability, is dramatically higher for lower viscosities of any phase, and slightly higher for the shear flow induced coalescence than for the extensional flow. The choice of the model of interfacial mobility used to describe drainage of the matrix between flattened drops (JH or PMI) has a strong effect on the calculated R_c value. Plausibility of these models for various systems should be the subject of further investigation.

Increased matrix elasticity, related to the relaxation time of its Maxwell model, reduces the coalescence probability, causes its decrease with shear or elongation rate even for spherical particles, and causes a decrease in both critical droplet radius R_c and minimal shear and elongation rates from which P_c starts decreasing steeply. The effect of the matrix elasticity is stronger for extensional than for shear flow if equal values of shear and elongation rates and the same other system parameters are considered.

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ПОТОКОВА ІНДУКОВАНА КОАЛЕСЦЕНЦІЯ В ПОЛІМЕРНИХ СУМІШАХ

Анотація. *Розроблена модифікована теорія коалесценції індукованої екстенсіональним потоком в полімерних сумішах з ньютонівськими крапельками у в'язкоеластичній матриці. Результати теорії порівняні з результатами теорії зсуву поточної індукованої коалесценції. Встановлено, що еластичність матриці приводить до зменшення ймовірності коалесценції.*

Ключові слова: *коалесценція, полімерні суміші, екстенсіональний потік, в'язкоеластичність.*