Coalescence of polymer droplets: experiments on collision

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Abstract - The coalescence of polymer droplets is a fundamental phenomenon which appears for example when mixing two polymers. When two polymeric droplets collide, a transient regime appears, which results from a competition between interfacial and viscoelastic effects : the spherical droplets deform to give birth to a new drop in a short time (t_C) and the drop shape stabilizes after a long time.

A novel method is proposed to study experimentally under a microscope the collision between two droplets of one polymer in another one, with different viscosity ratios. This allows to determine the characteristic time t_C which defines this phenomenon. The experiments actually show that t_C varies like the geometric mean of the viscosities of the two polymers, for the case of a polydimethylsiloxane/polyisobutylene system.

Coalescence de gouttelettes de polymères : expériences de collision

Résumé - *La coalescence de gouttelettes de polymères est un phénomène fondamental qui intervient par exemple lorsque l'on mélange deux polymères. Lorsque deux gouttelettes de polymères rentrent en collision, un régime transitoire apparaît, qui est régi par la compétition entre les effets de surface et les effets viscoélastiques : les gouttelettes sphériques se déforment pour donner naissance à une nouvelle goutte dans un temps rapide (t_C) et la forme de cette goutte se stabilise dans un temps long.*

Une nouvelle méthode est proposée pour étudier expérimentalement sous microscope la collision de deux gouttelettes d'un polymère dans un autre en faisant varier le rapport des viscosités. Ceci permet d'avoir accès au temps caractéristique t_C qui définit le phénomène. Les expériences montrent que t_C est en fait proportionnel à la moyenne géométrique des viscosités des deux polymères, dans le cas d'un système polydiméthylsiloxane/polyisobutylène.

Key words: coalescence - collision - droplet - polymer - interfacial tension

Mots-clés: coalescence - collision - gouttelette - polymère - tension interfaciale

Version française abrégée - Le terme de coalescence désigne en général le mécanisme global de rencontre de deux gouttes d'un milieu 1 placées dans un milieu 2. Ce processus peut être dû à des forces de natures différentes (mouvement Brownien, forces de van der Waals, forces extérieures comme un cisaillement, ...) et on peut le décomposer en plusieurs phases:

I. l'approche des gouttelettes avec le drainage du fluide interstitiel
II. l'ouverture d'un trou
III. la collision

La première étape a été bien décrite précédemment [1], en faisant plusieurs hypothèses concernant la nature de l'interface, mobile, partiellement mobile, ou fixe. La seconde étape est plus délicate mais

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* Dedicated to Professor Daniel D. Joseph, on the occasion of his 70th Birthday.

suppose que lorsque l'écart entre les deux gouttelettes correspond à une distance caractéristique petite (de l’ordre de 50 Å), il se crée un trou permettant la réunion des deux gouttelettes.
C'est la troisième et dernière étape qui nous intéresse ici ; en outre elle a été peu étudiée dans la littérature. Il s’agit de comprendre les mécanismes qui régissent la déformation de la surface libre, à savoir l’influence couplée des effets de surface et viscoélastiques, afin de prédire quels sont les paramètres qui contrôlent réellement cette étape.
Pour cela, nous utilisons deux polymères fondus transparents, le polydimethylsiloxane (PDMS) et le polyisobutylene (PIB), en se plaçant sous un microscope. Sous l’action des seules forces de van der Waals, deux gouttelettes se rapprochent et se réunissent, ceci étant filmé à l'aide d'une caméra vidéo. Dans le système considéré, les effets élastiques sont négligeables.
Les résultats montrent qu’un première phase très rapide intervient, où la surface libre se déforme soumise à l’action prépondérante des forces de surface. Ensuite une deuxième étape plus longue se déroule (relaxation), pendant laquelle la goutte nouvellement formée atteint sa forme sphérique finale.
Le temps caractéristique t_c de la première phase est mesuré en prenant l'inverse de la pente de la courbe $D(t)/D_0$ en fonction du temps t (D(t) longueur totale de la nouvelle goutte, D_0 longueur initiale) et il est porté sous forme adimensionnelle $\sigma t_c/\eta_1 R_1$ (σ est la tension interfaciale et R_1 le rayon de la grosse gouttelette) en fonction du rapport des viscosités $\eta 1/\eta 2$. La pente obtenue, pour différentes combinaisons de viscosités η_1 et η_2, est environ -1/2, ce qui veut dire que t_c varie à peu près comme la moyenne géométrique des viscosités $\sqrt{\eta_1\eta_2}$.

1. INTRODUCTION. -

Coalescence usually describes the global mechanism by which two drops of a fluid 1 meet in a fluid 2. This process may be due to different forces (Brownian forces, van der Waals ones, or exterior forces like shear, etc.) and can be divided into three different phases :
I. the approach of the droplets with the draining of the interstitial fluid
II. the opening of a hole
III. the collision
The first stage has been well described previously [1], several approaches consider mobile, partially mobile or immobile interfaces. The second stage is more delicate and requires a physical hypothesis assuming that a hole will appear when a certain small characteristic distance exists between the two droplets (typically 50 Å), then the droplets meet.
We consider here the final stage. In addition it has not been studied so much in the literature. Understanding the mechanisms of deformation of the free surface are essential, i.e. the competition between interfacial tension and viscoelasticity, in order to determine which are the relevant parameters governing this phenomenon.
In order to do so, we use two transparent polymer melts, a polydimethylsiloxane (PDMS) and polyisobutylene (PIB) and put this system under a microscope. Under the action of van der Waals forces only, two spherical droplets get closer and eventually meet, this being filmed using a video camera. In this particular system, elastic effects can be neglected.
Results show that a first rapid phase occurs, where the surface moves due to surface forces mainly. Then a second and longer phase is observed, during which the newly formed drop changes shape (relaxation) until it becomes spherical.
The characteristic time t_c of the first stage is measured from the slope in the diagram $D(t)/D_0$ versus time t (D(t) total length of the new drop, D_0 initial length) and is plotted in its dimensionless form $\sigma t_c/\eta_1 R_1$ (σ is the interfacial tension and R_1 the radius of the large droplet) against the viscosity ratio η_1/η_2. The slope obtained for various combinations of the viscosities η_1 and η_2 equals roughly -1/2, which means that t_c varies roughly like the geometric mean of the two viscosities $\sqrt{\eta_1\eta_2}$.

2. COLLISION OF SPHERICAL DROPS . -

Literature

Coalescence and therefore collision are very important for they appear in various mixing problems (emulsions, blends) or in metallurgy (sintering of metallic powders [2]). They are also essential in colloids, coatings, foams and may be also relevant to cellular systems, in particular when discussing

coagulation or aggregation. The resulting microstructure of the system or material greatly depends on coalescence phenomena.
Coalescence and break-up [3-9] are actually often associated in these systems because they appear at the same time and it may be difficult to predict which one is the governing mechanism. Droplets in elongation and shear situations have already been considered [6-7]. The most complete work on drainage in a coalescence process is due to Chesters [1] where a systematic analysis of the flow of the interstitial fluid is analyzed analytically using different interfaces, fixed, mobile or partially mobile. Numerical work has also been proposed [10] showing the onset of flattening before opening of a hole.
When thinking about a two-drop system, Frenkel's solution [11] may be recalled as well as experiments by Kuczynski [2], both showing the evolution of the radius of the hole which is opening like $t^{1/2}$ (t is time). More recently a close solution [12-13] was obtained for two-dimensional cases using mapping functions. The neck growth problem [14] was again treated experimentally in a complete manner for a polymeric system, showing correlation of the neck radius with the compliance over several decades in time. On the other hand, a very recent study [15] has proved that the initial evolution of the hole radius is like $t^{1/7}$. But this study does not tell us how interfacial tension comes into this relation. In the same work, multiple air traps were computed numerically, which seems rather surprising.
Polymeric systems are also of interest. Models describing groups of droplets (blends) require a few statistical assumptions, in particular the number of droplets per unit volume and the probability for the drops to meet. Such models for coalescence [16-17] are based on the assumption that coalescence is possible only if draining of the interstitial fluid is fast enough. The study of copolymers has also been considered [18], showing their stabilizing effects, thus preventing coalescence. Models can finally predict the final diameter or its evolution in time [19-20]. It can be concluded that coalescence is more important than break-up in certain cases [21-23].
Nevertheless, the understanding of the coalescence process during collision is still not well understood, due to the strong nonlinearities involved (surface deformations, curvatures), therefore a careful experimental study is needed to understand this process and the governing parameters, and this is the aim of this work.

Governing parameters

Let us consider a system composed of two droplets of fluid 1 with viscosity η_1 and density ρ_1 in an outer fluid 2 of viscosity η_2 and density ρ_2 (figure 1). They have radii R_1 and R_2 and σ is the interfacial tension.

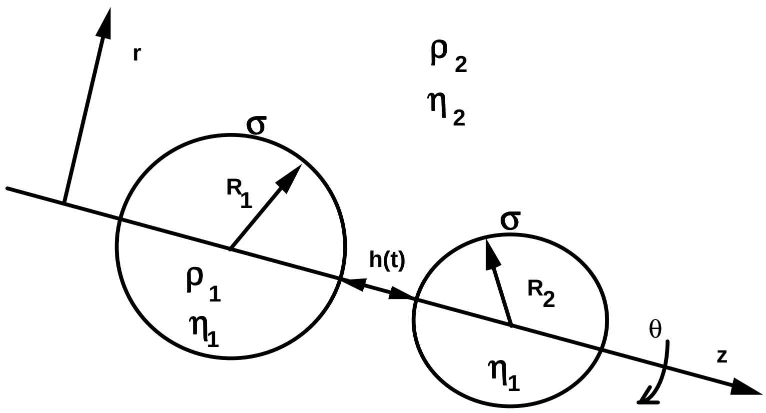


Fig. 1. - Sketch of the system
Fig. 1. - Schéma du système

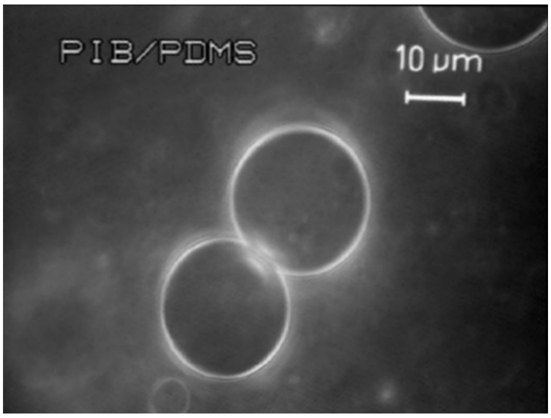
The five dimensionless parameters are the radius ratio R_1/R_2, the viscosity ratio η_1/η_2, the density ratio ρ_1/ρ_2, a capillary number, say $\eta_1 R_1/\sigma t_c$ (where t_c is the characteristic time of the phenomenon, therefore a typical velocity is R_1/t_c) and the Suratman number $S=\sigma\rho_1 R_1/\eta_1^2$. In our case, we will neglect gravitational effects because close densities prevent sedimentation in the time interval considered. Furthermore $S<<1$, due to the high viscosities used. Therefore we will look for a relation between

$\eta_1 R_1/\sigma t_c$ and the ratios R_1/R_2 and η_1/η_2. The system will be considered axisymmetric around the z-axis (figure 1), and this is verified experimentally.

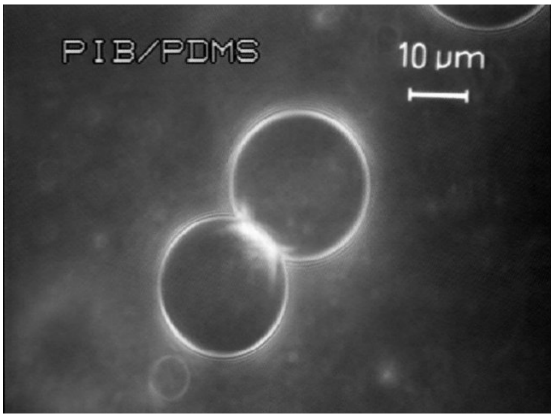
In this particular paper, we will neglect viscoelastic effects, which are not important due to the particular choice of the fluids. Systems including viscoelasticity should therefore also include other dimensionless numbers such as the Weissenberg numbers.

3. EXPERIMENTAL TECHNIQUE . -

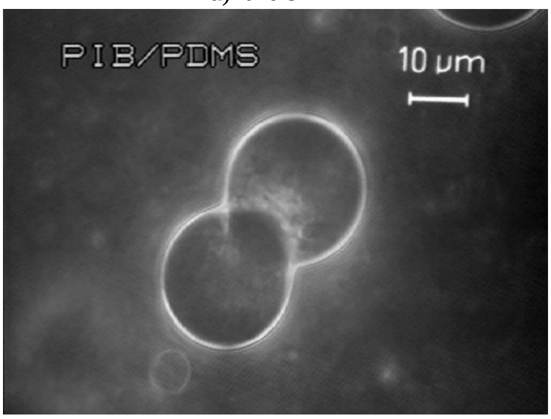
Two sets of polymers are used in the experiments. The first one is a series of polydimethylsiloxanes (PDMS, Rhône-Poulenc, 47VT series, three viscosities: 60 Pa.s, 100 Pa.s, 500 Pa.s at 20°C). The second polymer is polyisobutylene (PIB, BP chimie, D series, three viscosities: 58 Pa.s, 210 Pa.s, 705 Pa.s at 20°C). Therefore nine different viscosity combinations may be considered, according to the inner and outer polymers chosen, PDMS or PIB. This allows a range of viscosity ratios of about two decades. The interfacial tension σ is roughly 3mN/m, and is constant for the various systems. The relaxation times of these polymers are typically of the order of a few milliseconds, therefore elastic effects can be neglected, due to the longer times involved in the experiments.



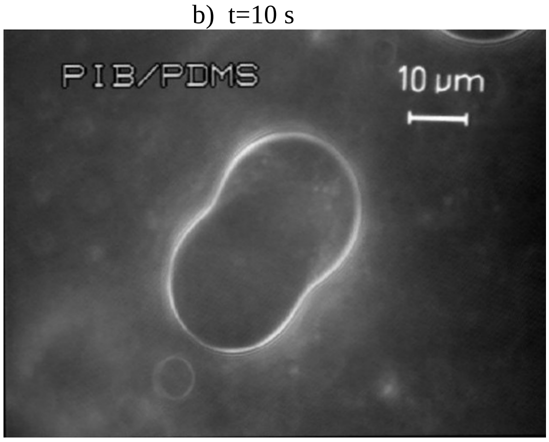
a) t=0 s



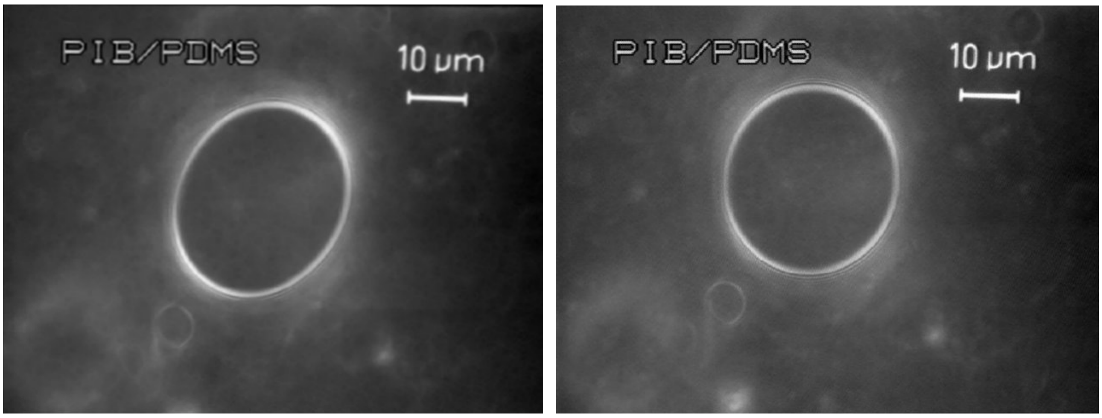
b) t=10 s



c) t=10.8 s



d) t=12.4 s



e) t=16.8 s f) t=21.6 s

Fig. 2. - Collision of droplets of PIB (705 Pa.s) in PDMS (60 Pa.s)
Fig. 2. - Collision de gouttelettes de PIB (705 Pa.s) dans du PDMS (60 Pa.s)

The fluids are prepared by hand-mixing without using compatibilizers. The volume concentration of fluid 1 is about 5%, so that a sufficient number of droplets is obtained and the droplets are not too close to each other. The resulting emulsion is placed between a glass plate and a micro cover glass, to be observed under a Leica microscope. Droplets are chosen in the middle of the glass plates, in order to avoid edge effects, so that we can consider that the motion is indeed three dimensional. The two droplets are located in the same plane so that both are in focus. This means that they should have about the same radius. They are not far from each other, so that the time to wait is not too long before they collide. Just before a hole is formed, the video camera is started and collision can be studied.
A typical experiment is depicted in the series of figures 2a-f. In this experiment, more viscous droplets (PIB, 705 Pa.s) are used in a matrix of less viscous fluid (PDMS, 60 Pa.s). We first start with two initial spherical droplets (figure 2a) almost touching. Then a hole is formed in about 10 seconds (figure 2b) and the droplets start to merge. After some short time (figure 2c), the droplets have already deformed under the action of interfacial tension. A little later (figure 2d), the newly-formed drop is showing a significant change. This drop is almost in its final equilibrium position after about 17 seconds (figure 2e), but more time is required for reaching equilibrium (figure 2f).
To determine the characteristic time of the rapid stage of the collision, we choose to represent the graph $D(t)/D_0$ versus time, sketched in figure 3. D(t) is the length of the final drop, and $D_0=2(R_1+R_2)$ is the initial length if the drops touch.

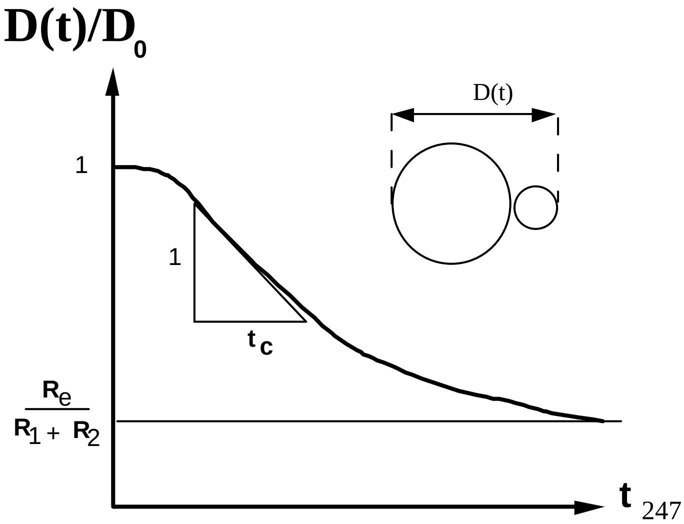


Fig. 3. - Determination of t_c from the plot of $D(t)/D_0$ vs. t
Fig. 3. - Détermination de t_c à partir de la courbe $D(t)/D_0$ vs. t

$D(t)/D_0$ equals roughly 1 at time 0, because of possible flattening effects. The interstitial fluid is finally removed until a hole is formed. Then a rapid decay is observed, where the slope $1/t_c$ is determined. This definition of t_c has been chosen because it is difficult to determine exactly when the hole opens up. As a consequence, it seems very difficult to measure the hole radius, so that is why the length D(t) is used instead. The final length of the drop is $2R_e$ (at infinite time) where $R_e^3 = R_1^3 + R_2^3$ from mass conservation. This final radius is obtained for infinite times, because of relaxational effects. The limiting value of $D(t)/D_0$ at infinite time is $R_e/(R_1+R_2)$. This limiting value as a function of R_1/R_2 decreases from 1 (R_1=0) to about 0.63 (R_1=R_2), then increases again to 1 (R_2=0). Therefore t_c, which is defined as the time required for a variation of 1 (of $D(t)/D_0$) may appear a bit large because $D(t)/D_0$ does not show variations larger than 0.37. In figure 4, the actual graph of D(t) deduced from figures 2 is shown.
We notice the plateau at short times corresponding to final drainage of fluid 2: the distance D(t) does not change much. A hole is opened at t~10s. The time t_c deduced from the slope is found to be t_c ~ 28s. This result corresponds to a viscosity ratio of η_1/η_2=11.75 (η_1=705 Pa.s, η_2=60 Pa.s). Using the value of the interfacial tension of 3mN/m, and the radii R_1=12.9µm and R_2=10.9µm, a corresponding reduced time $\sigma t_c/\eta_1 R_1$ of about 9 is found (see figure 5).
The capillary number, which is the inverse of the reduced time, according to our definition, is found to be always smaller than one, as expected, because this flow is governed mainly by interfacial effects.

4. RESULTS AND DISCUSSION . -

The results corresponding to different viscosity ratios are depicted in figure 5. Sixteen different experiments were performed. A log-log representation of the reduced time $\sigma t_c/\eta_1 R_1$ vs. the viscosity ratio η_1/η_2 has been used.

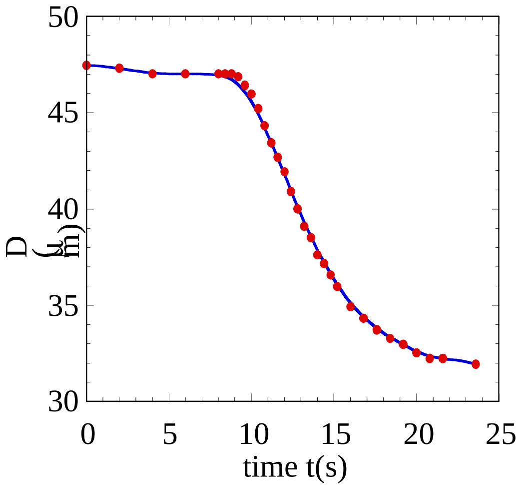


Fig. 4. - D(t) for droplets of PIB (705 Pa.s) in PDMS (60 Pa.s)

Fig. 4. - D(t) pour des gouttelettes de PIB (705Pa.s) dans du PDMS (60 Pa.s)

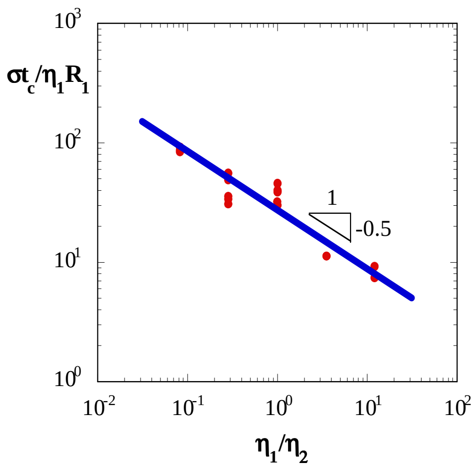


Fig. 5. - Reduced time $\sigma t_c/\eta_1 R_1$ versus η_1/η_2

Fig. 5. - Temps $\sigma t_c/\eta_1 R_1$ adimensionnel en fonction de η_1/η_2

In the experiments, the radius ratio of the drop does not change very much, a typical radius size for the drops is around 10µm. Indeed, droplets have similar sizes, because the focus is easier to make in such a case. Therefore, we may assume that the only varying parameter is η_1/η_2, the ratio R_1/R_2 remaining a constant close to 1. The slight scattering of the data is explained by differences in drop sizes. Nevertheless, the separate experiments (some repeated) were performed and the plot of $\sigma t_c/\eta_1 R_1$ vs. η_1/η_2 appears to show a typical slope of about -0.5, over two decades. This means that t_c varies like $\sqrt{\eta_1 \eta_2}$, in other words the geometric mean of the viscosities of the two fluids. t_c should increase when both viscosities increase, which is the case. Therefore it may be useful, in such a problem, to consider an

equivalent capillary number based on the so-called effective viscosity $\eta_e = \sqrt{\eta_1\eta_2}$. At this point, no clear evidence of the importance of this viscosity can be found or modeled in the literature. The characteristic time t_c varies like $t_c \sim \eta_e R_1/\sigma$. The influence of the other parameters is as expected. The larger the radius R_1, the larger the time t_c required to create the new surface. The larger the interfacial tension σ, the smaller the time (σ is the driving force).
This result is new and interesting because it shows the importance of an effective viscosity η_e responsible for the deformation of the interface, in a complex geometrical system where interfacial tension is the driving force.

5. CONCLUSION. -

It is often difficult to predict how the free surface of a two-phase system deforms when effects like interfacial tension and viscosities are present. This simple analysis of drop collision shows the role of an equivalent viscosity which may not have been guessed beforehand, in the case of a PDMS/PIB system.
In addition, this original set-up may be very useful for the investigation of other effects such as interfacial tension, the influence of compatibilizers at the interface, and may finally be used for understanding coalescence in general, including the drainage, pinching, and collision phases. Finally, it could be generalized to viscoelastic systems.

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