RHEOLOGY AND MORPHOLOGY DEVELOPMENT IN IMMISCIBLE POLYMER BLENDS

Peter Van Puyvelde, Paula Moldenaers

Katholieke Universiteit Leuven, Department of Chemical Engineering
W. de Croylaan 46, B-3001 Leuven (Belgium)

ABSTRACT

In this review, progress towards a fundamental understanding of the rheology-morphology relationship in immiscible polymer blends is discussed. The behaviour of biphasic polymer fluids, containing Newtonian components and subjected to simple shear flows is relatively well understood at present. The behaviour of these "simple" blends will be discussed first, as it serves as a reference for the other sections. In this overview, we will focus on studies that try to incorporate more complex but also more realistic aspects of blend behaviour. Firstly, structure development in compatibilized blends will be reviewed. Secondly, morphology generation in blends with viscoelastic components will be discussed. Thirdly, since blends are typically processed in mixing equipment in which the flow field is a complex combination of shear and elongation, the microstructural evolution in complex flow fields certainly deserves some attention. This includes the behaviour of polymer blends during special diagnostic flow conditions i.e. upon flow reversal and during LAOS. The overview closes with a discussion of blend morphology development in confined geometries.

KEYWORDS: Polymer blends

1. RELEVANCE

Most mixtures of molten polymeric materials are immiscible. This is due to their unfavourable interactions as well as to the small gain in entropy when mixing high molecular weight components. As a consequence, mixing polymers results in multiphasic structures, which can be optimised with respect to the needs of the end-use applications. Blending of immiscible polymers can generate materials with a wide range of mechanical and other properties that would be hard to obtain with their monophasic counterparts. In addition to desirable final properties, improved processing behaviour and cost reduction have also contributed to the success of polymeric blends as new high performance materials.

The final properties of a polymeric blend obviously depend on the properties of the components, the composition of the blend, the interfacial characteristics (e.g.

interfacial adhesion) and the morphology. Most commercial blends have a morphology that consists of droplets dispersed in matrix phase, but fibre-like structures and lamellar structures can also be made [1]. Co-continuous morphologies are another possibility; they can give rise to combinations of properties that would be hard to achieve with dispersed morphologies [2,3]. The morphology that is generated during processing has a significant impact on the blend properties. This is illustrated in figure 1. It shows the barrier properties of high density polyethylene filled with nylon [4]. Nylon has good barrier properties, but when present in the form of dispersed droplets, a substantial amount is needed to improve the barrier properties of the blend significantly. However, when the nylon has a layered or platelet-like structure, small amounts turn out to be very efficient in reducing the permeability.

Another example is toughening of relatively brittle, semi-crystalline polymers such as polyamides and polypropylene with a well dispersed rubbery phase [5]. It has been shown that the brittle/tough transition occurs at a critical interparticle distance. In this case the improved toughness at small interparticle distances was associated with interface-induced crystallization that percolates through the matrix phase.

2. STATE OF THE ART FOR 'SIMPLE' BLENDS

Major progress has been made in understanding the structure development of immiscible polymer blends during processing. Especially in the case of dilute blends, consisting of Newtonian components and subjected to shear flow, the rheological behaviour and morphology development is rather well understood. Scaling relations and sometimes quantitative relations have been developed for the different
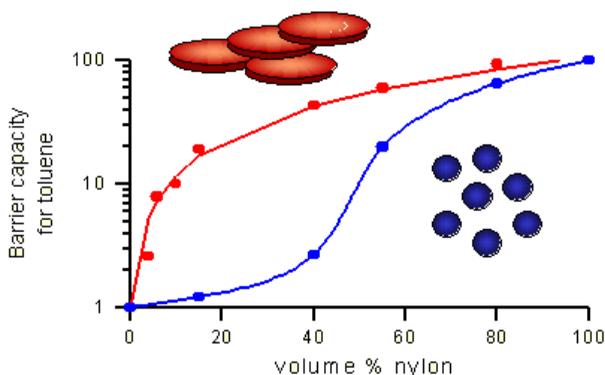

Figure 1: Influence of the morphology of a nylon dispersion on the barrier properties of a nylon/HDPE blend (adapted from [4])

mechanisms of microstructural change, such as droplet deformation and break-up, coalescence and droplet retraction. Most of the theoretical and experimental results that contributed to the understanding of the morphology evolution in these simple blends have been summarized in recent reviews by Ottino et al. [6], Tucker and Moldenaers [7] and Guido and Greco [8]. Hence we will not present an extensive discussion of the subject but rather present the major results that serve as a reference for the more complex blends discussed in the remainder of this review.

2.1 Microstructural changes

The microstructural changes in "simple" blends are governed by two dimensionless numbers: p and Ca. The factor p represents the viscosity ratio of the blend, i.e. the viscosity of the droplet phase (η_d) divided by that of the matrix phase (η_m). Ca represents the capillary number, which is defined as the ratio between the hydrodynamic stresses and the interfacial stresses:

$$Ca = \frac{\eta_m \dot{\gamma} R}{\alpha}$$

in which $\dot{\gamma}$ is the shear rate, R the radius of the droplet and α the interfacial tension.

During flow, the hydrodynamic forces will tend to deform and to orient the inclusions of a liquid/liquid dispersion. To what extent this happens depends on the viscosity ratio and on the relative effect of the restoring interfacial forces as expressed by the capillary number. The equilibrium droplet deformation has been studied, theoretically and experimentally, for small deformations of Newtonian fluids, as described in classical papers as those by Taylor [9] and by Rumscheidt and Mason [10]. The theory has been extended later by several authors, to take into account somewhat larger deformations. Major contributions in this area have been made by Acrivos and co-workers [11,12] and later by Leal [13,14] and co-workers, as reviewed by Rallison [15] and Stone [16]. Guido and Greco [17] reported very good agreement between "small" deformation theories and their experimental results, both with respect to deformation as well as to the orientation of droplets.

Applying flow to a biphasic liquid/liquid system does not only cause deformation and orientation of the inclusions, but it can also lead to droplet break-up. The latter occurs at a critical value Ca_c of the capillary number. Grace [18] provided systematic data of Ca_c as a function of viscosity ratio p in simple shear and extensional flows (see figure 2). Improvements have been made by Bentley and Leal [13-14] and an overview of the phenomenon is discussed in a review by Stone [16]. Jansen et al. [19] showed experimentally that the critical capillary number in simple shear flow decreases with increasing droplet concentration. They could however describe their data with the original critical capillary number, when replacing the matrix viscosity by the dispersion viscosity. Most of the basic work has been performed at conditions slightly above Ca_c. In that case relatively big droplets are split off at the ends of the original droplet, except at low values of p where tip-streaming becomes important.
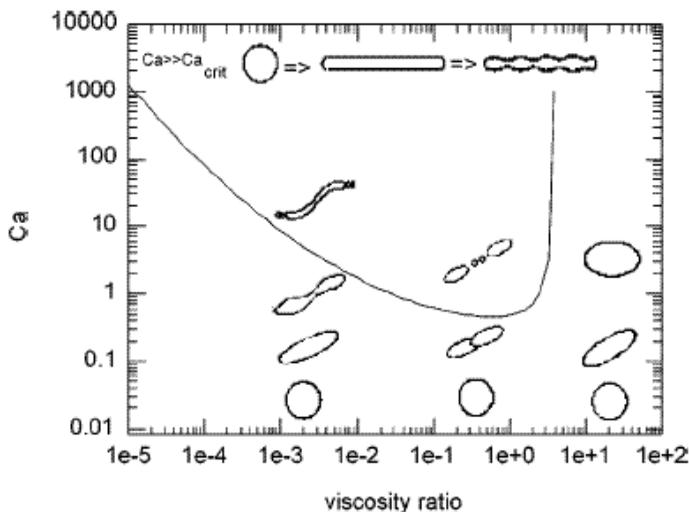
Figure 2: Schematic representation of the different modes of deformation and break-up in shear flow. The full line corresponds to an empirical fit for the critical capillary number through the data of Grace [18] (figure taken from [20]).

Droplet break-up can proceed by different mechanisms (see figure 2). When a relatively fast flow is applied to a liquid/liquid system, the droplet break-up is delayed. Whenever the capillary number at that stage is sufficiently large, the droplets will extend into very long threads, which finally break up in multiple droplets. This is due to an instability involving capillary waves at the surface of the thread (Rayleigh instability). Such a kind of break-up is often observed in polymeric systems [21]. The basic analysis for single filament break-up in quiescent liquid-liquid systems has been derived by Tomotika, using a linear perturbation theory [22]. More detailed numerical analysis are available (e.g. [23,24]) describing complex phenomena such as the formation of satellite droplets. The amplitude growth of the surface waves has also been used to determine the interfacial tension in polymer systems [25]. Knops et al. [26] demonstrated that for multiple threads there is a complex interaction between the break-up of neighbouring threads. In the situations of interest in blend processing, the break-up does however not occur in a stagnant fluid but during flow. The latter tends to stabilize the flow. An analysis of this case for Newtonian liquids in general linear flows is available [27], the predicted trends are confirmed by experiments [23].

When droplets come into contact, they can coalesce, thus coarsening the emulsion. During flow in viscous fluids the frequency of contacts between droplets will be determined by the number of flow-induced collisions. The efficiency with which these collisions result in coalescence depends on how effectively the matrix layer is squeezed out of the contact zone between the droplets ("film drainage"). When this layer is reduced to a critical thickness, instabilities will cause the film to rupture, resulting in coalescence. Approximate theories are available for the case of relatively dilute emulsions of Newtonian liquids and have been reviewed by Chesters [28] and by Ottino et al. [6]. In these theories a distinction is made between three types of film drainage, depending on the mobility of the interface: immobile (large p), fully mobile (low p) and partially mobile (moderate p). More detailed models have been developed, in which multiple trajectories of approaching droplets are simulated [29,30]. Droplet growth dynamics has been studied experimentally by various groups [e.g. 31-34]). There is evidence for a partially mobile interface in the case of polymeric blends [e.g. 35].

Upon cessation of flow, or after applying a step strain, the droplet deformation cannot be maintained. Driven by the interfacial tension, it will relax by one of several mechanisms, depending on the initial deformation of the droplet and on the viscosity ratio. This was mapped out for single droplets by Stone et al. [36] and by Stone and Leal [37]. Slightly deformed droplets will retract back to a spherical shape, very elongated droplets will relax into a string of droplets via capillary wave instabilities, whereas droplets with intermediate aspect ratio's will display end-pinching. Experimental evidence has been gathered on single droplet systems by microscopy (see [8] for a recent review). Rheological and rheo-optical techniques have also proven to be extremely useful in these investigations (see e.g. [38-40]). It was for example shown that retraction of a non-axisymmetric droplet is a two-step-process: the droplet cross section retracts very quickly towards a circle, whereas the retraction of the long axis is a slower process [41-43]. Both the Maffettone-Minale [44] model and the constrained volume model by Almusallam et al. [45] are capable of describing a two-step relaxation process. Finally, it can be mentioned that when the blend components are nearly inelastic, the elasticity of the blend can be used to study the morphology. This will be discussed in the next section.

2.2 Rheology

Considering the various changes in microstructure during flow, it is not surprising that polymer blends display a complex rheology. The basic theoretical framework for understanding blend rheology is provided by emulsion theory. Even when composed of purely viscous fluids, an emulsion will be viscoelastic because of the presence of the interface. This coupling of the blend elasticity with the morphology opens an interesting experimental route since it enables to use rheology as a morphology probe. For instance, Vinckier et al. [40] and Jansseune et al. [46] used G' and N_1 respectively to determine the size of dispersed droplets in a blend. Stress relaxation upon cessation of flow has also proven to be useful in this respect since it allowed to distinguish between the various relaxation mechanisms in blends [47].

Theoretical analyses are available for some simple cases, i.e. the Palierne model for small amplitude oscillatory flow of rather dilute systems of visco-elastic components [48,49]. A theory for steady state flow of systems containing Newtonian components is due to Choi and Schowalter [50]. It has been found appropriate to describe the limiting steady state rheological properties, including normal stresses, up to volume fractions of approximately 10% [51].

The concentration of the dispersed phase is rarely so low in industrial blends that really dilute dispersions are formed. A first attempt to tackle the rheology of concentrated systems has been made by Doi and Ohta [52]. Their model is based on the constitutive equations proposed by Batchelor [53] and by Onuki [54]. The total stresses in the blend are due to a contribution from the component polymers and a contribution caused by the presence of the interface. The contribution of the complex and variable interface is assumed to be proportional to the amount of interface/volume and to a tensorial entity $q_{\alpha\beta}$, which expresses the integrated interface orientation distribution. Transient stresses can be calculated from the time evolution of this entity, which is based, in a simplified fashion, on contributions from the flow field and from the interfacial relaxation. A distinct feature of the Doi-Ohta model is that the length scale arises dynamically from the interaction between flow and relaxation rather than being an intrinsic property of the material. This leads to specific scaling laws for the stress transients. These features have been confirmed experimentally for polymer mixtures [55,56]. The model fails to describe accurately the actual shape of the curves as the relaxational mechanisms have been strongly simplified. Extensions of the Doi-Ohta model such as those by Lee and Park [57] and by Lacroix et al. [58,59] include a somewhat more detailed picture of the structural evolution in the kinetic equations. It can also be noted that, in the absence of flow, the Doi-Ohta model predicts as the long-term equilibrium complete phase separation. Although this is thermodynamically correct, one often wants to halt the relaxation when the spherical shape is regained. This has been incorporated in the model by introducing an equilibrium length scale [60] or by imposing a constant droplet volume [45].

Another approach consists of modelling the droplet shape under flow. Once the droplet shape and its evolution are known, $q_{\alpha\beta}$ can be calculated and entered into the stress equation. For flows with relatively low capillary numbers, the Maffettone-Minale model [44] can be used to predict the steady state as well as the transient stresses. An extended version of this model, derived in the framework of nonequilibrium thermodynamics (GENERIC) was proposed by Grmela et al. [61], and later modified by Yu et al. [62]. For fast flows, the model of Wetzel and Tucker [63], which neglects interfacial tension effects, was found to be appropriate. The latter model was extended by Jackson and Tucker to incorporate interfacial tension effects [64].

In order to build a predictive model for both the rheology and morphology of immiscible polymer blends, one could try to integrate the various microstructural models that describe single structural events. Among these models, the one developed by Peters et al. should be mentioned [65]. The rheological model they propose is based on the Lee and Park model [57] in which several adaptations have been incorporated. These changes were largely inspired by experimental observations of morphology

development such as for instance a structure dependent relaxation time. In the same area, the recent model by Almusallam et al. [66] can be considered as a state-of-the art approach to describe the morphological changes in blends consisting of Newtonian components. The comprehensive constitutive model accounts for deformation, retraction, break-up and coalescence of droplets. The model allows a nearly perfect agreement with experimental droplet deformation data for shear rates below the critical conditions for break-up. However, the model is deficient in its prediction for transient behaviour of single droplets and dilute blends at large capillary numbers, although the qualitative trends are well captured.

Although various microstructural models have been suggested, none of them is able to predict all topological changes during flow without the need of phenomenological or adjustable parameters. An alternative approach is therefore the use of computational methods, in which the morphological changes follow automatically from solving the appropriate flow and composition equations. Compared to existing analytical models, these simulations combine an equally high level of accuracy with greater flexibility with respect to the applied flow fields. A major drawback of these numerical simulations is the computational expense because of the transition regions during break-up and coalescence. These transitional phenomena are characterized by very small size- and time-scales that need to be resolved by the numerical discretization and hence this requires a large number of computational domains. Cristini and Tan [67] have recently presented an excellent overview of the various numerical methods and their limitations. Basically, two major approaches exist to simulate multiphase flows, which differ by the way the presence of a variable interface is treated. A first class are the *interface tracking methods* or the so-called *sharp interface methods* in which the interface is tracked explicitly. Here the computational mesh elements lay on the fluid-fluid interface and information concerning location and curvature of the interface is explicitly available during the whole calculation process. Interface tracking methods, such as boundary integral methods (e.g. [68-72]) and finite element methods (e.g. [73-76]), are very accurate for simulating the morphological changes up to the onset of break-up and coalescence but become problematic to describe the subsequent transitions. This breaking down near break-up and coalescence is a generic problem of these sharp interface models, related to the formation of singularities in flow variables. In order to circumvent this problem, various adaptive meshing techniques have been proposed that greatly increase both the accuracy and computational efficiency of the interface tracking methods (e.g. [69-71]).

A second class of simulation methods is the so-called *interface capturing methods* (see [67]). Examples of such methods are the Lattice-Boltzmann (see [77]), the volume-of-fluid (e.g. [78,79]) and the diffuse interface approaches (e.g. [80-84]). These methods represent the interfacial tension as a body force or bulk stress distributed over a narrow region covering the interface. In addition, the fluid discontinuities, such as density and viscosity, are smoothed over the interfacial width. Consequently, the mesh elements do not lay on the interface but the interface evolves through the mesh that remains fixed during the computation. This approach leads to a powerful tool to incorporate topological changes during flow. A particularly intriguing method is the diffuse interface approach. It is based on free-energy functionals and

uses chemical diffusion in narrow transition layers between the fluid components as the physical mechanism to smooth flow discontinuities and to yield smooth evolutions through break-up and coalescence. Hence, interfaces are not modelled explicitly but result implicitly from the composition field. By using different energy formulations, components with varying degrees of interactions and with varying miscibilities can be described. Yue et al. [81] demonstrated that also viscoelasticity can be taken into account in this method. Keestra et al. [83] used the diffuse interface approach to simulate a step-shear experiment of a binary immiscible blend, using a modified Cahn-Hilliard formulation to incorporate immiscibility of the components. The interface tensor, a direct outcome of the calculation, is used to relate the microstructural evolution to rheology. The simulations results are in qualitative agreement with experimental evidence. However, Keestra et al. [83] and Khatavkar et al. [85] also pinpointed a serious drawback of the method. Essentially, the diffuse interface model is a small-scale model. If one wants to simulate realistic blend systems, a real interfacial thickness cannot be captured numerically anymore since it would lead to too costly computations. Such inconveniences can be solved by again using adaptive remeshing (e.g. [84]). Keestra et al. [83] demonstrated that none of the proposed scaling so far can capture all topological changes that occur during flow and clearly further research is required to elucidate this problem before these methods can become standardized simulations tools in immiscible polymer blends.

Despite the relative success in understanding the case of blends with Newtonian components in a simple shear flow field, real-life polymer blends are far from being understood because of additional complexities that come into play. Commercial blends typically consist of viscoelastic components, in addition these blends are often compatibilized, either reactively or physically. Blends are also processed under conditions in which the flow field is a complex mixture of shear and elongational components. Some progress has been made to bridge the gap between idealized and real industrial systems (see for instance [86] for a recent update). Here the morphology development in *compatibilized blends* will be reviewed first. This is clearly of industrial interest since compatibilizers are one of the main driving forces for future growth of the blend market (for a very recent review see [87]). Next, the discussion will focus on the integration of a variety of complexities that affect the morphology development in polymer blends. Since polymers are viscoelastic materials, effects of *component elasticity* on the structure development is of obvious interest. Moreover, if one wants to understand the structure development in real processing conditions, the behaviour of blends in *complex flow fields* has to be considered. Also some special diagnostic flow conditions such as flow reversals and large amplitude oscillatory shear flow will be dealt with. Finally, this review will discuss the evolution of blend structure in confined geometries.

3. MORPHOLOGY DEVELOPMENT IN COMPATIBILIZED BLENDS

The optimal morphology of a polymer blend often consists of small droplets dispersed in a matrix. It is however difficult to maintain such a morphology during processing, because the thermodynamic driving force causes the droplets to coalesce.

Incorporating block copolymers at the interface can stabilize the morphology substantially. Block copolymers can be kept at interfaces as a result of their dual chemical nature, their action being similar to that of surfactants in the stabilization of emulsions. The specific effect of compatibilizers on the deformation, break-up and coalescence in immiscible blends is a long-standing problem in blends research (see e.g. [88] for an overview). In physical compatibilization a third component (a block or a graft copolymer) is added which can promote the interactions between the dispersed phase and the matrix phase by positioning itself across the interface. Compatibilization may also be achieved in-situ during melt blending, by the addition of a reactive polymer, miscible with one of the blend components and reactive towards functional groups of the second component, to form in-situ block or graft copolymers [89,90]. The latter route has undoubtedly the advantage that the copolymer is generated at the site where it is needed, i.e. at the interface. In this section, the focus will be on the effect of compatibilizers on the various morphological processes rather than on discussing the effectiveness of compatibilization. Hence, no strict distinction will be made between the two compatibilization routes, since the observed phenomena seem to be generic in nature. Finally, a potentially attractive route to compatibilize polymer blends with (nano)-particles will be explored. This approach has already found many applications in emulsion technology (the so-called Pickering emulsions), but the implementation in blends of macromolecular components is new.

3.1 Physical and chemical compatibilization

Adding a compatibilizer to a blend has several advantages: it provides the necessary adhesion between the constituent phases, it allows achieving a finer dispersion and finally it stabilizes the morphology in time. Earlier, it was generally accepted that the refinement of the dispersion was solely a consequence of a decreased interfacial tension [e.g. 91]. This view has however been challenged by Sundararaj and Macosko [92], who where the first to suggest that the main contribution of a compatibilizer to structure generation is a suppression of coalescence rather than a mere reduction of interfacial tension. Sundararaj and Macosko observed a substantial increase of the steady state droplet diameter with increasing volume fraction in uncompatibilized blends whereas the droplet size was shown to become independent of volume fraction in the compatibilized equivalent blend. Since then, it is generally accepted that coalescence suppression is one of the most important aspects of compatibilization [34,93-99]. The precise mechanism however has not yet been fully elucidated.

At least two physical mechanisms have been postulated to explain coalescence suppression by compatibilization. One is based on the presence of so-called Marangoni stresses as is illustrated in figure 3a. When the matrix fluid is swept out of the gap between colliding droplets, the compatibilizer is dragged along. This introduces a gradient in compatibilizer concentration on the droplet surface, leading to an interfacial tension gradient and the associated, opposing Marangoni stress. The latter slows down the film drainage and will drastically reduce the coalescence efficiency. It was shown by Ha et al. [100] that the very weak flows, typically
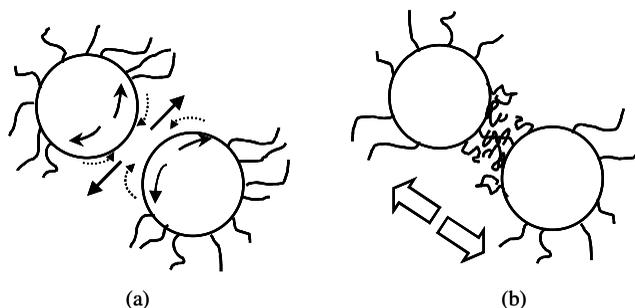
(a)   (b)

Figure 3: Schematic representation of the basic hypotheses to explain coalescence suppression in compatibilized polymer blends. (a) Bulk flow squeezes the compatibilizer out of the gap between approaching droplets resulting in a gradient in interfacial tension, which induces a Marangoni stress that retards drainage of the film between the droplets. (b) Squeezing of the block copolymers leads to a repulsion between the droplets (suppression due to steric hindrance).

associated with film drainage in a coalescence event, can be sufficient to generate significant Marangoni stresses. Gradients in block copolymer concentration during flow were indeed shown to be present in polymeric systems by visualizing a fluorescently labelled PS-PMMA block copolymer at the surface of a PMMA droplet in a PS matrix [101].

A second hypothesis to explain coalescence suppression is based on the squeezing of the compatibilizer block extending into the matrix phase when droplets approach each other (figure 3b). This squeezing can generate an elastic repulsion between the droplets or at least provides a barrier against coalescence (steric hindrance). Although different in nature, the two phenomena do not have to be mutually exclusive. Both phenomena have been shown to be present at the same time in water-in-oil emulsions in which adsorbed proteins reduce the film drainage due to concentration gradients but also stabilize the emulsion by steric hindrance [102]. In the case of polymer blends, the situation is less clear although Fortelny [103] recently argued, based on theoretical considerations, that steric repulsion can manifest itself only if the Marangoni effect is negligible.

Similar to surfactants, the presence of compatibilizer molecules at an interface causes a complex interfacial rheology that cannot be described anymore by a simple interfacial tension. Recently, attempts have been made to link interfacial rheology to the morphology development in polymer blends. Several research teams observed an additional slow relaxation process in small amplitude oscillatory shear experiments on both physically and chemically compatibilized blends, a phenomenon that is attributed to interfacial elasticity [104-109]. The rheological properties of the components,

together with the properties of the interface, give rise to the rheological fingerprint of the blend. This was mathematically treated by Palierne [48,49]. Palierne's model has already proven its usefulness for uncompatibilized blends, where it relates the oscillatory flow behaviour to the underlying morphology of the blends. In its simple form it predicts a relaxation shoulder in the linear dynamic moduli. This characteristic is associated with the shape relaxation of the droplets and is governed by the droplet radius and the interfacial tension as shown by:

$$t_s = \frac{R_v \eta_m}{4\alpha} \cdot \frac{(19p+16)(2p+3-2\varphi(p-1))}{10(p+1)-2\varphi(5p+2)}$$

in which t_s is the shape relaxation time of the droplets, R_v is the volume averaged radius and φ is the volume fraction of dispersed phase.

In its most general form Palierne's model contains additional parameters that are related to interfacial rheological properties such as an interfacial dilation modulus and an interfacial shear modulus (see e.g. Jacobs et al. [106] for a detailed discussion of the model). Independent measurements of these quantities would allow the prediction of the rheological properties of compatibilized blends. Although this approach might be more easily applied to low molecular weight emulsions (see e.g. [110,111]), such measurements are not easy to perform on polymeric systems because measuring the interfacial properties of highly viscous, molten polymers is not trivial. Nevertheless, the full Palierne model still provides an explanation for the additional low frequency relaxation process that has been observed in compatibilized blends.

Riemann et al. [104,105] were the first to fit the full Palierne model to the linear dynamic moduli that displayed this double relaxation process, providing values for both the shape relaxation time t_s and the interfacial relaxation time t_β. A systematic study of the influence of compatibilizer concentration on t_s and t_β was performed by Van Hemelrijck et al. [109]. To fit the linear dynamic spectrum with two distinct relaxation mechanisms, Van Hemelrijck et al. [109] fitted the Palierne model using an interfacial shear modulus, thus associating it with a concentration gradient of block copolymer along the interface. An illustration of the dynamic moduli of compatibilized blends for various compatibilizer loadings is shown in figure 4. The uncompatibilized blend (dotted lines) only shows a single shoulder (t_s) that reflects the shape relaxation of the droplets. The second relaxation mechanism (t_β) becomes apparent in compatibilized blends at relatively low frequencies. The solid lines represent fits with the Palierne model. As can be seen on this figure, the value of t_β strongly depends on the compatibilizer concentration. Van Hemelrijck et al. [109] also studied the time evolution of t_s and t_β upon step-down in shear rate (coalescence experiments). The evolution of t_s, through its relation with the radius of the droplets, reflects the ability of the compatbilizer to suppress coalescence. In addition, Van Hemelrijck et al. investigated the effect of block copolymer architecture (molecular weight and asymmetry of the blocks) on t_s and t_β [112]. It was demonstrated that symmetric block copolymers with a high overall molecular weight show more coalescence suppression for the same concentration. A simple first order scaling relation for the interfacial relaxation time t_β was proposed that correlates experimental
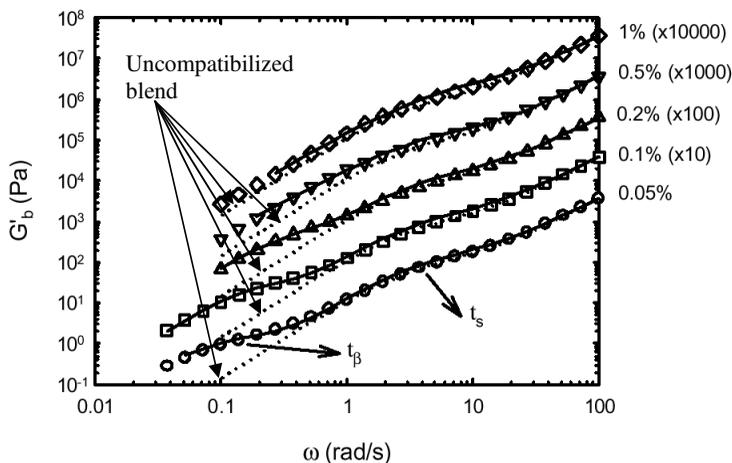
Figure 4: Storage moduli for compatibilized blends (10% PDMS in PI) with compatibilizer concentrations ranging from 0.05 wt% to 1% (concentrations expressed with respect to the amount of dispersed phase, preshear of 4.8 s^{-1}). Curves are vertically shifted for clarity (adapted from 112).

data for various block copolymer architectures, flow conditions and blend systems [112]:

$$t_\beta \quad \left[\frac{c_0}{R_v} \cdot \frac{1}{\eta_m} \cdot \frac{d\alpha}{dc} \cdot \delta^{2/3} \cdot p \right]^{-1}$$

in which c_0 is the equilibrium surface coverage of a droplet with compatibilizer and δ represents the asymmetry of the block copolymer. δ is defined here simply as the ratio of the molecular weight of the short and the long block. The key aspect of this scaling is the sensitivity of the interfacial tension to block copolymer coverage, $d\alpha/dc$, hence supporting the hypothesis of Marangoni stresses. Although this interfacial rheology might be an intriguing issue in compatibilized polymer blends, the efficiency of a compatibilizer will be judged on its ability to suppress. Up to now, no direct correlation between the interfacial relaxation time and coalescence suppression has been found.

In addition to affecting the coalescence, compatibilizers also influence the deformation and break-up of droplets. A compatibilizer might reduce the interfacial tension, thereby lowering the hydrodynamic stress required to break droplets of a certain size. However, some other phenomena might interfere. As explained above,

flow can induce gradients in the compatibilizer concentration along the droplet surface. This is confirmed by numerical simulations [113-117]. Large gradients in the interfacial tension develop when its sensitivity to block copolymer concentration becomes important, thus substantially affecting the local deformation and the break-up of the droplet. This is illustrated in figure 5 for different ranges of capillary number with respect to the critical one and the surfactant concentration. This figure represents break-up modes in extensional flow; break-up in shear flow proceeds by similar modes [e.g. 118,119].

Ramic *et al.* [96] concluded that small amounts of compatibilizer did not affect droplet breakup. This conclusion was derived from measuring steady drop size only and not from dynamic studies of deformation and breakup, hence the results might be affected by interference of coalescence. Hu *et al.* [118] evaluated the physical phenomena in figure 5 for compatibilized PDMS drops in a polybutadiene matrix, deformed by planar extensional flow. The compatibilizer was found to stabilize drops with a viscosity ratio larger than one, i.e. drops at a given *Ca* deformed less when a compatibilizer was added, and Ca_{cr} increased with compatibilization. In systems with a low viscosity ratio, drops on the other hand were destabilized, often breaking by modes (b) and (c) of figure 5, the broken-off tips typically sweeping away a majority of the block copolymer. The latter phenomenon entails a significant complexity when analyzing compatibilized droplet/matrix blends because the various droplets could have different degrees of compatibilizer loadings and hence different interfacial tensions.
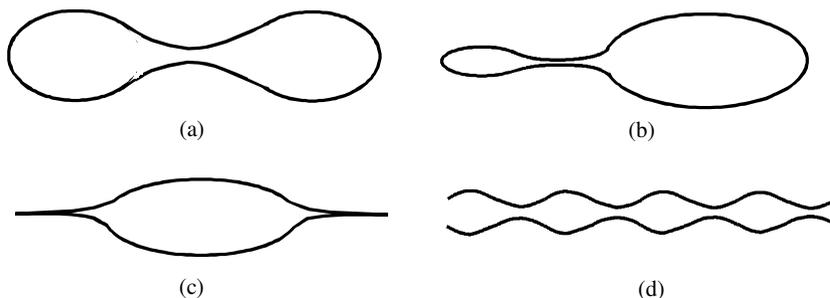

Figure 5: Modes of drop breakup in extensional flow. (a) Simple breakup by waist-thinning occurs when $Ca > Ca_{cr}$; (b) Asymmetric breakup by waist-thinning, probably requires a minimum of surfactant; (c) Tip streaming, requires a minimum of surfactant; (d) Capillary breakup occurs when $Ca \gg Ca_{cr}$.
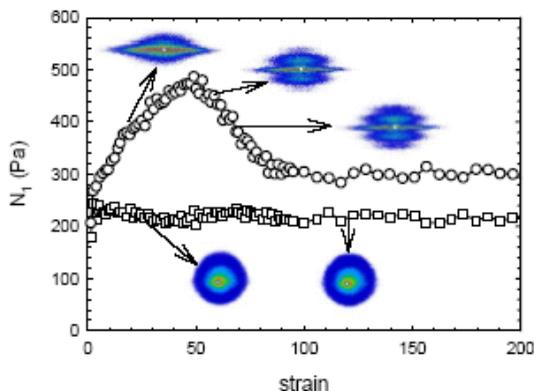
Figure 6: Evolution of the first normal stress difference (10% PDMS in PI) and the SALS patterns (1% PDMS in PI) during a start-up in shear rate. (0: uncompatibilized blend; □: 10% compatibilized blend) [121].

In addition to the aforementioned complexities, it has been observed that the presence of compatibilizer could lead to the formation of long, sheet-like droplets, i.e. the transition from affine to fibres with circular cross-section was delayed by the presence of a compatibilizer [101,120]. In some cases, compatibilized droplets even displayed widening [120], i.e. the dimension along the vorticity direction was larger than the original droplet diameter.

One of the key parameters during melt processing is the viscosity of the blend. Very few systematical studies have been published on the effect of compatibilizers on the rheological behaviour of blends. Iza et al. [122] showed that the addition of a compatibilizer did not affect the steady shear properties but significantly modified the behavior during start-up of shear flow. Start-up flows of uncompatibilized blends with Newtonian components typically show an overshoot in the first normal stress difference, which is accompanied by a minimum in the shear stress [56]. These transients can be explained on the basis of the evolution of the interfacial geometry: droplet deformation, fibril formation and finally fibril break-up. Van Hemelrijck et al. [123] reported that, for blends with small amounts of compatibilizers, the characteristic overshoot of the first normal stress difference (N_1) was similar to that of uncompatibilized blends, but it shifted to shorter times, indicative of a faster breakup process. Highly compatibilized systems did however not show any overshoot in N_1, suggesting the absence of any substantial deformation and break-up of the compatibilized droplets. The droplet behavior actually became rather suspension-like. This is illustrated in figure 6, where the transient normal stresses of an uncompatibilized and a 10% compatibilized blend are shown together with the corresponding SALS images. The latter clearly shows the flow-induced anisotropy for

the uncompatibilized blends. Blends with a substantial amount of compatibilizer on the other hand display isotropic SALS patterns during start-up experiments, indicating that the droplets do not deform or breakup under these conditions.

Steady state viscosity curves on reactively compatibilized blends have been reported by Moan et al. [107]. The viscosity curves showed two plateau regions, respectively at low and at moderate frequencies. It is now clear that this low frequency plateau stems from the interfacial rheology as described by the Palierne model. Recently, Velankar et al. [124] discussed the steady state rheological properties of compatibilized blends, consisting of Newtonian components with a viscosity ratio ranging from 0.1 to 2.65. The steady shear viscosity of the compatibilized blends was found to be higher than for the corresponding uncompatibilized blends for all viscosity ratios. Moreover, compatibilized blends were found to be less shear-thinning than uncompatibilized ones. In addition, the relative interfacial normal stress was higher for the compatibilized blends at low viscosity ratios, but at high values of p hardly any effect of the compatibilizer was observed, although it needs to be stressed that at high p, the deformability of droplets becomes small and hence, no significant effects on N_1 are to be expected. These observations are qualitatively consistent with the presence of Marangoni stresses that stabilize droplets against deformation in shear flow.

Since many years various reports on anomalously low viscosities for immiscible blends have appeared [125, 126]. In some cases the blend viscosity even becomes lower than that of the pure components. Zhao and Macosko [127] showed that systems that are more incompatible i.e. having a larger Flory-Huggins interaction parameter have larger negative viscosity deviations. Interfacial slip has been proposed to account for these anomalies: in the interfacial region polymer chains are less entangled, thus facilitating the occurrence of slip. This hypothesis is supported by viscosity measurements on multilayer structures [127,128]. Addition of a pre-made block copolymer was able to suppress interfacial slip, at least after a sufficiently long time to allow for the compatibilizer to diffuse to the interface. *In situ* formed compatibilizers, however, directly suppressed slip.

Co-continuous blends can however offer better combinations of the component properties than is possible on the basis of dispersed structures [2]. Co-continuous morphologies are often encountered as intermediate stages during the initial morphology development. The composition range over which stable co-continuous structures are found is usually very narrow, low interfacial tensions typically leading to a broader composition range of co-continuous structures ([129]; for an extensive review on the formation of co-continuous structures, see [1]). One of the effects of the presence of a compatibilizer is indeed a reduction of the interfacial tension, thus favoring the formation and stability of co-continuous structures. Other effects, such as coalescence suppression can however hinder the formation of a co-continuous structure. Due to these competing influences no a priori effect can be predicted.

3.2 Compatibilization with nano-sized particles

When stabilizing emulsions, colloidal particles are an alternative to the use of surfactants. In these so-called "Pickering emulsions" the particles are being trapped at the interface. The effectiveness of particles in stabilizing an emulsion depends on their size, relative wettability, their initial location and the level of interparticle interactions [130,131]. The mechanisms by which particles stabilize emulsions are not completely understood at present, but it has been shown that stable emulsions can be obtained with very low surface coverage. Another observation was that particles were able to bridge two droplets by means of a particle monolayer, thus inhibiting coalescence [132]. Vermant et al. [133] recently illustrated the potential of nano-sized silica particles to stabilize model polymer-polymer blends. These authors used the same experimental protocols as those typically employed in the study of flow-induced coalescence of blends that are stabilized by block-copolymers; data analysis was performed with the Palierne model. For blends of 30 % PIB in PDMS, coalescence was observed to be substantially reduced for silica at weight fractions as low as 0.01 of the total blend. This alternative compatibilization route might open new interesting technological perspectives. This was for instance demonstrated by Feng et al. [134], who investigated the effect of clay on the morphology of blends of PP and PA. It was found that the amount of clay drastically influenced the structure of the blend, a feature that was attributed to both the melt rheology and the compatibilizing action of the clay.

4 BLENDS WITH VISCOELASTIC COMPONENTS

As already mentioned in the introduction, industrial polymer blends consist of high molecular weight polymers, which typically show a significant degree of viscoelasticity. At present, the effect of non-Newtonian properties of the components, such as a shear rate dependent viscosity and normal stress differences, on the morphology development in polymer blends is not fully understood. The complex rheological nature of polymers hampers the theoretical analysis and numerical simulations as well as systematic experimental investigations of these effects. Nevertheless, experimental and theoretical results are at present emerging. In this part of the review, focus will be on deformation and breakup rather than on coalescence. This is because coalescence in blends consisting of viscoelastic components is still poorly understood. Indeed, even for Newtonian components, only a few studies have examined this problem in some detail, even at the scale of single droplets which is commonly accepted as the benchmark problem before tackling more concentrated and hence more difficult systems [e.g. 135,136].

From the large number of available experimental studies, the general effect of viscoelasticity on the deformation of droplets can be deduced: droplet elasticity leads to less deformed, more stable droplets as compared to the Newtonian case [e.g. 137-150]. Matrix elasticity on the other hand tends to deform the droplets more. A number of authors investigated the fate of viscoelastic droplets in a Newtonian matrix [e.g. 149, 151-153]. The critical capillary number and the break-up time of the droplets were found to increase with droplet elasticity, whereas droplet deformation decreased.

These observations hold in shear flow as well as in extensional flow. When the droplet phase consisted of a Boger fluid, the droplets could display the common behavior of having their long axis in the gradient-velocity plane and becoming more oriented in the velocity direction when the velocity was increased [154]. Yet, in apparently rather similar systems the droplet has been found to orient in the vorticity direction at higher elasticities, at least for sufficiently large droplets [e.g. 155-157]. The orientation in the vorticity direction is attributed to the high normal forces in the droplets and the presence of closed streamlines that form in the flow-gradient plane, causing the droplets to expand in the vorticity direction.

The opposite case, i.e. Newtonian droplets in a viscoelastic matrix, has been studied as well. This work goes back to the pioneering studies of Flumerfelt [138]. In shear flow, the deformation of the droplets and their degree of orientation in the flow direction, the critical capillary number and the break-up time all increased with increasing elasticity of the matrix fluid [149, 158-160]. However, in extensional flow, recent calculations by Maffettone [161] predict a decrease in the critical capillary number for a Newtonian drop in a viscoelastic matrix, a trend that is in qualitative agreement with experimental results of Tretheway and Leal [147].

Also, systems in which both phases are viscoelastic have been investigated. Levitt et al. [162] observed droplet widening in the neutral direction of a shear flow when isolated polypropylene droplets were sheared in a highly viscoelastic polystyrene matrix. The effect was associated with the large differences in elasticities between the droplet and matrix phase. As mentioned above, highly elastic droplets can align in the vorticity direction rather than in the flow direction [155-157]. The type of deviation with respect to systems with Newtonian components seems to be determined by the relative elasticity of the components, but the absolute elasticities seem to play a role as well. Also the transient behaviour is affected by viscoelasticity. Cherdhirankorn et al. [163] determined the dynamics of deformation of a viscoelastic droplet in a viscoelastic matrix with viscosity ratios close to unity. The droplet deformation displayed complex, oscillating changes of the different major axes. This is illustrated in figure 7, which shows the time evolution of the principle axis c in the vorticity direction with respect to the initial diameter of the droplet D_0 for a PS/HDPE blend. It can be seen that initially, no change of dimension in the vorticity direction is observed. Eventually however, the droplet dimension starts to oscillate after which the droplet finally reaches its steady state deformation. In highly elastic systems, the shape could oscillate several times before reaching its steady state.

Van Oene [137] studied the deformation of droplets in a viscoelastic mixture of molten polymers in a Kenics static mixer. It was demonstrated that the droplet deformation could be qualitatively captured by modifying the interfacial tension with a term depending on the first normal stress differences of the components.

The theoretical work on droplet deformation at small capillary numbers indicated that viscoelasticity did not affect the steady state deformation at that level [e.g. 147,151]. Greco [164] presented a perturbative analysis for small, steady state, deformations in dilute blends subjected to a general linear flow. It was assumed that the components were second order fluids. In addition to the viscosity ratio and the
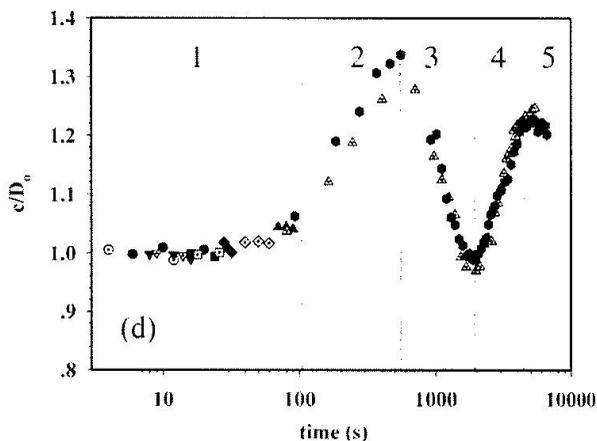
Figure 7: Time dependent deformation of the major axis in the vorticity direction of a blend consisting of highly elastic PS/HDPE after start-up of steady shearing. (figure adapted from [163]).

capillary number, four extra dimensionless parameters then come into play: the ratios of the second to first normal stress coefficients of the matrix and droplet materials and the respective Deborah numbers of the components. The analysis presented by Greco [164] describes the general trends for droplet deformation as seen in the experiments.

Two extensions for larger deformations have been proposed very recently. They are both based on the phenomenological model for droplet deformation of Maffettone and Minale, originally developed for blends with Newtonian components [44]. The extensions made by Maffettone and Greco [167] and by Minale [168] differ in the manner the second order expansion of the droplet shape with the capillary number is carried out. Calculations show that both models predict a larger effect of component elasticity on drop deformation when the matrix is viscoelastic as compared to the case where the droplet is viscoelastic. Both models give similar predictions for the orientation angle between the major axis of the droplet and the flow direction. The extension by Maffettone and Greco [167] predicts a smaller drop deformation when the matrix phase is viscoelastic than when it is Newtonian whereas Minale's extension [168] then predicts a larger droplet deformation. This is shown in figure 8 for different Deborah numbers of the matrix.

The model extension by Maffettone and Greco [167] also has the tendency to predict an overshoot for the droplet deformation during transient shear flow whereas Minale's model [168] predicts, for the same flow conditions, a more monotonous evolution towards steady state deformation. Finally, the model extension by Minale predicts a larger effect on the deformation of the ratio between the second and the first
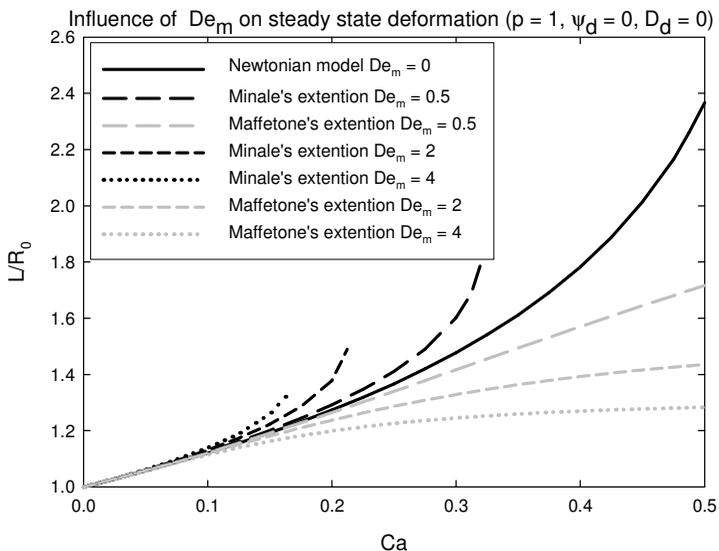
Figure 8: Effect of the matrix Deborah number on the deformation of the major droplet axis L. The black lines represent the extension by Minale, the grey lines the extension by Maffettone and Greco. The solid line is the prediction of the original Maffettone-Minale mode [169].

normal stress coefficient of the droplet phase. This parameter cannot be changed easily in a systematic way, which might hamper a critical evaluation of these models. Maffettone and Greco [167] also showed a strong dependency of the drop shape relaxation on the matrix elasticity. The latter also implies that relaxation data must be used with caution when extracting the interfacial tension for blends consisting of viscoelastic components.

Dressler and Edwards [165,166] followed a non-equilibrium thermodynamic approach, using a droplet shape tensor, to study the rheology of blends with a viscoelastic matrix. They could predict droplet widening at high shear rates. Yu et al. [170] developed a small deformaion theory for blends containing two components with linear viscoelastic properties. In addition, the model of Yu et al. [170] also predicts stress transients. They could retrieve the general effects of droplet and matrix elasticity as described above.

Blends containing a liquid crystalline polymer (LCP) as the dispersed phase constitute a special and interesting case and this for two reasons [171]. Firstly, the liquid crystalline phase can relatively easy form fibrillar inclusions in some processing flows, resulting in so-called 'in-situ composites' or 'self-reinforced' blends [171-174].

Secondly, the liquid crystalline phase can act as a processing aid to reduce the viscosity of the blend below that of the matrix. The unique rheology of the LCP phase is thought to play a crucial role in determining the rheology and morphology of these blends. Van Eijndhoven-Rivera et al. [175] observed that such blends formed stable fibres in a specific concentration range of the LCP. They concluded that the formation of such a highly microfibrillated morphology is coupled with an increase of the molecular orientation in the liquid crystalline polymer. Kernick and Wagner [176] demonstrated that LCP inclusions deform less than expected at low shear rates, and transform into fibres at higher shear rates. The specific trends they observed can be explained by considering the viscoelastic contrast imparted by the unique behaviour of the first normal stress difference of the LCP phase (the Van Oene rule). They could qualitatively predict deviations from Newtonian behaviour and provide a semi-quantitative prediction of the onset of fibre formation.

Lee and Denn [177] demonstrated that the Palierne model could describe the linear viscoelastic response for blends containing thermotropic LCP droplets, if the droplet size is much larger than the size if a liquid crystalline domain, which means that the model can only be used when the director orientation in the nematic can be ignored. Similar observations were made by Riise et al. [178] on a very different blend that consisted of liquid crystalline hydroxypropylcellulose (HPC)-water system in polydimethylsiloxane. Size effects have also been reported by Lee and Denn [179] , when observing the deformation and retraction of LCP droplets in a flexible polymer matrix. They demonstrated that the scaling derived from the Doi-Ohta theory [52] was also valid for blends with a liquid crystalline phase. However, a large negative deviation for the shear stress at the lowest concentrations of dispersed phase can be observed in a specific shear rate range. Although some trends can already be explained qualitatively, these observations point to the need for a theory that explicitly takes into account the liquid crystalline nature of the dispersed phase.

5 MORPHOLOGY DEVELOPMENT IN COMPLEX FLOWS

The thermal and mechanical histories in compounding and mixing equipment are more complicated than those in rheometrical flows. Some authors have attempted to investigate the morphology evolution in processing flows such as twin screw extruders. Typically the microstructure was analysed *post-factum*, after solidification of the product [180-182]. Recently, some in-line measurements of the microstructure have been performed on an extrusion line [183-185]. Although this approach has several useful applications (e.g. empirical optimisation of screw design in extrusion), it is difficult to gain fundamental insight in the phenomena causing the morphology development. Processing flows are typically a combination of shear and extension. Previous reviews [6-8] have mainly focussed on the morphology evolution in shear flow; here the work on the morphology development during uniaxial extensional flow is reviewed. Subsequently, a summary will be given of studies related to structure development in the simplest combinations of shear and elongation, i.e. in divergent or convergent channels.

5.1 Elongational flow

Elongational flow contributions can be significant in polymer processing operations such as blow molding or fibre spinning. Nevertheless, not many studies on the structure development of multiphase systems in elongational flows are available. This is, to a large extent, due to the inherent difficulties associated with elongational experiments. The deformation and break-up of single Newtonian droplets in a Newtonian medium was tackled theoretically and experimentally by Taylor [9] and by Grace [18]. The latter determined the critical capillary number for break-up as a function of viscosity ratio by gradually increasing the strain rate until break-up occurred. He demonstrated that extensional flow is more effective than simple shear flow in breaking-up droplets: for the same viscosity ratio, a smaller value of Ca_{cr} is obtained for elongational flow than for shear flow. In addition, elongational flows are capable of breaking droplets at viscosity ratios larger than 4, which is impossible in shear flow.

An extensive data set on deformation and break-up of single drops, was provided by Bentley and Leal [13]. They conducted experiments in a four-roll mill using Newtonian components, including planar extensional as well as flows intermediate between simple shear and elongation thus generating critical capillary numbers for combined flow conditions. Uniaxial elongational experiments have been performed by Delaby et al. on blends of viscoelastic components [186-189]. These authors determined the droplet deformation, based on the observation of a number of droplets before and after stretching the melt. The shape of the droplets was frozen by fast quenching and subsequently observed by scanning electron microscopy. It was found that droplets deform less than the macroscopic deformation of the sample when they were more viscous than the matrix. They deformed more than the matrix (approximately 5/3 times) whenever the droplets were less viscous than the matrix. Delaby et al. did, however, not consider the possible shape retraction during the quenching phase. Such a phenomenon is clearly visible in the experiments of Gramespacher and Meissner, who performed uniaxial elongation tests on PS-PMMA blends followed by recovery [190]. These authors showed that the process proceeds in two steps: viscoelastic recovery followed by shape recovery of the deformed droplets due to the restoring action of the interfacial tension. These two mechanisms occur on different time scales: the former taking place within the first few seconds of the recovery process whereas the latter can exceed this by orders of magnitude. Similar results were obtained by Mechbal and Bousmina, on a dilute PS-PMMA blend [191], who showed that the model proposed by Yu et al. [170] could describe both the stress and the shape recovery due to the interfacial tension.

Very recently, Oosterlinck [192] performed uniaxial elongation experiments on similar PS/PMMA blends. The stress measurements were supplemented by measurements of the conservative dichroism during elongation, the latter being a measure of the anisotropy. An example of such measurements is shown in figure 9.

For a series of elongational rates well above the critical capillary number, the increase of the dichroism was found to be determined by the strain. Moreover, the data
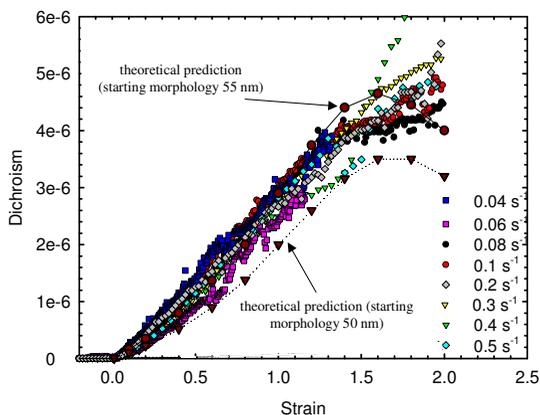
Figure 9: Dichroism versus Hencky strain at different elongational rates (1% PMMA in PS, 170°C). A comparison with theory is given, for two different initial droplet sizes (adapted from [192]).

was found to be consistent with theoretical calculations based on Rayleigh-Gans-Debye scattering, assuming affine deformation.

5.2 Controlled complex flows

In most processing applications, a complex flow field is encountered with both shear and elongational components. Complex flow fields are also important when analysing rheological measurements. This can be demonstrated by the data of Han et al. [193] who found that capillary and cone and plate measurements can differ for immiscible polymer blends due to the morphological changes that take place in the entrance region of the capillary. Only a few papers deal with morphology development during complex flow and most often entry flows are considered. In the entrance zones, typically substantial Hencky strains, i.e. of the order of 5, can be obtained. Such high values lead to the fibrillation of droplets [194-196].

Han and Funatsu [197] studied the deformation of single droplets in a complex flow field using a sudden contraction. They found that the extensional flow field led to drop deformation in the entry section; fibril break-up by Rayleigh instabilities only sets in after entering the contraction. In addition, they also observed that, as in shear flow, viscoelastic droplets were more stable than Newtonian ones, a results that was also obtained by Chin and Han [198] who used a gradually converging channel. A similar geometry was used by Van der Reijden-Stolk and Sara [199]. By using an approximate analysis to describe the flow field kinematics, they showed that the theory

of Cox [200] was able to predict relatively well the observed drop deformation. A limitation of these studies [197-199] is that the droplet size was comparable to the transverse dimension of the flow field. Under such conditions, the presence of a droplet can be expected to alter significantly the flow field and effects of confinement might interfere with the conclusions (see section 6.3). To overcome such problems, somewhat more concentrated blends, containing a large population of micron sized droplets, are used to obtain quantitative information on the morphology development [201-203]. Recently, Oosterlinck [204] investigated the usefulness of the Tomotika [22] theory for describing the break-up of of fibrils due to Rayleigh instabilities during capillary flow of dilute blends. The original theory by Tomotika was developed for break-up of a fibril in a quiescent matrix. It turns out that this theory is capable of qualitatively describing the observations, provided the viscosities at the relevant shear rates are used.

The morphology development, after a sudden contraction and in a gradually converging channel followed by a sudden expansion, has been studied by Testa et al. [203]. The flow-induced morphological evolution could be predicted, at least semi-quantitatively, by assuming that the effects of extensional and shear components are additive. The general criterion derived from these experiments is that droplet break-up takes place when either the local shear or stretching rate, which can be determined by computer simulations, exceeds the critical value for break-up as obtained from steady homogeneous flow data. Similar conclusions were drawn by Priore and Walker [205,206], based on small angle light scattering experiments. The conclusions drawn by Testa et al. [203] and by Priore and Walker [205,206] were however based on the average shear and elongational rates over the thickness of the slit die and were focussed on observations along the centreline of the geometry. This limits to a certain extent the applicability of their conclusions for real complex flows since their flows are certainly dominated by elongation.

Various other experimental set-ups have been used to study the morphology development in immiscible polymer blends [6,207-211]. Noteworthy in this respect are studies in which flow generated between eccentric cylinders is used to disperse one polymer into another. Such flow fields can be considered as 'real' complex flows since they provide a balanced mixture of shear and elongational components. This work was pioneered by Ottino and co-workers who focussed on chaotic flows produced in eccentric journal bearing flows [212-214]; it has recently received renewed interest [e.g. 215]. More specifically, the dynamics of droplet elongation, folding and break-up was studied experimentally in such a geometry. In particular, Tjajhadi and Ottino [213] observed that the critical capillary number for threads is often lower than for droplets. Therefore, if the primary aim is to produce the smallest possible droplet sizes, the transient break-up mechanism is more effective than repeated droplet break-up at the critical capillary number, a conclusion that was also drawn by Janssen and Meijer in a cross-slot configuration [23]. Based on these studies, one comes to the same conclusion as in the case of contraction flows: as long as the system is dilute, a simple calculation of the velocity field and the local stretching rates is sufficient to predict the morphology generation in immiscible fluids.

The results described above are essentially limited to dilute blends with Newtonian components. In the case of more concentrated systems, in which coalescence can no longer be neglected, and in the case of blends with viscoelastic components, more research is needed in order to fully understand the morphology evolution, the ultimate goal being the prediction and optimalization of the morphology evolution in real-life processing equipment such as twin-screw extruders. A first step in that direction was taken by Jun et al. [216] who investigated deformation and break-up of a drop in a screw channel flow, which mimics the flow in the metering section of a single screw extruder (see figure 10).
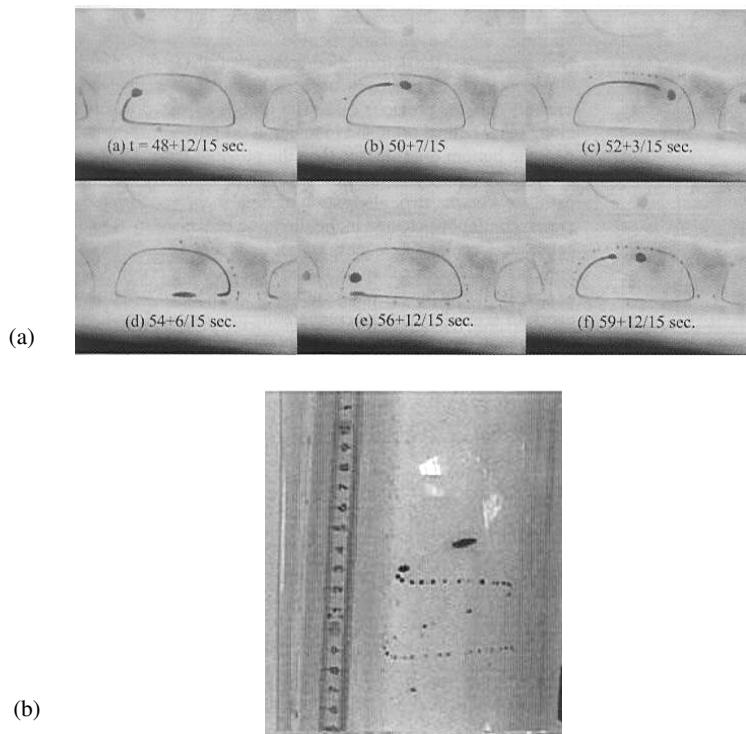
(a)

(b)

Figure 10:   Three-dimensional flow in an unwound screw channel (model for metering flow in single screw extruder). Time evolution of the droplet deformation in a cross sectional view (a) and a snapshot of a top view (b) (adapted from [216]).

6 DIAGNOSTIC FLOW CONDITIONS

In this section we will present some recent results that were obtained during special flow conditions that have been used specifically as tools to study detailed aspects of flow-induced morphological changes. First the blend response to flow reversal will be dealt with. Subsequently large amplitude oscillatory flow experiments on blends will be summarized. In both cases the flow field is still simple shear flow, but the behaviour of the blends can be rather complex. This renders these flow conditions suitable for the evaluation of model descriptions. Finally we will give an overview of the blend morphology development during flow in confinements.

6.1 Flow reversal

The experimental protocol of a flow reversal experiment consists of applying a shear flow, typically until steady state conditions have been reached, after which the flow direction is reverted. Flow reversals experiments have already been applied successfully to investigate textured materials such as for instance liquid crystalline polymers (e.g. [217-218]), but have only been used to a limited extent in structural studies of immiscible blends. Minale et al. [219] reported transient first normal stress differences and shear stresses of dilute polymer blends when reversing the flow direction after a short stepwise increase in shear rate ($Ca > Ca_{cr}$). They identified two different types of stress patterns, depending on whether the flow has been reversed before or after reaching the maximum in normal stress, i.e. when the interface of the stretched droplets starts to be distorted as a first step towards breaking up. In the first case, the normal stress passes consecutively through a well-defined minimum and maximum before reaching the final steady-state value. In case the normal stress has peaked before reversing the flow, no pronounced minimum or maximum could be detected anymore upon reversing the flow direction.

Minale et al. [219] attempted to model the transient stresses by considering two hypotheses concerning the droplet deformation. The first one was based on affine retraction of the droplet towards a sphere followed by affine stretching until break-up. The second hypothesis considered the case of rigid tumbling of the deformed droplets towards the complementary orientation angle, followed by affine stretching. It was demonstrated that the first hypothesis led to better agreement with the experimental data. Important quantitative differences remained however. A pronounced but non-zero minimum is observed in the first normal stress difference during flow reversal (see figure 11). The affine deformation hypothesis results in a minimum with N_1 equal to zero, when the droplets retract to a spherical shape before being deformed in the reverse direction. Dichroism measurements during similar flow histories did not go through zero either (Minale et al. [219] and Van Puyvelde et al. [220]), suggesting that a residual stretching pertains throughout the experiment.

The evolution of single, Newtonian droplets during flow reversal was studied microscopically by Guido et al. [221]. They observed two types of response: at low capillary numbers, the deformed drop evolves towards the new steady state in the reverse direction passing through an apparent spherical shape. At higher capillary
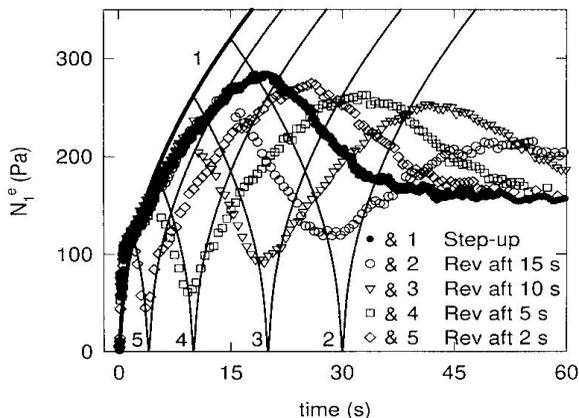
Figure 11: Comparison between the excess first normal stress difference (symbols) and theoretical predictions (full lines) based on the affine deformation hypothesis (adapted from [219]).

numbers, the drop remains elongated during the transient and rotates towards the new steady state. This rotation is however in the opposite direction of that of a rigid body. For low capillary numbers, the behaviour can be described by the Maffetone-Minale model [44].

6.2 Large amplitude oscillatory flow

Oscillatory flows are an elegant class of complex flows to probe microstructured fluids. At small amplitudes, they provide morphological information using the Palierne model (see earlier). Large Amplitude Oscillatory Shear flow (LAOS) has been proposed to highlight non-linear effects [222-225]. Even in the case of ordinary polymer melts, the LAOS response becomes quite complex due to the appearance of higher harmonics in the stress response, that is most often analysed in the Fourier domain [223].

The droplet dynamics under LAOS, using a single Newtonian droplet dispersed in a Newtonian matrix has been investigated by Guido et al. [226]. It was demonstrated that, above a certain threshold value of the applied strain, the droplet undergoes a complex oscillatory motion characterized by several excursions both in orientation and in deformation. For instance, the droplet orientation experiences fast oscillations around the velocity direction. Moreover, it was shown that at these non-linear conditions, the droplet does not oscillate around a spherical but rather around an ellipsoidal shape (see also [227]). When the applied strain amplitude was increased,

the oscillations became more structured and higher harmonics started to appear. The periodic nature of the response however did not change with increasing amplitude. The features reported in the work of Guido et al. are quite similar to those reported for other liquids such as for instance polymeric melts [e.g. 224,225] where they reflect the intrinsic non-linearities of the material. However, Guido et al. [226] suggested an explanation based on the presence on a non-affine deformation of the droplet phase indicating that the non-linearity has a morphological cause.

6.3 Morphology development during flow in confinements

Recently, the ability to create structures on micron and sub micron length-scales has triggered the development of a wide variety of micro devices to transport and manipulate fluids and to pattern surfaces. Engineers are hence faced with the challenge to control features at length-scales that are approaching the molecular ones [228]. Modern developments in this area of microfluidics have found many applications ranging from the life science industries (e.g. pharmaceutical industry for drug design) to industrial applications of combinatorial synthesis (e.g. rapid chemical analysis and high throughput screening of new materials). These micro and nano-scale technologies are an interesting research area in which polymer blends could play an important role. However, the physics of processing polymer blends and emulsions when the droplet size becomes comparable to the sample dimension is yet poorly understood although some remarkable phenomena have been observed.

Migler, for example, discovered a droplet-string transition in polymer blends, which occurs when the size of the dispersed droplets becomes comparable to the gap between the shearing surfaces [229] (see figure 12). This transition proceeded through coalescence of droplets: first there was an increase in the average droplet size, followed by a self-organization into pearl necklace structures. Eventually, the aligned droplets coalesced to form strings. This string state is stabilized by a suppression of Rayleigh instabilities due to the finite size effects. The latter observation was confirmed by Son et al. [230] and Hagedorn et al. [231]. This can be compared with the string formation that occurs in blends where the different phases cause some sort of confinement. Hagedorn et al. [231] and Dreyfus et al. [232] demonstrated that fluid-substrate thermodynamic interactions (the so-called 'wetting') can be expected to have a large influence on the stabilization of both ribbon and confined thread structures.

Pathak et al. [233] studied the influence of composition on the steady state morphology in the transition zone from bulk-like behaviour to string formation. Their results could be presented in a morphology diagram that describes the microstructure in confined PIB/PDMS emulsions in the parameter space of mass fraction, shear rate and gap size. In addition to the formation of strings, they observed that for certain combinations of concentration and shear rate the droplets organize themselves into a stable layered structure. The physics behind the formation of this layered morphology is not completely understood at present. Nevertheless, such layered structures could have a potential in the field of tissue engineering where ultra thin biopolymeric scaffolds could be processed.
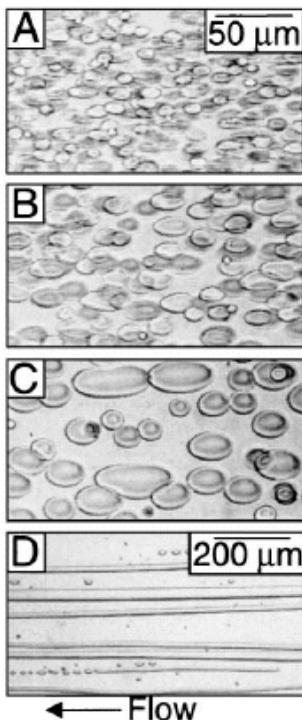
Figure 12: Droplet-string transition in immiscible sheared polymer blends (28 % PIB in PDMS). Images are in the plane containing the flow and vorticity directions. The distance between the plates is 36 micron. The various pictures are taken respectively at shear rates of 6.4 s^{-1} (A), 4.1 s^{-1} (B), 2.62 s^{-1} (C), 2.48 s^{-1} (D) (adapted from [229]).

Pathak and Migler also investigated the effect of confinement on droplet deformation [234]. It was shown that the aspect ratio of a droplet is unaffected by the proximity of a neighbouring droplet as long as the droplets are separated by a distance larger than their characteristic size. Moreover, confinement allowed for larger droplets to exist than predicted by the critical capillary number. Although no complete physical picture exists concerning the various morphological processes in confinements, some interesting applications have already emerged [e.g. 235-239]. For instance, Link et al. [237] demonstrated that microfluidic technology offers capabilities for the precise handling of small fluid volumes dispersed as droplets. Rather simple microfluidic configurations (i.e. a T-junction and flow past obstacles) could be used to design dispersions with controlled droplet sizes and hence with small polydispersities. A

fundamental understanding of the phenomena could lead to a wide variety of applications in small-scale equipment, typically employed in high throughput screening of materials. Such a microfluidic approach would facilitate the use of droplets as micromixers [237] and chemical reactors [239].

CONCLUSIONS

In this review, advances in understanding the morphology-rheology relationship in immiscible polymer blends have been discussed. More specifically, it has been attempted to summarize recent work that tries to incorporate more realistic features to bridge the gap between the idealized model of blends consisting of Newtonian components and real industrial blends. Such commercial polymer blends typically consist of viscoelastic components, are often compatibilized and are processed in rather complex flow fields. Although no complete picture has emerged so far, it is encouraging to observe that a significant effort is put into the quest of mechanistically understanding the individual phenomena, rather than focusing on the combination of all effects. It is our belief that, in the long run, such an approach will lead to a scientifically based design approach for blends optimally structured at the appropriate scale that is necessary to tailor the property profile.

ACKNOWLEDGEMENTS

REFERENCES

1.	Pötschke, P and Paul, D R, *Formation of co-continuous structures in melt-mixed immiscible polymer blends*, J. Macromol. Sci., Polym. Rev., C43 (2003) 87-141.

2.	Utracki, L A, *Commercial polymer blends*, Chapman and Hall, London, UK, (1998).

3.	Utracki, L A, *Polymer Blends Handbook*, Kluwer Academic, Dordrecht, (2003).

4.	Subramanian, P M, *Permeability barriers by controlled morphology of polymer blends*, Polymer Engineering and Science, 25 (1985) 483-487.

5.	Muratojlu, O K, Argon, A S, Cohen, R E and Weinberg, M, *Toughening mechanism of rubber-modified polyamides*, Polymer, 36 (1995) 921-930.

6.	Ottino, J M, De Roussel, P and Hansen, S, *Mixing and dispersion of viscous liquids and powered solids*, Adv. Chem. Eng., 25 (1999) 105-204.

7.   Tucker, C L and Moldenaers, P, *Microstructural evolution in polymer blends*, Ann. Rev. Fluid Mech., 34 (2002) 177-210.

8.   Guido, S., Greco, F., *Dynamics of a liquid drop in a flowing immiscible liquid*, *Rheology Reviews 2004*, The British Society of Rheology, (2004) 99-142

9.   Taylor G I., *The viscosity of a fluid containing small drops of another fluid*, Proc. R. Soc. (London), A 138, (1932) 41-48.

10.   Rumscheidt F D and Mason, S G, *Particle motions in sheared suspensions: XII: deformation and burst of fluid drops in shear and hyperbolic flow*, J. Colloid Sci., 16 (1961) 238-262.

11.   Barthes-Biesel, D and Acrivos, A, *The constitutive equation for a dilute emulsion*, J. Fluid Mech., 44 (1970) 65-78.

12.   Frankel, N A and Acrivos, A, *Deformation and burst of a liquid droplet freely suspended in a linear shear field*, J. Fluid Mech., 61, (1973) 1-21.

13.   Bentley, B J and Leal, L G, *A computer controlled four roll mill for investigations of particle and drop dynamics in two-dimensional linear shear flows*, J. Fluid Mech., 167 (1986) 219-240.

14.   Bentley, B J and Leal, L G, *An experimental investigation of drop deformation and breakup in steady two-dimensional linear flows*, J. Fluid Mech., 167 (1986), 241-283.

15.   Rallison, J M, *The deformation of small viscous drops and bubbles in shear flows*, Annual Rev. Fluid Mech., 16 (1984) 45-66.

16.   Stone H A, *Dynamics of drop deformation and breakup in viscous fluids*, Annual Rev. Fluid Mech., 26 (1994) 65-102.

17.   Guido, S and Greco, F, *Drop shape under slow steady shear flow and during relaxation. Experimental results and comparison with theory*, Rheol. Acta, 40 (2001) 176-184.

18.   Grace H P, *Dispersion phenomena in high viscosity immiscible fluid systems and application of static mixers as dispersion devices in such systems*, Chem. Eng. Commun., 14 (1982) 225-277.

19.   Jansen, K M B, Agterof, W G M and Mellema, J, *Droplet breakup in concentrated emulsions*, J. Rheol., 45 (2001) 227-236.

20.   Van Puyvelde, P, *Flow-induced morphology changes in immiscible polymer blends: a rheo-optical study*, PhD. Thesis, K U Leuven, (1999).

21.   Elemans P H M, Bos, H L, Janssen, J M H and Meijer, H E H, *Transient phenomena in dispersive mixing*,, Chem. Eng. Sci., 48 (1993) 267-276.

22.   Tomotika, S, *On the instability of a cylindrical thread of a viscous liquid surrounded by another viscous fluid*, Proc. R. Soc. (London), A 150 (1935) 322-337.

23. Janssen, J MH and Meijer, H EH, *Droplet breakup of liquid threads in linear flow*, J. Rheol., 37 (1993) 597-608.

24. Tjahjadi M, Stone, H A and Ottino, J M, *Satellite and subsatellite formation in capillary breakup*, J. Fluid Mech., 243 (1992) 297-317.

25. Elemans, P H M, Janssen, J M H and Meijer, H E H, *The measurement of interfacial tension in polymer/polymer systems: the breaking thread method*, J. Rheol. 34 (1990) 1311-1325.

26. Knops, Y M M, Slot, J J M, Elemans, P H M and Bulters, M J H, *Simultaneous breakup of multiple viscous threads surrounded by viscous liquid*, AIChE Journal, 47 (2001) 1740-1745.

27. Khakhar, D V, Ottino, J M, *Breakup of liquid threads in linear flow*, Int. J. Multiphase Flow, 13 (1987) 71-86.

28. Chesters, A K, *The modeling of coalescence processes in fluid-liquid dispersions*, Trans. I. Chem. E., 69A (1991) 259-270.

29. Rother, M A and Davis, R H, *The effect of slight deformation on droplet coalescence in linear flows*, Phys. Fluids, 13 (2001) 1178-1190.

30. Wang, H, Zinchenko, A Z and Davis, R H, *The collision rate of small drops in linear flow fields*, J. Fluid Mech, 265 (1994) 16-188.

31. Vinckier, I, Moldenaers, P, Terracciano, A M and Grizzuti, N, *Droplet size evolution during coalescence in semiconcentrated blends*, AIChE J., 44 (1998) 951-958.

32. Rusu, D and Peuvrel-Disdier, E, *In-situ characterization by small angle light scattering of the shear-induced coalescence mechanism in immiscible polymer blends*, J. Rheol., 43 (1999) 1391-1409.

33. Ramic, A.J., Hudson, S.D., Jamieson, A.M., Manas-Zloczower, I., *Temporary droplet size hysteresis in immiscible polymer blends*, Polymer, 41 (2000) 6263-6270.

34. Lyu, S P, Bates, F S and Macosko, C W, *Coalescence in polymer blends during shearing*, AIChE J., 46 (2000) 229-238.

35. Minale, M, Moldenaers, P and Mewis, J, *Effect of shear history on the morphology of immiscible polymer blends*, Macromolecules, 30 (1997) 5470-5475.

36. Stone, H A, Bentley, B J and Leal, L G, *An experimental study of transient effects in the breakup of viscous drops*, J. Fluid Mech., 173 (1986) 131-158.

37. Stone, H A and Leal, L G, *Relaxation and breakup of an initially extended drop in an otherwise quiescent fluid,* J. Fluid Mech., 198 (1989) 399-427.

38. Vermant, J, Van Puyvelde, P, Moldenaers, P, Mewis, J and Fuller, G G, *Anisotropy and orientation of the microstructure in viscous emulsions during*

flow, Langmuir, 14 (1998) 1612-1617.

39.　Van Puyvelde, P, Yang, H, Mewis, J and Moldenaers, P, *Rheo-optical probing of relaxational phenomena in immiscible polymer blends*, J. Coll. Interf. Sci., 200 (1998) 86-94.

40.　Vinckier, I, Moldenaers, P and Mewis, J, *Relationship between rheology and morphology of model blends in steady shear flow*, J. Rheol., 40 (1996) 613-631.

41.　Yamane, H, Takahashi, M, Hayashi, R, Okamoto, K, Kashihara, H and Masuda, T, *Observation of deformation and recovery of polyisobutylene droplets in a polyisobutylene/polydimethylsiloxane blend after application of step shear strain*, J. Rheol., 42 (1998) 567-580.

42.　Okamoto, K, Takahashi, M, Yamane, H, Kashihara, H, Watanabe, H and Masuda, T, *Shape recovery of a dispersed droplet phase and stress relaxation after application of step shear strains in a polystyrene polycarbonate blend melt*, J. Rheol., 43 (1999) 951.

43.　Guido, S and Villone, M, *Three dimensional shape of a drop under simple shear flow*, J. Rheol., 42 (1998) 395-415.

44.　Maffettone, P L and Minale, M, E*quation of change for ellipsoidal drops in viscous flows*, J. Non-Newtonian Fluid Mech., 78 (1998) 227-241. (+ Erratum: J. Non-Newtonian Fluid Mech., 84 (1999) 105-106.)

45.　Almusallam, A S, Larson, R G and Solomon, M J, *A constitutive model for the prediction of ellipsoidal droplet shapes and stresses in immiscible polymer blends*, J. Rheol., 44 (2000) 1055-1084.

46.　Jansseune, T, Mewis, J, Moldenaers, P, Minale, M and Maffettone, P L, *Rheology and rheological morphology determination in immiscible two-phase model blends*, J. Non-Newtonian Fluid Mech., 93 (2000) 153-165.

47.　Vinckier, I, Mewis, J and Moldenaers, P, *Stress relaxation as a microstructural probe for immiscible polymer blends*, Rheol. Acta, 36 (1997) 513-523.

48.　Palierne, J F, *Linear rheology of viscoelastic emulsions with interfacial tension*, Rheol. Acta, 29 (1990) 204-214.

49.　Palierne, J F, Erratum, Rheol. Acta, 30 (1991) 497-497.

50.　Choi S J and Schowalter, W R, *Rheological properties on nondilute suspensions of deformable particle*s, Phys. Fluids, 18 (1975) 420-427.

51.　Vinckier, I, Minale, M, Mewis, J and Moldenaers, P, *Rheology of semi-dilute emulsions: viscoelastic effects caused by the interfacial tension*, Colloids and Surfaces, 150 (1999) 217-228.

52.　Doi, M and Ohta, T, *Dynamics and rheology of complex interfaces I*, J. Chem. Phys., 95 (1991) 1242-1248.

53.　Batchelor, G K, *The stress system in suspensions of force-free particles*, J.

Fluid Mech., 41 (1970) 545-570.

54.   Onuki, A, *Viscosity enhancement by domains in phase separating fluids near the critical point: proposal of critical rheology*, Phys. Rev. A, 35 (1987) 5149-5155.

55.   Takahashi, Y, Kurashima, N, Noda, I and Doi, M, *Experimental test of the scaling relation for textured materials in mixtures of two immiscible fluids*, J. Rheol., 38 (1994) 699-712.

56.   Vinckier, I, Moldenaers, P and Mewis, J, *Transient rheologcial response and morphology evolution of immiscible polymer blends*, J. Rheol., 41 (1997) 705-718.

57.   Lee, M L, Park, O O, *Rheology and dynamics of immiscible polymer blends*, J. Rheol., 38 (1994) 1405-1425.

58.   Lacroix, C, Grmela, M and Carreau, P J, *Relationships betwee rheology and morphology for immiscible molten systems of polypropylene and ethylene copolymers under shear flow*, J. Rheol, 42 (1998) 41-62.

59.   Lacroix, C, Grmela, M and Carreau, P J, *Morphological evolution of immiscible polymer blends in simple shear and elongational flow*, J. Non-Newtonian Fluid Mech., 86 (1999) 37-59.

60.   Wagner, N J, Ottinger, H C and Edwards, B J, *The Doi-Ohta model for multiphase flow developed and analyzed through the GENERIC formalism*, AIChE J., 45 (1999) 1169-1181.

61.   Grmela, M, Bousmina, M and Palierne, J F, *On the rheology of immiscible blends*, Rheol. Acta, 40 (2001) 560-569.

62.   Yu, W, Bousmina, M, Grmela, M, Palierne, J F and Zhou, C X, *Quantitative relationship between rheology and morphology in emulsions*, J. Rheol., 46 (2002) 1381-1399.

63.   Wetzel, E D and Tucker, C L, *Droplet deformation in dispersions with unequal viscosities and zero interfacial tension,* J. Fluid Mech., 426 (2001) 199-228.

64.   Jackson, N E and Tucker, C L, *A model for large deformation of an ellipsoidal droplet with interfacial tension,* J. Rheol., 47 (2003) 659-682.

65.   Peters, G W M, Hansen, S and Meijer, H E H, *Constitutive modelling of dispersive mixtures*, J. Rheol., 45 (2001) 659-689.

66.   Almusallam, A S, Larson, R G and Solomon, M J, *Comprehensive constitutive model for immiscible blends of Newtonian component*s, J. Rheol., 48 (2004) 319-348.

67.   Cristini, V and Tan, Y, *Theory and numerical simulation of droplet dynamics in complex flows – a review*, Lab Chip, 4 (2004) 257-264.

68.   Zinchenko, A Z, Rother, M A and Davis, R H, *Cusping, capture and breakup of interacting droplets by a curvatureless boundary integral algorithm*, J. Fluid

Mech., 391 (1999) 249.

69.   Cristini, V, Blawzdziewicz, J and Loewenberg, M, *Drop breakup in three-dimensional viscous flows*, Phys. Fluids, 10 (1998) 1781.

70.   Cristini, V, Blawzdziewicz, J and Loewenberg, M, *An adaptive mesh algorithm for evolving surfaces: simulations of drop breakup and coalescence*, J. Comput. Phys., 168 (2001) 445.

71.   Bazhlekov, I B, Anderson, P D and Meijer, H E H, *Nonsingular boundary integral method for deformable drops in viscous flows*, Phys. Fluids, 16 (2004) 1064-1081.

72.   Feigl, K, Kaufmann, S F M, Fischer, P and Windhab, E J, *A numerical procedure for calculating droplet deformation in dispersing flows and experimental verification*, Chem. Eng. Sci., 58 (2003) 2351-2363.

73.   Wilkes, E D, Phillips, S and Basaran, O, *Computational and experimental analysis of dynamics of drop formation*, Phys. Fluids, 11 (1999) 3577.

74.   Hooper, R, Cristini, V, Skakya, S, Lowengrub, J, Macosko, C W and Derby, J J, in *Computational Methods in Multiphase Flow*, Ed. Power, H and Brebbio, C A, Wessex Institute of Technology Press, 29 (2001).

75.   Hooper, R, Toose, M, Macosko, C W and Derby, J J, *A comparison of boundary element and finite element methods for modeling axisymmetric polymeric drop deformation*, Int. J. Num. Mech. In Fluids, 37 (2001) 837-864.

76.   Hooper, R W, de Almeida, V F, Macosko, C W and Derby, J J, *Transient polymeric drop extension and retraction in uniaxial extensional flows*, J. Non-Newtonian Fluid Mech., 98 (2001) 141-168.

77.   Fredrickson, G H, Ganesan, V and Drolet, F, *Field-theoretic computer simulations for polymers and complex fluids*, Macromolecules, 35 (2002) 16-39.

78.   Renardy, Y Y, Renardy, M and Cristini, V, *A new volume-of-fluid formulation for surfactants and simulations of drop deformation under shear at a low viscosity ratio*, Eur. J. Mech. B/fluids, 21 (2002) 49-59.

79.   Li, J, Renardy, Y Y and Renardy, M, *Numerical simulation of breakup of a viscous drop in simple shear flow through a volume-of-fluid method*, Phys. Fluids, 12 (2000) 269-282.

80.   Anderson, D M, McFadden, G B and Wheeler, A A, *Diffuse-interface methods in fluid mechanics*, Annual Rev. Fluid Mech., 30 (1998) 139-165.

81.   Yue, P T, Feng, J J, Liu, C and Shen, J, *A diffuse-interface model for simulating two-phase flows of complex fluids*, J. Fluid Mech., 515 (2004) 293-317.

82.   Roths, T, Friedrich, C, Marth, M and Honerkamp, J, *Dynamics and rheology of the morphology of immiscible polymer blends*, *on modeling and simulation*, Rheol. Acta, 41 (2002) 211-222.

P. V. Van Puyvelde and P. Moldenaers, Rheology Reviews 2005, pp 101 - 145.

83. Keestra, B J, Van Puyvelde, P C J, Anderson, P D and Meijer, H E H, *Diffuse interface modeling of the morphology and rheology of immiscible polymer blends*, Phys. Fluids, 15 (2003) 2567-2575.

84. Barosan, I, Anderson, P D and Meijer, H E H, Computers and Fluids, in press, (2005).

85. Khatavkar, V V, Anderson, P D and Meijer, H E H, *On scaling of diffuse-interface models*, Chem. Eng. Sci., submitted, (2005).

86. *Phase morphology and interfaces in micro- and nanostructured multiphase polymer blend systems*, (Editors: Harrats, C, Thomas, S and Groeninckx, G, Hanser), in press, (2005).

87. Ruzette, A V and Leibler, L, *Block copolymers in tommorow's plastics*, Nature Mat., 4 (2005) 19-31.

88. Van Puyvelde, P, Velankar, S and Moldenaers, P, *Rheology and morphology of compatibilized polymer blends*, Curr. Opinion in Coll. & Interf. Sci., 6 (2001) 457-463.

89. Lorenzo, M L D, *Compatibilization criteria and procedures for binary blends: a review*, J. Polym. Eng., 17 (1997) 429-459.

90. Koning, C, Van Duin, M, Pagnoulle, C and Jerome, R, *Strategies for compatibilization of polymer blends*, Prog. Polym. Sci., 23 (1998) 707-757.

91. Paul, D R and Newmann, S, *Polymer Blends*, Volume 2, Academic Press, New York, (1978).

92. Sundararaj, U and Macosko, C W, *Drop breakup and coalescence in polymer blends – the effects of concentration and compatibilization*, Macromolecules, 28 (1995) 2647-2657.

93. Lepers, J C, Favis, B D and Lacroix, C, *The influence of partial emulsification on coalescence suppression and interfacial tension reduction in PP/PET blends*, J. Polym. Sci. Polym. Phys., 37 (1999) 939-951.

94. Lyu, S P, Jones, T D, Bates, F S and Macosko, C W, *Role of block copolymers on suppression of droplet coalescence*, Macromolecules, 35 (2002) 7845-7855.

95. Van Puyvelde, P, Velankar, S, Moldenaers, P and Mewis, J, *Effect of Marangoni stresses on the deformation and coalescence in compatibilized immiscible polymer blends*, Polym. Eng. Sci., 42 (2002) 1956-1964.

96. Ramic, A J, Stehlin, J C and Hudson, S D, *Influence of block copolymer on droplet breakup and coalescence in model immiscible polymer blends*, Macromolecules, 33 (2000) 371-374.

97. Hudson, S D, Jamieson, A M and Burkhart, B E, *The effect of surfactant on the efficiency of shear-induced drop coalescence*, J. Colloid Int. Sci., 265 (2001) 409-421.

98.   Nandi, A, Mehra, A and Kakhar, D V, *Suppression of coalescence in surfactant stabilized emulsions by shear flow*, Phys. Rev. Lett., 83 (1999) 2461-2464.

99.   Nandi, A, Khakhar, D V and Mehra, A, *Coalescence in surfactant stabilized emulsions subjected to shear flow*, Langmuir, 17 (2001) 2647-2655.

100.   Ha, J W, Yoon, Y and Leal, L G, *The effect of compatibilizer on the coalescence of two drops in flow*, Phys. Fluids, 15 (2003) 849-867.

101.   Jeon, H K and Macosko, C W, *Visualization of block copolymer distribution on a sheared drop*, Polymer, 44 (2003) 5381-5386.

102.   Walstra, P, *Principles of emulsion formation*, Chem. Eng. Sci., 48 (1993) 333-349.

103.   Fortelny, I, *An analysis of the origin of coalescence suppression in compatibilized polymer blends*, Europ. Polym. J., 40 (2004) 2161-2166.

104.   Riemann, R E, Cantow, H J and Friedrich, C, *Rheological investigation of form relaxation and interface relaxation processes in polymer blends*, Polym. Bull., 36 (1996) 637-643.

105.   Riemann, R E, Cantow, H J and Friedrich, C, *Interpretation of a new interface-governed relaxation process in compatibilized polymer blends*, Macromolecules, 30 (1997) 5476-5484.

106.   Jacobs, U, Fahrlander, M, Winterhalter, J and Friedrich, C, *Analysis of Palierne's emulsion in the case of viscoelastic interfacial properties*, J. Rheol., 43 (1999) 1495-1509.

107.   Moan, M, Huitric, J, Mederic, P and Jarrin, J, *Rheological properties and reactive compatibilization of immiscible polymer blends*, J. Rheol., 44 (2000) 1227-1245.

108.   Asthana, H and Jayaraman, K, *Rheology of reactively compatibilized polymer blends with varying extent of interfacial reaction*, Macromolecules, 32 (1999) 3412-3419.

109.   Van Hemelrijck, E, Van Puyvelde, P, Velankar, S, Macosko, C W and Moldenaers, P, *Interfacial elasticity and coalescence suppression in compatibilized polymer blends*, J. Rheol, 48 (2004) 143-158.

110.   Janssen, J J M, Boon, A and Agterof, W G M, *Influence of dynamic interfacial properties on droplet breakup in simple shear flow*, AIChE J., 43 (1997) 1436-1447.

111.   Peters, G W M, Zdravkov, A N and Meijer, H E H, *Transient interfacial tension and dilatational rheology of diffuse polymer-polymer interfaces*, J. Chem. Phys., in press, (2005).

112.   Van Hemelrijck, E, Van Puyvelde, P, Macosko, C W and Moldenaers, P, *The effect of block copolymer architecture on the coalescence and interfacial elasticity in compatibilized polymer blends*, J. Rheol., in press, (2005).

P. V. Van Puyvelde and P. Moldenaers, Rheology Reviews 2005, pp 101 - 145.

113.   Stone, H A and Leal, L G, *The effects of surfactants on drop deformation and breakup*, J. Fluid Mech., 220 (1990) 161-186.

114.   Milliken, W J and Leal, L G, *The effect of surfactant on the transient motion of Newtonian drops*, Phys. Fluids, 5 (1993) 69-76.

115.   Li, X and Pozrikidis, C, *The effect of surfactants on drop deformation and on the rheology of dilute emulsions in Stokes flow*, J. Fluid Mech, 341 (1997) 165-194.

116.   Pawar, Y and Stebe, K, *Marangoni effects on drop deformation in an extensional flow: the role of surfactant physical chemistry, I. Insoluble surfactants*, Phys. Fluids, 8 (1996) 1738-1751.

117.   Eggleton, C D and Stebe, K J, *An adsorption-desorption controlled surfactant on a deforming droplet*, J. Coll. Int. Sci., 208 (1998) 68-80.

118.   Hu, Y T, Pine, D J and Leal, L G, *Drop deformation, breakup and coalescence with compatibilizer*, Phys. Fluids, 12 (2000) 484-489.

119.   Velankar, S, Van Puyvelde, P, Mewis, J and Moldenaers, P, *Effect of compatibilization on the breakup of polymeric drops in shear flow*. J. Rheol., 45 (2001) 1007-1019.

120.   Levitt, L and Macosko, C W, *Shearing of polymer drops with interface modification*, Macromolecules, 33 (1999) 6270-6277.

121.   E. Van Hemelrijck, *Effect of physical compatibilization on the morphology of immiscible polymer blends*, PhD. Thesis, K U Leuven, (2005).

122.   Iza, M, Bousmina, M and Jérôme, R, *Rheology of compatibilized immiscible viscoelastic polymer blends*, Rheol. Acta., 40 (1999) 1999.

123.   Van Hemelrijck, E, Van Puyvelde, P and Moldenaers, P, *Rheology and morphology of compatibilized and uncompatibilized polymer blend*s, Proceedings of the meeting of the European Polymer Processing Society, Guimaraes, Portugal, (2002).

124.   Velankar, S, Van Puyvelde, P, Mewis, J and Moldenaers, P, *Steady-shear rheological properties of model compatibilized blends*, J. Rheol., 48 (2004) 725-744.

125.   Utracki, L A and Kamal, M R, *Melt rheology of polymer blends*, Polym. Eng. Sci., 22 (1982) 96-114.

126.   Utracki, L A, *Melt flow of polymer blends*, Polym. Eng. Sci., 23 (1983) 602-609.

127.   Zhao, R and Macosko, C W, *Slip at polymer-polymer interfaces: rheological measurements on coextruded multilayers*, J. Rheol., 46 (2002) 145-167.

128.   Van Puyvelde, P, Oommen, Z, Koets, P, Groeninckx G and Moldenaers, P, *Effect of reactive compatibilization on the interfacial slip in nylon-6/EPR*

blends, Polym. Eng. Sci., 43 (2003) 71-77.

129. Willemse, R C, *Co-continuous morphologies in polymer blends: stability*, Polymer, 40 (1999) 2175-2178.

130. Brinks, B P, *Particles as surfactants- similarities and differences*, Curr. Opin. Colloid In., 7 (2002) 21-41.

131. Aveyard, R, Brinks, B P and Clint, J H, *Emulsions stabilized solely by colloidal particles*, Adv. Colloid. Interfac. Sci., 100 (2003) 503-546.

132. Stancik, E J, Kouhkan, M and Fuller, G G, *Coalescence of particle-laden fluid interfaces*, Langmuir, 20 (2004) 90-94.

133. Vermant, J, Cioccolo, G, Golapan Nair, K and Moldenaers, P, *Coalescence suppression in model immiscible polymer blends by nano-sized colloidal particles*, Rheol. Acta, 43 (2004) 529-538.

134. Feng, M, Gong, F L, Zhao, C G, Chen, G M, Zhang, S M and Yang, M S, *Effect of clay on the morphology of blends of poly(propylene) and polyamide 6/clay nanocomposites*, Polym. Int., 53 (2004) 1529-1537.

135. Guido, S and Simeone, M, *Binary collisions of drops in simple shear flow by computer-assisted video optical microscopy*, J. Fluid Mech., 357 (1998) 1-20.

136. Yang, H, Park, C C, Hu, Y T and Leal, L G, *Coalescence of two equal-sized drops in a two-dimensional linear flow*, Phys. Fluids, 13 (2001) 1087-1106.

137. Vanoene, H, *Modes of dispersion of viscoelastic fluids in flow*, J. Colloid Int. Sci., 40 (1972) 448-467.

138. Flumerfelt, R W, *Drop breakup in simple shear fields of viscoelastic fluids*, Ind. Eng. Chem. Fundam., 11 (1972) 312-318.

139. Bartram, E, Goldsmith, G L and Mason, S, *Particle motions in non-Newtonian media*, Rheol. Acta, 14, 776-782 (1975).

140. Chin, H B and Han, C D, *Studies on droplet deformation in extensional flows*, J. Rheol., 23 (1979) 557-590.

141. Elmendorp, J., *A study on polymer blending microrheology*, PhD Thesis, Technical University of Delft, The Netherlands, (1986).

142. de Bruijn, R A, *Deformation and breakup of drops in simple shear flow*, PhD Thesis, Technical University Eindhoven, the Netherlands, (1989).

143. Milliken, W and Leal, L G, *Deformation and breakup of viscoelastic drops in planar extension flows*, J. Non-Newtonian Fluid Mech., 40 (1991) 335-379.

144. Varanasi, P P, Ryan, M E and Stroeve, P, *Experimental study on the breakup of model viscoelastic drops in uniform shear flow*, Ind. Eng. Chem. Res., 33 (1994) 1858-1866.

145. Sundararaj, U, Dori, Y and Macosko, C W, *Sheet formation in immiscible polymer blends: model experiments on initial blend morphology*, Polymer, 36

(1995) 1957-1968.

146.   Mason, T G and Bibette, J, *Shear rupturing of droplets in complex fluids*, Langmuir, 13 (1997) 4600-4613.

147.   Tretheway, D C and Leal, L G, *Deformation and relaxation of Newtonian drops in planar extensional flows of a Boger fluid*, J. Non-Newtonian Fluid Mech., 99 (2001) 81-108.

148.   Mighri, F, Ajji, A and Carreau, P J, *Influence of elastic properties on drop deformation in elongational flow*, J. Rheol., 41 (1997) 1183-1201.

149.   Mighri, F, Carreau, P J and Ajji, A, *Influence of elastic properties on drop deformation and breakup in shear flow*, J. Rheol., 42 (1998) 1477-1490.

150.   Mighri F and Huneault, M A, *Drop deformation and breakup mechanisms in viscoelastic model fluid systems and polymer blends*, Can. J. Chem. Eng., 80 (2002) 1028-1035.

151.   Tretheway, D C and Leal, L G, *Surfactant and viscoelastic effects on drop deformation in 2-D extensional flow*, AIChE J., 45 (1999) 929-937.

152.   Lerdwijitjarud, W, Sirivat, A and Larson, R G, *Influence of elasticity on dispersed-phase droplet size in immiscible polymer blends in simple shearing flow*, Polym. Eng. Sci., 42 (2002) 798-809.

153.   Lerdwijitjarud, W, Larson, R G, Sirivat, A and Solomon, M J, *Influence of a weak elasticity of dispersed phase on droplet behaviour in sheared polybutadiene/poly(dimethylsiloxane) blends*, J. Rheol., 47 (2003) 37-58.

154.   Lerdwijitjarud, W, Sirivat, A and Larson, R G, *Influence of dispersed phase elasticity on steady-state deformation and breakup of droplets in simple shearing flow of immiscible polymer blends*, J. Rheol., 48 (2004) 843-862.

155.   Migler, K B, *Droplet vorticity alignment in model polymer blends*, J. Rheol., 44 (2000) 277-290.

156.   Mighri, F and Huneault, M A, *Dispersion visualization of model fluids in a transparent Couette flow cell*, J. Rheol., 45 (2001) 783-797.

157.   Hobbie, E K and Migler, K B, *Vorticity elongation in polymeric emulsions*, Phys. Rev. Lett., 82 (1999) 5393-5396.

158.   Guido, S, Simeone, M and Greco, F, *Deformation of a Newtonian drop in a viscoelastic matrix under steady shear flow: Experimental validation of slow flow theory*, J. Non-Newtonian Fluid Mech., 114 (2003) 65-82.

159.   Guido, S, Simeone, M and Greco, F, *Effects of matrix viscoelasticity on drop deformation in dilute polymer blends under slow shear flow*, Polymer, 44 (2003) 467-471.

160.   Sibillo, V, Simeone, M and Guido, S, *Breakup of a Newtonian drop in a viscoelasic matrix under simple shear flow*, Rheol. Acta, 43 (2004) 449-456.

161.   Maffettone, P L, personal communication, (2005).

162.   Levitt, L, Macosko, C W and Pearson, S D, *Influence of normal stress difference on polymer drop deformation*, Polym. Eng. Sci., 36 (1996) 1647-1655.

163.   Cherdhirankorn, T, Lardwijitjarud, W, Sirivat, A, Larson, R G, *Dynamics of vorticity stretching and breakup of isolated viscoelastic droplets in an immiscible viscoelastic matrix*, Rheol. Acta, 43 (2004) 246-256.

164.   Greco, F, *Drop deformation for non-Newtonian fluids in slow flows*, J. Non-Newtonian Fluid Mech., 107 (2002) 111-131.

165.   Dressler, M and Edwards, B J, *Rheology of polymer blends with matrix-phase viscoelasticity and a narrow droplet size distribution*, J. Non-Newtonian Fluid Mech., 120 (2004) 189-205.

166.   Dressler, M and Edwards, B J, *The influence of matrix viscoelasticity on the rheology of polymer blends*, Rheol. Acta, 43 (2004) 257-282.

167.   Maffettone, P L and Greco, F, *An ellipsoidal drop model for single drop dynamics with non-Newtonian fluids*, J. Rheol., 48 (2004) 83-101.

168.   Minale, M, *Deformation of a non-Newtonian ellipsoidal drop in a non-Newtonian matrix: extension of Maffettone-Minale model*, J. Non-Newtonian Fluid Mech., 123 (2004) 151-160.

169.   Verhulst, K and Moldenaers, P, *Transient and steady deformation of a single droplet in polymer blends with viscoelastic components*, Proceedings 8th European Symposium on Polymer Blends and Eurofillers, Brugge (in press), (2005).

170.   Yu, W, Bousmina, M, Zhou, C X and Tucker, C L, *Theory for drop deformation in viscoelastic systems,* J. Rheol., 48 (2004) 417-438.

171.   Dutta, D, Fruitwalai, H, Kohlii, A and Weiss, R A, *Polymer blends containing liquid crystals : a review*, Polym. Eng. Sci., 30 (1990) 1005-1018.

172.   Weiss, R A, Huh, W and Nicolais, L, *Novel reinforced polymers based on blends of polystyrene and a thermotropic liquid crystalline polymer*, Polym. Eng. Sci., 27 (1987) 684-691.

173.   Handlos, A A and Baird, D G, *Processing and associated properties of in-situ composites based on thermotropic liquid crystalline polymers and thermoplastics*, J. Macromol. Sci. Rev. Macromol. Chem., C35 (1995) 183-238.

174.   DeSouze, J P and Baird, D G, *In-situ composites based on blends of a polyehterimide and thermotropic liquid crystalline polymers subjected to shear free deformations*, Polym. Comp., 17 (1996) 578-595.

175.   Van Eijndhoven-Rivera, M J, Wagner, N J and Hsiao, B, *Correlation of the minor-phase orientation to the flow-induced morphological transitions in*

thermotropic liquid crystalline polymer/PBT blends, J. Polym. Sci., Part B: Polym. Phys., 36 (1998) 1769-1780.

176. Kernick, W A III and Wagner, N J, *The role of liquid-crystalline polymer rheology on the evolving morphology of immiscible blends containing liquid-crystalline polymers*, J. Rheol., 43 (1999) 521-549.

177. Lee, H S and Denn, M M, *Rheology of a viscoelastic emulsion with a liquid crystalline polymer dispersed phase*, J. Rheol., 43 (1999) 1583-1598.

178. Riise, B L, Mikler, N and Denn, M M, *Rheology of a liquid crystalline polymer dispersed in a flexible polymer matrix*, J. Non-Newtonian Fluid Mech., 86 (1999) 3-14.

179. Lee, H S and Denn, M M, *The deformation and retraction of thermotropic LCP droplets in a flexible polymer matrix*, J. Non-Newtonian Fluid Mech., 93 (2000) 315-323.

180. Oommen, Z, Thomas, S, Aravind, I and Groenincxk, G, *Phase morphology development in uncompatibilized and reactively compatibilized nylon-6/ethylene propylene rubber (EPR) blends: effect of mixer type on morphology*, J. Macromol. Sci. Phys. B43 (2004) 1025-1043.

181. Breuer, O, Sundararaj, U and Toogood, R W, *The design and performance of a new miniature mixer for speciality polymer blends and nanocomposites*, Polym. Eng. Sci., 44 (2004) 868-879.

182. Tol, R T, Groeninckx, G, Vinckier, I, Moldenaers, P and Mewis, J, *Phase morphology and stability of co-continuous PPE/PS-PA6 and PS-PA6 blends: effect of rheology and reactive compatibilization*, Polymer, 45 (2004) 2587-2601.

183. Schlatter, G, Serra, C, Bouquey, M, Muller, R, Terrisse, J, *Online light scattering measurements: a method to assess morphology development of polymer blends in a twin-screw extruder*, Polym. Eng. Sci., 42 (2002) 1965-1975.

184. Serra, C, Schlatter, G, Bouquey, M, Muller, R and Terrisse, J, *Online light scattering measurements as a means to assess influence of extrusion parameters on non-reactive polymer blend morphology: experimental procedure and preliminary results*, Can. J. Chem. Eng., 80 (2002) 1036-1043.

185. Covas, J A, Carneiro, O S, Costa, P, Machado, A V and Maia, J M, *Online monitoring techniques for studying evolution of physical, rheological and chemical effects along the extruder*, Plastics Rubber Comp., 33 (2004) 55-61.

186. Delaby, I, Ernst, B, Germain, Y and Muller, R, *Droplet deformation in polymer blends during uniaxial elongational flow: influence of viscosity ratio for large capillary numbers*, J. Rheol., 38 (1994) 1705-1720.

187. Delaby, I, Ernst, B and Muller, R, *Drop deformation during elongational flow in blends of viscoelastic fluids: small deformation theory and comparison with*

experimental results, Rheol. Acta, 34 (1995) 525-533.

188. Delaby, I, Ernst, B, Froelich, D and Muller, R, *Droplet deformation in immiscible polymer blends during transient elongational flow*, Polym. Eng. Sci., 36 (1996) 1627-1635.

189. Delaby, I, Ernst, B and Muller, R, *Drop deformation in polymer blends during elongational flow*, J. Macromol. Sci., B35 (1996) 547-561.

190. Gramespacher, H and Meissner, J, *Melt elongation and recovery of polymer blends : morphology and influence of interfacial tension*, J. Rheol., 41 (1997) 27-44.

191. Mechbal, N and Bousmina, M, *Uniaxial deformation and relaxation of polymer blends: relationship between flow and morphology development*, Rheol. Acta, 43 (2004) 119-126.

192. Oosterlinck, F, Mours, M, Laun, H M and Moldenaers, P, *Morphology development of a PS/PMMA blend during start-up of uniaxial elongational flow*, submitted to J. Rheol., (2005).

193. Han, J H, Chin, C F, Li, D J and Han, C D, *Effect of flow geometry on the rheology of dispersed 2 phase blends of polystyrene and poly(methylmethacrylate)*, Polymer, 36 (1995) 2451-2462.

194. Dreval, V E, Vinogradov, G V, Plotnikova, E P, Zabugina, M P, Krasnikova, N P, Kotova, E V and Pelzbauer, Z, *Deformation of melts of mixtures of incompatible polymers in a uniform shear field and the process of their fibrillation*, Rheol. Acta, 22 (1983) 102-107.

195. Tsebrenko, M V, Yudin, A V, Ablazova, T I and Vinogradov, G V, *Mechanism of fibrillation in flow of molten polymer mixtures*, Polymer, 17 (1976) 831-834.

196. Vinogradov, G V, Krasnikova, N P, Dreval, V E, Kotova, E V, Plotnikova, E P and Pelzbauer, Z, *Effect of rheological properties of compounds on fiber formation in mixtures of incompatible polymers*, Int. J. Polym. Mater., 9 (1982) 187-200.

197. Han, C D and Funatsu, K, *Experimental study of droplet deformation and breakup in pressure driven flows through converging and uniform channels*, J. Rheol., 22 (1978) 113-133.

198. Chin, H B and Han, C D, *Studies on droplet deformation and breakup. 2. breakup of a droplet in nonuniform shear flow*, J. Rheol., 24 (1980) 1-37.

199. Van der Reijden-Stolk, C and Sara, A, *A study on polymer blending microrheology. 3. deformation of newtonian drops submerged in another newtonian fluid flowing through a converging cone*, Polym. Eng. Sci., 26 (1986) 1229-1239.

200. Cox, R G, *The deformation of a drop in a general time-dependent fluid flow*, J. Fluid Mech., 37 (1969) 601-623.

P. V. Van Puyvelde and P. Moldenaers, Rheology Reviews 2005, pp 101 - 145.

201.   Godbille, F D and Picot, J J C, *Drop breakup in combined shear and elongational flow conditions*, Adv. Polym. Techn., 19 (2000) 14-21.

202.   Khayat, R E, Luciani, A, Utracki, L A, Godbille, F D and Picot, J J C, *Influence of shear and elongation on drop deformation in convergent-divergent flows*, Intern. J. Multiphase Flow, 26 (2000) 17-44.

203.   Testa, C, Sigillo, I and Grizzuti, N, *Morphology evolution of immiscible polymer blends in complex flow fields*, Polymer, 42 (2001) 5651-5659.

204.   Oosterlinck, F, Mours, M, Laun, H M and Moldenaers, P, *Morphology development of a PS/PMMA polymer blend during flow in dies*, Rheol. Acta, in press, (2005).

205.   Priore, B E and Walker, L M, *Coalescence analysis through small angle light scattering*, AIChE Journal, 47 (2001) 2644-2652.

206.   Priore, B E and Walker, L M, *Small angle light scattering analysis of morphology development of a model immiscible polymer blend in transient slit-contraction flows*, J. Rheol., 45 (2001) 383-402.

207.   Sau, M and Jana, S C, *Effect of waveforms on morphology development in chaotic mixing of polymers*, AIChE J., 50 (2004) 2346-2358.

208.   Sau, M and Jana, S C, *A study on the effect of chaotic mixer design and operating conditions on morphology development in immiscible polymer systems*, Polym. Eng. Sci., 44, 407-422, 2004.

209.   Kwon, O and Zumbrunnen, D A, *Production of barrier films by chaotic mixing of plastics*, Polym. Eng. Sci., 43 (2003) 1443-1459.

210.   Zumbrunnen, D A, Inamdar, S, Kwon, O and Verma, P, *Chaotic advection as a means to develop nanascale structures in viscous melts*, Nano Letters, 2 (2002) 1143-1148.

211.   Zumbrunnen, D A and Chibber, C, *Morphology development in polymer blends produced by chaotic mixing at various composition*s, Polymer, 43 (2002) 3267-3277.

212.   Ottino, J M, Leong, C W, Rising, H and Swanson, P D, *Morphological structures produced by mixing in chaotic flows*, Nature, 333 (1988) 419-425.

213.   Tjahjadi, M and Ottino, J M, *Stretching and breakup of droplets in chaotic flows*, J. Fluid Mech., 232 (1991) 191-219.

214.   Kusch, H A and Ottino, J M, *Experiments on mixing in continuous chaotic flow*, J. Fluid Mech., 236 (1992) 319-348.

215.   Feigl, K, Kaufmann, S F M , Fischer, P and Windhab, E J, *A numerical procedure for calculating droplet deformation in dispersing flows and experimental verification*, Chem. Eng. Sci., 58 (2003) 2351-2363.

216.   Jun, H S, Hwang, W R and Kwon, T H, *Experiments on characteristic deformation and breakup behaviours of an immiscible drop in a screw channel*

flow, Int. Polym. Proc., 3 (2004) 218-224.

217. Moldenaers, P, Fuller, G G and Mewis, J, *Mechanical and optical rheometry of polymer-liquid-crystal domain structure*, Macromolecules, 22 (1989) 960-965.

218. Hongladarom, K and Burghardt, W R, *Molecular alignment of polymer liquid crystals in shear flows: 2. Transient behaviour in poly(benzyl glutamate) solutions*, Macromolecules, 26 (1993) 785-794.

219. Minale, M, Moldenaers, P and Mewis, J, *Transient flow experiments in a model immiscible polymer blend*, J. Rheol., 43 (1999) 815-827.

220. Van Puyvelde, P and Moldenaers, P, *Orientation of droplets in immiscible polymer blends during a flow reversa*l, Proceedings of the XIIIth International Congress on Rheology, (Editors: Binding, D M, Hudson, N E, Mewis, J, Piau, J-M, Petrie, C J S, Townsend, P, Wagner, M and Walters, K), volume 3, Cambridge, (2000) 134-136.

221. Guido, S, Minale, M and Maffettone, P L, *Drop shape dynamics under shear-flow reversal*, J. Rheol., 44 (2000) 1385-1399.

222. Giacomin, A J and Dealy, J M, *Large amplitude oscillatory shear, In: Collyer A.A., editor, Techniques in rheological measurements*, Chapman and Hall, London, (1993) 99-121.

223. Wilhelm, M, Maring, D and Spiess, H W, *Fourier-transform rheology*, Rheol. Acta, 37 (1998) 399-405.

224. Debbaut, B and Burhin, H, *Large amplitude oscillatory shear and Fourier-transform rheology for a high-density polyethylene: experiments and numerical simulation*, J. Rheol., 46 (2002) 1155-1176.

225. Neidhöfer, T, Wilhelm, M and Debbaut, B, *Fourier transform rheology experiments and finite-element simulations on linear polystyrene solutions*, J. Rheol., 47 (2003) 1351-1371.

226. Guido, S, Grosso, M and Maffettone, P L, *Newtonian drop in a Newtonian matrix subjected to large amplitude oscillatory shear flows*, Rheol. Acta, 43 (2004) 575-583.

227. Yu, W, Bousmina, M, Grmela, M and Zhou, C, *Modeling of oscillatory shear flow of emulsions under small and large deformation fields*, J. Rheol., 46 (2002) 1401-1418.

228. Stone, H A and Kim, S, *Microfluidics: basic issues, applications and challenges*, AIChE Journal, 47 (2001) 1250-1254.

229. Migler, K B, *String formation in sheared polymer blends: coalescence, breakup and finite size effects*, Phys. Rev. Lett., 86 (2001) 1023-1026.

230. Son, Y, Martys, N S, Hagedorn, J G and Migler, K B, *Suppression of capillary instability of a polymeric thread via parallel plate confinement*, Macromolecules, 36 (2003) 5825-5833.

P. V. Van Puyvelde and P. Moldenaers, Rheology Reviews 2005, pp 101 - 145.

231. Hagedorn, J G, Martys, N S and Douglas, J F, *Breakup of a fluid thread in a confined geometry: droplet-plug transition, perturbation, sensitivity and kinetic stabilization with confinement*, Phys. Rev., E, 69, 0563121-05631218, (2004).

232. Dreyfus, R, Tabeling, P and Willaime, H, *Ordered and disordered patterns in two-phase flows in microchannels*, Phys. Rev. Lett., 90, 144505-1-4, (2003).

233. Pathak, J A, Davis, M C, Hudson, S D and Migler, K B, *Layered droplet microstructures in sheared emulsions: finite-size effects*, J. Coll. Interf. Sci., 255 (2002) 391-402.

234. Pathak, J A and Migler, K B, *Droplet-string deformation and stability during microconfined shear flow*, Langmuir, 19 (2003), 8667-8674.

235. Sugiura, S, Nakajima, M, Iwamoto, S and Seki, M*, Interfacial tension driven monodispersed droplet formation from microfabricated channel array*, Langmuir, 17 (2001) 5562-5566.

236. Thorsen, T, Roberts, R W, Arnold, F H and Quake, S R, *Dynamic pattern formation in a vesicle-generating microfluidic device*, Phys. Rev. Lett., 86 (2001) 4163-4166.

237. Link, D R, Anna, S L, Weitz, D A and Stone, H A, *Geometrically mediated breakup of droplets in microfluidic devices*, Phys. Rev. Lett., 92, no. 054503, (2004).

238. Burns, M A, Johsnson, B N, Brahmasandra, S N, Handique, K, Webster, J R, Krishnan, M, Sammarco, T S, Man, P M, Jones, D, Heldsinger, D, Mastranglo, C H and Burke, D T, *An integrated nanoliter DNA analysis device*, Science, 282 (1998) 484-487.

239. Song, H, Tice, J D and Ismagilov, R F, *A microfluidic system for controlling reaction networks in tim*e, Ang. Chem., Int. Ed., 42 (2003) 768-772.