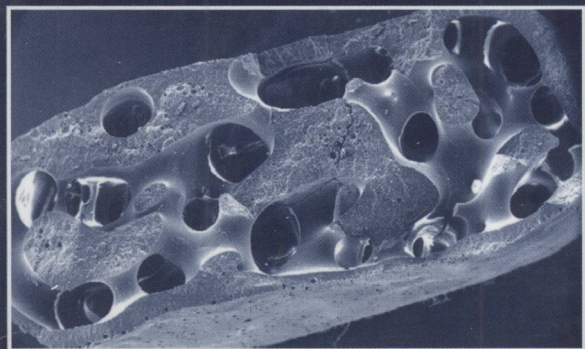
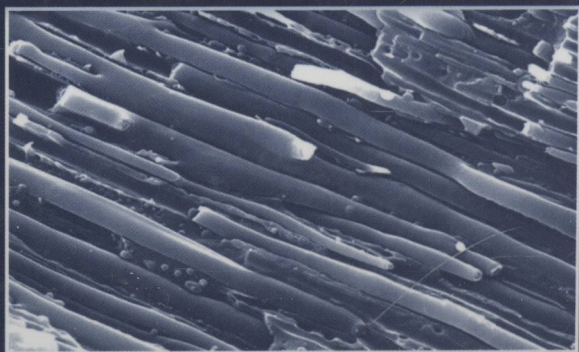
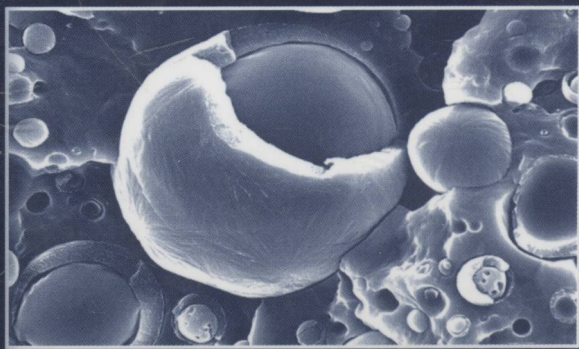
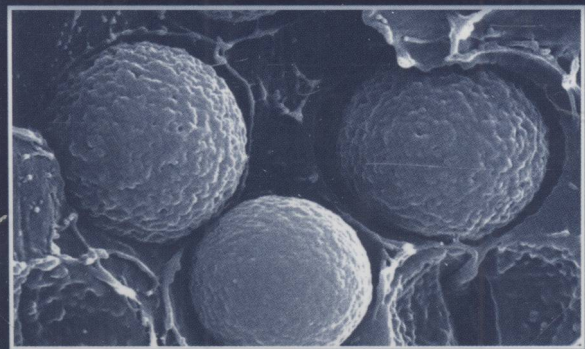


# Multiphase Polymer-Based Materials

An Atlas of Phase Morphology at the  
Nano and Micro Scale



Charef Harrats



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# Multiphase Polymer-Based Materials

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An Atlas of Phase Morphology at the  
Nano and Micro Scale

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## ***Dedication***

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*I dedicate this book to my wife, Ralisa, and my daughters, Meriem, Nejda, Hinde, and Watitou.*

*I also dedicate the work to my two sons, Kais (age 16) and Mohamed-Wassim (age 4).*

*Although it was very funny to see Mohamed-Wassim play  
in my home office, he was also a disturbance.*

*To Professor Gabriel Groeninckx, thank you very much for the scientific, education,  
and social atmospheres you have created for us in your Laboratory for  
Macromolecular Structural Chemistry at the Katholieke Universiteit Leuven  
during our fruitful collaboration in the period from 1997 to 2005.*

*You were not only the scientist we know, but a very sensitive and warm person to your  
collaborators. The door to your office was always open for us.*

*You shared everything you could with your students, postdocs, and associates.*

*You encouraged and financed even first year Ph.D. students to participate in seminars, colloquium,  
and congresses worldwide. Very rare are those who do so. We won't forget that.*

*My present modest words would not be enough to fully express  
my acknowledgments and recognition to you.*

---

## Preface

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Phase morphology in multicomponent polymer-based systems—including thermoplastics/thermoplastics, thermoplastics/thermosets and thermoplastics/rubbers (called thermoplastic vulcanizates), and polymer matrices where inorganic or organic fillers are dispersed via various processing strategies—constitutes the core physical characteristic to carefully control when designing and studying plastic materials. A huge volume of scientific literature and industrial patents is continuously devoted to research where the interrelation of phase morphology with physical and chemical properties of the materials is considered in controlling the performance of polymer-based materials.

In 2006, I coedited with T. S. Thomas and G. Groeninckx a book on the micro- and nanostructured multiphase polymer blends systems titled *Micro- and Nanostructured Multiphase Polymer Blend Systems: Phase Morphology and Interfaces*. The focus of that book was on the research achieved in multiphase polymer blends, with an emphasis on both theoretical and experimental aspects of their formation, their properties, and their processing in relation to the parameters used in their control.

This book, which can be considered as a complementary work to the 2006 book, utilizes a more practical and straightforward approach in dealing with the microscopic observation of phase morphology in multicomponent polymer blends and nanocomposites. It deals exclusively with the study of phase morphology of materials made of one, two, or more polymers, polymers and nonpolymers, copolymers, and combinations thereof. It targets students, technicians, and phase morphology analysts as it explains the various methods by which phase morphology can be directly observed. It also targets more experienced researchers and professionals as it gives a huge variety of good-quality photographs and illustrations provided by authors accumulating a large expertise in the field.

As it is not the objective of this book to include a detailed discussion of the images, a succinct and brief description is given in addition to the legend for each photomicrograph. In some cases, extended information is provided to help the reader clearly understand the content and features of the images. This is the case where many photomicrographs are grouped in one figure and compared. However, a deeper understanding requires the reading of the source of the photograph. For that, each image is associated with the full reference of the article where extended discussions are given.

Chapter 1 provides a brief introduction on the basics and fundamentals in phase morphology of polymer blends. This topic is frequently reported in a very extended way in open literature, usually in the reviews and also in the books and articles dealing with phase morphology in polymer blends. In Chapter 2, the microscopic tools, tips, and some selected scanning electron photomicrographs are provided as illustrations to the practical methods described for the investigation of morphology. The images presented in Chapter 3 contain morphological features of nanocomposites constituting a variety of polymer matrices where silicates clay was dispersed in an exfoliated or intercalated state. Chapter 4 relates photomicrographs of thermoplastics/thermoplastics, thermoplastics/thermosets, and some selected thermoplastic vulcanizates in which the phase morphology is not particularly cocontinuous. Chapter 5 is fully devoted to microscopic photomicrographs of blend systems where the phase morphology is of the cocontinuous type.

I would like to emphasize that the present book could be of encyclopedia size, as more than one million microscopic pictures on phase morphology of polymer blends are available in literature and are excellent candidates to integrate herein. However, difficult decisions were made in the selection of images. On writing this, I would like to apologize to the many scientists and authors who have published excellent work in this area and that either I passed over by ignorance or I could not really include as I had made a selection of work similar or closer in content to their own.

**Charef Harrats**  
Liege, Belgium

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## *Acknowledgments*

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I would like to thank Professor Gabriel Groeninckx, one of my two coeditors of our 2006 book on phase morphology in micro- and nanostructured multiphase polymer blend systems, for his encouragement and advice as I prepared this book.

I also thank Dr. T. S. Omonov, the author of the Ph.D. thesis on phase morphology of polymer blends carried out at MSC Laboratory at Katholieke University Leuven. Professor Groeninckx and I supervised his thesis with pleasure, aware of the author's skillful research. A large number of excellent-quality pictures from this thesis are used in this book.

I should not forget all the scientists who provided me with their excellent-quality microscopy images on phase morphology.

---

## *About the Author*

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**Charef Harrats, Ph.D.**, obtained his engineering degree in plastics in 1986 from the Algerian Institute of Petroleum (IAP) in Boumerdes (Algeria). The plastic and rubber department at IAP was a cofoundation of the Algerian Ministry of Energy and the Michigan Institute of Technology in New Jersey (USA). He worked as a process engineer at the National Company for Rubber and Plastics (ENPC-Algeria) and then moved to the University of Liège in Belgium, where he worked as a research engineer on industrial research projects at the Center for Education and Research on Macromolecules (CERM). He obtained his Ph.D. in 1996 in the field of polymer blends and composites under the supervision of Prof. Ph. Teyssié, Prof. R. Jérôme, and Dr. R. Fayt.

After spending 1 year as a postdoc at the Max-Planck Institute for Polymer Research in Mainz, Germany, Dr. Harrats joined Prof. G. Groeninckx's group at KULeuven. His main research areas are the material development and design of polymers, polymer blends, and composites. Dr. Harrats has conducted numerous research projects in collaboration with companies such as General Electric (USA), Alcatel-Alsthöm (France), DSM Research (Netherlands), and Redco-Eternit (Belgium).

He has joined the group of Prof. P. J. Lemstra at the Technical University of Eindhoven for a 2-year sabbatical under the Marie-Curie Research Project for Experienced Researchers.

Dr. Harrats has also actively participated in Europe–South Mediterranean Collaboration Tempus programs with Algerian universities including Ecole Nationale Supérieure de l'Enseignement Technique (ENSET) and Université des Sciences et Technologie d'Oran (USTO Oran).

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# Basics in Phase Morphologies of Multicomponent Polymer-Based Materials

## 1.1 Phase Morphology Development in Polymer Blends

The blending process generally starts with the components in the form of pellets of 3 mm or powder of 0.2  $\mu\text{m}$  in approximate size. However, the target morphologies for the final product often require domain sizes in the range of 0.1 to 10  $\mu\text{m}$  in order to achieve superior performance characteristics. This means that a size reduction of about three orders of magnitude is imposed on the initially introduced components in the mixing equipment [1]. Phase morphology development in immiscible polymer blends can be considered as the big change in dimension and shape the components undergo during their transformation and compounding operations. The minor phase in an immiscible polymer blend in the melt is deformable, as opposed to composite materials, which contain a rigid minor phase. Depending on the components characteristics and the blending conditions, a wide range of sizes and shapes (spherical, ellipsoidal, cylindrical, ribbon-like, sheet, platelet, cocontinuous, etc.) can thus be obtained for the dispersed phase during processing [2,3]. The final phase morphology in a blend is the result of a balance between deformation-disintegration phenomena and coalescence.

### 1.1.1 Deformation, Breakup, and Coalescence Phenomena during Melt-Blending

#### 1.1.1.1 Basic Principles

Historically, Einstein was the first to derive an expression for the viscosity of hard spheres in a dilute suspension [4]. Later, Oldroyd [5] considered the case where the spheres are themselves liquid. Taylor extended the study to a system where the suspending medium, as well as the dispersed spheres, are Newtonian liquids [6,7]. It was observed that when the radius of the drop is great enough or the rate of distortion is high, the drop breaks up. Taylor derived the following two equations:

$$Ca = \eta_m R \dot{\gamma} / \sigma \quad (1.1)$$

$$E = Ca[(19p + 16)/(16p + 16)] \quad (1.2)$$

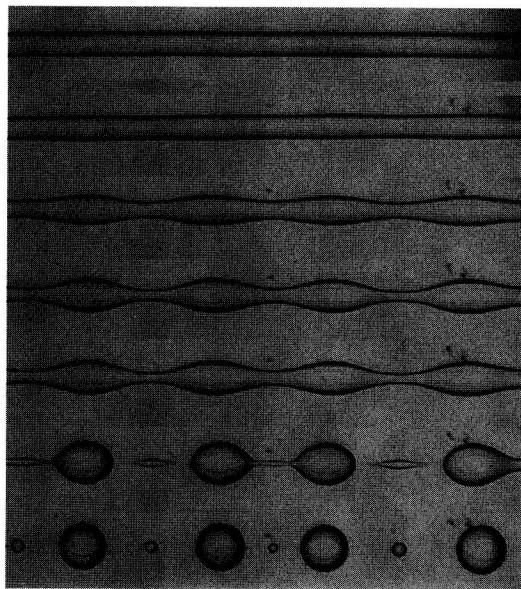
From the above equations it is possible to calculate the size of the largest drop that exists in a fluid undergoing distortion at any shear rate. In these equations, the governing parameters for droplet breakup are the viscosity ratio  $p$  (viscosity of the dispersed phase to that of the matrix); the type of flow (elongational, shear, combined, etc.); the capillary number  $Ca$ , which is the ratio between the deforming stress  $\eta_m \dot{\gamma}$  (matrix viscosity  $\times$  shear rate) imposed by the flow on the droplet; and the interfacial forces  $\sigma/R$ , where  $\sigma$  is the interfacial

tension and  $R$  is the radius of the drop. If  $Ca$  is small, the interfacial forces dominate and a steady drop shape develops. Upon exceeding a critical value  $Ca_{crit}$ , the drop becomes unstable and finally breaks up. A dimensionless parameter,  $E$  (Equation 1.2), was derived which allows one to describe dispersed-particle disintegration for Newtonian systems in shear-flow fields. According to Taylor [6,7], the apparent deformation  $D$  (Equation 1.3) of the droplet has a value of 0.5, where  $L$  is the length of the particle and  $B$  is the breadth:

$$D = (L - B)/(L + B) \quad (1.3)$$

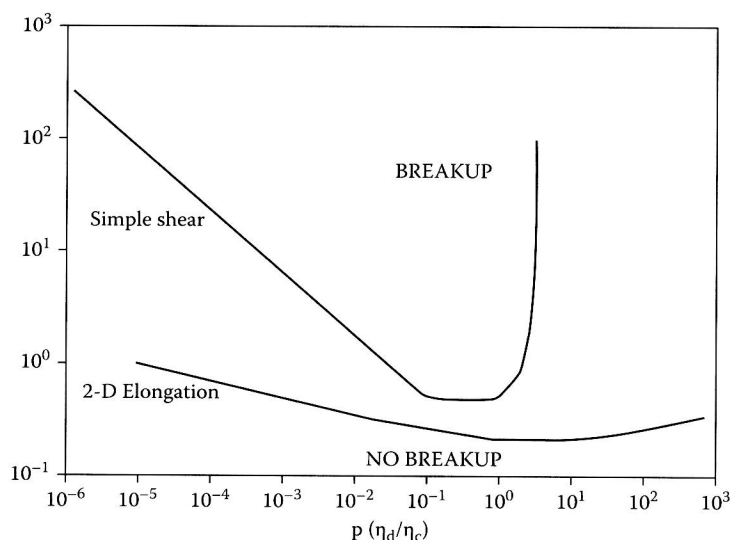
It has been demonstrated experimentally by Taylor [6,7] that for values of  $p$  from 0.1 to 1, droplet breakup occurred at  $D$  values between 0.5 and 0.6. The expression of  $E$  in Equation 1.2 indicates that the viscosity ratio, the shear stress, the droplet diameter, and the interfacial tension are critical variables to consider in controlling particle deformation and breakup in Newtonian fluids. In that equation, however, the coalescence, which has been later found to be critical in a breakup process, has not been considered. Figure 1.1 shows a nice illustration of the process of breakup of a polymer fiber (polyamide) in a polymer matrix (polystyrene).

Grace [6] has constructed a plot of the critical capillary number as a function of the viscosity ratio,  $p$ , under two types of flow: a simple shear flow and a hyperbolic (elongational) flow field (Figure 1.2). It is shown that droplets are stable when their  $Ca$  number is below a critical value; the deformation and breakup are easier at  $P$  within a 0.25 to 1 range for shear flow, and the elongational flow field is more effective for breakup and dispersion than the shear flow. It can also be seen that at a viscosity ratio  $p > 4-5$ , it is not possible to break up the drop in simple shear flow.



**FIGURE 1.1**

Sinusoidal distortions on a polyamide 6 (PA6) thread, with diameter 54  $\mu\text{m}$ , embedded in a polystyrene matrix. The measurement was performed at 230°C; the times for subsequent photographs are 0 sec, 183 sec, 300 sec, 340 sec, 396 sec, 494 sec, and infinite. (From Y. Son, *Polymer* 42, 1287–1291, 2001. With permission.)

**FIGURE 1.2**

Critical capillary number versus viscosity ratio in simple shear and plane hyperbolic (two-dimensional elongational) flow. (From H. P. Grace, *Chem. Eng. Commun.* 14, 225, 1982. With permission.)

### 1.1.2 Effect of Component Characteristics on Phase Morphology

Favis [7] has summarized in a well-structured chapter the effect of the viscosity ratio, blend composition, elasticity, shear stress, and interfacial modification in immiscible blends on the final phase morphology.

#### 1.1.2.1 Viscosity Ratio

In a binary blend, the ratio of the viscosity of the dispersed phase to that of the matrix is one of the most critical variables for controlling the phase morphology. In many situations, if the minor phase has a lower viscosity than the major one, the minor phase will be finely dispersed. In contrast, if the major phase exhibits a lower viscosity than the minor phase, a coarse dispersed phase will be developed.

#### 1.1.2.2 Blend Composition

In a binary blend A/B, the phase morphology can be of an A-droplet-in-B-matrix when A is minor, a B-droplet-in-A-matrix when B is minor, and a third particular situation in between where the two phases A and B are cocontinuous.

As the output phase morphology in a blending operation is a balance between particle breakup and coalescence, increasing the concentration of the A component in an A/B blend will favor coalescence because of the increased particle-to-particle collision probability resulting in an increased particle size. Coalescence has been reported to start at concentration of the dispersed phase as low as 1 wt% [8]. Below a given concentration (depending on the viscoelastic characteristics of the blend constituents) the particle size gradually increases as a function of the concentration. Around that critical concentration

the dimensions of the particles become very sensitive to the concentration. Whereas within a concentration window, a phase inversion region is delimited where phase cocontinuity occurs, no more particle breakup is possible and the two phases are interconnected in a tortuous structure throughout the whole blend volume. The width of this concentration window at which the phases are cocontinuous depends on the viscoelastic characteristics of the blend constituents [9].

#### 1.1.2.2.1 Role of Coalescence

Several authors have developed empirical equations to predict the effect of coalescence on the phase morphology of binary polymer blends. Equation 1.4 relates the particle size of the dispersed phase at equilibrium to its composition in the blend [10]. This equilibrium equation was derived from a more complex expression where a rate constant for breaking the drops and one for their coalescence have been defined to account for the continuous process of phase morphology development resulting from a competition between breakup and coalescence.

$$d_e \approx \frac{24P_r\sigma}{\pi\tau_{12}} \left( \Phi_d + \frac{4P_rE_{DK}}{\pi\tau_{12}} \Phi_d^2 \right) \quad (1.4)$$

$\tau_{12}$  is the shear stress,  $\sigma$  is the interfacial tension,  $\Phi_d$  is the volume fraction of the dispersed phase,  $E_{DK}$  is the bulk breaking energy, and  $P_r$  is the probability that a collision between two close particles will result in coalescence leading to phase coarsening. It is clear from the expression that the particle size at equilibrium diminishes as the shear stress increases, the interfacial tension decreases, and the volume fraction of the dispersed phase decreases. This theory has been verified experimentally for several immiscible blends where a master curve of particle size as a function of composition was found to follow a  $\Phi_d + k \Phi_d^2$  dependence [11]. Fortelny et al. [12] have proposed an expression (Equation 1.5) that accounts for a drop breakup (the first term in Equation 1.5) and a coalescence process (the second term in Equation 1.5):

$$R = (\sigma_{12}(We)_c / (\eta_m \gamma)) \times (\sigma_{12} \alpha \phi / (\eta_m f_1)) \quad (1.5)$$

where  $R$  is the particle radius,  $(We)_c$  is the critical Weber (or capillary) number,  $\eta_m$  is the viscosity of the matrix,  $\sigma_{12}$  is the interfacial tension,  $\gamma$  is the shear rate,  $\alpha$  is the probability of coalescence after collision,  $\phi$  is the volume fraction of the dispersed phase, and  $f_1$  is the slope of the function  $F(We)$ , which describes the frequency of phase breakup at the critical Weber number.

Elmendorp and Van der Vergt also developed an expression to describe shear-induced coalescence of spherical particles [8]. A critical coalescence time has been defined which accounts for the time that passes between the arrival of a droplet at a liquid–liquid interface and the rupture of the intervening film. The critical coalescence time  $t_c$  has been defined as:

$$t_c = (3\eta_m R / 2\sigma) \ln(R / 2h_c) \quad (1.6)$$

The above discussion clearly reveals that particle size versus composition dependence, which is affected by coalescence, is controlled to a large extent by the interfacial tension between the two phases of a binary blend. Several reports showed that the coalescence can be suppressed

or at least its role minimized over a wide composition range. For example, it has been demonstrated that in a polyvinyl chloride/polyethylene (PVC/PE) blend of a low interfacial tension of 3.4 mN/m, the particle size reduction (suppressed coalescence) is much more significant than in a polyamide (PA)/PE blend having an interfacial tension as high as 14 to 18 mN/m [13–15].

The interfacial tension in immiscible polymer blends is reduced by the addition of suitable interfacial agents such as block or graft copolymers, preformed or generated *in situ* during the blending or the processing operation. The action of adding these agents to immiscible blends in an attempt to decrease their interfacial tension and reduce the coalescence phenomena during phase morphology development is called compatibilization. Literature reporting on the compatibilization of polymer blends is too extensive to be exclusively listed in this section. Addition of hydrogenated polybutadiene-*b*-polystyrene block copolymers as compatibilizing agents to polyethylene/polystyrene immiscible blends has been extensively investigated by Fayt et al. [16–20]. Diblock copolymers were found to be more efficient than graft, triblock, or star-shaped copolymers. In these studies the most efficient interfacial agents were reported to be diblock copolymers of a well-balanced composition. As far as the copolymer concentration is considered, stable dispersions were produced by adding as low as 1 to 2 wt% of an efficient copolymer.

### 1.1.2.3 Effect of Elasticity

In addition to interfacial tension, composition, and viscosity, the elasticity of the components, although not thoroughly studied, has also been considered in the understanding of the phase morphology buildup. The role of this parameter is the least understood among all parameters considered. Van Oene [21] was the first who pointed out that in capillary flow the dispersion of particles undergoes stratification and droplet–fiber formation. In addition to the role of the particle size and the interfacial tension, these two morphologies were also controlled by the differences in viscoelastic properties between the two phases. For example, in a polystyrene/polymethyl methacrylate (PS/PMMA) blend, the PMMA phase, having the largest normal stress function (more elastic than PS), exhibits a droplet morphology type in the PS matrix. After the addition of a low-molecular-weight PMMA to the blend, a stratified PMMA phase was obtained. It was also noted that when the droplet size was smaller than 1  $\mu\text{m}$ , the difference in morphologies (stratified versus droplet type) disappeared. It was concluded that the elastic contribution to the interfacial tension was no longer dominant. The statement of Van Oene is that the phase of higher elasticity has the tendency to encapsulate the one with lower elasticity. He showed that it is difficult to deform a highly elastic material. He could then develop an expression where the contribution of material elasticity to the interfacial tension is considered:

$$\sigma_{\text{eff}} = \sigma + \frac{d}{12} [(N_2)_d - (N_2)_m] \quad (1.7)$$

where  $\sigma_{\text{eff}}$  is the effective interfacial tension under dynamic conditions,  $\sigma$  is the static interfacial tension,  $d$  is the droplet diameter, and  $N_{2d}$  and  $N_{2m}$  are the second normal stress functions for the dispersed phase and for the matrix, respectively. Furthermore, it has been also shown that in an extensional flow field when a Newtonian droplet is deformed by a viscoelastic matrix, no lower limiting droplet size exists beyond which disruption of particles becomes impossible [22,23]. Elmendorp and Maalcke [24] demonstrated experimentally that the normal stress exhibited by a droplet in a viscoelastic fluid stabilizes it, as predicted by

Van Oene, Levitt et al. [25] have observed that polypropylene droplets were elongated perpendicular to the flow direction in a polystyrene matrix that was highly elastic. The extent of particle stretching in the perpendicular direction of flow was found to be proportional to the normal stress differences between the phases. Particle contraction was observed upon cessation of the shearing action, which confirms the role of the elasticity on deformation.

The shear stress,  $\tau_{12} = \eta_m \dot{\gamma}$  ( $\tau_{12} = \eta_m \dot{\gamma}$ ), which is a machine parameter, has a direct effect on particle deformation. The particle size is inversely proportional to the applied shear stress. Increasing the shear stress results in a particle size reduction. This interrelation has been verified unambiguously in a polystyrene/polyethylene immiscible blend [26]. It has been shown that increasing the shear stress resulted in a much finer particle size and also that the viscosity ratio was less predominant compared to the shear stress. The morphology was not influenced by variations in the molecular weight of polyethylene or by an increase in the mixing temperature. Other authors reported that a variation of the shear stress by a factor of 2 or 3 does not influence significantly the particle size [27–29]. Apparently, the variation of shear stress should be much higher in order to be effective in affecting predominantly the size of the particles.

The shear stress was reported to have an effect on the shape of the dispersed phase. In a polyamide/polyethylene blend extruded through a slit die, an increase of shear stress from 17 kPa to 29 kPa resulted in a change of the nylon phase from a spherical to a fiber-like particle shape [30].

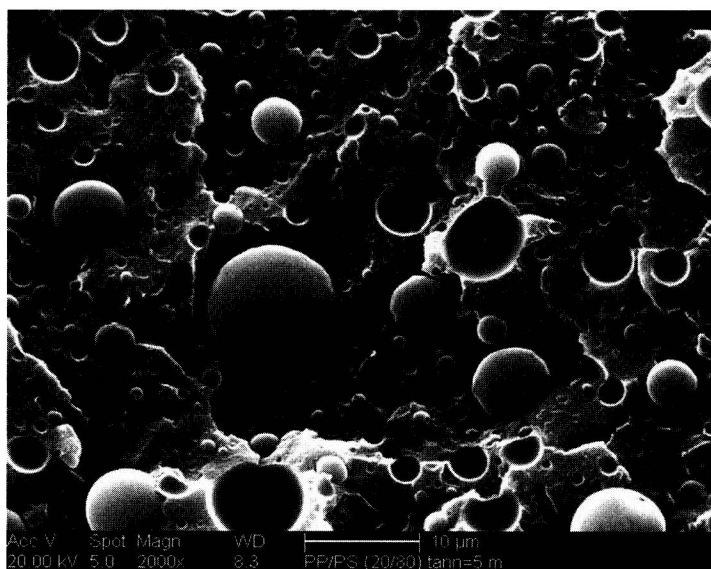
#### 1.1.2.4 Role of the Mixing Equipment and Compounding Conditions

The mixing conditions play a crucial role in the development of phase morphology. These include the mixing equipment and the mixing parameters such as the mixing temperature, the mixing time, and the rotation speed of the mixing elements. Three major types of equipment are employed in the processing of polymer blends: internal mixers and extruders (single- and twin-screw extruders) and injection molding, which is used to shape an already compounded blend. These devices are equipped with screws or rotor blades revolving in a closed chamber or a barrel, respectively. The design and condition of the screws or the rotor blades determines the type of flow fields to which the polymer melts are subjected.

Internal mixers are mainly used for rubber-based blends, but they are also useful on a laboratory scale for blending a wide range of thermoplastics. They are practical for blending small amounts of material and allow a monitoring of torque (a viscosity-dependent parameter). Favis has reported on the influence of the mixing time on the size of the dispersed phase in a Brabender mixer [28]. By using polycarbonate/polypropylene immiscible blends, the most significant particle size reduction or phase morphology generation took place within the first 2 min of the mixing operation. Between 2 and 20 min of mixing time, very little particle size reduction of the dispersed phase was noticed. An increase in rotor speed had only a minor effect on further size reduction. Similar observations were also made by Schreiber and Olguin in polyolefin/elastomer blends prepared using internal mixer [31].

Single-screw extruders, although limited in developing high shear rates and good distributive mixing, remain, nevertheless, a widespread tool for blending polymers. Lindt and Ghosh have studied phase morphology evolution in a single-screw extruder. It was revealed that the blend undergoes a continuous change in its developing morphology during the passage through the melting zone. Within a fraction of a second, the length scale of the dispersed phase drops by several orders of magnitude [32].

The most appropriate mixing tool and the most widespread in processing polymer blends is the twin-screw extruder. Corotating and counterrotating twin-screw extruders

**FIGURE 1.3**

Typical droplet-in-matrix (or dispersed type) phase morphology in melt-blended binary blend. Scanning electron microscopy (SEM) photomicrograph of a cryofractured surface of 80 wt% polystyrene/20 wt% polypropylene melt-mixed blend. (From G. Lei, *Development of Three Phase Morphologies in Reactively Compatibilized Polyamide 6/Polypropylene/Polystyrene Ternary Blends*, master's thesis, Katholieke Universiteit Leuven, Belgium, 2004.)

are high-intensity mixing devices consisting of two screws with a kneading section for intensive mixing. An entire screw can be built using a set of kneading elements to meet specific mixing requirements. Many studies were devoted to the comparison of the mixing efficiency between a static mixer and a twin-screw extruder [33,34]; the static mixer produced a coarser dispersion than the twin-screw extruder (a factor of 2 has been reported). The dependence of phase size on the viscosity ratio for blends prepared in a twin-screw extruder was found to resemble that observed for Newtonian fluids in an elongational flow field. Detailed aspects on phase morphology development in a twin-screw extruder are well documented elsewhere [7].

### 1.1.3 Main Types of Phase Morphologies

There exist in polymer blends two or three major types of phase morphologies, depending on whether the encapsulated structures (composite droplets) are considered as a class apart. The most common is the droplet-in-matrix (as, for example, Figure 1.3), the (droplet-in-droplet)-in-matrix (as, for example, Figure 1.4), and the cocontinuous phase morphology where both phases are mutually interconnected throughout the whole volume of the blend (as, for example, Figures 1.5 and 1.6).

#### 1.1.3.1 Droplet-in-Matrix Phase Morphology (Dispersed Morphology)

The mechanism and the parameters that control the droplet formation in a binary immiscible blend have been discussed in the preceding section. The size of the dispersed phase in a polymer blend is measured on images observed by microscopy. For well-mixed