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Extruder Processing for Nanoblends and Nanocomposites

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Summary: Structuring multiphase polymer materials to a micrometer scale (*micro-structuration*) is a facile engineering practice. However, structuring them to a nanometer scale (*nano-structuration*) is a formidable engineering challenge. In this paper, it is shown first why traditional extruder compounding processes only lead to micro-structuration and then how one may use the extruder type of mixer to structure multiphase polymer materials at a nano-meter scale to obtain nanostructured polymer blends (*nanoblends*) and nanostructured polymer composites (*nanocomposites*).

Keywords: compounding; mixing; nanoblends; nanocomposites; reactive extrusion

Introduction

Nowadays "nano" is used as a prefix for almost all scientific and technical terms. Among the numberless examples are nano-materials and nano-technology. By "nano" it is usually meant that the scale of objects or structures is of the order of 100 nm or below. Nano-materials science aims at answering questions as to when nanometer scale structures comes into play and what properties they can bring about. Nano-materials engineering strives to develop methodologies which allow to structure materials at a nanometer scale. This paper is concerned with the nano-structuration processes of multiphase polymer materials (polymer blends and polymer composites).

Polymer-Polymer Mixing vs. Polymer-Powdered Solids Mixing

It has been common practice to use extruder compounding processes to fabricate polymer blends (*polymer-polymer mixing*) and polymer composites (*polymer – filler mixing*). The common goal of these processes is to mix mixtures of polymers or polymers and fillers in granular or powdered form to materials structured at microscopic levels. The scale of dispersion (structuration) that such processes can achieve is typically of the order of a few sub-micrometers to a few micrometers. In other words, they are *micro-dispersion* processes and not *nano-dispersion* ones. Why is it so?

This may be understood qualitatively by analyzing polymer-polymer mixing and polymer-powdered solids mixing processes (Figure 1). There are similarities and substantial differences between these two processes. As pointed out by Ottino et al.[1], polymer blending is the result of complex interactions between flow and events occurring at droplet-length scales: deformation,

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breakup, coalescence, and hydrodynamic interactions. Similarly, polymer compounding is the result of complex interactions between flow and events occurring at agglomerate-length scales: deformation (it may be small), fragmentation, and hydrodynamic interactions. Whether or not a droplet breaks up depends on the *capillary number, Ca*, which is the ratio of deforming viscous stress to resisting interfacial stress (equation 1). Similarly, whether or not an agglomerate fragments depends on the *fragmentation number, Fr*, which is the ratio of deforming viscous stress to resisting cohesive strength of the agglomerate (equation 2).

$$\mathrm{Ca} = \frac{\text{Deforming viscous stress}}{\text{Resisting interfacial stress}} = \frac{\eta\dot{\gamma}}{\sigma/R}\left(\text{simple shear flow}\right) \tag{1}$$

$$\mathrm{Fr} = \frac{\text{Deforming viscous stress}}{\text{Cohesive strength of agglomerates}} = \frac{\eta\dot{\gamma}}{T}\left(\text{simple shear flow}\right) \tag{2}$$

where η is viscosity, $\dot{\gamma}$ shear rate, σ interfacial tension, R radius of the droplet, and T cohesive strength of the agglomerate. The latter corresponds to interparticle bonds due to electrostatic charges and van der Waals forces.

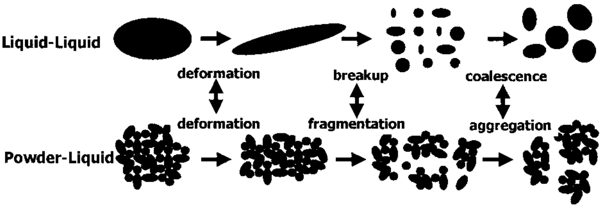


Figure 1. Schematic representation illustrating the analogies between dispersion of immiscible liquids (polymer blending) and powdered solids (polymer compounding). Adopted from ref. 1.

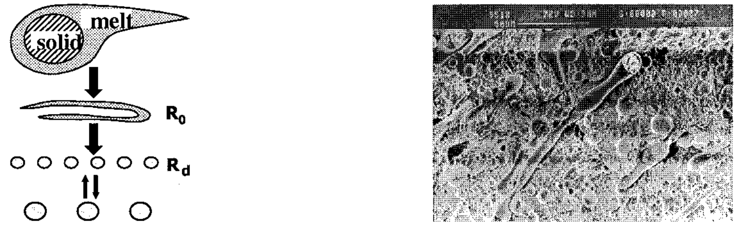
For breakup of a droplet to occur, Ca has to exceed a critical value, $\mathrm{Ca_c}$[2]. Similarly, for fragmentation of an agglomerate to take place, Fr should be above a critical value, $\mathrm{Fr_c}$. Thus, the value of $\mathrm{Ca_c}$ gives the *maximum* droplet size that can survive in a given flow in the absence of coalescence. For two immiscibles liquids, the maximum droplet radius R_{max} is given by the following equation:

$$R_{max} = \frac{\sigma}{\eta\gamma}\mathrm{Ca_c} \tag{3}$$

If they are of equal viscosity, the value of $\mathrm{Ca_c}$ is close to unity. Take the values of σ, η and $\dot{\gamma}$ as 1×10^{-2} N/m, 100 Pa.s and 100 s^{-1}, respectively. The corresponding value of R_{max} is equal to 1 μm. This implies that under such typical processing conditions, droplets bigger than 1 μm in radius will not be stable and will be broken down to smaller ones. Those whose radii are smaller than 1 μm will be stable, if no coalescence occurs.

What is the size of droplets upon breakup of threads? Figure 2a depicts the morphology formation process of polymer blending starting from polymer granules or powder. It is composed of four steps: melting/plastification, deformation of polymer melt to thread, breakup of thread to droplets and coalescence of droplets to larger ones[3]. This process is confirmed by controlled experiments in a twin screw extruder (Figure 3)[4]. Both threads undergoing breakup and droplets are observed. According to Tomotika's analysis[5], the radius of droplets resulting from breakup of an infinitely long and viscous thread embedded in a quiescent matrix of an immiscible and viscous liquid, $R_{droplet}$, is related to its initial radius, R_0, by the following equation:

$$R_{droplet} = \left(\frac{3\pi}{2X_m}\right)^{1/3} R_0 \qquad (4)$$



(a)

(b)

Figure 2. Extruder compounding processes to fabricate polymer blends starting from polymer granules of 1 to 5 mm in size (a) and polymer composites starting from polymer granules and powdered solids (b). Adopted from Refs. 3 and 4, respectively.

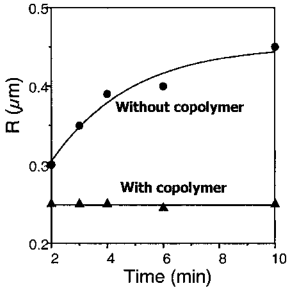


Figure 3. Evolution of the radius of PA 6 particles in the PP matrix for PP/PA 6 (100/0.5) blends with and without a graft copolymer of PP and PA 6 as a compatibilizer. Adopted from Ref. 3.

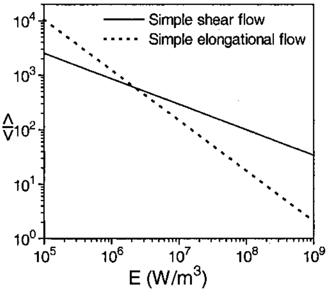


Figure 4. Average number of particles <i> in final fragments of arbitrary shape composed of spherical particles of radius R as a function of dissipation energy E for simple shear and simple elongational flows.

where X_m is the dominant wave number of the thread leading to breakup and is a function of viscosity ratio, p, between the thread and the matrix. For $p = 1$, $X_m = 0.56$. Equation (4) then becomes $R_{droplet} \approx 2R_0$ (5)

This equation indicates that the thinner the thread upon breakup, the smaller the droplets formed. In order for the radius of droplets to be smaller than 100 nm, that of the thread upon breakup has to be smaller than 50 nm. While this is theoretically possible under certain circumstances, it has not been feasible in practice. For a real polymer blending process in which the melting temperature of the polymer of the dispersed phase is higher than that of the matrix, the most favorable conditions for obtaining fine morphology are the following[3]: the rate of melting is much smaller than the sum of the rates of melt deformation and thread breakup. Moreover, the rate of coalescence is zero. Such conditions can be met when the volume fraction of the dispersed phase is very small and an efficient compatibilizer is present during the entire blending process. Figure 3 shows the evolution of the morphology development of polypropylene and polyamide 6 PP/PA 6 (100/0.5) blends with and without a compatibilizer (a graft copolymer of PP and PA 6) in a batch mixer. Note that while the particle radius remains constant at 0.25 μm during the entire blending process in the presence of the compatibilizer, it increases constantly without the compatibilizer due to coalescence. This indicates that the minimum attainable radius is 0.25 μm, far above 100 nm, which is typical of melt polymer blending.

Mixing and dispersion of powdered solids in viscous liquids is much less well understood. For agglomerates whose particles are bound by van der Waals forces, the average number of particles in final fragments <i> is directly related to the dissipation energy imposed by flow, E, by the following equations[6]:

$\langle i \rangle = 5.57 \mathrm{x} 10^5 E^{-0.468}$ for simple shear flow (6)

$\langle i \rangle = 3.20 \mathrm{x} 10^7 E^{-0.798}$ for simple elongational flow (7)

This is shown in Figure 5 for simple shear and simple elongational flows. It is evident that nano-dispersion is possible only when agglomerates are composed of nanoparticles and when <i> is unity. For simple shear flow, in order for <i> to be unity, E has to be 1.89 x 10^{12} W/m^3. This is simply not attainable in extruders. In practice, E ranges from 10^4 to 10^9 W/m^3. Even in the upper limit, <i> is 34. If the radius of particles is 50 nm, that of the final fragments will be 1.7 μm.

The above analyses show that it is very difficult, if not possible at all, to reach nano-dispersion starting from polymer granules/powder and powdered solids. In other words, “from millimeter to nanometer” is likely impossible.

Nano-Structuration Methodologies

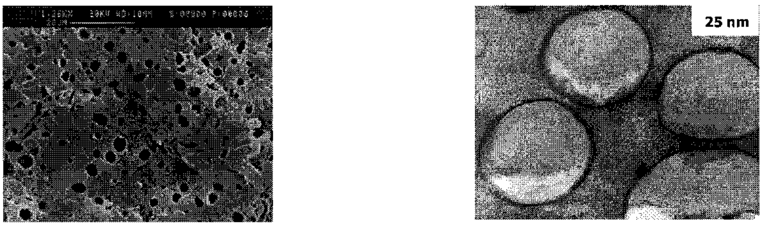
Instead of mixing and dispersing polymer granules/powder or powdered solids which likely does not lead to nano-dispersion, the nano-structuration methodologies proposed here are from "nanometer to nanometer". They consist in dispersing nanometer-scale or finer objects in polymers. In such a way, dispersive mixing will not have to be important. Only is distributive mixing needed to achieve uniform spatial distribution of fine objects. In addition to distributive mixing, stabilization of those fine objects with an appropriate stabilizer/compatibilizer against coalescence or aggregation will remain very important.

Examples of Nano-Structuration of Polymer Blends and Polymer Composites

In what follows, two examples will be given in a concise manner because of space limitations to illustrate how to achieve nano-structuration of polymer blends and polymer composites using the above mentioned "from nanometer to nanometer" methodologies.

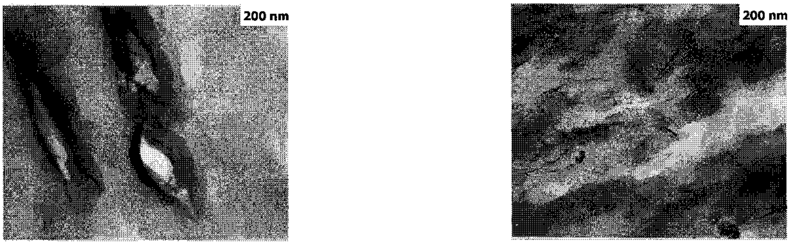
PA 6 can be obtained by polymerization of ε-caprolactam (ε-CL) in the presence of a catalyst such as sodium caprolactam and an activator such as an isocyanate compound. It is a very fast process and is compatible with the residence time of reactive extrusion processes. When this polymerization reaction is carried out in the presence of PP, a PP/PA 6 blend is obtained. The morphology of the final blends would be similar to that obtained by melt blending PP and PA 6. However, if a fraction of PP chains bear isocyanate moieties, then nano-structuration may be possible. In such a case, there is competition between homopolymerization of ε-CL leading to PA 6 and copolymerization of ε-CL onto PP chains leading to a copolymer of PP and PA 6. Thus the final morphology depends on the relative importance of their rates. As shown in Figure 6a, polymerization of a mixture of ε-CL and PP (30/70) in a twin extruder, leads to PA 6 particles of 3.5 μm in diameter[7]. When a fraction of PP is replaced by isocyanate bearing PP, the PA 6 particles are only 50 nm in diameter (Figure 6b)[8]. Such a nano-blend can not be obtained otherwise by melt blending of PP and PA 6, whatever the compatibilization method employed.

Nano-composites based on montmorillonite (MMT) have been subjected to many studies. Melt compounding of MMT with polymers does not lead to nano-dispersion if MMT is not treated. Quaternary amine salts are often used for such treatment. Why is such treatment needed? First, it allows to improve the compatibility between MMT and the polymer matrix. Second, it intercalates MMT interlayer distances allowing for polymer chains to get in. Third, it allows to reduce cohesive strength of MMT by reducing both electrostatic forces and van der Waals forces. Only significant reduction in cohesive strength together with improved compatibility will nano-dispersion of MMT be possible. Treatment of MMT is usually done ex-situ. In-situ treatment during extruder compounding is possible. Figure 6 compares the state of dispersion of MMT in two systems: PA 6/non-treated MMT (95/5) and PA 6/MMT treated in-situ during extruder compounding (one-step extruder compounding). In the first case, the size of the MMT is on the micrometer scale. In the second case, it is dispersed in a nanometer scale. Both the types of intercalant and stabilizer and processing conditions are very important for such processes.



(a) (b)

Figure 5. (a) SEM micrograph of polymerized ε-CL/PP system (30/70), (b) TEM micrograph of polymerized ε-CL/(PP+ isocyanate bearing PP) system (30/70). Adopted from refs.7 and 8.



(a) (b)

Figure 6. TEM micrographs of PA 6/ non-treated MMT (95/5) (a) and PA 6/MMT treated in-situ (95/5) systems (b).

Conclusion

Extruder processing for nano-blends and nano-composites is quite challenging. New engineering principles and methodologies need to be developed. This paper proposed a so-called "from nanometer to nanometer" approach toward that direction. More works are being undertaken.

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