

Continuous Preparation of Polymer Nanocomposites for Applications in Novel Substrates, Multilayered Materials, and 3D Printing

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ABSTRACT

Polymer nanocomposites are composed of a nanofiller, such as nanoclay, carbon nanotubes, graphene, and nanosilver, in a polymer matrix. Depending on the choice of filler, these nanocomposites exhibit unique material properties, including improved barrier properties, flame retardance, mechanical properties, and electrical properties. The critical barrier to obtaining optimal properties is the need for excellent dispersion of the nanofiller throughout the polymer matrix and retaining this dispersion during subsequent melt forming processes. This paper (1) reviews experience with industrially-relevant, continuous melt mixing processes, specifically twin screw extrusion, in creating nanocomposites with low filler loadings, (2) recent efforts in extending melt mixing methods to polymer systems with high loadings of nanofillers, and (3) issues when melt mixing of nanocomposites with a high speed twin screw extruder. Also discussed is the behavior of these nanocomposites in commercial-scale melt forming processes, specifically extrusion of multilayer films, extrusion of novel filament for 3D printing processes, and injection molding of 3D parts.

Key words: nanocomposites, multilayer films, additive manufacturing

PREPARATION OF NANOCOMPOSITES

Polymer nanocomposites consist of a nanofiller in a polymer matrix. These nanocomposites exhibit unique material properties, such as improved barrier properties, flame retardance, mechanical properties, and better electrical and/or thermal properties. A wide range of nanofillers or nanoparticles, including nanoclays, silicas, carbon nanotubes, graphene, nanoalumina, and nanosilver, have been employed to prepare nanocomposites. The critical barrier to obtaining optimal properties, however, is the need for excellent dispersion of the nanofiller throughout the polymer matrix and retaining this dispersion during subsequent melt forming processes (e.g., injection molding and extrusion). Although the nanofillers may be added as nano or microscale particles, when they are exfoliated into individual nanoparticles, there is (1) extensive interfacial area per volume of particles - i.e., 10^3 to 10^4 m²/ml, (2) a large number of particles per unit volume - i.e., 10^6 to 10^8 particles/mm³, (3) particle-particle correlation (orientation and position) arising at low volume fractions - i.e., $f < 0.001$, (4) short distances between particles, typically, 10 to 50 nm at ~1-8 vol%, and (5) comparable size scales among the particles, distance between particles, and polymer chains.

Melt Compounding of Nanocomposites

Although nanocomposites can be prepared by solution processing or in-situ polymerization, the industrially-relevant process is melt mixing. With thermoplastic polymers, this melt mixing typically is performed in a continuous twin screw extrusion compounding process, whereas with thermoset rubbers, the mixing can occur in batch mixers, such as Banbury mixers, or in continuous processes like twin screw extrusion. In melt mixing, the nanoparticles are added to a relatively high molecular weight polymer. Therefore, mixing depends on the compatibility of the nanoparticles with the polymer matrix, the molecular weight of the polymer (which affects its melt viscosity), the mixing equipment, the mixing parameters, and interactions of these factors. A comparison of nanoalumina dispersion in batch and continuous mixers is presented in Figure 1.

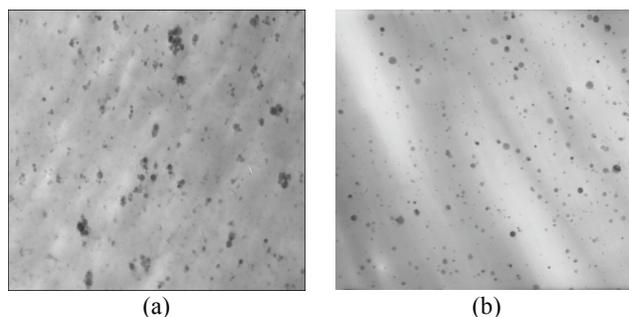


Figure 1. Dispersion of nanoalumina particles with a diameter of 45 nm in polyethylene terephthalate (PET) using a (a) batch mixer and (b) twin screw extruder.

Surface chemistry dictates interaction of the nanoparticles with other particles and with the polymer melt. When the surface chemistry of the particles does not match that of the polymer, the result is poor dispersion of the nanoparticles in the polymer matrix. To improve dispersion, nanoparticles are often surface treated - i.e., the chemistry of the nanoparticle surface is modified - or a compatibilizer, usually a lower molecular weight material that has polar and non-polar functionality, is added to the mixture of nanoparticles and polymer. The selection of a surface treatment or compatibilizer depends on the nanoparticle chemistry, the polymer system, and the processing equipment and temperatures. Reactions between the particles' surfaces and treatments or compatibilizer dictate the selection of surface treatment or compatibilizer. For example, quaternary ammonium salts can react with polar surfaces of nanofillers like nanoclays. These salts can have alkyl hydrocarbon chains that mix readily with non-polar polymers like polypropylene or carboxylic acid groups that are more

machines. This work has shown that the higher screw speeds produce degradation of polymers [4-5], even relatively-stable like polypropylene. As shown in Figure 3b, the degradation was reduced by eliminating most of the kneading blocks along the screw. With the modified screw designs, the higher screw speeds induce “turbulence.” Therefore, dispersion improves with increasing screw speed [6-7].

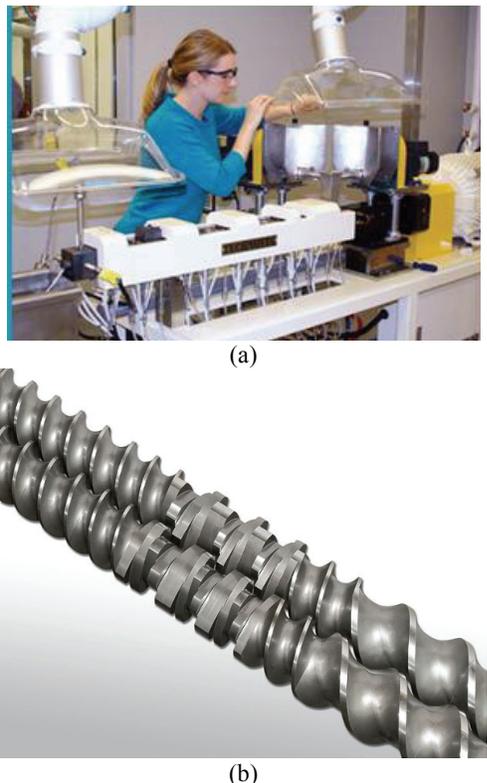


Figure 3. Compounding using a high speed twin screw: (a) 15-mm twin screw extruder and (b) modified screw design for the twin screw extruder.

FORMING OF NANOCOMPOSITES

Polymer nanocomposites generally perform well in standard polymer forming processes (extrusion, injection molding, blow molding, thermoforming, and rotational molding). The low level of nanoparticles can increase the viscosity of the polymer melt, particularly at low shear rates. The higher viscosity requires greater injection pressures, higher torques in extrusion, and greater forming forces in blow molding and thermoforming. The nanoparticles also can act as nucleating agents, causing changes in the crystallization of semi-crystalline polymers like polyethylene, polypropylene, polyamides, and polyesters. Thermally-conductive nanoparticles usually increase the cooling rate in these forming processes. Typical solutions have been increases in temperatures and changes in product design to prevent the melt from solidifying too rapidly (and creating defects in the products).

Nanocomposite Film and Sheet

As shown in Figure 4, nanocomposite pellets produced from twin screw compounding can be fed into a single screw extruder where the pellets are melt and forced through a conventional film or sheet die. The sheet of melt exiting the die is stretched, cooled, and sometimes, embossed in a chill roll stack and then wound on a roll. The flow and stretching can create significant alignment of fibrous nanoparticles, like carbon nanotubes, in the machine direction. The new materials can retain their anisotropic properties or undergo post-extrusion stretching operations to create more biaxial orientation of the nanoparticles.

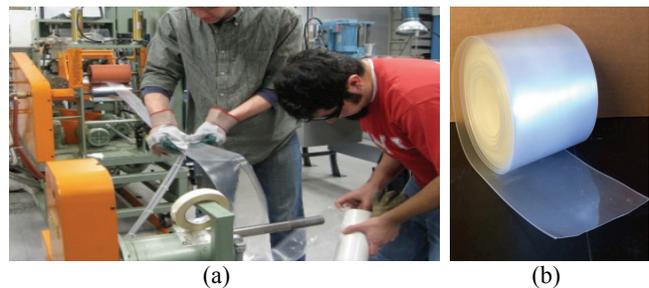


Figure 4. Extrusion of nanocomposite sheet and film: (a) sheet extrusion line and (b) roll of film.

With multilayer film or sheet, the melt exiting two or more extruders is split and restacked by layer multiplying elements (LMEs) to create as many as 2000 horizontal or vertical layers (Figure 5). Nanocomposite materials can be incorporated into one or more of the extruders, creating materials with enhanced electrical, thermal, and barrier properties. The greater viscosity of the nanocomposites can cause imbalances in the melt viscosity of filled and neat polymer layers, producing layer instabilities. These instabilities can be eliminated by changes in melt temperature, changes in flow rate (from the extruders), and changes in LME design.

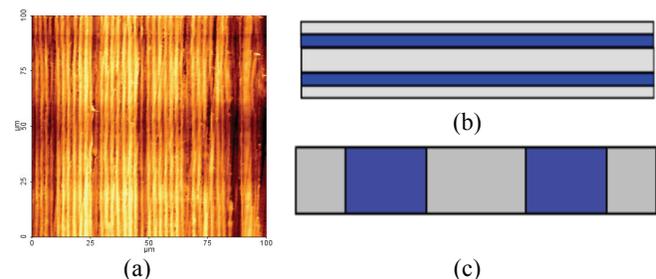


Figure 5. Multilayer extrusion of film and sheet: (a) atomic force microscopy of cross-section from sheet with over 600 layers, (b) horizontal layering, and (c) vertical layering.

Overall, monolayer and multilayer extrusion of nanocomposite film and sheet enables continuous manufacturing of substrates that can easily be about 900 to 1800 mm (3 to 6 feet) wide and produced at extremely high rates.

Production of Nanocomposite Filaments for Additive Manufacturing Processes

Additive manufacturing processes, including fused deposition modelling (FDM), have limited materials. The available materials – i.e., filaments – also do not meet the dimensional tolerances required to create parts that are similar to those produced by forming processes like injection molding and extrusion. The nanocomposites offer an opportunity to easily create novel filaments tailored for specific applications.

As shown in Figure 6, filament can be produced by feeding the nanocomposite pellets produced in the twin screw compounding process into a single screw extruder. The extruder melts the pellets and forces the melt through an filament die. While the molten filament is stretched by a puller, it passes through a cooling station (e.g., water bath) where the filament is solidified. The filament dimensions are measured between the cooling station and puller.



Figure 6. Filament extrusion line: extruder with die (right back), water bath (right front), filament gauging system (center), and puller (left).

Extrusion of neat polymer and nanocomposite filament was a relatively straight forward process. Maintaining uniform dimensions, however, was not. Stabilization of the extrusion process (as determined by the head pressure and drive torque) and the puller speed (as measured during the process) – along with a feedback loop provided some improvements in the filament dimensions. Greater improvements required changes to the geometry of the filament die. The improved die designs permitted extrusion of filaments from a range of polymer materials, including polypropylene, ABS, and polycarbonate, as well as nanocomposites and customer-specified materials.

CONCLUSIONS

Polymer nanocomposites can be produced in large amounts by melt mixing using twin screw extrusion compounding. Although mixing conditions must be adjusted for different polymer and nanoparticle combinations, the overall compounding process is well understood. Use of novel high speed twin screw extruders has required significant changes in screw design to prevent polymer degradation. Good mixing, however, has been achieved with new screw designs and higher screw speeds that create turbulence in the melt. Very high loadings (up to 90 wt %) of nanoparticles have been

incorporated into a range of polymer materials. The mixing processes have required splitting the feeding of the fillers, and sometimes, two passes through the twin screw extruder.

The polymer nanocomposites usually have been easy to form into parts using standard plastics forming processes. The nanocomposites often have higher viscosities, can nucleate semi-crystalline polymers, and may cause issues with faster cooling. These materials are routinely formed into monolayer sheet and film (including blown film), multilayer film and sheet, and injection molded parts. New filament materials for fused deposition modelling processes are also being investigated. With very high filler loadings, however, the nanocomposites are much more difficult to form. The filler loadings require changes in the design (e.g., lower compression ratios) of single screws used in extrusion, injection molding, and blow molding. Moreover, the limited amount of polymer melt in these systems has produced changes in melt fronts and required changes in processing conditions and tooling designs.

Other studies have shown that nanocomposites can be recycled with limited changes in some properties as well as no emission of the nanoparticles into the environment.

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REFERENCES

- [1] I. Manas-Zloczower, A. Nir, and Z. Tadmor, *Rubber Chemistry and Technology*, 57(3), 583-620 (1984)
- [2] D. Kim, J. S. Lee, C. F. Barry, and J. L. Mead, *J. Applied Polymer Science*, 109(5), 2924-2934 (2008).
- [3] T. Lan, Q. Qian, Y. Liang, and J. W. Cho, Nanocor, from: http://www.nanocor.com/tech_papers/FRApplsPlastic.asp, last accessed March 14, 2016.
- [4] M. J. Egan, Doctoral Dissertation, University of Massachusetts Lowell (2013).
- [5] A. Farahanchi, R. Malloy, and M. J. Sobkowicz, *Polymer Engineering and Science* (2016) *in press*.
- [6] J. Gug and M. J. Sobkowicz *Journal of Applied Polymer Science* **2016** (doi: 10.1002/APP.43350).
- [7] X. Chen and M. J. Sobkowicz, *Journal of Polymer Science Part B: Polymer Physics* (in revision).
- [8] J. Zhang, A. Panwar, D. Bello, T. Jozokos, J. A. Isaacs, C. Barry, and J. Mead, *Environmental Science: Nano* (2016) - DOI: 10.1039/C5EN00253B