Building better plastics with supercritical carbon dioxide

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Supercritical CO₂ can aid the dispersal of nanoscale clay fragments during the synthesis of polymer nanocomposites, provided that it can be concentrated at the clay-compatibilizer interface.

Nanocomposite plastics are a promising class of materials with a range of applications, particularly in the automotive industry. By incorporating mineral material of nanoscale dimensions, the mechanical properties of the bulk plastic, such as strength, thermal stability, and flame retardance, are drastically improved, with little to no impact on other favorable properties such as low weight. In these composites, uniform dispersal (exfoliation) of the mineral filler throughout the polymer matrix is a key factor. However, this is nontrivial due to the inherent chemical incompatibility of the inorganic clay mineral with the organic polymer of the plastic and the strong internal forces holding together the closely spaced stacks of silicate sheets that make up these clays. Improving dispersal can be accomplished using organoclays. Here, the stacked structure of the clay mineral is expanded by replacing internal inorganic ions with organic ions (surfactants), and the use of small organic polymers (compatibilizers) that can interact with both the hydrophilic clay and the hydrophobic plastic. These measures have had some success in enhancing exfoliation of the filler, but technologies are needed that can achieve more complete exfoliation.

Several technologies have recently been presented in the literature for using supercritical CO₂ (scCO₂) to improve organoclay exfoliation in polyolefins.1–5 ScCO₂ can permeate the composite or its components during processing, acting as a solvent to enable more effective exfoliation, and is readily available and environmentally benign. A key distinction between the proposed methods is which of the nanocomposite components (organoclay, compatibilizer, or polymer matrix) is present with the scCO₂ during processing. The effectiveness of each approach depends on the influence of the scCO₂ on the material or materials. However, the function of CO₂ in these methods has not been studied until now.

Detailed batch studies with scCO₂ and the components of a polyolefin nanocomposite have shown that the gas acts to plasticize the materials present.6–8 For an organoclay alone, this plasticization causes excess surfactant trapped at the peripheries of the silicate sheets to mobilize and become more uniformly distributed over all the internal surfaces of the mineral, but does not change the stacking structure. This plasticizing influence of scCO₂ allows functionalized polymers (the compatibilizers) to enter more deeply into the gaps between stacked sheets. But the absence of shear stress measurements in previous studies has limited our understanding of its practical use. Our more recent work was performed in a 27mm co-rotating twin screw extruder (Leistritz). This enabled us to take shear stresses into account as we evaluated three methods for varying the component present with scCO₂ and thus to assess the effectiveness of each approach.9

The simplest method, due to its similarity to polymer foaming, is referred to as direct gas injection (DI), where scCO₂ is injected into the extruder after all components of the composite material have been melt-mixed together.5 X-ray diffraction (XRD) analysis of the state

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of organoclay exfoliation in the resulting thermoplastic olefin (TPO) nanocomposite (5 : 5 : 90% clay : compatibilizer : matrix) found no change in structure (see Figure 1). Transmission electron microscopy (TEM) found the clay had simply broken into smaller fragments: see Figure 2(a). As a result, it was not surprising to find that the storage modulus, a measure of stiffness, differed little from the conventionally prepared sample, nTPO (see Figure 3). Thus, when the matrix resin is present, the plasticizing effect of scCO\(_2\) is too highly diluted for any beneficial change to occur in the state of clay exfoliation.

The other two methods proved more effective for clay exfoliation: using pretreated organoclay (PO), prepared alone with scCO\(_2\) prior to mixing; and masterbatch-scCO\(_2\) injection (MS), combining the organoclay and compatibilizer together with scCO\(_2\) prior to mixing with molten TPO. XRD analysis of nanocomposites prepared via these methods showed no detectable basal spacing for the organoclay (see Figure 1), indicating that the organoclay platelets are well dispersed. TEM images of the PO nanocomposite also show a more highly exfoliated state within the polymer compared to nTPO: see Figure 2(b). However, this composite displayed a particular susceptibility to shear stresses and its storage modulus is lower than that of nTPO (see Figure 3) despite the higher clay dispersion. We suspect that this outcome is related to the more uniform surfactant coating found for pretreated organoclay\(^8\), preventing functional groups of the compatibilizer from linking to the silicate sheets with strong bonds.

For the MS method, we observed two outcomes. If the scCO\(_2\) used remained present as the compatibilizer-clay mass was mixed into the TPO, then poorly dispersed clusters of expanded but ordered silicate sheets were obtained—see Figure 2(c)—and the storage modulus of the nanocomposite differed little from nTPO (see Figure 3). Conversely, if the CO\(_2\) did not remain in the extruder during mixing, then the shear stress response was not diminished by plasticization and the clay showed a state of exfoliation similar to the PO method: see Figure 2(d). The storage modulus of the nanocomposite obtained via the MS method is higher than that obtained via the PO method but still did not exceed the stiffness of nTPO.

It is evident that these three methods using scCO\(_2\) to aid clay exfoliation were not improvements over the conventional method (nTPO). However, focusing attention on the clay-compatibilizer interface, as in the case of the MS method, seems the most favorable approach to develop a technology. We believe it is possible for the MS method, with its highly exfoliated clay, to create a stiffer nanocomposite than nTPO if the extensive thermal degradation of the compatibilizer that occurs during the annealing under scCO\(_2\) can be prevented. Future work will focus on approaches to melt-mix the organoclay and compatibilizer in the presence of scCO\(_2\) to avoid degradation issues related to prolonged heating.

![Figure 2](image1.png)

*Figure 2. Transmission electron microscopy images showing clay dispersion in the nanocomposite prepared by (a) DI, (b) PO, (c) MS with scCO\(_2\) in the extruder, and (d) MS without scCO\(_2\) in the extruder.*

![Figure 3](image2.png)

*Figure 3. Storage modulus curves determined at 190°C by parallel plate rheometry.*
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