

# Structure and Rheology of Supercritical Carbon Dioxide Exfoliated Polymer Nanocomposites

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## ABSTRACT

A major technological barrier to achieving superior properties of nano-structured composite materials is the difficulty of dispersing fillers uniformly in a host matrix. The existing nanocomposite manufacturing processes achieve property improvements through chemical modifications of filler structures and utilization of chemical interactions between the chemically modified fillers and matrix polymers. We have developed a novel and efficient supercritical fluid processing method for extensively exfoliating and coating nano-scale fillers for use in polymeric nanocomposites. The filler material, consisting of aggregated or layered particles, is contacted with a supercritical fluid containing a soluble organic material for a certain time, the soak step, followed by a catastrophic depressurization step. During the soak step, under the selected processing conditions, the mixture of the supercritical fluid and the organic material diffuses between the layers or bundles. Depending on the selected conditions and the solubility of the organic material in the supercritical fluid, the mixture can be a gas-expanded liquid phase or a dense-gas solution. The high diffusivity and low viscosity of the mixture enable efficient kinetics of this step. During depressurization, expansion of the gas between the layers or bundles pushes them apart causing extensive exfoliation while the organic material remains between the layers and bundles, coating the surfaces of the layers or bundles, thus preventing the reformation of the layered structure. We investigated the structure and rheology of several nanocomposites prepared by the supercritical carbon dioxide exfoliation and coating process: Thermoplastic polyurethane (TPU)/graphite nanocomposite Polydimethylsiloxane (PDMS)/natural clay nanocomposite Polyvinylmethylether (PVME)/I30P (a chemically modified clay). The morphology of the samples was studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM) and the steady-shear and oscillatory-shear measurements were performed on the Rheometrics ARES and the Rheometrics RSA II rheometers, respectively.

**Keywords:** supercritical fluids, exfoliation, coating, clays, graphite, PDMS, PVME, TPU

## 1 INTRODUCTION

The field of polymer/silicate nanocomposites has recently gained substantial momentum. Polymer/clay nanocomposites with attractive property profile such as improved stiffness, barrier resistance, thermal stability, and

flame retardancy have been developed with minimal increase in density due to the low inorganic loading requirements [1,2,3,4,5]. The dramatic enhancements in properties can be attributed to a decrease in particle size (particles ~ 100-1000 nm in diameter and 1 nm thick) and an increase in aspect ratio. If the layered silicate can be efficiently dispersed throughout the polymer matrix, a small fraction can easily generate significant interfacial area (~760m<sup>2</sup>/g). Two recent research efforts have made significant contributions to the revival of these materials: First, the report of a Nylon-6 montmorillonite material from Toyota research where very moderate inorganic loadings resulted in concurrent and remarkable enhancements of thermal and mechanical properties [6,7]. And second, Giannelis et. al. found that polymers and clays could be melt-mixed, without organic solvents, resulting in intercalated nanocomposites [8].

Layered silicates are a family of smectic clays with a 2:1 layered structure and typical aspect ratios ranging from 100 to 1000, which is an order of magnitude greater than conventional fillers such as mica and talc. Polymer/silicate hybrids are typically classified into three categories according to the degree of silicate dispersion: immiscible, intercalated, and exfoliated [9]. *Immiscible* corresponds to a composite system where the layered fillers exist in their original state of aggregated layers with no penetration of the polymer matrix into the inter-gallery spacing (interaction is on the micro-scale level like traditional composites). Systems where the extended polymer chains penetrate between host layers, resulting in increased repeat stacking distances of a few nanometers, are *intercalated*. And nanocomposites where the individual filler layers are dispersed throughout a continuous polymer matrix are referred to as *exfoliated* [10]. Typically, a nanocomposite is considered to be exfoliated when the polymer increases the initial separation in the clay platelets an additional 80 Å [11]. Further characterizations include more complex morphologies like disordered intercalated phases, house of card structures, partially exfoliated phases, and structures resembling nematic phases [12]. In order to correctly characterize polymer/clay nanocomposites a variety of devices must be used. Of these devices wide-angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) are the most common. WAXD is best suited for determining the d-spacing in intercalated and immiscible nanocomposite systems.<sup>13</sup> And TEM is useful for providing a qualitative spatial relationship between clay platelets in the polymer matrix.

In addition to WAXD and TEM, rheology can be employed as another tool to characterize polymer/clay nanocomposites. In order to effectively process nanocomposites, the detailed melt rheological behavior of these materials must be understood. This is important not only for gaining a fundamental knowledge of the processability, but also for elucidating the structure-property relationships [13]

The use of supercritical fluid treatment appears to be another promising technique to produce intercalated/exfoliated polymer clay nanocomposites. Supercritical fluids (SCF) have been proposed as environmentally friendly solvents for a range of materials synthesis and processing applications including: polymerization processes, polymer purification and fractionation, coating applications, and powder formation [14]. In particular, supercritical carbon dioxide (scCO<sub>2</sub>) has emerged as a powerful alternative to traditional solvents due to its many desirable attributes such as low cost, abundance, and low toxicity. In general supercritical fluids offer mass transfer advantages over conventional organic solvents because of their gas-like diffusivity, low viscosity, and surface tension [15]. When CO<sub>2</sub> is raised above its critical point ( $T_c = 31.1\text{ }^\circ\text{C}$ ;  $P_c = 73.8\text{ bar}$ ;  $\rho = 0.472\text{ g/mL}$ ), its physicochemical properties (i.e., density, dielectric constant) can be continuously tuned between vapor-like and liquid-like limits by varying the system pressure and/or temperature.

We have a novel method for developing new classes of supercritical fluid exfoliated nanocomposites. The supercritical fluid based process (**Figure 1**) involves contacting the aggregated or layered particles (A) with a supercritical fluid containing a soluble organic material for a certain time (B) followed by a catastrophic depressurization step (C). The particles can be aggregated or layered nanoplatelets, nanofibers, or nanotubes. The organic material can be a pre-polymer, polymer, or monomer soluble in the supercritical fluid under the processing conditions. At the elevated pressures, the supercritical fluid with the soluble organics diffuses between the layers or bundles. During depressurization, expansion of the gas (depressurized fluid) between the layers or bundles pushes them apart causing extensive exfoliation while the solubility of the organic material drastically drops causing the organic material to precipitate and deposit on the surfaces of the layers or bundles, thus preventing the reformation of the weak bonds. The supercritical fluid based process creates ready-to-use exfoliated and coated nanoplatelets, nanofibers, or nanotubes. The ready-to-use nanoparticles can further be introduced into any polymer matrix and in any specified quantity by standard methods of polymerization, melt mixing, or extrusion.

## 2 RESULTS AND DISCUSSIONS

We have conducted preliminary studies on the morphology and rheology of several nanocomposites manufactured by employing the scCO<sub>2</sub> exfoliation and coating process. These include: Polydimethylsiloxane (PDMS)/natural clay nanocomposite, Polyvinylmethylether (PVME)/I30P (a chemically modified clay) nanocomposite, Thermoplastic polyurethane (TPU)/ graphite nanocomposite.

The morphology of the samples was studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Steady-shear and oscillatory-shear measurements were performed on the TA/Rheometrics ARES and the TA/Rheometrics RSA II rheometers, respectively.

### 2.1 Polydimethylsiloxane (PDMS)/natural clay nanocomposite (Polymer/clay dispersion in scCO<sub>2</sub>):

This nanocomposite contains Cloisite Na<sup>+</sup> (from Southern Clay Products), which is a naturally occurring montmorillonite with a cation exchange capacity of 93meq/100g clay, in a PDMS matrix. The clay was first blended with a low molecular weight PDMS (MW=38,900 g/mole, the coating polymer) at a ratio of 50 wt% clay and 50 wt% polymer. The blended clay and coating polymer was introduced into the matrix PDMS (MW=400,000 g/mole) and processed with scCO<sub>2</sub> at 14 MPa and 75°C ( $d_{\text{CO}_2} = 0.40\text{g/cm}^3$ ) for 24 hours. Then the system was depressurized at a rate of 5.4 cm<sup>3</sup>/s.

The structural features of Cloisite Na<sup>+</sup> and nanocomposites processed with scCO<sub>2</sub> are displayed in **Figure 2**. The XRD scan of the as-received Cloisite Na<sup>+</sup> has a characteristic peak at  $2\theta = 6.8^\circ$  corresponding to a basal spacing  $d_{001} = 1.29\text{ nm}$ . Pure PDMS shows a broad peak at  $2\theta = 12^\circ$  ( $d = 0.774\text{ nm}$ ) attributed to its amorphous halo (Figure 2A). The XRD scan of the nanocomposite with 5 wt% clay content shows no basal spacing peak of clay, suggesting significant degree of exfoliation and dispersion. The XRD scan of the nanocomposite with 15 wt% clay content has a very low intensity broad peak at  $2\theta = 6.1^\circ$  corresponding to  $d_{001} = 1.44\text{ nm}$ . This peak emanates from the clay dispersion and indicates a small degree of intercalated structure. **Figure 3** shows the TEM of the nanocomposite. The single platelets and more complex structure are very clear from these images.

The linear viscoelastic properties of the PDMS/ Cloisite Na<sup>+</sup> nanocomposite with 15 wt% clay showed marked enhancement at all frequencies and loadings. An improvement in storage modulus ( $G'$ ) of about 100% over the matrix polymer was observed over the entire frequency range (**Figure 4**). This improvement is a factor of 2 higher than those observed for nanocomposites prepared by

dispersing chemically modified clays in PDMS by solution mixing techniques.

## 2.2 Polyvinylmethylether(PVME)/I.30P nanocomposite:

This nanocomposite contains a chemically intercalated clay, I.30P, dispersed in a PVME matrix. I.30P has 25-30% of the natural clay cations replaced by trimethyl-octadecylamine onium ions  $[\text{CH}_3(\text{CH}_2)_{17}\text{N}^+(\text{CH}_3)_3]$  resulting in doubling of the distance between natural clay layers. The clay was blended with PVME (MW=90,000 g/mole) and was processed with  $\text{scCO}_2$  at 14 MPa and  $75^\circ\text{C}$  for 24 hours followed by depressurization at  $5.4 \text{ cm}^3/\text{s}$ . The motivation for using PVME is its compatibility with polystyrene, an extensively studied commercial polymer.

The rheological characterization and the structure of the PVME/I.30P nanocomposite indicate a very significant improvement in the storage modulus and the presence of intercalated structures in the processed nanocomposite (Figure 5). The XRD scan of I.30P has a characteristic peak at  $2\theta=3.8^\circ$  corresponding to  $d_{001}=2.7 \text{ nm}$ . The XRD scan of the  $\text{scCO}_2$  processed nanocomposite with 15 wt% clay content displays a highly intercalated structure, evident by the shift of the clay's characteristic sharp peak to lower  $2\theta$  value corresponding to  $d_{001}=3.6 \text{ nm}$ . TEM images also confirms the intercalated structure (Figure 6). A ten-fold increase in the storage modulus,  $G'$ , of the nanocomposite relative to pure PVME is measured over a wide frequency range. Some of the increase of the modulus is attributable to favorable interactions via H-bonding between the onium ions of the clay and the ether functions of PVME. Even in the absence of H-bonding, for  $\text{scCO}_2$  processed PVME/natural clay nanocomposite, with 15 wt% clay content, greater than 100% improvement in modulus was observed.

## 2.3 Thermoplastic polyurethane (TPU)/ Graphite nanocomposite:

Thermoplastic polyurethanes are semirigid linear block copolymers consisting of soft segments, such as polyethers or polyesters and hard segments. The preparation of the TPU graphite nanocomposite combined the SCFP of graphite with prepolymer followed by the polymerization step. The graphite and the prepolymer, an ether-based polyol, were first processed with  $\text{scCO}_2$  at 14 MPa and  $75^\circ\text{C}$  for 24 hours and depressurized at  $5.4 \text{ cm}^3/\text{s}$ . The resultant prepolymer coated graphite was reacted with diisocyanates (hard segments) and chain extenders to form the TPU/graphite nanocomposite. The control experiment involved mechanically blending the prepolymer with graphite followed by the polymerization step.

In the XRD scan of the nanocomposite prepared by the conventional method, the characteristic peak of graphite at

$2\theta=26.36^\circ$  ( $d_{002}=0.34 \text{ nm}$ ) is clearly observed while the corresponding scan of the nanocomposite prepared by the supercritical carbon dioxide processing method shows a very small peak, indicating substantial reduction of the layered structure and better dispersion of graphite (Figure 7B). The rheological characterization of pure TPU, TPU/graphite nanocomposite prepared by conventional method and TPU/graphite nanocomposite prepared by the SCFP method were done at  $190^\circ\text{C}$  (Figure 7A). The storage modulus of the  $\text{scCO}_2$  processed nanocomposite was improved by a factor of 5 over a wide frequency range when compared to the modulus of the nanocomposite prepared by the conventional method.

### FIGURES:

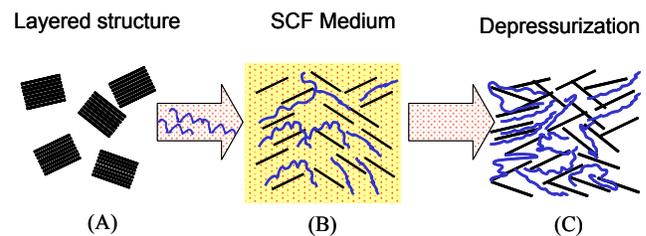


Figure 1: The supercritical fluid based process

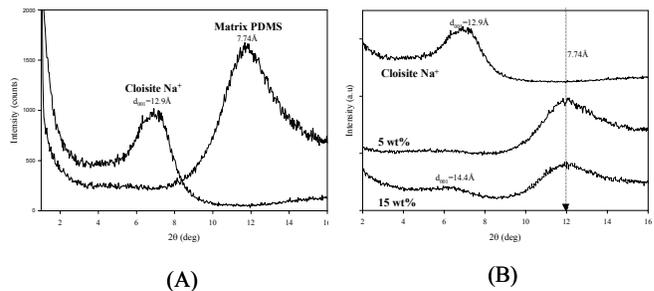


Figure 2: PDMS/Cloisite  $\text{Na}^+$  system: A) XRD-scan of Cloisite  $\text{Na}^+$  and pure PDMS matrix polymer. B) XRD scans of Cloisite  $\text{Na}^+$  (as received),  $\text{scCO}_2$  processed PDMS/ Cloisite  $\text{Na}^+$  nanocomposite (5 wt%) and PDMS/ Cloisite  $\text{Na}^+$  nanocomposite (15 wt%).

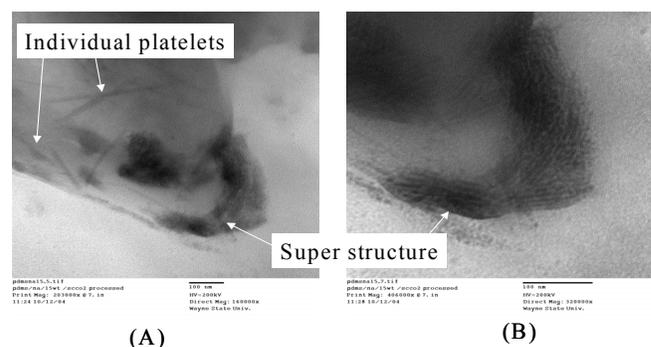


Figure 3: TEM images of PDMS/ Cloisite  $\text{Na}^+$  nanocomposite

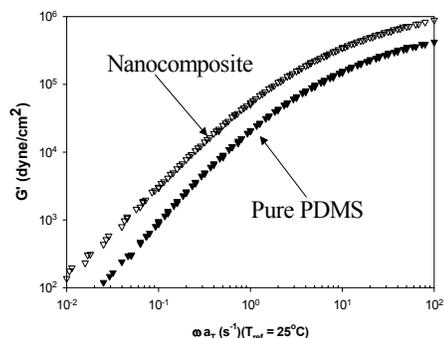


Figure 4: PDMS/Cloisite Na<sup>+</sup> nanocomposite (15 wt% clay): Storage modulus of pure PDMS (dark) and PDMS/Cloisite Na<sup>+</sup> nanocomposite (open) at 25°C. G' of nanocomposite was improved by approximately 100% compared to pure PDMS.

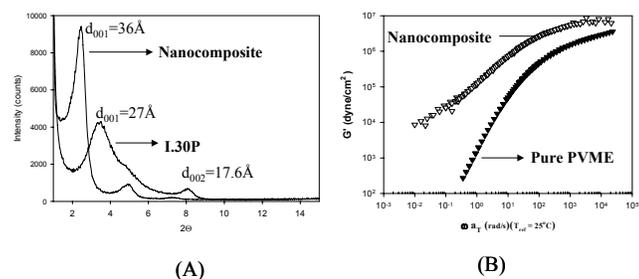


Figure 5: PVME/I.30P nanocomposite (15 wt% clay): A) XRD-scan of I.30P as received and PVME/I.30P nanocomposite. B) Storage modulus of pure PVME (dark) and PVME/I.30P nanocomposite (open) at 25°C.

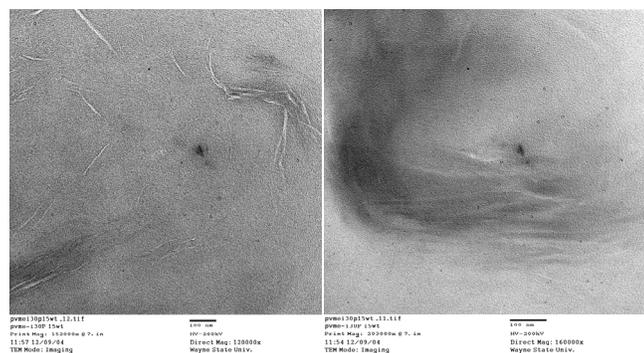


Figure 6: TEM images of PDMS/ Cloisite Na<sup>+</sup> nanocomposite

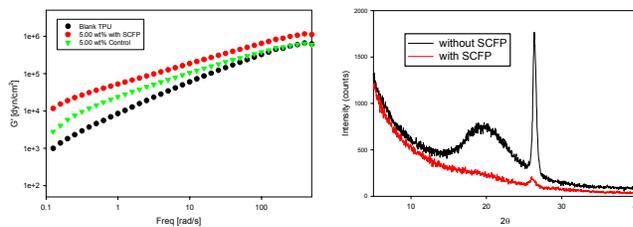


Figure 7: TPU/Graphite Nanocomposite (5 wt% graphite): A) Storage modulus of pure TPU (black), and control TPU/Graphite nanocomposite (green) and supercritical fluid processed (SCFP) TPU/graphite nanocomposite (red) at 190°C. B) XRD-scan of the control (black) and the SCFP (red) nanocomposite.  $d_{002}$ =0.34 nm peak of graphite is diminished for the SCFP nanocomposite indicating an exfoliated graphite structure.

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