

SUPERCRITICAL FLUID TREATMENT METHOD FOR DELAMINATING AND COATING OF LAYERED MATERIALS

Gulay K. Serhatkulu and Esin Gulari*

Chemical Engineering and Materials Science Department

Wayne State University

Detroit, MI 48202

Email: egulari@nsf.gov, Fax: 313-577-3810

The dispersion of nanolayers of clay or graphite enhances the properties of polymers, particularly their thermal stability, mechanical strength, and flame retardancy. The objective of this research is directed to the delamination of layered materials such as organically modified or natural clays and graphite. Supercritical CO₂ was chosen as a processing aid to delaminate the layered platelets. CO₂-soluble additives, such as low molecular weight polymers, oils, or monomers are used to coat the delaminated layered surfaces during supercritical process treatment. The organic coating prevents the reformation of the layered structure during the depressurization of carbon dioxide. Examination of the supercritical fluid treated layered materials by Wide-Angle X-Ray Diffraction (WAXD) and Transmission Electron Microscopy (TEM) confirms that the treatment is effective in exfoliation of layers. Pressure, temperature and processing time have strong effects on the degree of delamination and coating of layers.

INTRODUCTION

Studies by researchers at Toyota have demonstrated a tremendous increase of tensile modulus and heat distortion temperature of Nylon-6/clay nanocomposites [1]. The recent applications of nanocomposites using thermoplastics and thermosets have seen varying degrees of success. Several strategies have been considered to make polymer clay nanocomposites including solution mixing [2], melt blending [3], in-situ polymerization [4] and template synthesis [5]. All these methods necessitate the penetration of polymers or monomers into layered silicates by solvents or shear forces. Some of these methods are limited by the immiscibility of the clay with a polymer matrix or a polymer solution.

In its natural state, clay is made up of stacks of individual particles held together by ionic forces. The spacing between the layers is on the order of 1nm, which is smaller than the radius of gyration of typical polymers. Consequently there is a large entropic barrier that inhibits the polymer from penetrating this gap and intermixing with the clay [6]. Organically treated clays are achievable by performing intercalation chemistry to exchange a naturally occurring inorganic cation with a bulky organic cation. This process increases the interlayer spacing between layers, lessening the attractive forces and allowing the clay to be compatible with polymers for subsequent polymerization or compounding. While this strategy is effective in more polar systems such as nylon, efforts to extend the same strategy to non-polar polymers have limited success. Furthermore, the high melt viscosity of many thermoplastics prohibits uniform dispersion of the layered silicates [7]. Even when the layers are successfully separated and interspersed into the polymer matrix, the high aspect ratio platelets

tend to form ordered structures under shear within the polymer or can phase separate from the matrix material [6].

SCF solvents have been proposed as candidate media for polymerization processes, polymer purification and fractionation, coating applications and powder formation [8]. Recently Caskey *et al* [9] have used supercritical carbon dioxide as a processing aid in the fabrication of composite materials. Any gaseous compound becomes supercritical when compressed to a pressure higher than its critical pressure (P_c) above its critical temperature (T_c). One of the unique characteristics, which distinguish supercritical fluids from ordinary liquids and gases, is that some properties are tunable, simply by changing the pressure and temperature. In particular, density and viscosity change drastically at conditions close to the critical point. Generally, diffusion is faster and viscosity is lower than a liquid while liquid-like densities or solvent power are achievable. Supercritical carbon dioxide ($scCO_2$) is readily accessible with a T_c of 31 °C and a P_c of 73atm. It is abundant, inexpensive, non-flammable, non-toxic and environmentally benign [10]. Non-polar organic compounds have substantial solubility in $scCO_2$.

Supercritical fluids have been used for delaminating layered silicate materials without the coating agents earlier [11]. 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, oil 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 the depressurization, the expansion of the gas (depressurized fluid) between the layers or bundles pushes them apart causing extensive exfoliation. The solubility of the organic material drastically drops during depressurization 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.

There are many advantages of our method; i) The exfoliation and the coating are done in a single step process producing totally exfoliated and economical silicate materials, graphite and carbon nanotubes. ii) This method of producing the coated silicate materials, graphite and carbon nanotubes is environmentally friendly because the chemical processes such as ion exchange process is eliminated. iii) Ready to use products can be applied to practically any polymer matrix because the coating material and the polymer matrices can be miscible or immiscible. iv) This method enables preparation of polymer blend nanocomposites, which is very hard to achieve with the conventional techniques due to the complex chemistry necessary between the intercalated ions and the polymer matrices. v) This technique enables the use of naturally occurring, hydrophilic, inorganic silicate layered materials to prepare nanocomposites with hydrophobic polymers as well. vi) This technique is not structure-oriented so it enables to use mixed fillers/polymer nanocomposites such as different silicate materials, silicate materials with graphite, or carbon nanotubes with graphite etc. to prepare nanocomposites with unique properties.

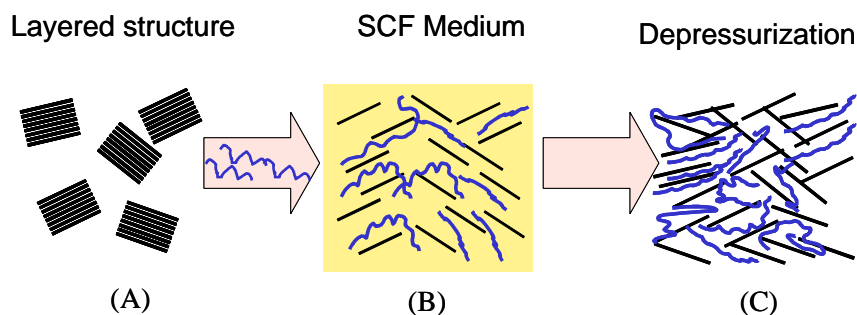


Figure 1: The supercritical fluid based process involves contacting the aggregated or layered particles (A) with a supercritical fluid containing a soluble organic material for a certain time (B) followed by a catastrophic depressurization step (C). The supercritical fluid with the soluble organics diffuses between the layers (B). Upon depressurization, expansion of the fluid pushes the layers apart causing extensive exfoliation and the organic material precipitates and deposits on the surfaces of the layers (C).

I-MATERIALS AND METHODS

The clays used in this study were obtained from Southern Clay Products (Cloisite Na⁺). Cloisite Na⁺ is a natural montmorillonite with cation exchange capacity of 92.6meq/100g clay. Synthetic graphite powder (<20 micron) was purchased from Aldrich. PDMS (polydimethylsiloxane) standards were purchased from Scientific Polymer Products, with $M_w=170300$, 90200, 38900 and $M_n=97200$, 46000, 13700 respectively. Solution of PVME (polyvinylmethylether) in water was purchased from Scientific Polymer Products. The weight average molecular weight is 90,000. It is dried for several days in freeze dryer. In order to remove impurities it was dissolved in toluene, then filtered and re-dried.

Coating Process

Clay or graphite sample with the coating agent was blended to form a paste which was placed into a glass vial. The glass vial was packed by a porous membrane and sealed with Teflon thread. These sample packs were placed into the pressure vessel, which is heated by a heating jacket. The vessel was pressurized and clays were exposed to scCO₂ for a definite period. Then the vessel was rapidly depressurized and the samples were removed from the vessel.

Characterization

Wide-angle X-ray diffraction (XRD) data was collected using a Rigaku Rotaflex powder diffractometer. X-ray source is CuK α radiation ($\lambda=1.54056\text{\AA}$) with 40kV and a current of 150mA). The 00l reflections vary in position according to the separation of the structural layers. This separation is influenced by the following factors: the exchangeable cations present, the nature of the liquid absorbed between layers, the quantity of liquid, the nature of the montmorillonite itself, and the chemical reactions clay may have been subjected to [12]. Non-separated montmorillonite layers, after introduction into the polymer, are often referred to as tactoids. The term intercalation describes the case where a small amount of polymer moves into the gallery spacing between the clay platelets, but causes less than 20-30 \AA of additional separation between the platelets. Exfoliation and delamination occur when polymer further separates the clay platelets by 80-100 \AA or more [13].

Rheology of the various poly-layered silicate (PLS) nanocomposites was performed using a Rheometrics RSA II and/or ARES rheometer. All tests on the RSA II were run in the shear-sandwich geometry (15.95 mm x 12.6 mm x 0.47 mm) and all tests on the ARES were run in the cone and plate configuration (cone angle of 0.1 rad, gap of 0.05 mm, and a plate diameter of 25.0 mm). The nanocomposites were subjected to oscillatory shear, with the RSA II, over a frequency range of 10^{-2} to 10^2 rad/s and a temperature range of 25 to 70°C. To ensure all rheology, with the RSA II, was done in the linear viscoelastic region strain sweeps were performed at each temperature. Consequently, strains of 15-20% were used at low frequencies and strains of 1-3% were used at high frequencies. Specifically, at all temperatures and a frequency range of 10^2 to 10^1 rad/s the commanded strain was 1-3% while for the frequency range of 10^{-1} to 10^{-2} rad/s the commanded strain was 15-20%. Furthermore, to ensure no permanent orientation was occurring, dynamic frequency sweeps at high strains (15-20%) were repeated and the data compared with the previous sweep. No such orientation was observed. The steady-shear viscosity, for the PLS, was determined using the ARES rheometer. The steady-shear viscosity was measured at shear rates ranging from 10^{-2} to 10^2 s⁻¹ at a fixed temperature of 25°C.

II-RESULTS AND DISCUSSIONS

We have investigated the morphological and rheological properties of nanocomposites prepared by supercritical carbon dioxide (scCO₂) exfoliated clay and graphite. Three different polymers were studied; poly(vinylmethylether) (PVME), poly (dimethylsiloxane) (PDMS) and thermoplastic polyurethane (TPU). PVME and PDMS, soluble in supercritical carbon dioxide under the processing conditions, were used as the coating material. The first clay is a *natural montmorillonite* with interlayer spacing of 12.6Å ($2\theta=6.836^\circ$) (**Figure 2A**) and second is Cloisite 30B, which is a natural montmorillonite surface modified with ternary ammonium salt. All the nanocomposites have 15-wt% clay. The basal spacing peak of the natural clay disappears in the X-Ray Diffraction (XRD) scans of the nanocomposites, indicating an exfoliated structure (Figure 2A). The degree of exfoliation is much more extensive than that has been achieved *even* with the organically modified clays [14]. Consequently, significantly better improvements in mechanical properties compared to the literature were observed. The storage modulus (G') of PVME/ Cloisite 30B nanocomposite demonstrated substantial increase of over 500% (at 10 rad/s) (**Figure 2B**). Similarly 160% (at 1 rad/s) enhancement in storage modulus was observed for PDMS/ Na⁺-montmorillonite nanocomposite (**Figure 2B**).

We have also studied thermoplastic polyurethane (TPU)/Graphite nanocomposites. Graphite layers were first coated with ether-based pre-polymer in the supercritical fluid-processing step. Then, the coated graphite was polymerized with the chain extender and diisocyanate. The graphite/TPU nanocomposite contains 5 wt% of graphite. The results indicate that exfoliation of graphite flakes in TPU is successful, which is clear from the disappearance of $2\theta=26.36^\circ$ ($d_{002}=0.34\text{nm}$) peak of graphite in XRD scans (Figure 3A). The storage modulus of the nanocomposite was improved by 515% (at 1 rad/s) compared to pure TPU (Figure 3B). Moderate improvements in other properties, such as electrical conductivity, elongation at break, E modulus, were also observed.

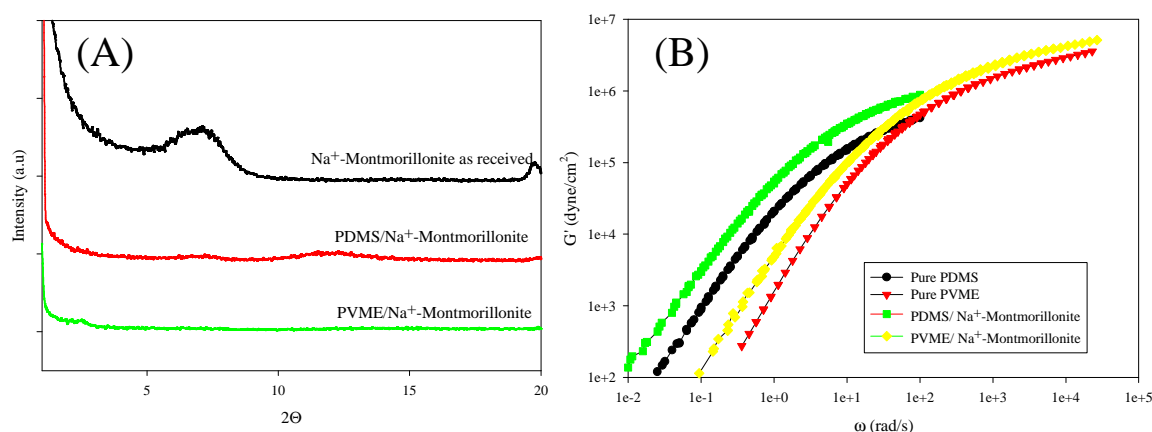


Figure 2: Morphological and Rheological Properties of PDMS/Na⁺-Montmorillonite, PVME/Na⁺-Montmorillonite, PVME/Cloisite 30B Nanocomposites: A) X-Ray Diffraction of Na⁺-Montmorillonite as received and PDMS/Na⁺-Montmorillonite and PVME/Na⁺-Montmorillonite Nanocomposites. B) Storage Modulus of pure PVME, pure PDMS, PDMS/Na⁺-Montmorillonite and PVME/ Cloisite 30B Nanocomposites. The substantial improvement in modulus upon adding exfoliated filler is shown. For PDMS nanocomposites, approximately 160% improvement in G' is observed whereas in PVME nanocomposites over 500% improvement is observed.

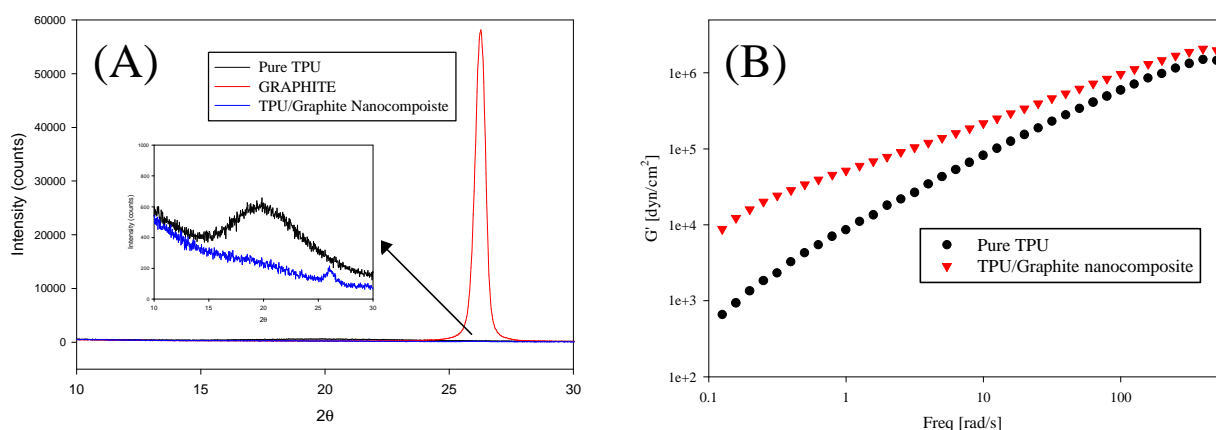


Figure 3: TPU/Graphite Nanocomposite (5 wt% graphite): A) X-Ray Diffraction of Pure TPU, Graphite and TPU/Graphite Nanocomposite. The insert is the XRD scan of the nanocomposite and pure TPU showing the d_{002} peak on an expanded scale. $d_{002}=0.34\text{nm}$ peak of graphite is diminished indicating an exfoliated structure. B) Storage modulus of pure TPU, and TPU/Graphite nanocomposite at 190°C. G' of nanocomposite was improved by approximately 515% compared to pure TPU.

CONCLUSION

The use of supercritical fluids for exfoliating clay is a novel process. There are several advantages of using this new technique with regards to the final applications. It is an environmentally friendly process because it can be performed in closed CO₂ cycle to reduce the generation of chemicals. We have investigated the structure and linear viscoelastic properties of PDMS/Na-MMT, PVME/Na-MMT and TPU/Graphite nanocomposites formed

by supercritical fluid processing method. XRD studies confirm that all the nanocomposites are totally exfoliated.

The linear viscoelastic properties for the series of exfoliated poly-layered silicate and graphite nanocomposites demonstrated significant improvements. Specifically, for the 15-wt% clay-loaded PVME and PDMS nanocomposites, the storage modulus was enhanced by 100% or more. For the 5wt% loaded TPU/graphite nanocomposites, the storage modulus was improved over 500%. The latter results are significantly greater than those reported in the literature.

REFERENCES:

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- ¹ Kojimo, Y., Usuki, A., Kawasumi, M., Okada, A., Fukushima, Y., Kurauchi, T., Kamigaito, O., *J Mater Res.* Vol. 8, **1993**, p. 1185
 - ² Zhao, X., Urano, K., Ogasawara, S., *Colloid Polym. Sci.*, Vol. 267, **1989**, p 899.
 - ³ Kato, M., Usuki A., Okada, A., *Macromolecules*, Vol. 30,**1997**,p 6333.
 - ⁴ Lee, D.C., Jang, L.W., *J. Apply. Polym. Sci.*, Vol. 61, **1996**, p 1117.
 - ⁵ Alexandre, M., Dubois, P., *Materials Sci. and Eng.*, Vol. 28, **2000**, p 1.
 - ⁶ Ginzburg, V. V., Singh, C., Balazs, A.C., *Macromolecules*, Vol. 33, **2000**, p 1089.
 - ⁷ Mielewski D.F., Lee, E.C.C., Manke, C.W., Gulari, E., U.S. Patent Number: 0082331A1,**2002**.
 - ⁸ Kirby, F.C., McHugh, M.A., *Chem. Rev.* Vol. 99, **1999**, p. 565.
 - ⁹ Caskey T.C., Zerda, A.S., Lesser, A.J., *ANTEC*, **2003**, p 2250.
 - ¹⁰ Nielsen, A.K., Glaney, W.C., USA Patent No 5,509,959, **1996**.
 - ¹¹ Manke, C. W., Gulari E., Mielewski D. F., Lee E. C., US Patent Number 6,469,073, **2002**.
 - ¹² Brown, G., *The X-ray Identification and Crystal Structure of Clay Minerals*, Mineralogy Society, London, **1989**.
 - ¹³ Dennis, H.R., Hunter, D.L., Chang, D., Kim, S., White, J.L., Cho, J.W., Paul, D.R., *Polymer*. Vol. 42, **2001**, p. 9513.
 - ¹⁴ Krishnamoorti R., Yurekli, K., *Current Opinion in Colloid & Interface Science*, Vol.6, **2001**, p.464.