

Notes

Characterization of the Dispersion of Clay in a Polyetherimide Nanocomposite

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Introduction

Polymer layered silicate nanocomposites (PLSNs) have attracted a great deal of interest because they often exhibit improved mechanical, thermal, and flammability properties.^{1–6} Thermoplastic-type PLSNs are of special interest because of facile processing and recycling capability. If such a thermoplastic nanocomposite also had reduced flammability, there would be widespread appeal for many applications for use in ultra-fire-safe materials including aircraft cabin materials.⁷ Recent reports on polyetherimide (PEI)–clay nanocomposites^{8–11} have found them to be difficult to process or intractable with high melting temperatures and viscosity and not very soluble. While low-melting aliphatic polyimide PLSNs have been made,¹² the use of a relatively lower-melting aromatic PEI in preparing a PLSN would be of great interest and led us to pursue the synthesis of a thermoplastic PEI nanocomposite.

Several ways to make polymer clay nanocomposites have been demonstrated, including solution mixing, melt blending, and in situ polymerization.^{13–15} All of these methods are limited by the miscibility of the polymer with the clay. Using an organically treated clay can improve the miscibility of the clay with a polymer matrix or in a polymer solution. For melt blending, one of the most commonly used methods, the main limitation of these organically treated clays is lower thermal stability relative to the high melting temperature of many high-performance polymers.¹⁶ Therefore, melt blending is feasible only if the organic treatment on the clay is stable at the high-temperature processing conditions required. Because there are currently no organic treatments commercially available that can withstand typical processing temperatures for thermoplastic aromatic PEIs (≥ 350 °C),¹⁵ solution blending and in situ polymerization routes remain as the most likely to succeed in producing a PEI–clay nanocomposite. This work describes the synthesis and characterization of

poly(ether imide) PLSNs using an in situ polymerization in solution.

Experimental Section¹⁸

All organically treated clays (sodium montmorillonite (Na-MMT), montmorillonite treated with *n*-dodecylamine ammonium salt (MMT-C12), montmorillonite treated with 12-aminododecanoic acid ammonium salt (MMT-C12Acid)) were provided by Southern Clay Products. The syntheses of the PEI nanocomposites are described elsewhere.⁶ Wide-angle X-ray diffraction (XRD) data were collected on powder specimens with a Philips diffractometer using Cu K α radiation ($\lambda = 0.1505945$ nm) with a 0.02° 2θ step size and a 2 s count time. Bright-field transmission electron microscopy (TEM) images of PEI nanocomposites were obtained at 120 kV, at low dose conditions, with a Philips 400T electron microscope. All samples were ultramicrotomed with a diamond knife on a Leica Ultracut UCT microtome at room temperature to give sections with a nominal thickness of 70 nm. The sections were transferred from water to carbon-coated Cu grids of 200 mesh.

Results and Discussion

Since Na-MMT has a thermal stability suitable for the PEI **1**'s typical processing conditions of 350 °C, we attempted to synthesize a PEI PLSN by melt blending PEI **1** (Figure 1) with Na-MMT. This was unsuccessful as determined by XRD. This is probably because the Na-MMT has no organic treatment; thus, it is highly immiscible with the polymer, and no intercalation or exfoliation of the clay occurred during melt blending. Therefore, an in situ approach^{1,14,15} was used to prepare PEI PLSNs, using two organically treated clays (Figure 1). Since *N,N*-dimethylacetamide (DMAc) is the solvent of choice for the polymerization of **1**, we chose two organically treated clays which were shown by light scattering to disperse in DMAc.^{18,19} The MMT-C12Acid has the potential for reacting with the monomers during polymerization, creating a "tethered" polymer clay nanocomposite (Figure 1). The PEI precursor (polyamic acid) was first synthesized from 1,3-phenylenediamine and bisphenol A dianhydride (BPADA) in the presence of MMT-C12 or MMT-C12Acid in DMAc to give a polyamic acid–clay solution. The solvent was then removed, and the polyamic acid was imidized to PEI in a vacuum oven at 250 °C for 2 h. We then characterized the resulting material by XRD and TEM.

When using XRD to analyze a polymer–clay nanocomposite, there are three descriptive categories commonly used: *immiscible*, *intercalated*, and *exfoliated*.¹ It should be noted that these definitions are based on XRD results and are for ideal cases only, assuming that the degree of dispersion falls into only one of the three categories. Using XRD, we investigated how well the clay was dispersed in PEI **1** (Figure 2). XRD measured an increase in *d* spacing in MMT-C12Acid from 1.36 to 1.92 nm, following the in situ solution polymerization. This indicates that an *intercalated* PEI nanocomposite had been synthesized. However, no *d* spacing change

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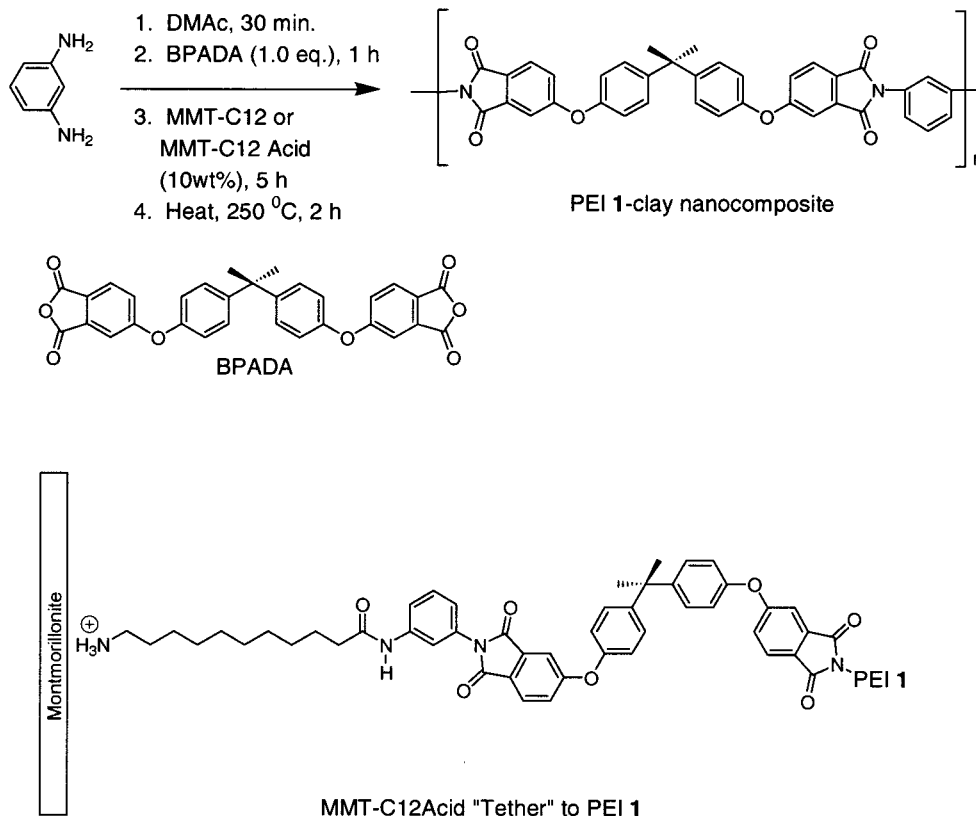


Figure 1. Synthesis of PEI 1-clay nanocomposites via in situ method (top). Tethering of PEI 1 to the montmorillonite surface via 12-amino-1-dodecanoic acid ammonium salt that occurs with MMT-C12Acid (bottom).

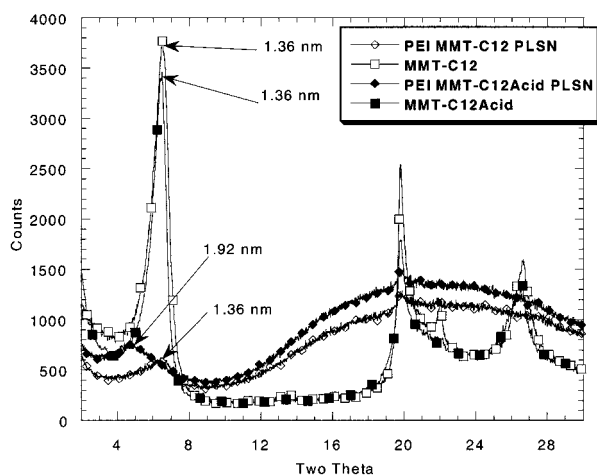


Figure 2. XRD plot of PEI 1 + mass fraction of 10% MMT-C12, MMT-C12, PEI 1 + mass fraction of 10% MMT-C12Acid and MMT-C12Acid.

occurred when MMT-C12 was used during the synthesis of the polyetherimide. This would suggest that an *immiscible* blend had been synthesized.

TEM analysis tends to support the findings from XRD but also shows that the clay is well dispersed at the microscale in both systems, including the immiscible MMT-C12/1 system. To clarify the issue of dispersion, two scales of dispersion must be discussed: microscale and nanoscale. Low-magnification TEM images showed that the clay was homogeneously dispersed throughout both MMT-C12/1 and MMT-C12Acid/1 at scales of 1 μ m or larger; therefore, they were well-dispersed at the microscale. Higher-magnification TEM images show the nanoscale dispersion to not be uniform. A well-dispersed

uniform nanoscale dispersion would be an *exfoliated* nanocomposite, and the systems presented here are not pure *exfoliated* nanocomposites, even though they contain some *exfoliated* clay regions. Therefore, the systems presented here are well-dispersed at the microscale, but not at the nanoscale.

In Figures 3 and 4, the darker lines are the clay layers and the polymer matrix is gray. TEM for MMT-C12/1 (Figure 3) shows that where multilayer tactoids exist, the clay layers are tightly packed together, but there are no large, undispersed clay tactoids. A fair number of single layers were also observed. This indicates that the MMT-C12 was well dispersed and exfoliated in the DMAc before polymerization, but no polymer chains intercalated between the layers of this material during polymerization. Therefore, the clay layers that were exfoliated in the solvent were enveloped by the polymer during polymerization, leaving them in an exfoliated state. Multilayer tactoids in the solvent were similarly enveloped by the polymer, leaving their original *d* spacing intact. Given the combined XRD and TEM data, this nanocomposite may be the first example of an *exfoliated-immiscible* nanocomposite defined as such. Work by Yano¹⁶ on polyimide nanocomposites using a synthetic procedure similar to our own obtained what was identified as an *exfoliated* nanocomposite. Closer examination of the data presented in that paper suggests that while it is predominantly *exfoliated*, some *immiscible* clay regions exist, as seen in our MMT-C12 system. The degree of nanoscale exfoliation in Yano's polyimide nanocomposite is most likely superior to our own, as his material shows no peak by XRD, indicating a small concentration of *immiscible* clay tactoids. Since we observe a peak by XRD in our systems, we must conclude that our MMT-C12 system contains more

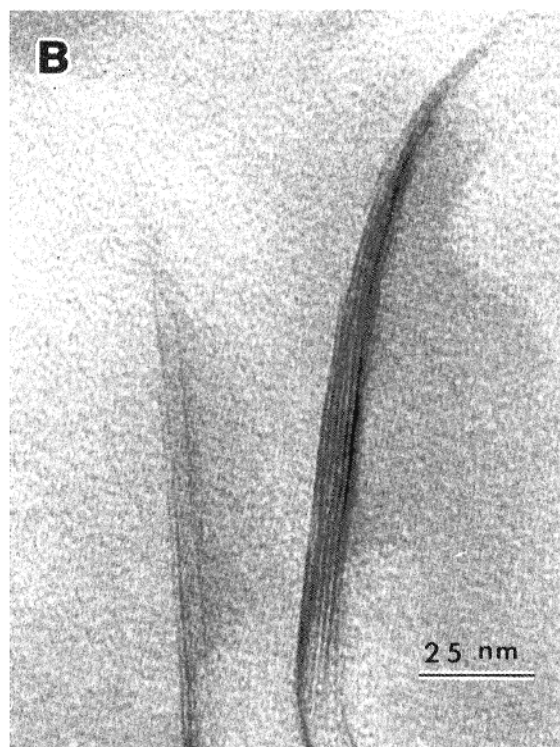
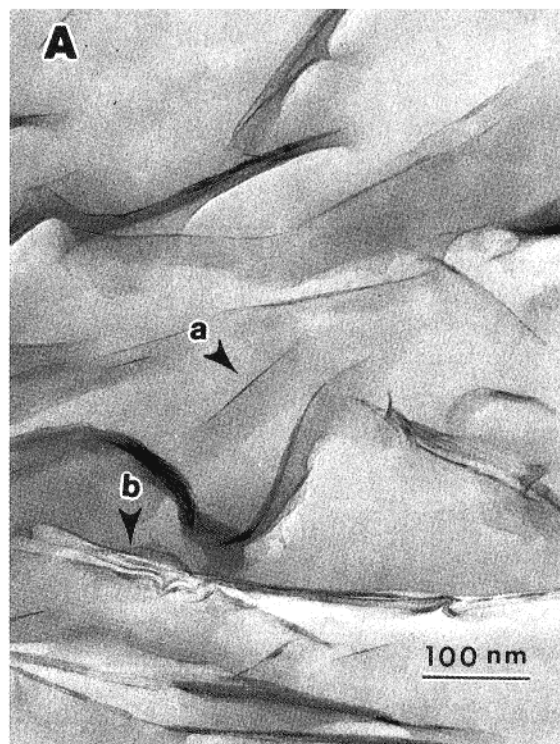


Figure 3. (A) TEM micrograph of PEI **1** + mass fraction of 10% MMT-C12. Note single layers (a) as well as multilayer tactoids (b) present in the material. (B) High magnification TEM micrograph of PEI **1** + mass fraction of 10% MMT-C12 showing a multilayer tactoid (d spacing 1.36 nm by XRD).

immiscible than *exfoliated* clay or our *immiscible* clay is highly ordered while the clay in Yano's material is not.

The MMT-C12Acid nanocomposite shows both elements of an *exfoliated* and *intercalated* system in that single clay layers are observed in abundance (Figure 4), and where multilayer clay tactoids exist, there is an

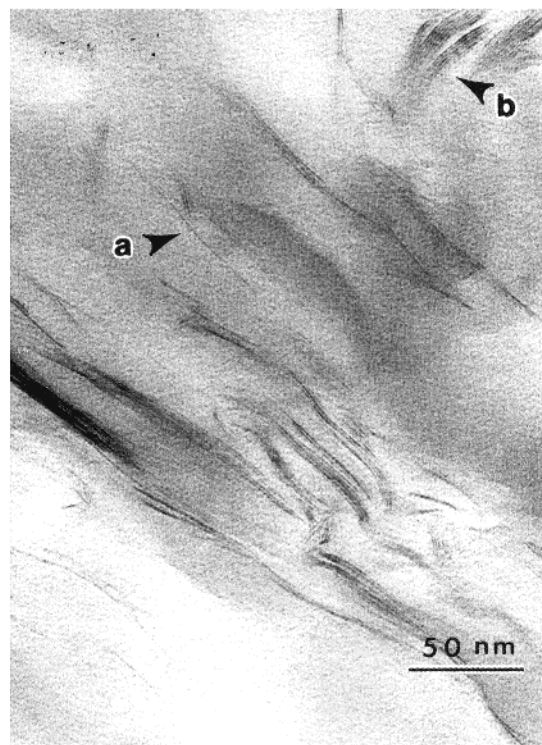


Figure 4. High magnification picture of PEI **1** + mass fraction of MMT-C12Acid. Some single layers (a) are present as well as multilayer intercalated tactoids (b) (d spacing 1.92 nm by XRD).

increase in d spacing. TEM of the MMT-C12Acid/**1** system indicates that the clay was well dispersed, and some polymer intercalated in between the clay layers (Figure 4). Not as many single layers were seen in this system, but some did exist. The MMT-C12Acid/**1** system has some intercalated domains, but also some single layers, making it neither fully *intercalated* nor *exfoliated*. Given this observation, it should probably be defined as an *exfoliated-intercalated* nanocomposite. Intergallery reaction with the 12-ammonium dodecanoic acid (Figure 1) which forms a tether to the clay may have facilitated the intercalation. This reaction does not occur with the MMT-C12 system, thus giving the *immiscible* tactoids seen in Figure 3.

To conclude, we were able to successfully synthesize PEI nanocomposites using MMT-C12 and MMT-C12Acid via an in situ solution polymerization approach. Using TEM and XRD to analyze these materials revealed two nanocomposites whose exact dispersion could not be accurately described by XRD alone. While XRD showed no d spacing increase for the PEI-**1**/MMT-C12 nanocomposite, TEM showed *exfoliated* single clay layers and some undispersed multilayer clay tactoids (particles). Combining the observations from TEM and XRD indicated that the PEI **1**/MMT-C12 was an *exfoliated-immiscible* nanocomposite. For the MMT-C12Acid/PEI **1** nanocomposite, XRD observed an increase in d spacing, indicating an *intercalated* nanocomposite. However, when this datum was combined with the TEM images, the MMT-C12Acid/PEI **1** nanocomposite was shown to be an *exfoliated-intercalated* nanocomposite. Since the clays (MMT-C12 and MMT-C12Acid) were well dispersed in the DMAc solvent prior to the in situ polymerization, they gave rise to the resulting *exfoliated-immiscible* and *exfoliated-intercalated* nanocomposites.

Given the structure of PEI **1**, we had hoped to synthesize a thermoplastic PEI PLSN which could be melt processed. We chose the in situ route in an effort to avoid the thermal decomposition of the clay's organic treatment which would have occurred if the clay was melt processed when synthesizing the PEI nanocomposites. Recent studies on the thermal stability of alkylammonium treatments on clays¹⁵ have shown that the PEI nanocomposite we synthesized cannot be processed at typical melt conditions. The specific reason for this is that the organic treatment will thermally decompose during melt processing, even though it is intact in the polymer *before* melt processing. This thermal decomposition will eliminate the benefits we had hoped to achieve in making a PEI nanocomposite via the in situ process. The thermal stability of the organic treatment on the clay needs to be improved, and efforts are currently underway in this area.¹⁵

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- (18) Certain commercial equipment, instruments, materials or companies are identified in this paper in order to adequately specify the experimental procedure. This in no way implies endorsement or recommendation by NIST.

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