

Assessing Organo-Clay Dispersion in Polymer Nanocomposites

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ABSTRACT: Organo-clay polymer nanocomposites offer improved material properties at very low filler loadings making them of immediate interest for application in body panels, claddings, and instrument panels. This improvement in properties requires that the organo-clay be well dispersed if not completely exfoliated. Conventionally, the dispersion and exfoliation of the organo-clay is evaluated using transmission electron microscopy (TEM) and X-ray diffraction (XRD). Although both TEM and XRD data were found to correlate with flexural modulus of thermoplastic olefin nanocomposite materials, only TEM proved successful in

quantifying the dispersion of the organo-clay in all nanocomposite materials (exfoliated, tactoid, or agglomerated tactoid). XRD was found to be capable of detecting exfoliation and intercalation but is limited because of clay dilution, preferred orientation, mixed-layering, and other peak broadening factors. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1110–1117, 2004

Key words: nanocomposites; TEM; WAXS; XRD; microstructure

INTRODUCTION

Organo-clay polymer nanocomposites, more simply referred to as polymer nanocomposites, are a rapidly developing class of materials.^{1–17} Polymer nanocomposites are attractive because they offer the potential to improve mechanical properties,^{1–3} thermal properties,^{1,4} barrier properties,^{1,5} and flame-retardant properties.^{1,6} This can be accomplished at very low filler loadings, typically 5 wt % (3 vol %) compared to the 10–70 wt % filler in traditional polymer composites. The low filler loadings and the small particle size of the filler offer the increased benefit of processing flexibility, lower density, and reduced costs. These advantages have prompted researchers to investigate polymer nanocomposites with a diverse variety of polymers. This includes thermosets such as epoxy,^{7–9} thermoplastics such as poly(methyl methacrylate),^{10,11} nonpolar polymers such as polypropylene,^{12,13} polar polymers such as nylon,^{2,14} elastomers such as butadiene acrylonitrile copolymer,¹⁵ and conductive polymers such as polyaniline.¹⁶

Polymer nanocomposites can be differentiated from traditional polymer composites by the size of the filler. Ideally, the filler in a nanocomposite consists of individual silicate sheets, on the order of 1-nm thick, dispersed in a polymer matrix. The silicate sheets are

derived from clay, a layered silicate mineral. Although both naturally occurring and synthetic clays are used to form nanocomposites, the clay must allow the exchange of interlayer inorganic cations such as Na⁺ or Ca²⁺ with organic cations such as alkylammonium cations. The exchange of the interlayer cations is required to improve the compatibility of the organophobic silicate sheets with the polymer matrix, thus permitting the silicate sheets to be dispersed as discrete layers. While the specific alkylammonium ion exchanged is normally tailored to the polymer matrix, sodium montmorillonite [a naturally occurring clay having the empirical formula Na_{0.33}(Al_{1.67}Mg_{0.33})Si₄O₁₀(OH)₂] is the most commonly used clay.

In reality, the silicate sheets in polymer nanocomposites do not always disperse as discrete silicate sheets but can form much larger and more complicated structures. These organo-clay structures can be simply classified as exfoliated, tactoid, or agglomerated tactoid. The exfoliated structure, frequently referred to as delaminated, is a clay silicate layer dispersed as a discrete sheet with the individual sheets having no observable association with other silicate sheets. The tactoid structure is clay particulates in which the silicate sheets are stacked face to face. The space between stacked sheets is often referred to as the interlayer or gallery spacing. The agglomerated tactoid structure is clay particulates made of multiple tactoids. This range in clay structures results in a range of dispersion of the filler in polymer nanocomposites.

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Characterizing the dispersion and structure of the organo-clay in polymer nanocomposites has been performed by atomic force microscopy (AFM),¹⁷ X-ray diffraction (XRD),¹⁻¹⁶ and transmission electron microscopy (TEM).¹⁻¹⁵ AFM has only recently been used and the usefulness of this technique is still questionable. XRD has long been used for the characterization of clay minerals. It is based upon the interference pattern produced by repetitive structures in the organo-clay, in particular, the periodic structure associated with the tactoids. TEM is based upon electron density and diffraction contrast differences between the clay structures and the polymer matrix. Unlike XRD, TEM permits the direct observation of the clay structures.

XRD and TEM are the most widely used techniques to characterize clay dispersion in polymer nanocomposites; yet with only a few exceptions,^{12,14,18} both techniques are used qualitatively. Therefore in this paper we assess the use of TEM and XRD in characterizing and quantifying the dispersion and structure of the organo-clay in polymer nanocomposites.

EXPERIMENTAL

Materials

Organo-clay fillers and organo-clay nylon nanocomposites were obtained from Southern Clay Products Inc. (Gonzales, TX). Polyolefin materials were obtained from Basell Polyolefin (Troy, MI), Thermoplastic urethane materials were obtained from A. Schulman, Inc. (Akron, OH), Polyolefin nanocomposites and thermoplastic urethanes were compounded using a Midi 2000 extruder and microinjection molder system (DMS, The Netherlands). Compression-molded samples were prepared by melting chopped pellets between glass plates. Injection-molded samples were prepared with the DMS microextruder/injection molder system.

Transmission electron microscopy

TEM was performed with a Philips 430 T TEM operating at 300 kV. Specimens were prepared by cryoultramicrotomy. Thin sections, nominally 80-nm thick, were sliced at -60°C using a diamond knife.

X-ray diffraction

XRD data were collected with a Siemens D5000 diffractometer using copper K-alpha radiation. The diffractometer was configured in the parallel beam geometry using a Göbel mirror on the primary beam, a lithium fluoride diffracted beam monochromator, and an auxiliary knife-edge slit placed above the specimen.

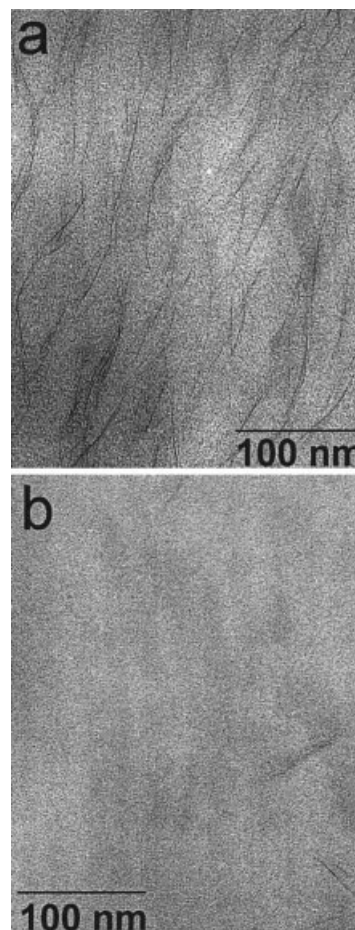


Figure 1 TEM micrograph of nylon nanocomposite microtomed (a) perpendicular to the molding direction and (b) parallel to the molding direction.

The auxiliary knife edge slit allowed data to be collected at lower 2θ values.

RESULTS AND DISCUSSION

Transmission electron microscopy

TEM characterization of polymer nanocomposites differs from the TEM characterization of other polymer systems in that it requires no staining for sufficient contrast. In fact, staining with common heavy metal stains (RuO_4 and OsO_4) can obscure the clay. The organo-clay structures in a polymer nanocomposite naturally appear as dark features in the TEM micrographs. If the structures are sufficiently thick, that is, thicker than the microtomed sections, they can easily be observed independent of the orientation of the silicate layers. As the thickness of the structures approaches the width of a single silicate layer, they can only be observed edge on. This is illustrated in the micrographs of the injection-molded nylon nanocomposite shown in Figures 1(a) and 1(b). In this sample, the injection molding has forced the silicate sheets to

align parallel to the molding direction. Therefore, in the sample microtomed perpendicular to the molding direction [Fig. 1(a)], numerous silicate sheets are observed; while in the same sample microtomed parallel to the molded surface [Fig. 1(b)], few silicate sheets can be observed.

Qualitatively, the organo-clay particles can be described as either exfoliated, tactoid, or agglomerated tactoid. A micrograph from a nylon nanocomposite exhibiting an exfoliated structure is shown in Figure 1(a). Nylon's polar nature facilitates complete exfoliation of the organo-clay. The exfoliated organo-clay particles are discrete monolayer sheets of the parent clay. Because the sheets are discrete monolayers, they have a disordered appearance, showing no obvious association between silicate sheets. The individual sheets appear as relatively straight to slightly curved dark lines. In Figure 1(a), the dark lines are estimated to be around 1-nm thick, consistent with the thickness of the 2 : 1 silicate sheets in the parent montmorillonite clay. The silicate sheets show some variation in length, but are generally less than 200 nm, consistent with previous observations.^{12,18}

A micrograph from a thermoplastic urethane nanocomposite illustrating numerous tactoid structures is shown in Figure 2(a). The moderate polarity of thermoplastic urethanes makes it difficult to achieve an exfoliated structure. The tactoids are the structures with discrete clay layers stacked face to face. When viewed on edge, the tactoids appear as multiple parallel dark lines [enlargement, Fig. 2(b)]. The structure in the tactoids is generally, though not necessarily,⁷ highly ordered, with the discrete silicate layers being nearly equally spaced. Tactoids tend to be less than 100 silicate sheets thick and can range down to just a few layers thick.

An agglomerated structure from a poorly compounded thermoplastic olefin nanocomposite is shown in the micrograph in Figure 3(a). Because of the nonpolar nature of thermoplastic olefins, agglomerated structures can occur quite readily in improperly compounded materials. The agglomerates in any material can be rather large, sometimes several microns across. As shown in the enlargement in Figure 3(b), these agglomerates are comprised of loosely bound tactoids. The agglomerated tactoids can be distinguished from nonagglomerated tactoids by their relatively close proximity to one another relative to the overall dispersion of the clay and by the large range in direction of the silicate sheets. Because most TEM sections are much thinner than the diameter of an agglomerate and because the sections are normally a random slice through the sample, the actual size of the observed agglomerate is usually larger than that observed in the microscope. The plate-like nature of the tactoids typically results in alignment close to a dominant axis. The agglomerates tend to have very low

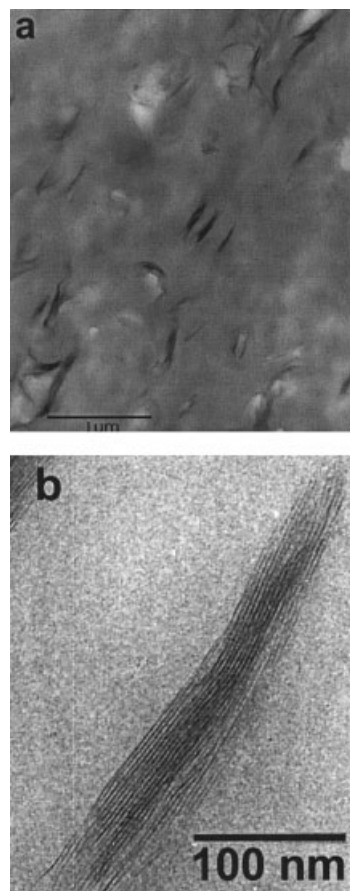


Figure 2 TEM micrograph of a thermoplastic urethane (a) illustrating tactoid structures and (b) illustrating highly ordered, equally spaced silicate layers—enlargement of (a).

aspect ratios and are usually a detriment to material properties. The agglomerates may either be from undispersed starting material or, as suggested from samples containing other fillers such as titania, from re-agglomeration of the tactoids during processing.

The qualitative description of the clay structure is insufficient to adequately describe the clay dispersion and may be misleading for several reasons. First, the small areas examined by TEM may not be representative of the overall microstructure. Second, a nanocomposite can be comprised of multiple structures. Third, the structures can have a range of sizes. Therefore, we felt it was necessary to quantify the dispersion.

To quantify the dispersion, we considered measuring the particle size, particle density, and linear intercept distance. Particle size measurements, like one used by Nam et al.,¹² are tedious and require an excessively large sample; therefore, we did not perform this measurement. Particle density measurements were calculated similar to those by Dennis et al.¹⁴ and Fornes et al.¹⁸ For our measurements, the magnification and total area sampled were adjusted to accommodate the wide range in dispersion. A higher particle density at a fixed or normalized organo-clay

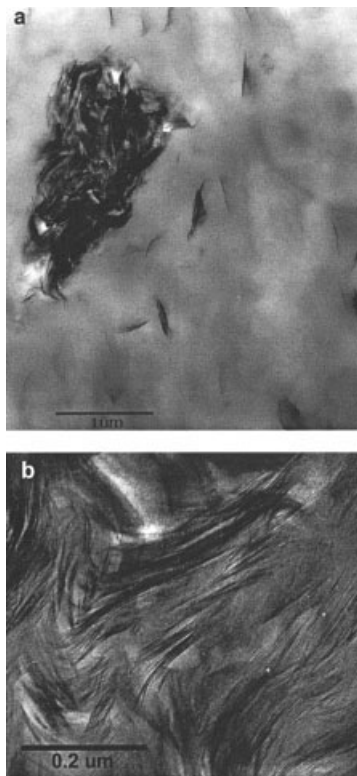


Figure 3 TEM micrograph of a thermoplastic olefin nanocomposite (a) exhibiting an agglomerated structure and (b) illustrating loosely bound tactoids—enlargement of (a).

volume fraction indicates better dispersion. Linear intercept measurements were performed by placing an array of parallel lines over the micrograph and then dividing the total length of the lines by the number of times the lines intersect the clay. In samples with highly oriented clay particles, the array of lines was placed perpendicular to the dominant clay axis. The magnification and total area sampled were adjusted to accommodate for the wide range in dispersion. A smaller linear intercept distance indicates better dispersion.

The graph in Figure 4 shows a comparison of the two measurements. The population density is plotted as $(\text{Particle Density})^{-0.5}$ for a direct comparison. The data in Figure 4 cover materials with an organo-clay volume fraction of 3–4 vol %. The data also cover a wide range of dispersion from materials with an agglomerated tactoid structure (upper right corner) to those with an exfoliated structure (bottom left corner). The samples showing an exfoliated structure have a linear intercept distance of less than 0.1 μm .

Although the particle density and the linear intercept distance both provide a quantitative method for measuring the clay dispersion, we feel the linear intercept method has several advantages. First, we believe the linear intercept method is quicker, less tedious, and more objective. Second, for exfoliated nanocomposites, the particle density depends on the length of the silicate sheets while the linear intercept does not. That is, the exfoliated nanocomposites with smaller clay silicate sheets will have a larger particle density than one with larger silicate sheets, and thus appear to have better delamination of the silicate sheets. Last, the theoretical mean linear intercept distance can be calculated for an aligned exfoliated nanocomposite simply by dividing the interlayer spacing of the original organo-clay by the organo-clay volume fraction in the nanocomposite. For the case of the data presented in Figure 4, the theoretical values of 0.05–0.08 μm compare well with the measured values of 0.04–0.06 μm . The measured values tend to be slightly smaller (i.e., better dispersion) than the theoretical values. This is a stereological error¹⁹ arising from the image projection of a microtomed section. The error increases with thicker sections and smaller particles. This error affects both the linear intercept and the population density measurements.

The disadvantage of the linear intercept method is the dependence on the orientation of the clay particles. Clay particles showing random orientation in the microtomed plane will have a larger linear intercept

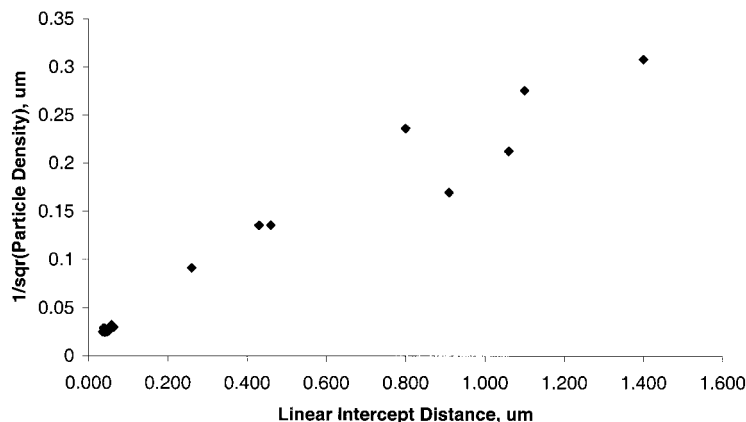


Figure 4 Comparison of TEM particle density and linear intercept measurements used to quantify clay dispersion.

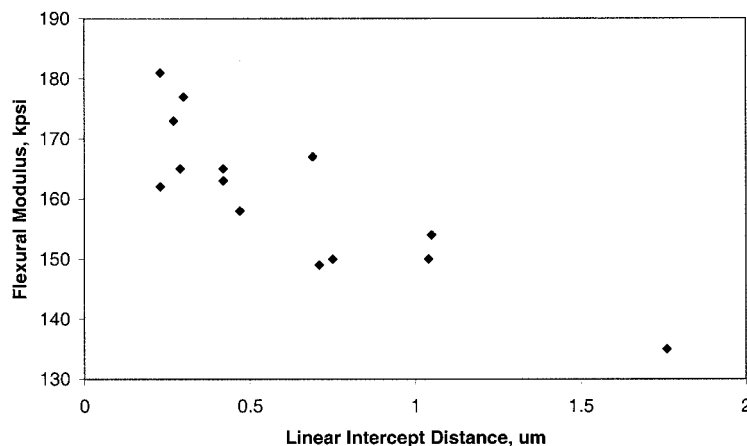


Figure 5 Comparison of flexural modulus properties and TEM linear intercept distance from a series of thermoplastic olefin nanocomposite materials.

distance than those with a preferred in-plane orientation. This type of orientation will have little influence on the particle density.

The graph in Figure 5 shows a comparison of mean linear intercept distance with flexural modulus for a set of thermoplastic olefin (TPO) samples. The composition of the samples was kept constant but the dispersion was varied by changes in the processing conditions. Not surprisingly, the samples with the better dispersion (a smaller linear intercept distance) showed a better flexural modulus.

X-ray diffraction

XRD is an attractive method for the characterization of organo-clay particles in polymer nanocomposites because it is easy, quick, inexpensive, and more accessible than TEM. Yet, ambiguities in the XRD data can complicate the characterization of these materials. In a well-ordered layered structure, the basal reflections conform to the Bragg law, forming a harmonic series of diffraction peaks. Yet, as demonstrated by the diffraction patterns in Figure 6, the basal reflections for organo-clay materials do not always form a harmonic series. For example, the diffraction patterns in Figure 6 were obtained from neat Cloisite® 15a (montmorillonite clay modified with a dimethyl, dehydrogenated tallow quaternary ammonium salt) and several different Cloisite® 15a polymer nanocomposite materials. The diffraction pattern for neat Cloisite® 15a (Fig. 6, diffraction pattern D) shows four basal reflections at 2θ of 2.8, 4.4, 7.2, and 10.1° ; giving d -spacings of 31.1, 20.0, 12.3, and 8.8 Å obviously not conforming to the Bragg law. This is not unprecedented and can easily be explained by a mixed-layering in the clay,^{20,21} where the spacing between the silicate sheets is a mixture of two or more types. Clay minerals are considered mixed-layered if their peak position about

their nominal Bragg position exceeds 0.75%. Mixed-layering generates uncertainty in the interlayer spacings, the type of ordering, and therefore the exact structure of the clay.

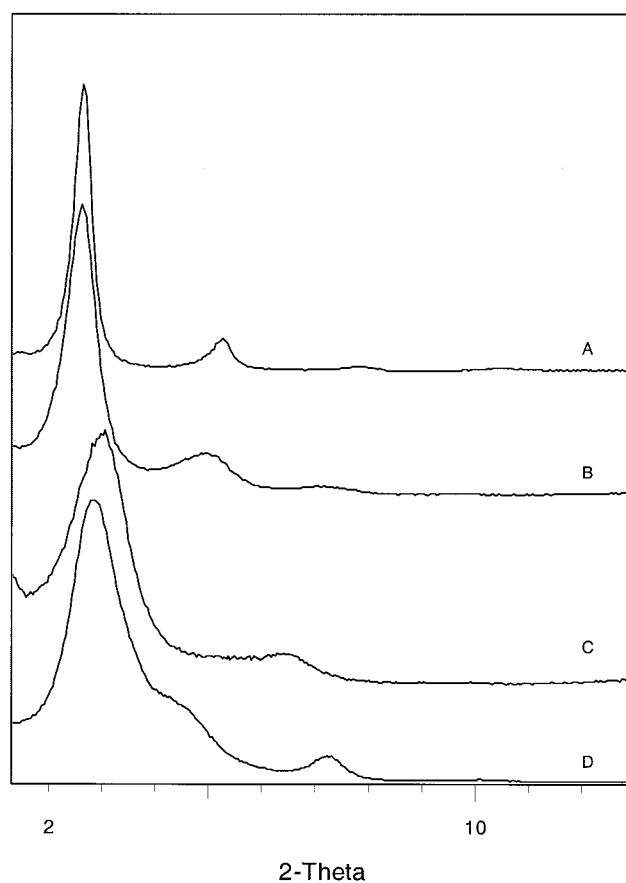


Figure 6 XRD data from Cloisite® 15A - based polymer nanocomposites: (A) thermoplastic urethane, (B) thermoplastic olefin #1, (C) thermoplastic olefin #2, and (D) neat Cloisite® 15A.

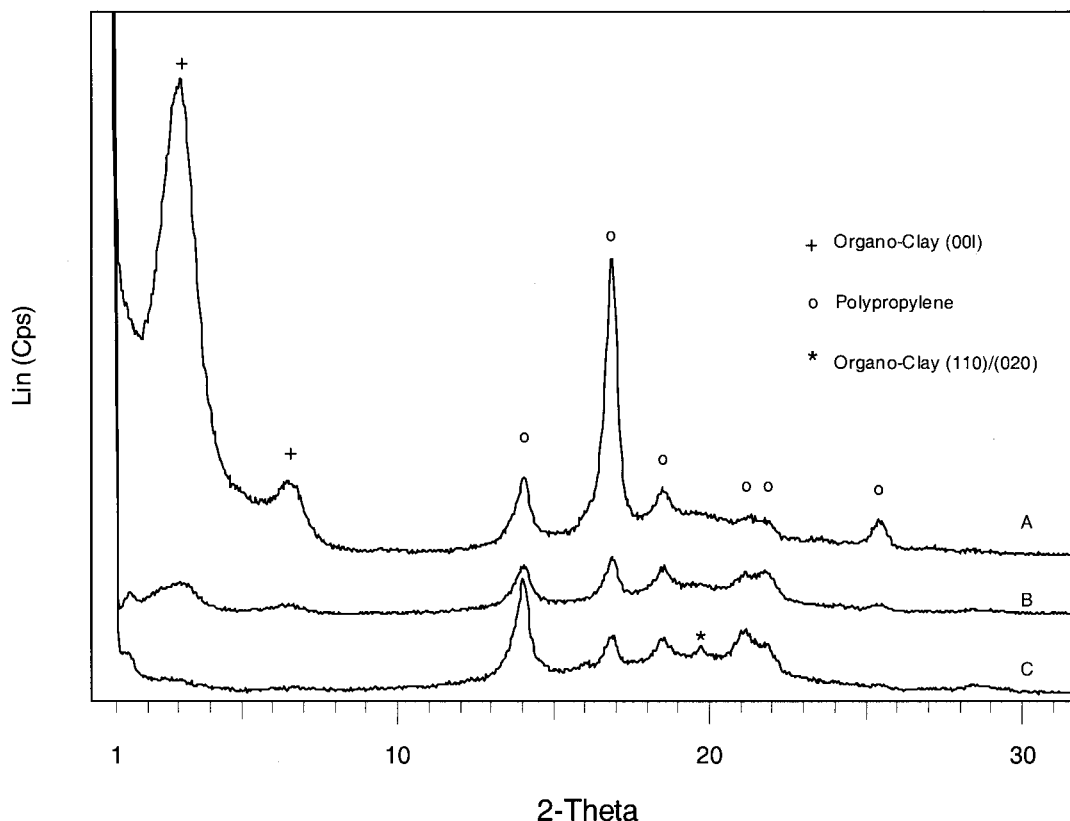


Figure 7 Thermoplastic olefin nanocomposite XRD data: (A) injection molded and aligned parallel to the diffractometer axis; (B) compression molded and aligned parallel to the diffractometer axis; and (C) injection molded and aligned perpendicular to the diffractometer axis.

Changes in the organo-clay diffraction patterns, as shown in the other diffraction patterns in Fig. 6, are an indication of the interaction between organo-clay and polymer matrix, but the structures formed and the nature of the interaction are difficult to discern from these data. Diffraction patterns B and C are from two different polypropylene-based nanocomposites. Both diffraction patterns differ from each other and from the neat organo-clay. Only two basal reflections are observed in C, 30.5 and 13.7 Å, again suggesting a mixed-layered clay, but different from that of the neat Cloisite® 15a (diffraction pattern D). Three basal reflections are observed in B: 34.3, 18.0, and 13.7 Å, much closer to the harmonic series expected for a single-layered clay, but still indicative of a mixed-layered structure. A more dramatic change observed in the organo-clay diffraction pattern occurs in the Cloisite® 15a thermoplastic urethane nanocomposite material (Fig. 6, diffraction pattern A). In contrast to the previous three diffraction patterns, seven basal reflections are observed, all showing an excellent harmonic relationship (33.7, 16.9, 11.3, 8.42 Å, etc.), indicative of a monolayered clay.

It is also important to note the changes in the diffraction peak widths in the diffraction patterns shown in Figure 6. The diffraction peaks in pattern C are

broader than the neat organo-silicate clay (diffraction pattern D) while those in pattern A and B are sharper. Instrumental parameters, particle size, defect density, strain effects, and mixed-layering²⁰ can all affect the observed peak width. Instrumental broadening is expected to contribute no more than 0.2° 2θ , much less than the observed 1.3 – 0.5° 2θ . For the diffraction patterns with broader peaks, particle size and strain effects are also unlikely sources of this broadening and are not consistent with the TEM data. It is interesting to note that the diffraction patterns with the broadest diffraction peaks are also the diffraction patterns in which the peak position deviates the most from the peak position expected by the Bragg law, again consistent with mixed-layering.

Because of the plate-like nature of the clay particles, preferred orientation can have a large effect on the observed XRD data. Figure 7 shows three diffraction patterns from the same thermoplastic olefin nanocomposite. Diffraction pattern A is an injection-molded sample, while diffraction pattern B is a compression-molded sample. The positions of the clay basal reflections are the same in both samples. However, the intensity is an order of magnitude larger in the injection-molded samples, indicating significant preferred orientation. Similar differences can be seen in the

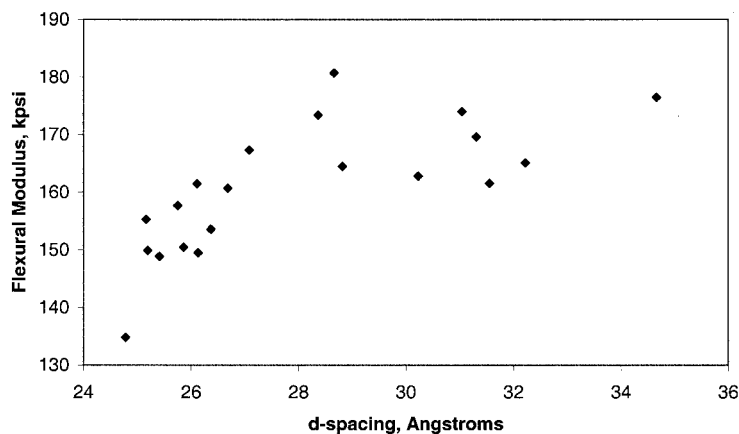


Figure 8 Comparison of flexural modulus properties and XRD d -spacing measurements of the largest clay basal reflection from a series of thermoplastic olefin nanocomposite materials.

polypropylene reflections, with the injection-molded sample showing preferred orientation. The third diffraction pattern, C, is also from the injection-molded sample. These data were collected from a cross-sectioned sample oriented with the molded surface perpendicular to the diffractometer axis instead of the more typical method with the molded surface parallel to the diffractometer axis. To cover the entire incident beam, several cross-sectioned pieces were ganged together prior to data collection. The intensities of the polypropylene peaks were similar to the two other patterns, indicating that the sampling volume is about the same. The data from the cross-sectioned sample show no clay basal reflections but now show the clay (110)/(020) reflection, corroborating the preferential orientation of the clay silicate sheets with the molded surface.

Because of the difficulties in interpretation, XRD characterization of polymer nanocomposites is problematic at best. Consequently, XRD is usually limited to detection of clay exfoliation and polymer intercalation.¹ Exfoliation can be determined by the absence of the clay basal reflections, while intercalation is determined by an increase in the d -spacing of the basal reflections. Although the presence or absence of the basal reflections can indicate whether exfoliation has occurred, other factors such as clay dilution, preferred orientation, and peak broadening need to be considered. Simple dilution of the clay or factors contributing to peak broadening can result in the false conclusion that exfoliation has occurred. Conversely, preferred orientation effects can result in the false conclusion that exfoliation has not occurred. Similarly,

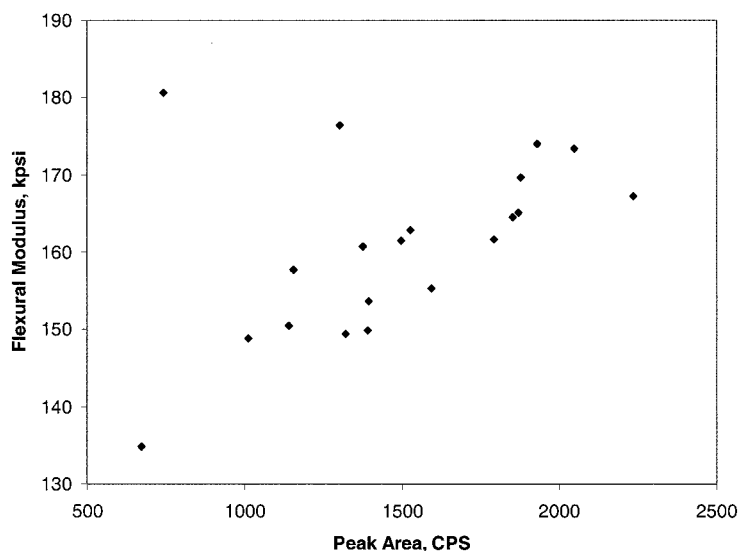


Figure 9 Comparison of flexural modulus properties and XRD peak intensity measurements of the largest clay basal reflection from a series of thermoplastic olefin nanocomposite materials.

identification of polymer intercalation can be muddled, especially by the presence of mixed-layered clay.

Even though XRD data is difficult to interpret, features in the diffraction pattern are easily quantified (e.g., peak areas and d -spacings). The simplistic approach is to compare these quantifiable features and attempt to use them as an indicator of performance. A comparison of the flexural modulus and d -spacing of the largest basal reflection is shown in Figure 8. These data are from the same set of materials discussed in Figure 5. All samples show an increase in the original d -spacing of the organo-clay used to prepare these materials. The materials with the larger d -spacing do appear to have a higher flexural modulus; however, the exact relationship is not clearly defined. A similar comparison of the flexural modulus and peak area of the largest basal reflection is shown in Figure 9. Intuitively, one would expect the flexural modulus to increase with better clay dispersion, thus, resulting in lower peak areas for these materials. The data in Figure 9 contradict this. More likely the materials with better dispersion have increased preferred orientation; thus accounting for the greater peak intensity.

CONCLUSION

The organo-clay dispersion and exfoliation in polymer nanocomposites can be evaluated using TEM. Both the particle density and the linear intercept provide a quantitative measure of the clay dispersion. The linear intercept measurement is slightly more useful because it can be compared to the theoretical limit for the completely exfoliated nanocomposite. XRD was found inferior in evaluating both organo-clay dispersion and exfoliation in polymer nanocomposites. XRD cannot be used to quantify the dispersion. Dilution of the clay, preferred orientation, mixed-layering, and other peak broadening factors make XRD characterization of polymer nanocomposites susceptible to errors.

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