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Characterization of Nanoclay Nanocomposites

By

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Abstract

One of the challenges encountered when characterizing nanocomposites is quantifying the levels of dispersion and exfoliation. This paper attempts to take into consideration many of the relevant methods currently available to the producer of nanocomposites as a guide to the limitations and successes seen with each basic analytical system. The samples used in this study were created at an independent lab using a sonic mixer and contain different levels of nanoclay loading. The samples were subsequently evaluated using multiple techniques to try to determine the level of exfoliation and dispersion of the nanoclay through a polyester base resin. While there is currently no single system that can describe both the levels of exfoliation and dispersion of the nanoclays with complete certainty, some methods can impart more information than others. Of the analysis methods investigated, x-ray diffraction coupled with TEM microscope analysis appears to be the most reliable and is currently the most often used to examine clay containing nanocomposites. However, this study shows that TGA coupled with particle size analysis and x-ray diffraction could be a more global method to quantify levels of dispersion and exfoliation when coupled with TEM analysis for local visual confirmation.

Introduction

The aim of this study was to examine current commons approaches to analyzing resin containing nanoclays with the goal of determining a method to quantify the level of dispersion and exfoliation of the nanoclay in the samples.

Dispersion is a measure of how thoroughly mixed the clay is with the resin. Analysis techniques try to determine that the clay is evenly distributed amongst the resin by examining for locations where there is no clay present. Exfoliation is a measure of how separated the nanoclay platelets are. Analysis techniques attempt to quantify the number of platelets in each particle or determine the average spacing between platelets.

Understanding the level of dispersion and exfoliation is important to properly analyze how well a process is performing. In many cases, clays are added to improve barrier properties which if they are sheared into singular platelets (fully exfoliated), less material would be necessary to achieve a required level of permeation. These platelets would also need to be well dispersed to ensure that every location has the same number of platelets for uniformity in barrier properties.

The samples examined were Closite 30B clay from Southern Clay in a polyester resin CCP Stypol 040-8086. They were created at an independent test lab using a Sonolator sonic mixer. The clay was loaded at 3%, 6.5%, or 10% and then passed through the sonolator a number of times to induce both dispersion and exfoliation. A sonolator generates eddy currents to shear the platelets apart by forcing the resin/clay mixture over a sharp blade.

The samples produced were labeled based on weight percent of clay added to the polyester and number of passes the resin and clay made through the high pressure sonolator. Five specimens were made in this manner: 3%-5p, 3%-7p, 6.5%-5p, 6.5%-10p, and 10%-6p. There was also a neat resin sample which was casted from the same batch of resin for comparison.

The samples were then analyzed using a variety of methods including X-ray diffraction, TGA, TEM, EDAX, ESEM, and SEM analysis.

Theory

X-Ray Diffraction

This analytical tool probes the crystal lattice structure of the nanocomposite. An x-ray is projected into the sample. The distance between the waves as they exit the sample is due to the diffraction of the waves by the basal plane. This d-spacing refers to the spacing between planes of the crystal lattice. When different lattice structures or spacings between platelets are present, there will be multiple peaks on the resulting graph.

Transmission Electron Microscopy (TEM)

This analytical tool is fashioned after a traditional light microscope. However, instead of transmitting light it uses electron beams which can give a higher resolution picture due to the decrease in wavelength. An electron gun emits an electron beam which moves through a condenser aperture and then bombards the specimen. The beam that passes through the sample is then filtered and magnified. The electrons impact a phosphor screen which allows for the viewing of the image.

Scanning Electron Microscopy (SEM)

This analytical tool can be used to view samples in three dimensions. The scanning electron microscope differs from the TEM by the fact that the beam is used to scan across the surface of the specimen. Secondary electrons are released from the specimen due to the increased energy are then detected by a phosphor screen producing the image shown.

Environmental Scanning Electron Microscopy (ESEM)

This analytical tool is similar to SEM but allows for the manipulation of environment parameters such as temperature, pressure, humidity, and composition of the ambient gas or liquid. It also allows for a non-conductive sample to be viewed without sputter coating provided the sample does not retain the increase energy generate by bombarding the specimen. This often causes the sample to product artifacts resembling a glow known as charging.

Electron Dispersive X-ray Spectroscopy (EDS/EDAX)

This analytical tool utilizes energy dispersive x-ray analysis. The atoms are bombarded with electrons from the beam in the scanning electron microscope. This energy knocks off some of the electrons in the atoms. The energy that is required to knock off electrons is recorded and allows for the atom composition of the sample to be recorded.

Thermogravimetric Analysis (TGA)

This analytical method utilizes a sensitive balance to determine weight loss of a sample through a range a temperatures. A sample is loaded onto a pan and then place on the balance. A furnace then encloses the sample and the temperature can be increase at a given rate and in a given environment. The constituents of the sample will burn off at different rates making the weight percents of the constituents determinable.

Results

X-Ray Diffraction

Figure 1 contains plots for three different samples: 10%-6p, 6.5-5p, and 3%-7p. The three plots were overlaid to highlight to the differences between samples. The optimum graph of results has no discernable peaks. If a peak is shown, the spacing between platelets can be determined and is shown in angstroms on the abscissa; however, if no peak is shown the spacing between platelets is large, meaning that the platelets are singular. As seen in Figure 1, the sample with 3% and 6.5% loading exhibit this behavior. However, the sample with 10% loading has a deviation from the desired graph around 44 angstroms. This is said to correspond with large clumps of platelets. This can only be confirmed with further microscopic analysis.

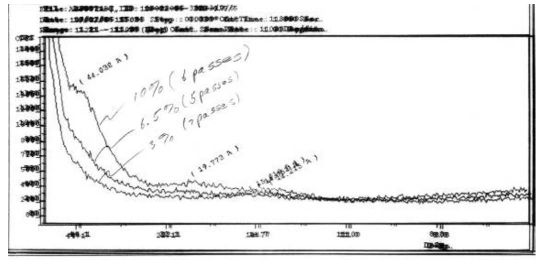

Figure 1 – X-Ray diffraction results Samples 3%-7p, 6.5%-5p, 10%-6p

TEM

Most of the time was spent analyzing the samples using TEM. Three samples were viewed using this method: 6.5%-5p, 6.5%-10p, and 10%-6p. The TEM gave a clear overview of the sample to determine dispersion as shown in Figure 2. However, it is very difficult to say definitively whether this is good dispersion or poor dispersion. The spots that seem to be light on particle could merely have better exfoliation in that area. Figure 3 shows a close up of one particle to show that it is possible to count platelets on individual particles with TEM, the software at the NEST laboratory also allows for the calculation of distances between platelets.

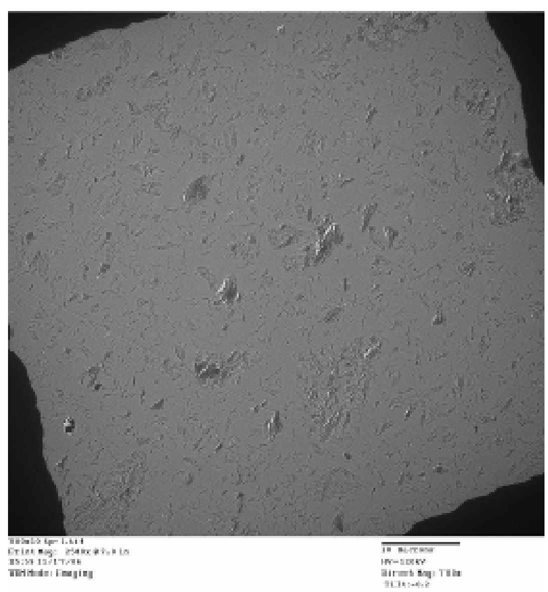

Figure 2 – 700x Sample 10%-6p

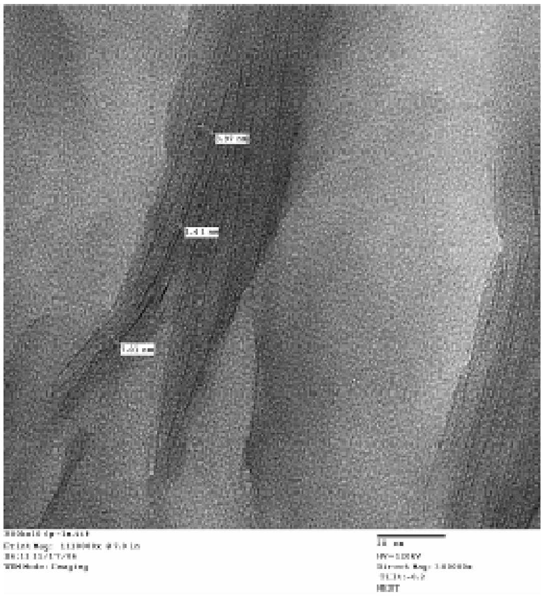

Figure 3 – 300,000x Sample 10%-6p

Figures 4 and 5 have the same loading of nanoclay of weight but look very different. This is most likely due to the difference in dispersion. Both specimens have the same amount of clay loading; however, the specimen shown in Figure 5 seems to have many more particles. One possible explanation for this is that the two specimens were not microtomed to the same thickness. Microtoming is a process which uses a diamond knife to make small slivers of specimens. The machine itself can be set to microtome a certain thickness (50nm) but it is not always the thickness that is actually achieved. If one sample is thicker than the other, the number of visible particle will increase due to the lack of transmission of electrons through the clay. This can skew the results making Figure 5 seem like there are more particle packed together when in fact the two specimens could truly have the same dispersion.

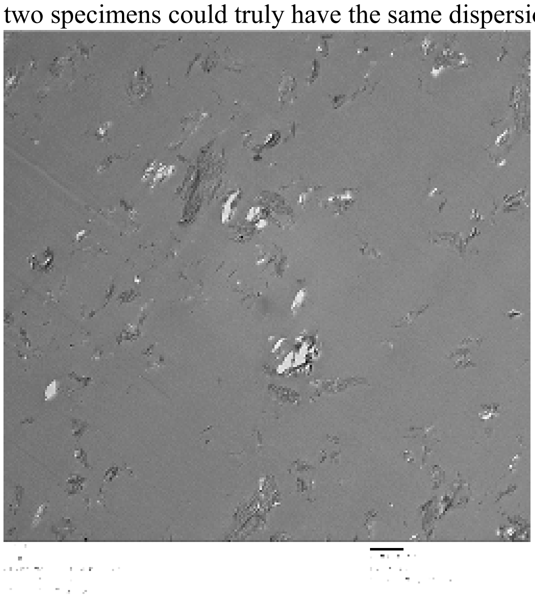

Figure 4 – 1000x Sample 6.5%-5p

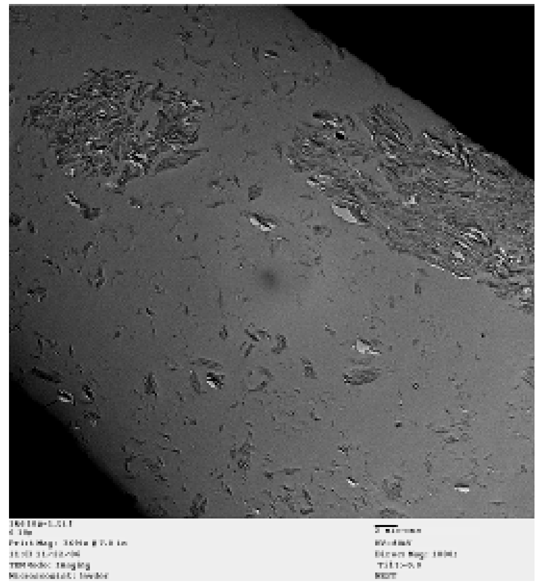

Figure 5 – 1500x Sample 6.5%-10p

In Figures 6 and 7, two parts of the same specimen are viewed. In Figure 7, there is a big area (1 micron squared) that has no visible nanoparticles at all. All around the empty resin are big groups of platelets. In another portion of the specimen, seen in Figure 6 (<1mm from this first point), the dispersion and exfoliation seems to be more desirable.

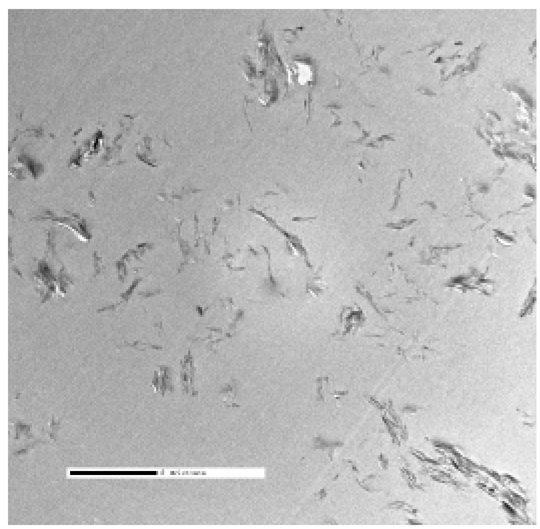

Figure 6 – 4000x Sample 6.5%-10p

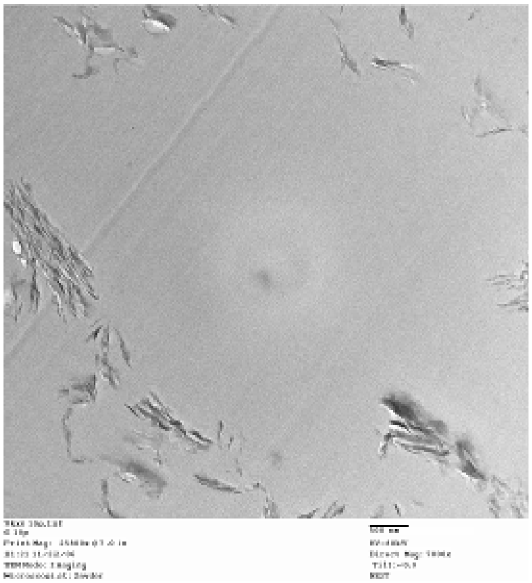

Figure 7 – 7000x Sample 6.5%-10p

In Figures 8 and 9, the specimens were zoomed in on to try to determine if increasing the number of passes through the sonolator increases the amount of exfoliation. It seems in Figure 9 that the largest particles are smaller and contain fewer platelets. Overall, the two samples seem to have the same average size particles. However, as seen previously in Figure 5, it is hard to determine whether or not this is true throughout the specimen.

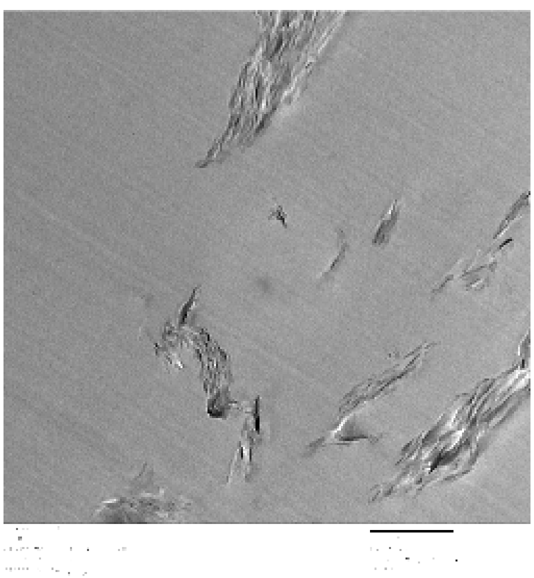

Figure 8 – 15000x Sample 6.5%-5p

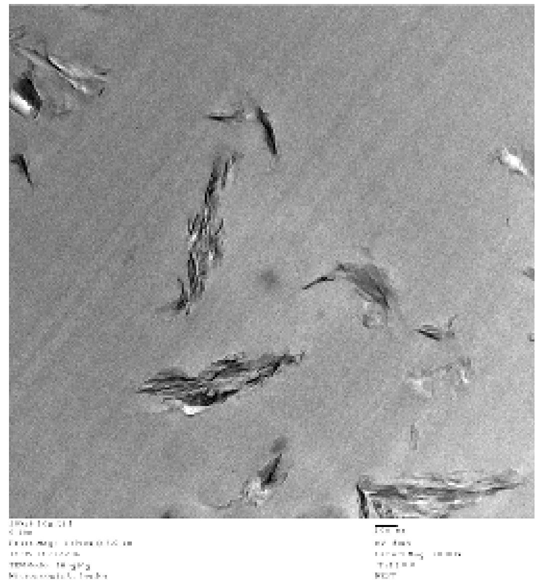

Figure 9 – 20000x Sample 6.5%-10p

SEM

A high resolution SEM was also used to view the specimens. This required the use of sputter coating to make the sample surface conductive. The SEM produced great pictures at low resolutions but failed to provide the detail required to accurately determine the exfoliation of particles. The pictures do however give a much better feel of the particles in 3-D space. Figure 10 shows the dispersion of the nanoparticles. Figure 11 demonstrates the resolution achievable by the SEM, but also shows that determination of the exfoliation of particles using SEM is very difficult.

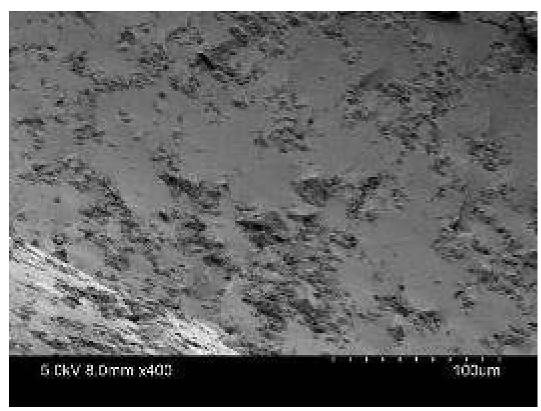

Figure 10 – 400x Sample 3%-5p

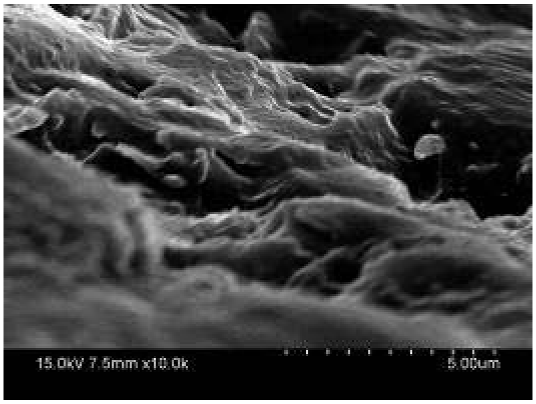

Figure 11 – 10000x Fracture surface of Sample 3%-5p

ESEM

The images produced by the ESEM were largely unhelpful. At first, the standard aperture was used and a lot of charging was seen. Then, the sample was sputter coated and the aperture was switched to a variable pressure aperture to eliminate the charging. Figure 12 is similar to the micrograph obtained in the SEM at a low magnification. As shown in Figure 13, the images that were produced did not have resolution sufficient to determine platelet count on any particles.

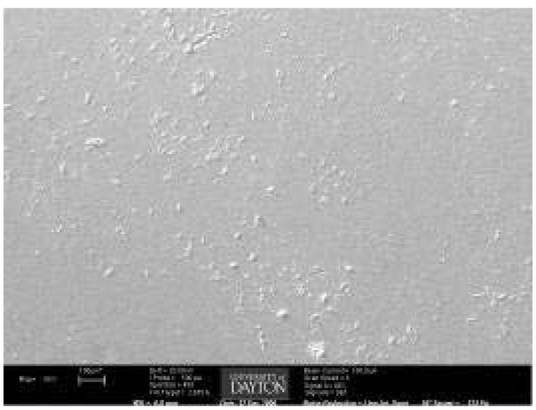

Figure 12 – 55x of sample 3%-5p

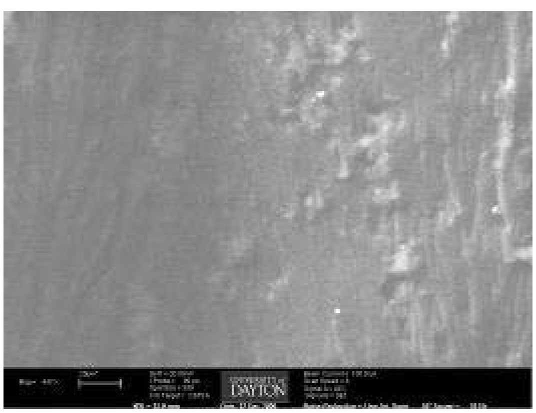

Figure 13 - 447x of sample 3%-5p

EDAX

The EDAX was used to explore its dispersion characterization capabilities by comparing one area of a sample to another and comparing the relative amounts of an atom specific to the clay such as silicon. This looks promising as one can pick individual parts of the screen to capture data from. The counts of silicon present in different specimens from one sample or in different locations within the same specimen may be related to the amount of clay in that part of the sample. This may be a technology that can be used to quickly determine clay dispersion in the future. The preparation of these samples is much less tedious than the preparation of TEM specimens. A graph showing the capability of the EDAX follows:

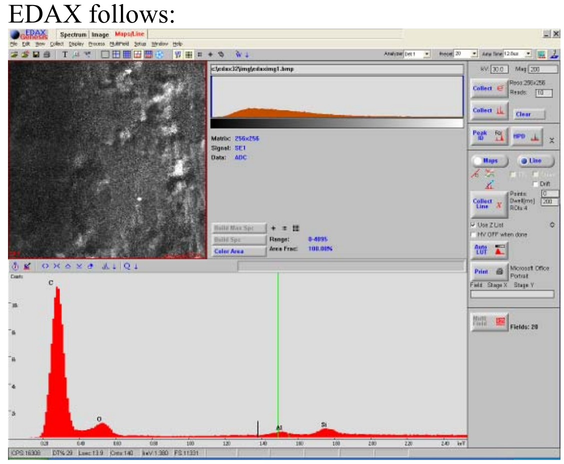

Figure 14 – EDAX graph from one portion of 3%-5p sample

TGA

TGA analysis was performed on 3 samples: neat resin, 3% - 7P, and 6.5% - 10P. The 3% - 7P sample was repeated 3 times to show repeatability. As seen in Table 1, the weight loss of each of the samples is roughly the same and does not correlate with the amount of nanoclay present in the sample.

Sample	Initial Weight of Sample (mg)	Residual (%)
Neat Resin	8.01	6.32
3% - 7P -1	4.70	6.72
3% - 7P -2	5.15	7.10
3% - 7P -3	9.22	6.94
6.5% - 10P	8.46	8.63

Table 1 – TGA analysis results

However, the derivative of the weight loss per degree Celsius change separates the samples based on nanoclay weight as shown in Figure 15. The polyester containing nanoclay begins burning off at a slightly lower temperature when compared to the neat polyester resin sample. Also, the derivative of the weight loss per temperature change shows that the samples containing nanoclay loss weight at a slower rate. This is repeatable as both the weight loss and the derivative of the weight loss with respect to temperature are almost identical for the three trials for the sample 3% - 7P regardless of initial sample weight. The amount of change seen in weight loss and its derivative that occur between sample containing differing weight percentages of clay do not have a linear relationship with respect to weight percent and therefore must be impacted by the extent of exfoliation.

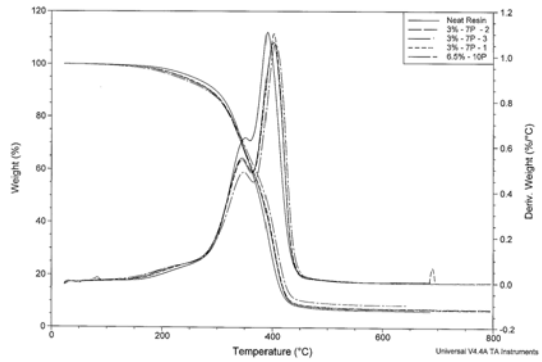

Figure 15 – TGA analysis of various samples

During the TGA experiments, a condensation particle counter was placed 1 inch from the outlet of the furnace. This particle counter condenses isopropyl alcohol on the surface of sub-micron particle in order to grow them to the point where an optical particle counter can sense it. It can be seen in Figure 16 that the amount of nanoparticles given off during the TGA experiments. In every case, nanoparticles are emitted during the weight loss portion of the TGA experiment.

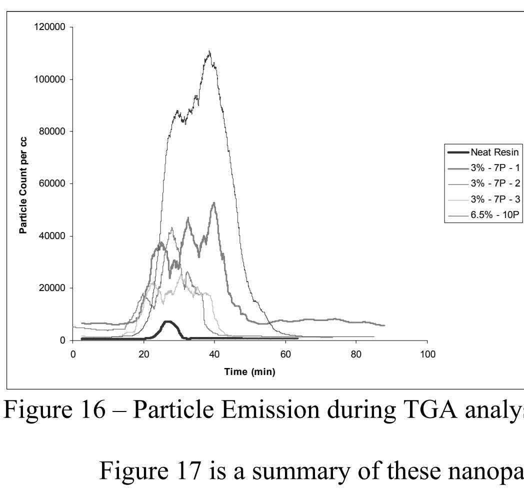

Figure 16 – Particle Emission during TGA analysis

Figure 17 is a summary of these nanoparticle emissions over the peak region which occurs during the weight loss of the sample. It can be seen that the average particle count increases linearly with weight percent of nanoclay in the sample.

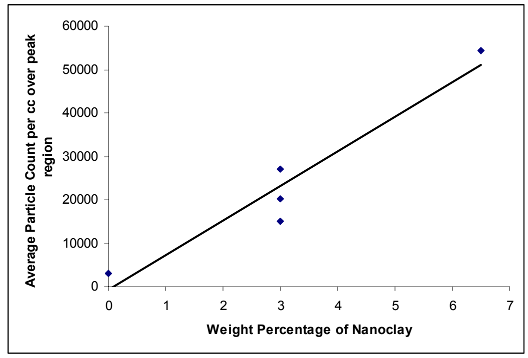

Figure 17 – Nanoparticle emissions based on weight percent of nanoclay

Discussion

From the analysis of these samples, it seems as though from the TEM pictures it can be assumed that increasing the number of passes of the samples through the sonolator increases the exfoliation seen in the sample. This could be confirmed with further tests involving x-ray diffraction of various numbers of passes at the same clay loading.

It also seems from the TEM that when the clay loading was increased from 6.5% to 10% while maintaining a similar number of passes, the average individual particle size increased. This is likely due to the increased contact between the smaller particles which then agglomerated.

The SEM and ESEM analysis yielded very good 3-D images of the fracture surface of the material but was of little use in determining the exfoliation of the particles due to the lack of resolution at higher magnitudes. The views which could be used for dispersion were just as easily obtained in the TEM analysis.

The EDAX analysis was able to show that the clay particles were detectable using the technology. Further analysis of this equipment may be required to fully explore its potential in regards to nanoclay analysis.

TGA analysis seems to be able to stratify the samples on a global level based on weight loss and its derivative. Although individual particles are not seen and analyzed for exfoliation, the weight loss characteristics of the samples change based on the weight percent of nanoclay and possibly based on the extent of exfoliation. The number of nanoparticles given off during TGA testing seems to echo the clay content in the samples. Also, multiple TGA experiments could be run to determine level of dispersion. If the results are exactly duplicated over several test specimens taken from different location in the sample, the sample can be described as perfectly dispersed.

The one downside with this method it that is requires many iterations to determine the correlation between exfoliation and change in weight loss characteristics seen through TGA analysis. This link can only be confirmed by methods which determines exfoliation locally such as TEM or by x-ray diffraction. Once this link is established, this method could then be used as a relatively quick method of determining quantitatively the levels of dispersion and exfoliation.

A good regiment to characterize nanoclay containing composites to quantify dispersion is x-ray diffraction, followed by multiple iterations of TGA analysis and particle sizing, with confirmation via TEM. The x-ray diffraction will determine global exfoliation. Multiple iterations of TGA analysis will determine the level of dispersion. Particle Size analysis should also confirm weight percentage contained in the sample as well as determine the range of particle sizes which can be helpful in determining whether or not the particles are all roughly the same size. TEM will give confirmation of all results on the local scale.

Recommendations

The samples that were prepared did not distinguish the effect of the sonolator. There were no samples prepared with less than 5 passes through the sonolator and the difference between samples prepared with 5 passes and those prepared with 10 passes were almost indistinguishable. Sample containing the nanoclays but with 0, 1, and 3 passes through the sonolator would be useful in determining the effect of the sonolator process.

A further investigation into the EDAX equipment may be fruitful as specimen preparation for the EDAX is minimal. If this technology is able to reliably compare two areas and their relative clay loadings, it could be used to distinguish between at least relative dispersions. However, EDAX is not generally used in the characterization of nanoclays.

Using a Scanning Mobility Particle Sizer or similar equipment to size the nanoparticles generated during the TGA test, as well as determine count, could help to determine the size distribution of the particles. The size distribution could help with quantification of exfoliation. Further experimentation utilizing TGA and particle size technology could firm links between TGA results, emitted nanoparticle size and number, nanoclay content by weight, dispersion, and exfoliation.