

# **Dispersion of Nanoclay in Linear Low-Density Polyethylene (LLDPE) and Maleated Linear Low-Density Polyethylene (LLDPE-g-MA) in Supercritical Carbon Dioxide**

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## **Abstract**

Addition of nanoclay to polymer is often desirable due to the ability of the nanoclay to improve the thermo-mechanical and barrier properties as well as flame retardancy of the polymer. The degree of property enhancement by the nanoclay is largely dependent on how well it is dispersed throughout the polymeric system. However, complete or nearly complete dispersion is difficult to achieve. Supercritical carbon dioxide is one technique that has the potential to achieve a high level of dispersion. Organo-nanoclay Cloisite 93A dispersion was attempted in linear low-density polyethylene (LLDPE) and linear low-density polyethylene grafted with maleic anhydride (LLDPE-g-MA) via supercritical carbon dioxide at various processing conditions. According to x-ray diffraction (XRD) analysis, both LLDPE and LLDPE-g-MA pellets experience nanoclay dispersion into the pellet, but these polymers have different run conditions that result in a better nanocomposite. This is most likely due to the grafted maleic anhydride that increases the compatibility between LLDPE and Cloisite 93A. Besides being a means of effective dispersion, it is conceivable that supercritical carbon dioxide may be used to exfoliate nanoclays which can further enhance the resultant nanocomposite properties.

## **Introduction**

The need is increasing for polymers to have their properties tailored for specified applications. One way to tailor the properties of a polymer would be to add fillers to it. A useful filler to enhance a polymer's mechanical, thermo-mechanical and barrier properties is nanoclay<sup>1-5</sup>. Nanoclays are environmentally friendly, in ample supply, and inexpensive<sup>4,6</sup>. Nanoclays have a high interfacial area when intercalated or exfoliated and thus the ability to greatly enhance a polymer's properties at low loadings<sup>1,2,6</sup>. The difficulty with nanoclays is completely exfoliating and uniformly dispersing them throughout the polymer matrix in order to achieve the maximum level of enhancement<sup>1,7</sup>. One method to increase the possibility of intercalation and exfoliation of nanoclays is to modify them to be compatible with the desired polymer matrix or processing medium. This article will focus on using modified nanoclays that are compatible with the processing medium.

Supercritical fluids pose a unique processing environment because they have a liquid-like density and a gas-like diffusivity, making them tunable fluids<sup>1,8</sup>. Carbon dioxide is an advantageous supercritical fluid and processing medium because it has a low toxicity, is highly abundant, inexpensive, non-combustible, and has easily achievable critical conditions ( $T_C =$

31.1°C,  $P_c = 7.4\text{MPa}$ )<sup>1,8,9</sup>. Supercritical carbon dioxide (scCO<sub>2</sub>) has been successfully used for a wide variety of applications such as extraction, purification, precision cleaning<sup>9</sup>, depolymerization, polymer grafting<sup>10</sup> and producing polymer membranes<sup>8</sup>. In addition to these applications, supercritical carbon dioxide has also been used to infuse different materials into polymers<sup>11</sup> and to exfoliate nanoclays<sup>1</sup>. Some polymers tend to swell in supercritical carbon dioxide<sup>11</sup>, which allows particles of materials that are soluble in this medium to more easily infuse into the swollen polymeric matrix. One such example of this is the infusion of sodium nitrite into a biodegradable polymer<sup>11</sup>. And when nanoclays are in a supercritical carbon dioxide medium, the carbon dioxide molecules can infuse between the intercalated clay platelets and break them apart into an exfoliated structure as they expand during depressurization<sup>1</sup>. Other techniques have been employed to aid in the delamination of clays within a polymer such as melt compounding<sup>3,7</sup>, extrusion<sup>2,7</sup>, solution casting, and *in-situ* polymerization<sup>1,2,8</sup>.

This article is concerned with the infusion of modified organic nanoclays into linear low-density polyethylene (LLDPE) and linear low-density polyethylene grafted with maleic anhydride (LLDPE-g-MA). The graft copolymer of LLDPE-g-MA was chosen for this study because maleic anhydride modifications are reported to aid in the dispersion of clay in a polymeric matrix<sup>3,7</sup>. Organo-nanoclay Cloisite 93A was chosen for this experiment because it has a high affinity for supercritical carbon dioxide as compared to other nanoclays, allowing easier transport from this medium into the polymer.

Clays have been successfully exfoliated and powders have been infused into polymers using scCO<sub>2</sub>. The purpose of this study is to determine if clay can be infused into LLDPE or LLDPE-g-MA using scCO<sub>2</sub>. Later, it will be tested if the two processes of exfoliating the clay and then infusing it into LLDPE or LLDPE-g-MA can be combined into one step. Once infusion is determined to have occurred, exfoliation and uniform dispersion of the nanoclay will be attempted.

## Experimental

### **Materials**

Cloisite 93A was obtained from Southern Clay Products, Inc. A quaternary ammonium salt (methyl, dehydrogenated tallow ammonium) modifies natural montmorillonite to create Cloisite 93A. The modifier concentration is 90meq/100g of clay. Ninety percent of the particles by volume are less than 13µm, 50% are less than 6µm, and 10% are less than 2µm. And the density of the clay is 1.88g/cc. All clay is dried at a temperature around 80°C in an oven for at least 24 hours before processing.

The polymers used in this experiment were linear low-density polyethylene (LLDPE, Dowlex 2517) and linear low-density polyethylene grafted with maleic anhydride (LLDPE-g-MA, Polybond® 3109). The LLDPE is in pellet form and has a melting point of 124°C, a specific gravity of 0.917 and a melt flow index of 25g/10min. The LLDPE-g-MA is in the also in the form of pellets with a density of 0.926g/cc and a melt flow index of 30g/10min. The grafting level of maleic anhydride is 1wt% in LLDPE-g-MA and the melting point is 123°C.

### **Processing Procedure**

The polymer samples and Cloisite 93A are placed in a stainless steel thimble and mechanically mixed until the polymer is thoroughly coated with the clay. Ten grams of the polymer and 2.5g of Cloisite 93A were used, giving a respective weight ratio of 4 to 1. The thimble is then put inside a stainless steel reactor with an impeller that is turned using a MagneDrive®. Cooling water is sent through the head of the reactor to help control the temperature. The impeller is started during heating to help keep the environment a uniform temperature. The impeller is kept at around 300rev/min. Once the desired temperature and pressure are attained, the run time is started. All runs have a run time of 3 hours and are carried out in a batch mode. After the run is complete, the reactor is depressurized. The processing conditions are displayed in Table 1.

**Table 1.** Processing Conditions in scCO<sub>2</sub> for Polymer-Clay Nanocomposites

<b>Run</b>	<b>T (°C)</b>	<b>P (MPa)</b>	<b>Wt. Ratio (Clay:Polymer)</b>
1	60.0	10.3	0.25 : 1
2	98.9	10.3	0.25 : 1
3	60.0	17.2	0.25 : 1
4	98.9	17.2	0.25 : 1
5*	98.9	17.2	0 : 1

\* LLDPE-g-MA only

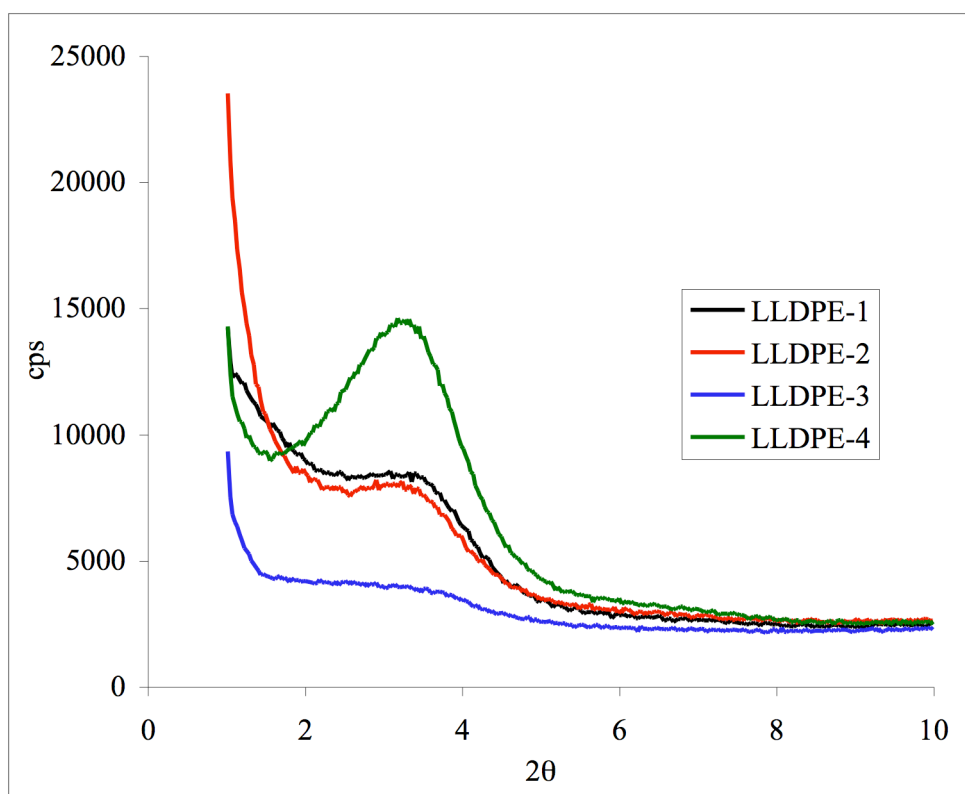
### **Characterization**

The infused polymer pellets are formed into coins that are 1mm thick so they can be analyzed by x-ray diffraction (XRD). The coins are made by heating them on a metal plate at 195°C until they are completely melted. Then a heated metal plate is placed on top of this lower plate with spacers in between them. This top plate is held in place until the polymer is hardened and the coin can be removed. All XRD analysis was done with a Philips X-Pert diffractometer with a Cu K $\alpha_1$  radiation source having a wavelength of 0.154056nm. The generator voltage was 45kV and the tube current was 40mA. The XRD data angle range was from 1° to 10° with an increment of 2 $\theta$ .

Differential scanning calorimetry (DSC) analysis was conducted on LLDPE-g-MA nanocomposite samples that weighed between 5 and 10mg. The instrument is a TA DSC 2010 that performs its analysis on the sample in a nitrogen environment. The nanocomposites are heated from room temperature to 190°C at a rate of 10°C/min. This temperature is held for three minutes and then the samples are cooled at the same rate to about 35°C. The same heating/cooling processes are then repeated again and the data is collected. The first heating/cooling is to remove any thermal history within the sample. The second heating/cooling is to obtain the melting and crystallization temperatures. The pressure is at typical atmospheric conditions.

## Results and Discussion

Cloisite 93A was processed with LLDPE in supercritical carbon dioxide. Four different run conditions were investigated in order to see if infusion occurred at any of these conditions and which conditions were best for the possible infusion. XRD analysis was conducted on the polymer pellets to determine if infusion had occurred. Cloisite 93A creates a peak on the XRD plot at a Bragg angle around  $3.4^\circ$  which corresponds to a  $d_{001}$ -spacing of  $2.59\text{nm}$ <sup>3</sup>. All runs display similar peaks around the same angle, indicating that infusion of Cloisite 93A occurred<sup>1,2,3,12</sup>. The sample LLDPE-3 has the lowest almost non-existent peak, which could indicate either the clay is well dispersed or almost no clay is in the polymer<sup>1,2,3,6</sup>, most likely the latter. Runs 1, 2 and 4 have clear peaks from the Cloisite 93A with  $d_{001}$ -spacings respectively of  $2.73$ ,  $2.81$ , and  $2.73\text{nm}$ . The increase in  $d_{001}$ -spacings as compared to pure Cloisite 93A could be due to the  $\text{scCO}_2$  and/or polymer diffusing in between the platelets and pushing them apart, making them closer to an exfoliated structure<sup>1,2,3,6,7</sup>. Sample LLDPE-2 with a low pressure and a high temperature had the largest increase in spacing between platelets. This sample experiences an increased platelet spacing possibly since the  $\text{CO}_2$  molecules and polymer chains are more mobile in a low pressure environment, making it easier for them to work their way between the platelets. And the high temperature helps the infusion of clay by softening the polymer. According to Horsch et al.<sup>1</sup>, larger intensities in XRD peaks can indicate an increase in tactoid size and parallel registry of the clay. The run with the highest conditions (LLDPE-4) had the largest peak intensity, possibly indicating that this environment could create larger clay tactoids within the polymer. The two low-pressure runs with similar peaks had a lower intensity, which might indicate that lower pressures create smaller tactoids and more exfoliated clay structures within the polymer. Figure 1 contains the XRD plot of LLDPE-Cloisite 93A nanocomposites.



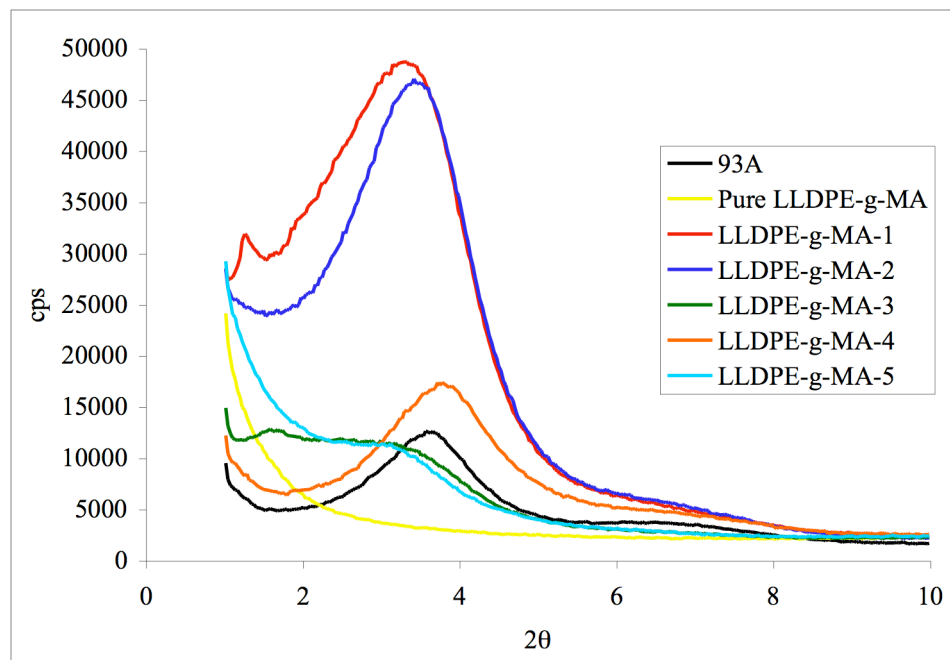
**Figure 1.** XRD Plot of LLDPE Processed with Cloisite 93A at Various Conditions (Pure Cloisite 93A Plot Left Off so Nanocomposite Peaks Could be Seen)

LLDPE-g-MA pellets were processed with Cloisite 93A in  $scCO_2$  at various temperatures and pressures. The resultant polymer was then analyzed using DSC and XRD. Differential scanning calorimetry analysis revealed that the melting temperature of the LLDPE-g-MA after  $scCO_2$  processing with Cloisite 93A was altered by a maximum of  $0.46^\circ C$  (LLDPE-g-MA-1) and that the crystallization temperature changed by a maximum of  $0.80^\circ C$  (LLDPE-g-MA-2). The changes seen from the addition of the nanoclay to the LLDPE-g-MA are not very significant, leading one to infer that the processing conditions of the nanocomposite should not change much from those for pure LLDPE-g-MA. Melting and crystallization temperatures for the nanocomposites are summarized in Table 2.

**Table 2.** Melting Point ( $T_{mp}$ ) and Crystallization Point ( $T_{cp}$ ) of LLDPE-g-MA-Cloisite 93A Nanocomposites Measured by DSC Analysis

Sample	$T_{mp}$ ( $^\circ C$ )	$T_{cp}$ ( $^\circ C$ )
Pure LLDPE-g-MA	122.58	108.67
LLDPE-g-MA-1	122.12	108.83
LLDPE-g-MA-2	122.56	109.47
LLDPE-g-MA-3	122.47	108.93
LLDPE-g-MA-4	122.66	109.08
LLDPE-g-MA-5	122.60	108.85

From the XRD analysis, it is apparent that 93A was successfully infused into the LLDPE-g-MA for run conditions 1, 2 and 4 since the 93A peak is present<sup>1,2,3,12</sup> (Figure 2). Runs 3 and 5 exhibit slight peaks in the XRD plot. But at this time it is unknown what the peak for run 5 is from, especially since run 5 was processed without 93A. The peak could be from the breakdown of maleic anhydride or some residual clay in the system could have found its way into the LLDPE-g-MA in run 5. Concerning the peak found in LDPEMA-3, a possible scenario could be that the clay is almost completely dispersed, giving little to no peak in the plot<sup>1,2,3,6</sup>. The  $d_{001}$ -spacings for the clay peaks found in runs 1, 2, and 4 are respectively, +0.24nm, +0.15nm, and -0.10nm in relation to that of 2.44nm for 93A<sup>3</sup>. These differences in distances may not be very large, but may still be significant, as a trend seems to exist. The  $d_{001}$ -spacings indicate that in runs 1 and 2, where the pressure was low, the spacing between clay platelets increased due to processing. In run 1, the lowest temperature and pressure environment, the largest increase in spacing between clay platelets occurred. Run 2 might not have realized such a large increase in spacing because the high temperature could have degraded the clay modifier<sup>1</sup>, working against the  $scCO_2$  and polymer getting between the platelets to expand the gap. And at a higher pressure seen in run 4, the spacing between clay platelets decreased. This decrease in spacing might in fact be due more to the high processing temperature also used in this run that could have caused the clay to lose some of its modifier<sup>1</sup>. Also, the higher pressure environment could have made the polymer chains less mobile so fewer were able to intercalate with the nanoclay particles. The increase in distance between platelets is favored over a decrease because it can indicate that polymer has found its way between the platelets, bringing the clay closer to an exfoliated structure<sup>1,2,3,6,7</sup>.



**Figure 2.** XRD Plot of LLDPE-g-MA Processed with Cloisite 93A at Various Conditions

## Conclusion

Indicated by XRD analysis, Cloisite 93A was successfully infused into both LLDPE and LLDPE-g-MA using supercritical carbon dioxide. Different peak relations are seen between LLDPE and LLDPE-g-MA because the grafted maleic anhydride alters the transport of the clay particles. The high temperature and low pressure run for LLDPE had the largest increase in spacing between clay platelets, indicating that these conditions for LLDPE are better when trying to achieve an intercalated or exfoliated clay structure. For LLDPE-g-MA nanocomposites, the melting and crystallization temperatures remained near to those for pure LLDPE-g-MA, revealing that the processing conditions of the nanocomposites should be similar as those for pure LLDPE-g-MA. LLDPE-g-MA experienced its best infusion conditions on the low temperature and pressure run, since the clay had the largest separation between platelets, bringing the process closer to clay intercalation or exfoliation. It is proposed that the maleic anhydride in LLDPE-g-MA allows the clay to more easily transport into the polymer at a lower temperature than that for LLDPE, which is why the largest separation between clay platelets was seen in a low temperature run for LLDPE-g-MA as opposed to a high temperature run for LLDPE. And a lower temperature would degrade less of the clay modifier, giving LLDPE-g-MA an advantage over LLDPE when using modified clays. In the future, FT-IR analysis will be used to determine the percentage of clay infused and TEM analysis will be used to help determine the degree of exfoliation of clay.

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