

Quantitative Analysis of Cloisite 93A Infused into Linear Low-Density Polyethylene and Maleated Linear Low-Density Polyethylene in a Supercritical Carbon Dioxide Medium

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ABSTRACT: Linear low-density polyethylene (LLDPE) is a widely used polymer that can benefit from the enhanced barrier, thermal, and mechanical properties offered by nanoclay fillers. However, optimal property enhancement requires complete exfoliation and uniform dispersion, both of which are difficult to achieve with nanoclay fillers. Supercritical carbon dioxide (scCO₂) processing is an inexpensive and environmentally benign method for exfoliating and dispersing clays into polymers. In a scCO₂ medium under controlled environments, the organically modified clay Cloisite 93A was infused into LLDPE and maleated linear low-density polyethylene (LLDPE-g-MA).

Upon microscopic inspection, it was evident that clay infusion was achieved near the surface of the polymer pellet, but no clay found its way into the interior of the pellet. In this article, we describe an analytical method for determining the amount of nanoclay infused into a polymer matrix via Fourier transform infrared analysis. Using this method, we determined the weight percentage of Cloisite 93A infused into LLDPE and LLDPE-g-MA. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3329–3333, 2012

Key words: compatibilization; FT-IR; nanocomposites; organoclay; polyethylene (PE)

INTRODUCTION

Property enhancements to commonly used polymers are possible with the addition or incorporation of nanoclay fillers; this incorporation results in enhancements in the barrier, thermal, and mechanical properties^{1–5} at low clay loadings. Abundant in nature, clays are inexpensive and environmentally friendly.^{4,6} Inherently, clays are in a stacked platelet configuration and agglomerated but offer many more polymer property enhancements when exfoliated into individual layers and homogeneously dispersed throughout a polymer matrix.^{1,2,6–8} However, individually and simultaneously, homogeneous distribution and clay platelet delamination is difficult to attain.^{1,7}

The incorporation of modified clays with modified polymers has the potential to increase the degree of exfoliation and dispersion of clay into a polymer matrix. This is possible because of the increased compatibility between the filler and the matrix that the modifications offer.^{1,3,6,7} With increased material compatibility, the clay is capable of imparting more of its properties onto the host polymer. Ryu and

Chang⁷ discovered that exfoliation was achieved when 10 wt % polyethylene modified with maleic anhydride (MA) was processed with clay and linear low-density polyethylene (LLDPE) in an internal mixer. The tensile modulus of the nanocomposites with various concentrations of maleated polyethylene increased by 40–50%, which the authors attributed to an increase in clay dispersion.⁷ Transmission electron microscopy analysis revealed to Peprnicek et al.⁹ that the organically modified clays (Cloisite 30B and Cloisite 93A) had a higher degree of intercalation and/or exfoliation than the unmodified clay (Cloisite Na⁺) in their poly(vinyl chloride)-paste/clay nanocomposites. However, in many cases, modified components alone have not been enough for the complete exfoliation and dispersion of clays.

The processing of nanoclays in supercritical carbon dioxide (scCO₂) is a method that has been successfully used to exfoliate nanoclays.¹ Exfoliation is accomplished when clay stacks are broken up into individual platelets by the expansion of scCO₂ molecules during depressurization.¹ This increases the clay-polymer interfacial area interaction, improving the transfer of properties from the clay to the polymer.^{1,2,6} In addition to exfoliating nanoclays, carbon dioxide is an environmentally friendly solvent that facilitates the infusion and dispersion of fine particles, such as powdered clay, into a polymer matrix

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by swelling the polymer.^{1,10,11} Supercritical carbon dioxide processing also keeps the organic component of a modified nanoclay in tact by operating at temperatures well below the decomposition temperature,^{2,3,5,12} which can start at temperatures as low as 160°C,¹² unlike temperatures seen with the use of melt mixers or extruders. When the clay modifications decompose, the subsequent molecules can then interact with the polymer matrix to adversely affect the resulting properties of the nanocomposite.¹² Furthermore, if degradation is avoided, the modification is still functional in allowing the clay to more easily disperse throughout the polymer and more efficiently transfer its properties to the polymer;^{2,12} this is a byproduct of the increased compatibility of the clay with the polymer.

In this study, LLDPE and maleated linear low-density polyethylene (LLDPE-g-MA) were processed with nanoclay Cloisite 93A in scCO₂ to assist in the infusion and dispersion of Cloisite 93A. Along with this new processing method and the confirmation of nanoclay infusion in scCO₂, an analytical technique was proposed and employed to determine the weight percentage of clay infused into a given polymer. The analytical technique was created out of necessity for a non-destructive method of analysis because of the low quantity of polymer/clay nanocomposite obtained from the scCO₂ infusion method with this setup.

EXPERIMENTAL

Materials

Southern Clay Products, Inc. (Gonzales, TX) supplied the organonano clay Cloisite 93A. The sizes of the clay particles by volume were as follows: 10% were less than 2 μm, 50% were less than 6 μm, and 90% were less than 13 μm in size. The room-temperature clay density was 1.88 g/cm³. Cloisite 93A is a natural montmorillonite that is modified with a quaternary ammonium salt (methyl, dihydrogenated tallow ammonium) in a concentration of 90 mequiv/100 g of clay. In comparison to other modified clays, Cloisite 93A has a greater compatibility with carbon dioxide.¹ Before the experiment, the Cloisite 93A underwent a drying process, where it was placed in an oven for 24 h at 80°C.

The LLDPE (Dowlex 2517, The Dow Chemical Company, Midland, MI) used in this work had a melting temperature of 124°C, a melt flow index of 2.5 g/min, and a specific gravity of 0.917 and was in the form of pellets. Also used in this experiment, the LLDPE-g-MA (Polybond 3109, Uniroyal Chemical Company, Middlebury, CT) had a MA graft level of 1 wt %. This graft polymer had a melting temperature of 123°C, a melt flow index of 3 g/min, and a density of 0.926 g/cm³ and was in pellet form. Also,

TABLE I
Polymer/Clay Nanocomposite scCO₂
Processing Conditions

Run	Pressure (MPa)	Temperature (°C)	Weight ratio (clay/polymer)
1	10.3	60.0	0.25 : 1
2	10.3	98.9	0.25 : 1
3	17.2	60.0	0.25 : 1
4	17.2	98.9	0.25 : 1

the MA modification made LLDPE-g-MA more compatible with the clay in comparison to the pristine LLDPE.^{3,5-7}

Preparation and processing procedure

We prepared the polymer/clay mixture by placing 10 g of polymer and 2.5 g of Cloisite 93A in a stainless steel thimble and mechanically mixing it until the polymer was thoroughly coated with the clay. The reactor used for the scCO₂ processing was a 300-cc autoclave reactor made of stainless steel 316 that was fitted with a magnetically driven impeller on the head of the reactor. During the experiment, we maintained a constant and uniform reactor temperature by flowing water through the reactor head and driving an impeller within the reactor, respectively. When the reactor reached the desired temperature and pressure, the experiment was deemed to have begun and was maintained in a batch mode for a duration of 3 h. Once the experiment reached completion, the reactor was rapidly depressurized into an open container, and the samples were recovered. Table I shows the experimental conditions.

Characterization

The amount of clay infused into the polymer samples was determined with the aid of Fourier transform infrared (FTIR) analysis. The equipment used was a Nicolet Nexus 470 FTIR ESP spectrometer (Nicolet Instrument Co., Madison, WI) that scanned the wave-number range from 400 to 4000 cm⁻¹ an average of four times. This spectrometer had a 4-cm⁻¹ resolution and a 1-cm absorption path length. Data from the spectrometer were collected with Omnic ESP 5.1 computer software (Nicolet Instrument Co., Madison, WI).

To determine the weight percentage of Cloisite 93A in the samples, initial calibration standards were made with a C. W. Brabender Instruments twin-screw extruder (South Hackensack, NJ) and an electric pelletizer. Used to estimate the quantity of clay in the processed samples, the first LLDPE/clay standards contained 0, 1, 5, and 13 wt % Cloisite 93A. Next, a batch mixer was used to produce LLDPE/clay calibration standards for determining precise amounts of

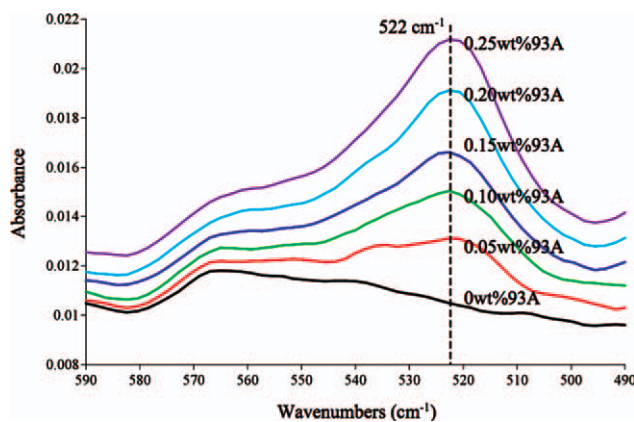


Figure 1 LLDPE/Cloisite 93A standard spectra with an absorbance peak at 522 cm^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

clay within the samples that had 0.25 wt % clay and less. These LLDPE/clay standards contained 0, 0.05, 0.10, 0.15, 0.20, and 0.25 wt % Cloisite 93A. Heated to 185°C, a Carver laboratory press (Carver model M) was used to create films for FTIR analysis by the compression of the polymer/clay samples at 10,000 psi for approximately 50 s. The LLDPE/Cloisite 93A films had thicknesses between 50 and 90 μm , and the LLDPE-g-MA/Cloisite 93A films had thicknesses ranging from 70 to 180 μm .

RESULTS AND DISCUSSION

FTIR method

Spectra obtained from the FTIR analysis of the calibration standards in conjunction with the resultant calibration curve were used to determine the amount of Cloisite 93A infused into the polymer. To accomplish this, the following technique adapted from Clark et al.¹³ was employed for calculating the weight percentage from the absorbance spectra. The absorbance for small concentrations of IR-absorbing species is approximated by the Beer–Lambert law:

$$A = \log\left(\frac{I_0}{I_T}\right) = \sum_i (K_i \delta C_i) \quad (1)$$

where A , I_0 , I_T , K_i , δ , and C_i are the absorbance, intensity of the incident IR beam, intensity of the transmitted IR beam, absorbance coefficient, absorbing layer thickness, and absorbing species concentration, respectively. In this technique, an absorbance equation with contributions from the clay and polymer was combined with an absorbance equation with only a polymer contribution. The Beer–Lambert law used to convey the absorbance equation for the nanocomposite of polymer (LLDPE or LLDPE-g-MA) and Cloisite 93A was

$$A_1 = K_1 \delta C_{93A} + K_2 \delta C_{\text{Polymer}} \quad (2)$$

where C_{93A} and C_{Polymer} are the concentrations of Cloisite 93A and the polymer (either LLDPE or LLDPE-g-MA), respectively. The absorbance of the polymer only was represented as

$$A_2 = K_3 \delta C_{\text{Polymer}} \quad (3)$$

To remove the absorbing layer thickness from the calculation and separate the polymer absorbance contribution from the clay absorbance contribution, a peak that had an absorbance contribution from both the polymer and Cloisite 93A was divided by a peak that only had an absorbance due to the polymer. This resulted in the linear equation

$$\frac{A_1}{A_2} = \left(\frac{K_1}{K_3}\right) \frac{C_{93A}}{C_{\text{Polymer}}} + \left(\frac{K_2}{K_3}\right) \quad (4)$$

The absorption peak attributable to clay within the polymer was found at 522 cm^{-1} on the spectra¹² and is shown in Figure 1. The absorption peak solely dedicated to the polymer (either LLDPE or LLDPE-g-MA) was found at 2019 cm^{-1} on all spectra and is displayed in Figure 2. The absorbance for each peak was determined by integration of the area under the peak. Using the previous linear absorbance equation and the spectra obtained from the polymer/clay standards (Fig. 1), we regressed a calibration curve; this is shown, along with a corresponding square of the Pearson autocorrelation coefficient, in Figure 3. Upon analysis, the absorbance ratios from the sample spectra were used with the calibration curve to calculate the weight percentage of Cloisite 93A infused into the polymer. Two calibration curves were used, one for samples with clay percentages ranging from 0 to 0.25 wt % and another for samples with clay percentages

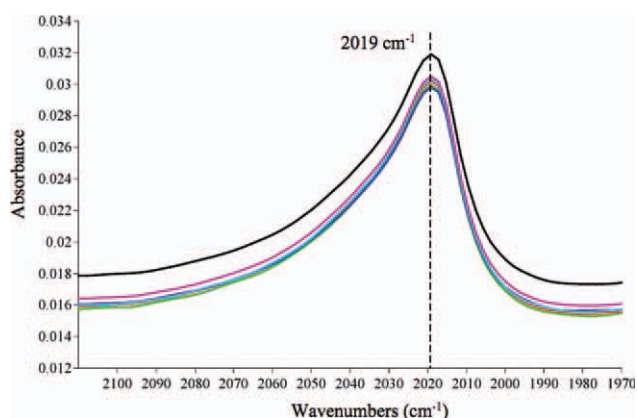


Figure 2 LLDPE/Cloisite 93A standard spectra with an absorbance peak of 2019 cm^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

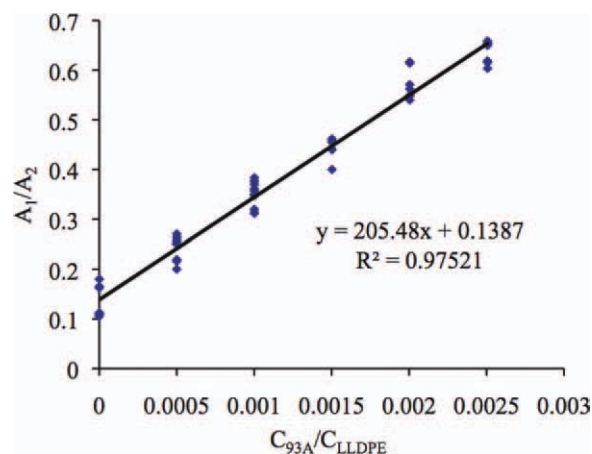


Figure 3 Calibration curve of the LLDPE/clay nanocomposites with various clay loadings. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

above 0.25 wt %. The larger range calibration curve used for clay amounts greater than 0.25 wt % contained a standard error of about 6%, whereas the standard error was about 3% for the smaller range calibration curve for 0–0.25 wt % clay.

This method is applicable to different types of natural and modified clay because all clays should possess an absorption peak identifiable by FTIR analysis that will increase with clay concentration. Careful choice of the absorption peaks (for either polymer or clay) is important, as a peak can be overlapped by other peaks or can contain signal noise that could result in the miscalculation of the peak absorbance and, thus, concentration. In addition, if the absorption peak chosen is indicative of the clay and not its modification, clay modifier degradation due to processing should not affect the results. However, polymer degradation could affect the results if the chosen absorption peak attributed solely to the polymer is altered by degradation. For this work, no degradation was expected because the processing conditions were below the degradation temperatures of the materials.

ScCO₂ clay-infusion results

FTIR analysis was employed to analyze the LLDPE/Cloisite 93A and LLDPE-g-MA/Cloisite 93A nanocomposite samples. First, we cleaned the pellets of residual clay on their surface by using a soft brush followed by wiping with a paper towel to ensure that the only clay detected was infused clay. The clay infused from the outer polymer surface inward. No clay was observed in the center of the pellet, and the majority of the clay remained near the polymer surface. Because clay infusion was not uniform throughout the pellets, the polymer/clay samples were melted, mixed manually, and then pressed into films for FTIR analysis. For the melt mixing, the pellets

TABLE II
LLDPE/Cloisite 93A Nanocomposite Average Clay Weight Percentages and Standard Deviations at Various Processing Conditions

Pressure (MPa)	Temperature (°C)	Average (wt %)	Standard deviation (wt %)
10.3	60.0	0.08	0.04
10.3	98.9	0.05	0.04
17.2	60.0	0.04	0.06
17.2	98.9	0.07	0.03

were placed on a metal plate on a heated film press platen. Once the pellets were melted, the molten polymer was mixed with a metal spatula to achieve a more uniform dispersion so an accurate bulk clay percentage in the polymer could be obtained.

LLDPE/Cloisite 93A nanocomposites showed little to no clay infusion, as determined by FTIR analysis. The maximum amount of clay infusion into LLDPE was 0.16 wt %, and the minimum was 0 wt %. As displayed in Table II, the lowest average clay infusion was found in the high-pressure and low-temperature run, whereas the highest average clay infusion seemed to have occurred in a low-pressure and low-temperature processing environment. In any event, the pressure and temperature effects still remained elusive as a result of the sample standard deviations being on the same order of magnitude as the average infusion amount; this resulted in an overlapping of values.

In terms of maximum clay infusion, nearly eight times more clay was infused into LLDPE-g-MA in comparison to the pristine LLDPE. Clay infusion into LLDPE-g-MA reached a maximum at 1.27 wt % and a minimum at 0.04 wt %. The lowest average clay infusion into LLDPE-g-MA was 0.07 wt % and occurred at in a high-pressure and low-temperature run, as exhibited in Table III. It is proposed that the high pressure reduced mobility of carbon dioxide molecules and clay particles and that the low temperature led to a lower diffusion rate and a harder polymer; this resulted in less clay moving to a polymer interface that was too hard to permit adequate infusion. At almost 12 times the lowest average clay

TABLE III
LLDPE-g-MA/Cloisite 93A Nanocomposite Average Clay Weight Percentages and Standard Deviations at Various Processing Conditions

Pressure (MPa)	Temperature (°C)	Average (wt %)	Standard deviation (wt %)
10.3	60.0	0.48	0.04
10.3	98.9	0.73	0.20
17.2	60.0	0.07	0.02
17.2	98.9	0.83	0.24

infusion for LLDPE-g-MA, high-pressure and high-temperature conditions produced the largest average clay infusion of 0.83 wt %. In actuality, these conditions could result in the same amount of clay infusion as the low-pressure and high-temperature run because their standard deviations gave overlapping values. These infusion results suggest that the reduced mobility from high pressures was less significant at high temperatures; when the fluid density was decreased, the diffusion rate was increased, and the polymer was sufficiently softened to promote infusion. Furthermore, the larger clay infusion amount into LLDPE-g-MA over that into pristine LLDPE was attributed to the greater compatibility of LLDPE-g-MA with the nanoclay offered by the MA modifications.^{3,5-7}

Although the aim of mixing was uniform clay dispersion, it was not achieved in most cases, as evidenced visually by white specs in the film and analytically by the large standard deviation present throughout a single sample. This may have been due to polymer pellets within the same processing environment being infused with different amounts of clay depending on their location in the reactor. To some extent, the large standard deviations in clay percentages were the cause of defects in the film samples, which resulted in oscillations or slight shifts in the spectra. The film defects, although minor, may have come from surface imperfections, that is, scratches and divots, in the brass plates that were transferred to the film during its preparation. Furthermore, improvements in the preparation of the polymer/clay standards and samples are expected to reduce the standard error contained within the calibration curves and reduce the standard deviation within the samples, respectively.

CONCLUSIONS

Linear low-density polyethylene/Cloisite 93A and LLDPE-g-MA/Cloisite 93A nanocomposites were successfully created via scCO_2 processing. The amount of clay within the nanocomposites was determined by an analytical method with FTIR analysis. In the explored processing environments, the near-zero clay infusion amounts in conjunction with the calibration curve and FTIR spectra inaccuracies made it difficult to ascertain the processing condition effects for LLDPE. In the case of LLDPE-g-MA, the MA modifications to LLDPE increased its compatibility with the nanoclay,^{3,5-7} thus giving it a greater infusion potential than pristine LLDPE and also increasing its clay-to-polymer property-transfer efficiency. The processing environment with the least potential for clay infusion into either polymer appeared to be a low-temperature and high-pressure environment.

Excluding this work, thus far, no apparent method has been formulated to quantify the amount of clay

added to a polymer. The creation of this method is needed for this particular process because the amount of clay infused into the polymer cannot be determined accurately by the simple weighing of the resultant nanocomposite and uninfused clay. This is due to the potentially unaccountable loss of clay within the system upon depressurization and recovery from the reactor. The simple weight increase of the polymer is also unhelpful because the polymer's weight undergoes changes not only due to clay infusion but also to the infusion of CO_2 into the polymer and weight losses due to polymer pellets scraping on the reactor walls, impeller, or each other. These weight-affecting factors might be small, but the amount of clay infused would be small as well, and this would obscure the results. The analytical method outlined in this work is a quick, simple, and nondestructive method for quantifying clay within a nanocomposite.

With this method, the amount of clay within a polymer system can be determined quickly and inexpensively. For manufacturers and researchers, knowing the precise amount of clay within the polymer will save time and money. If the optimization of this process is successful in leading to clay that is exfoliated, infused, and dispersed in polymer pellets, customers (viz., researchers and parts manufacturers) need only to melt the polymer into a desired shape or blend.

This research will allow the properties of polymers to be tailored for specific applications and broaden the applications for which a polymer can be used. It also adds an environmentally benign component to the polymer and the process because the filler is clay and scCO_2 is an environmentally friendly solvent. In other words, this research will allow inexpensive polymers to have a broader range of applications and to be more environmentally friendly.

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