

Intercalated Clays from Pentaerythritol Stearate for Use in Polymer Nanocomposites

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ABSTRACT: Smectite clays treated with quaternary ammonium salts have been utilized for decades in paints, greases, cosmetics, and personal care products as rheological modifiers. They have also been used in industrial wastewater treatment extensively. In more recent times these surface modified clays have demonstrated benefits in polymer/clay nanocomposites. The use of quaternary ammonium modifiers limits the usefulness of these composites in food packaging because they are not approved for direct food contact. It would be advantageous to have surface modifying chemicals acceptable for direct food contact in these composites. This article reports research conducted on a promising surface modifier pentaerythritol ste-

arate (PS), which is approved by the FDA for inclusion in food as a preservative. The surface modification of montmorillonite with PS is reported in detail as well as the production of nanocomposites with selected polymers made with the modified clay. Molecular modeling and purification of commercial PS samples indicate that the mono- and diesters are the critical surface modifiers, although the as received commercial material works well in forming intercalated clay complexes. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1908–1916, 2008

Key words: composites; molecular modeling; nanolayers; nanotechnology; organoclay

INTRODUCTION

The first attempt to chemically alter smectite clay galleries with various organic molecules was reported in the late 1940s.^{1–3} Research and eventual industrialization of quaternary ammonium chemicals, utilized in the fabric softener industry, met the world of clay chemistry when it was realized that the quaternary ammonium moiety could cation exchange with the sodium or other alkali metal cations on the surface of the clay. The hydrophobic tail tails of these quaternary amine species help to organophilize the clay platelets for potential exfoliation in solvents, or polymers as first noted in 1950.⁴ The mechanistic aspects and physical structure of these platelets has also been widely studied for non-polymeric media, such as in aromatic systems,⁵ as well as other organic matrices. Chemicals other than quaternary ammoniums, such as pyrrolidone and pyridinium compounds with long hydrophobic tails, can also modify clays in the same manner as their closely related ammonium cousins⁶ via ion dipole bonding and self assembly on the clay surface.⁷

Several problems and limitations arise from using quaternary ammonium as a cation exchange medium. Toxicity of these compounds, while mild, is

enough to raise concerns about direct contact with food. The Food and Drug Administration (FDA) have not approved quaternary ammonium compounds for direct food contact. To date this has largely limited polymer/clay nanocomposites applications involving quaternary ammonium to nonfood industries, such as automobile or electrical composites. The limited availability of different types of quaternary ammonium compounds is another factor. Six quaternary ammonium compounds are widely used commercially, typically, in the fabric softener industry. Alternative quaternary ammonium compounds are typically expensive to produce and have little to no market, while still carrying the issue of toxicity. Additionally, while these compounds are used to organophilize clays for polymers such as nylon-6, there is a rather large issue involving thermal stability of the quaternary ammonium moieties. Degradation of the organoclay can happen well under a polymer's melting point, leading to further composite contamination that could impart additional problems involving color, clarity, odor, and structure. The degradation byproducts of the quaternary ammonium ions present an additional regulatory concern.⁸

Because of toxicity and thermal stability issues with quaternary ammonium species, an interest in food safe intercalates has arisen. Clay intercalants that rely on ion-dipole interactions instead of cation exchange show considerable promise due to reasonable strength of interaction, wide commercial

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availability, high thermal stability, and no inherent toxicity.

This article reports the findings of an ordered study of intercalation and thermal stability of pentaerythritol stearate (PS) esters, which are approved by the FDA for inclusion in food as a preservative, particularly commercially available PS and purification and isolation of the tetra-, tri-, di-, and monoesters from the commercial material. Data on the intercalation behavior and thermal stability of these esters are presented with possible implications for polymer nanocomposites.

EXPERIMENTAL

Materials

The chemically and mechanically purified montmorillonite Cloisite Na⁺ was obtained from Southern Clay Products, Gonzales, TX. PS was obtained as a 500 g sample from Oleon, a Belgian fatty acid manufacturing company, in the form of Radiesurf[®] 7174 pentaerythritol monostearate. Another PS source was used, from Chem Service, also labeled pentaerythritol monostearate. For both chemicals it was found by Nuclear magnetic resonance (NMR) and liquid chromatography/mass spectrometry (LC/MS) that they contained substantial amounts of the tetra-, tri-, di-, and monoesters regardless of their respective labels as "monostearate." Most of the clay intercalation and polymer composites were made as it is, without further chemical purification or modification. Several clay intercalation experiments were performed with purified esters in order to understand the role of each ester in the overall intercalation behavior of the mixtures. There is no available commercial source for these purified esters.

Several polymers were used in compounding studies involving attempted exfoliation of PS organoclays. The polymers are all commonly used in the modern packaging industry, and were used as it is without any modifications: Ethylene vinyl acetate (Escorene LD-761, ExxonMobil), linear low density polyethylene (Dowlex 2045, Dow), isotactic polypropylene (Escorene PP-4792, ExxonMobil), and Nylon-6 (Ultramid B35, BASF).

Ester purification by preparative scale high performance low pressure liquid chromatography

PS esters were separated by preparative scale column chromatography. A 4.0 cm × 17.0 cm Michel-Miller column (RTSI-240) was prepacked with 80 g normal phase silica gel. The column was loaded with 1 g Oleon Radiesurf[®] 7174 preadsorbed on silica gel. The mixture was separated into four pure ester fractions, as determined by thin layer chroma-

tography, gel permeation chromatography (GPC), and LC/MS, using a two step solvent gradient starting from pure hexane and ramping to 11% ethyl acetate (25 mL fractions, 830 mL total) followed by a second gradient from 40% ethyl acetate/60% hexane to 100% ethyl acetate (25 mL fractions, 1100 mL total).

Ester purification by fractional recrystallization

Pentaerythritol fatty acid esters are generally obtained as mixtures of mono-, di-, tri-, and tetraesters. In addition, the carboxylic acid portion may be a practical mixture of varying hydrocarbon chain lengths. Recrystallization of this product from hot anhydrous ethanol afforded a first fraction (designated Oleon E-1) that was principally tetra- and triester with a trace of diester, and a second fraction (designated Oleon E-2) that was principally mono- and diester with a trace of triester. These fractions can be further purified by additions of appropriate amounts of water to the recrystallization solvent.

Preparation of intercalated clays

Initially, 10 g of Cloisite Na⁺ was treated with an equal weight water to hydrate the cations and expand the gallery and mixed in a mortar and pestle. The as received PS (MP of ~ 53°C) was melted in a double boiler system to facilitate addition to the clay. In total, 20 g (keeping a 2 : 1 chemical : clay ratio) of liquid PS was added into the swelled clay and ground for over 10 min. After mixing, the clay mixtures were dried in an 80°C oven overnight. Clays were ground to a fine powder using a commercial coffee grinder and sieved through a 325 mesh US standard sieve, typical particle size being equal to or less than 45 μm.

Secondary studies into intercalates formed as a function of clay PS were conducted by producing a ladder series based on milliequivalents, i.e., milliequivalents based on the sodium content of Cloisite Na⁺ (nominally 95 mequiv Na⁺/100 g clay), the point being to find an optimal minimal amount of chemical needed to swell the clay gallery completely. A 95 mequiv/100 g clay ratio (3.83 g chemical per 10 g clay), reflecting a 1 : 1 chemical : clay molar ratio of chemical to mole surface cation, was the center point of the secondary studies, from which 50 mequiv intervals were subtracted or added to form a concentration series. A typical study would have 45, 95, 145, and 195 mequiv per 100 g clay.

In addition, intercalates were made in an analogous procedure for the purified tetra-, tri-, di-, and monoesters at 95 mequiv/100 g of clay.

X-ray diffraction

Basal d -spacing of our organoclay along with Cloisite 20A, a quaternary ammonium cation exchanged organoclay, was determined on a Bruker D-8 X-ray diffractometer using a copper source ($K_{\alpha} = 1.541838 \text{ \AA}$). Samples were scanned in powder mode from 0.5° to 20° 2θ - Ω . Dry ($<2\% \text{ H}_2\text{O}$) Cloisite Na^+ only shows a d -spacing of 11.7 \AA (corresponding to a peak of 7.55° 2θ). Any additional intercalated agents will increase the clay gallery and, therefore, are easily detected by monitoring the basal d -spacing with X-ray diffraction.

Thermal gravimetric analysis

Thermogravimetric analysis (TGA) was performed on all organoclay samples produced to determine water content as well as decomposition peak for the organic molecules. TGA was also performed on a commercially available and widely known organoclay, Cloisite 20A, for comparison. The tests were performed on a TA Instrument's TGA Q50 with a scan rate of $20^{\circ}\text{C}/\text{min}$ under argon atmosphere from room temperature to 800°C .

Polymer compounding

All polymer compounding was accomplished via a Haake driven Rheomix 600 bowl mixer. All compounding was run at a 5% organoclay by weight in a 50 g polymer sample. Initially, the machine's three heating stages would be set to industrially utilize processing temperatures. Then the polymer would be introduced in pellet form at a low RPM paddle setting, generally 10 or lower. To this molten polymer the organoclay was added carefully and slowly, typically 1 g/min, by spatula. Once the organoclay was in the bowl mixer, the top air vent to the bowl mixer was lowered and the mixing was allowed to commence for 30 min at 50 rpm.

Organoclay polymer composite testing methods

Dynamic mechanical analysis (DMA) was performed on selected samples with a Rheometrics RSA-II Solids Analyzer using a fiber/film fixture. Samples were 3.0 mm wide by ~ 30 mm long, and nominal jaw separation following sample mounting was ~ 22.9 mm. Dynamic mechanical scan were obtained and reported by the procedures outlined in ASTM D 4065-89 and ASTM D 5026-90. The temperature of the sample was stepped from -25 to 150°C at 3°C increments, while allowing a 30 s delay for temperature equilibration between each step. Maximum strain amplitude was 0.2%, and the angular frequency was 22 rad/s.

Transmission electron microscopy (TEM) analysis was conducted at the Electron Microscopy Laboratory at Clemson University (Clemson, SC) by cryo-microtoming ~ 50 nm samples onto a carbon coated grid, and imaging on a Hitachi Model 250 Transmission Electron Microscope under a 100 kV accelerating voltage.

Molecular modeling

Molecular modeling was carried out utilizing the commercial Cerius two software package. All calculations were atomistic force field based and were conducted using the Universal force field. The models of the esters were produced using the 3D sketcher. The esters were then assigned charges in the Open force field setup module and minimized in open forcefield methods module. The clay model was generated using crystal builder based upon published structure parameters. The clay parameters were held constant and only the surface cations and ester molecules were allowed to undergo molecular dynamics and minimization.

RESULTS AND DISCUSSION

Basal d -spacing of the pentaerythritol stearate organoclays

The ladder series of pentaerythritol monostearate organoclays, along with Cloisite 20A for comparison, were analyzed by X-ray diffraction. Table I shows the d -spacings obtained from these scans, and Figure 1 shows the graphical data from the scans for the ladder series of Radiesurf 7174.

The results show that maximum intercalation for the Radiesurf 7174 organoclay occurs at 95 mequiv (3.83 g chemical per 10 g clay) and no large change in d -spacing occurs at higher concentration. A five-fold increase in gallery spacing is obtained when compared with dry Cloisite Na^+ , which exhibits a basal d -spacing of 1.17 nm. The low angle region of scattering in the X-ray pattern is somewhat broad,

TABLE I
Chart of Basal d -Spacings for Pentaerythritol Stearate Modified Organoclays as Compared to Cloisite Na^+ and Cloisite 20A

Organoclay	Primary d -spacing (nm)
Cloisite Na^+	1.17
45 mequiv Oleon Radiesurf 7174	1.54
95 mequiv Oleon Radiesurf 7174	5.5
145 mequiv Oleon Radiesurf 7174	5.6
195 mequiv Oleon Radiesurf 7174	5.9
Cloisite 20A	2.62
95 mequiv Chem Service PEMS	5.04

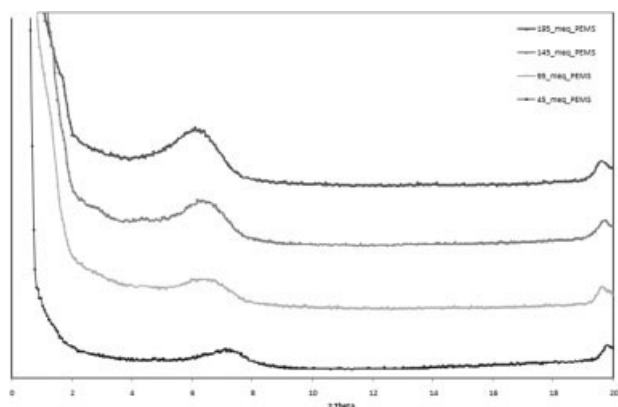


Figure 1 X-ray diffraction patterns for differing concentrations of pentaerythritol stearate organoclay.

and seems to run from ~ 1.00 to $1.90^\circ 2\theta$. This low angle peak would result in basal d -spacings that are in the range of 6 nm. Fortunately for the 95 and 145 mequiv clay intercalates the second, third, and fourth order peaks can be measured and were utilized to determine the d -spacings listed in Table I. The broadness of this low angle peak is somewhat surprising in light of previous work on intercalates of dodecyl pyrrolidone⁷ where relatively sharp peaks were observed. This led to the further analysis of the commercial monoesters utilized in the study. Molecular modeling indicates that the monostearate ester tail sticks straight up perpendicular to the clay surface, affording a large spacing between clay sheets. Figure 2 contains a molecular model of the mono-

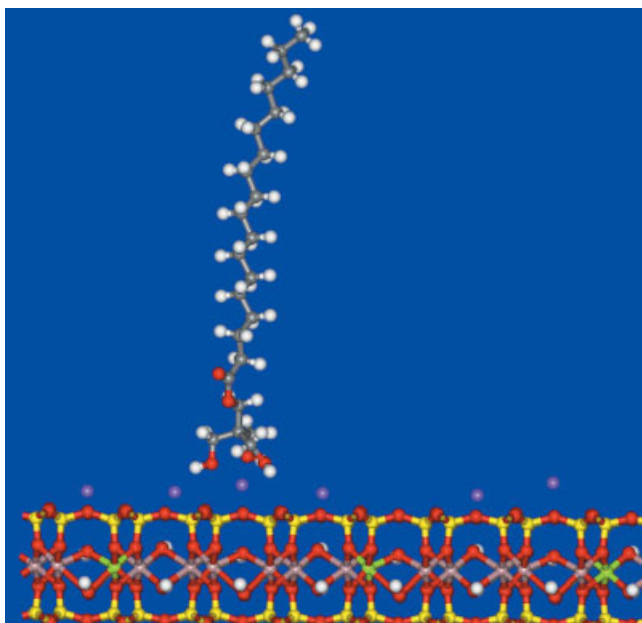


Figure 2 Molecular model of pentaerythritol monostearate ion dipole bonded to the sodium cation on the clay surface. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

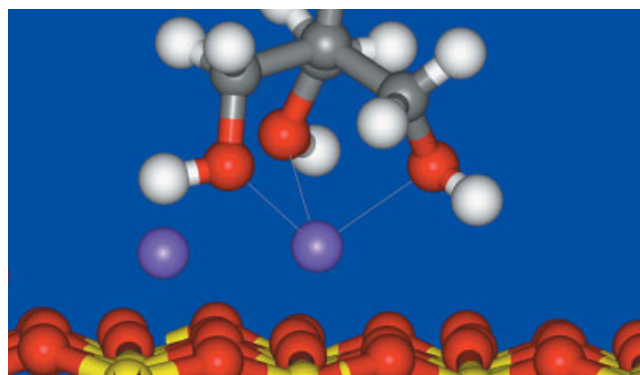


Figure 3 Molecular model of the bonding around the sodium cation with monostyrylpentaerythritol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ester bonded to a sodium atom on the clay surface. The three hydroxides are bonded to the sodium cation via ion-dipole interactions and give bond distances of 2.2 Å for two of the bonds and 2.3 Å for the third (see Fig. 3). This mode of bonding mimics the arrangement of water molecules where on average three water molecules normally hydrate the sodium cation on the surface of the clay. The distearate ester can also ion-dipole bond to surface cations similar to monostearate moieties, but the additional stearate arm is now oriented parallel to the clay surface $\sim 90^\circ$ to the initial one that is pointing up. This arrangement renders the stearate tail even more rigid than in the case of the monoester. The interaction of alkyl chains with the siloxane surface has been shown to be reasonably strong in several polymer systems. Figure 4 contains a molecular model of the distearate ester bonded to the clay surface. Figure 5 shows the bonding around the sodium cation and indicates that the bonding has changed from that seen in the monoester. Two of the hydroxides are still bonded at ~ 2.3 Å but now instead of the

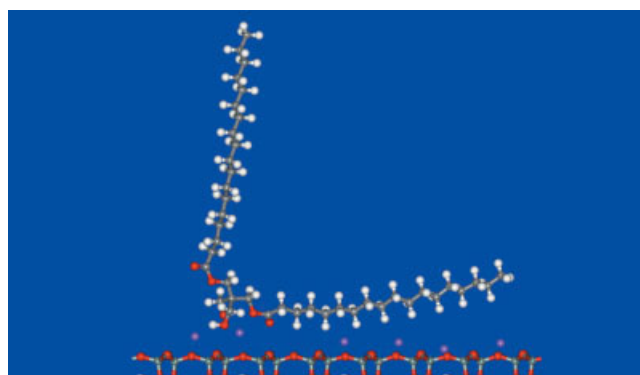


Figure 4 Molecular model of the distearate ester of pentaerythritol bonded to the sodium on the surface of the clay. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

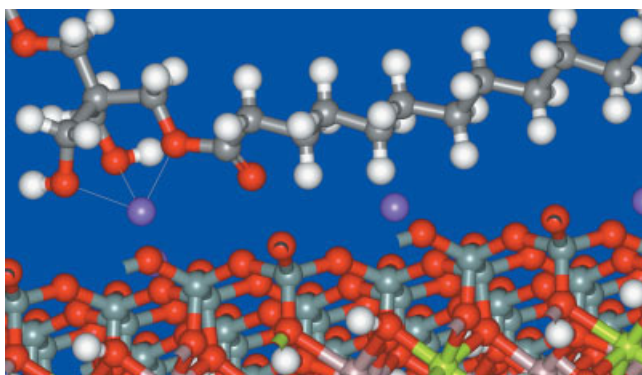


Figure 5 Molecular model showing the bonding around the sodium cation with the diester of pentaerythritol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

third bond being to a hydroxide it is to the oxygen in the ester linkage at 2.1 Å.

With the monostearate and distearate molecules bound to the surface, tri- and tetraester molecules slightly interdigitate with their stearate tails, showing van der Waal affinity to the surface bound molecules. This packing of the gallery by the tri- and tetraesters provides enough bulk to further separate the gallery, which explains the larger *d*-spacing.

Thermogravimetric analysis of pentaerythritol monostearate organoclay

TGA was performed on 95 mequiv/100 g organoclays of Radasurf 7174 PS (RPSC) and Chem Service PS. TGA was also performed on Cloisite 20A (20A) as a comparison study. The Radasurf 7174 PS organoclay performed exceedingly well, decomposing at 400°C, as compared to 20A whose organic intercalate (dimethyldihydrogenated tallow quaternary amine salt) decomposed at 313°C, a difference of 87°C. Xie et al.⁸ showed that the decomposition of dimethyldihydrogenated tallow quaternary amine salt is believed to take place via Hoffman elimination.⁸ Pentaerythritol esters on the other hand do not produce any detectable off odors during high temperature work; however, it should be noted that chemical separation/MS methods to determine degradation products have not been performed as of publication. RPSC in particular has a very late onset of degradation, into the region of Nylon processing (>220°C). Chem Service PS has a slow rate of degradation until ~ 350°C, when it begins to rapidly degrade. Both PS esters have extremely high degradation peaks. This is exciting from an industrial processing standpoint, as organoclay nanocomposites are limited by a number of important factors, including the modifier's breakdown temperature, tending to decompose if

mixed with Nylon. RPSC begins to degrade at 250°C, whereas 20A and Chem Service PS are already >10% degraded. Figure 6 contains a graph of the first derivative weight percent/degree versus temperature of RPSC compared to 20A. The first derivative curves were chosen because they illustrate the rate of degradation better than the weight loss curves.

The rounded low hump of 20A shows that the onset of decomposition is at a relatively low temperature (220°C which is well below the processing temperature commonly used of 270°C for nylon 6) and peaks at 315°C and continues up to 385°C. RPSC exhibits a much higher onset temperature of 265°C with a rapid increase in degradation rate at 370°C and peak degradation at almost 400°C. RPSC degrades ~ 30°C after Chem Service PS, indicating the existence of extra-gallery tri- and tetraester compounds, which would exit from the gallery faster than ion-dipole bound mono- and diesters. This indicates that the RPSC should be superior for producing nanocomposites since less degradation will occur during processing.

Purification of commercial pentaerythritol esters

The very broad diffraction peaks and the shape of the TGA curves indicated that the commercial pentaerythritol monoester is actually a mixture of mono-, di-, tri-, and tetraesters. By NMR the composition of Radasurf 7174 was found to be nominally 8.4 mol % monoester, 33.0 mol % diester, 43.5 mol % triester, and 15.2 mol % tetraester. As described in the experimental section, the commercial material was purified by column chromatography to isolate the individual ester species in the mixture, which were analyzed with NMR to identify each ester. It can be seen that the label of the commercial material as being a monoester is quite misleading.

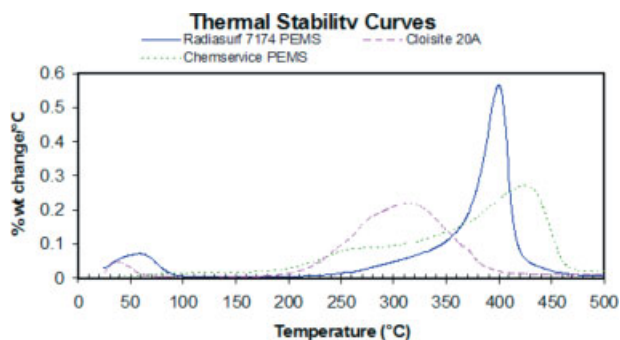


Figure 6 First derivative TGA mass loss plot of Radasurf 7174 PEMS blend, Chem Service PEMS and Cloisite 20A. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

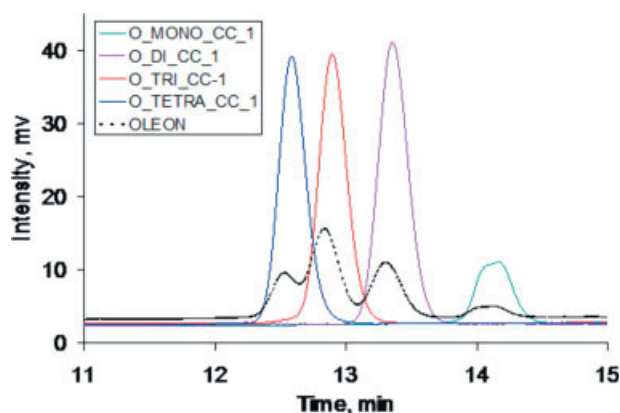


Figure 7 LC-MS chromatograms of the four pure fractions of OLEON Radasurf 7174 separated by column-chromatography, in which O_MONO_CC_1 denotes monostearate, O_DI_CC_1 denotes distearate, O_TRI_CC_1 denotes tristearate, and O_TETRA_CC_1 denotes tetrastearate fraction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Preparative scale high performance low pressure LC was utilized to separate four ester fractions from the commercial Radasurf 7174.

The following melting points were obtained for the four fractions: tetraester, m.p. = 64–69°C (O_Tetra_CC); triester, m.p. = 52–57°C (O_Tri_CC); diester, m.p. = 60–65°C (O_Di_CC); monoester, m.p. = 57–64°C (O_Mono_CC). LC/MS chromatograms of the pure ester fraction are shown in Figure 7. The two peaks seen for the mono ester are the result of C₁₆ and C₁₈ carbon chains. Similarly an increasingly complex pattern is seen for the di-, tri- and tetraesters because of statistical distribution of the differing chain lengths. It can be seen that the claim of the manufacturer that the Radasurf 7174 is predominately the monoester is grossly off. In fact it appears that the monoester is the smallest component with the di- and triesters predominating.

The original Oleon material and the four purified samples were further analyzed by GPC and a comparison was presented in Figure 8. Again it is clear that the claim of the manufacturer that the material is a monoester is incorrect. Recrystallization of this product from hot anhydrous ethanol afforded a first fraction (designated Oleon E-1) that was principally tetra- and triester with a trace of diester, and a second fraction (designated Oleon E-2) that was principally mono- and diester with a trace of triester. The Oleon E-1 fraction had a m.p. = 54–58°C and the E-2 fraction had a m.p. = 53–56°C.

By adding various portions of water to the recrystallization solvent, the ester composition of the various fractions can be manipulated. An 80% ethanol/water recrystallization produces a fraction that is essentially only mono- and diesters. Further recrystallization of Radasurf[®] 7174 from a mixture of 60%

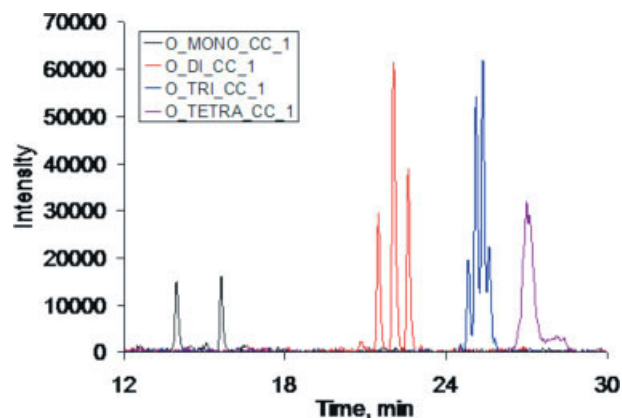


Figure 8 GPC chromatograms of the four pure fractions of OLEON Radasurf 7174 separated by column-chromatography, together with the original OLEON. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ethanol and 40% water afforded a first fraction (designated Oleon E60-1) that was principally tetra-, tri- and diesters, and a second fraction (designated Oleon E60-2) that was essentially monoester. In this manner, 434 g of Radasurf[®] 7174 was recrystallized to yield 19.6 g of high purity monostearate ester (yield, 4.5%, m.p. = 60–72°C). Although this fraction is virtually pure monoester, this melting point is still broad because the stearate portion is a mixture of various chain lengths, principally C₁₈ and C₁₆.

The separated fractions of the individual esters were further analyzed with wide angle X-ray diffraction (WAXD) as pure esters and also as intercalates with the smectite clay. The WAXD patterns for the mono-, di-, tri-, and tetraesters are contained in Figure 9. It can be seen that the X-ray patterns for the tetra-, tri-, and diesters exhibit very similar patterns with a sharp first order peak at 4.4 nm. The second

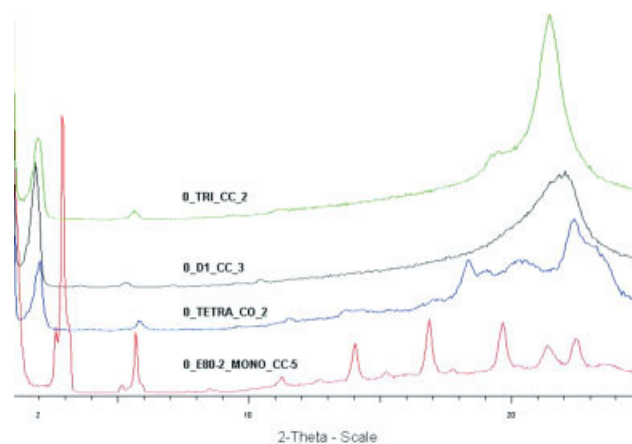


Figure 9 X-ray diffraction patterns of purified monostearate, distearate, tristearate, and tetrastearate of pentaerythritol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

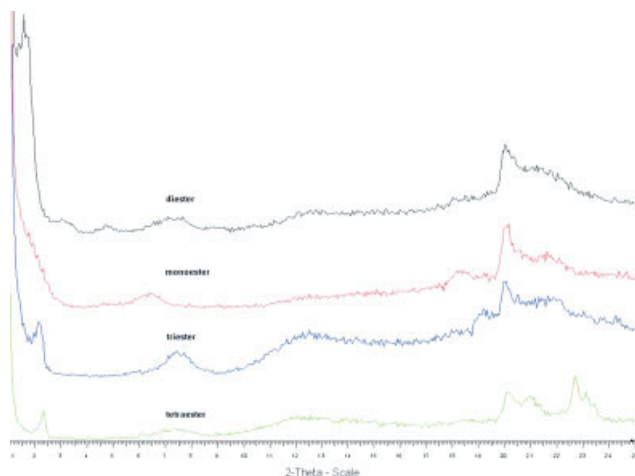


Figure 10 X-ray diffraction pattern of the clay intercalates of monostearate, distearate, tristearate, and tetrastearate of pentaerythritol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and third order peaks also show up but it is interesting to note that the intensity of the second order is lower than the third order peak. The mono ester has a sharp first order peak at 3.0 nm but the highest intensity peak is at 0.44 nm. The width at half max for all of these pure esters is $\sim 0.3^\circ 2\theta$. Small samples of clay were compounded with each of the pure esters in a mortar and pestle. These samples were then X-rayed to determine if any intercalation occurred. Figure 10 contains the WAXD patterns of the mono-, di-, tri-, and tetraesters mixed with clay, respectively. It can be seen that in the case of the mono- and diesters an intercalate has formed with the clay. This is indicated by three factors; first the peaks are much broader than in the pure esters exhibiting peak widths at half max of $0.6^\circ 2\theta$, which is characteristic of clay intercalated systems. Second, the absence of any peak at 1.2 nm which is the basal peak for unintercalated clay and finally the primary first order peak for the mono- and diester intercalates are 54.4 and 55.4 nm, respectively. These values are 2.4 and 1.1 nm larger than the pure ester peaks for the mono- and diesters, respectively. This is in reasonable agreement with a value of ~ 1.0 nm for the thickness of the clay layer for the diester but much larger than expected for the monoester. Molecular modeling conducted to predict the gallery spacing in the monoester was conducted at 95 mequiv loading and resulted in an interdigitated structure pictured in Figure 11 and a d -spacing of 4.1 nm. This is too small to explain the experimentally observed spacing. Further modeling was conducted at 103 mequiv and yielded a d -spacing of 5.2 nm, which is in very good agreement with the observed spacing of 5.4 nm. Figure 12 contains the molecular model of this system and highlights the extra molecule that is

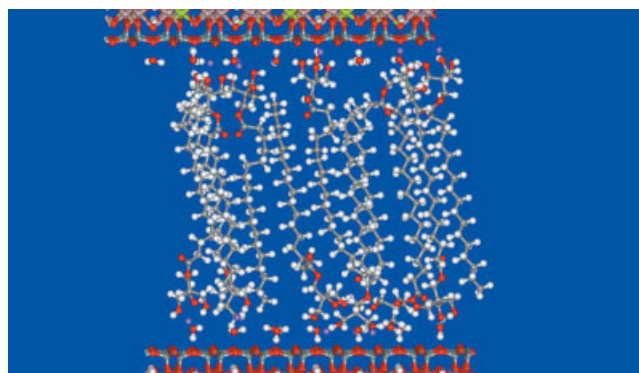


Figure 11 Molecular model of the gallery of monostearyl pentaerythritol at 95 mequiv. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

trapped and propping open the gallery. Similar modeling of the diester resulted in d -spacings of 4.8 and 5.6 nm for the 95 and 103 mequiv, respectively (Fig. 13). Again these numbers are in good agreement with the observed d -spacing of 5.5 nm. The triester complex with clay initially forms an intercalated structure that has a d -spacing of 5.3 nm but upon standing spontaneously deintercalates and forms a two phase system. In the mixture of the triester with the mono- and diesters the intercalated structure may be stabilized. It is also clear that the tetra ester does not intercalate at all since there is a broad peak at 1.2 nm for the unintercalated clay and a sharp peak at 1.57 nm corresponding to the pure tetra ester.

Pentaerythritol stearate polymer compounding results

Extent of exfoliation in polymer nanocomposites is semi-quantifiable through X-ray diffraction. An exfoliated polymer/clay nanocomposite system would

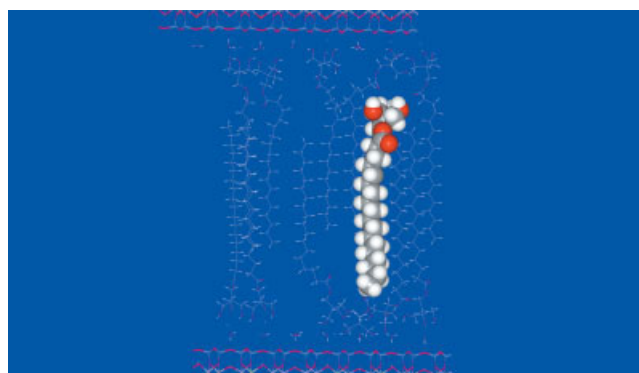


Figure 12 Molecular model of the gallery of monostearyl pentaerythritol at 103 mequiv. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

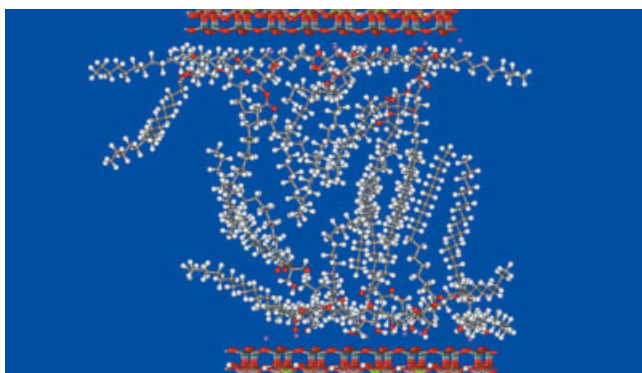


Figure 13 Molecular model of the gallery of distearyl pentaerythritol at 103 mequiv. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

have no additional X-ray peaks other than those of polymer crystallinity, signaling that the platelets are truly random and scattered. This system would then potentially provide the benefits expected.

Dry, unmodified montmorillonite does not exfoliate well into polymeric media. Therefore, any peaks for unmodified montmorillonite showing up in polymer composite X-ray data could mean one of two possibilities. Either the amount of chemical surface treatment was inadequate and there was still some latent unmodified montmorillonite, or during processing conditions the chemical treatment would be stripped off the surface. There is likely a mix of the two in any given final product, and only rigorous optimization individual to each organoclay would solve such problems.

Of the various polymer composites made, only 95 mequiv/100g clay RPSC was extensively studied in a good cross section of common commercially used

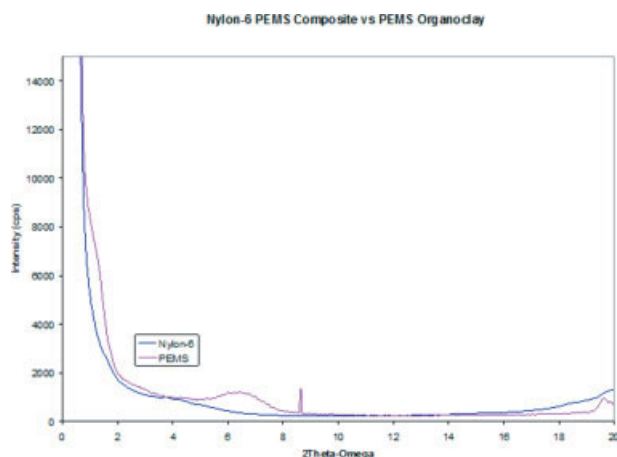


Figure 14 X-ray diffraction of 5% PEMS organoclay in Nylon-6 versus that of 95 mequiv/100 g clay Radi surf 7174 PEMS organoclay. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

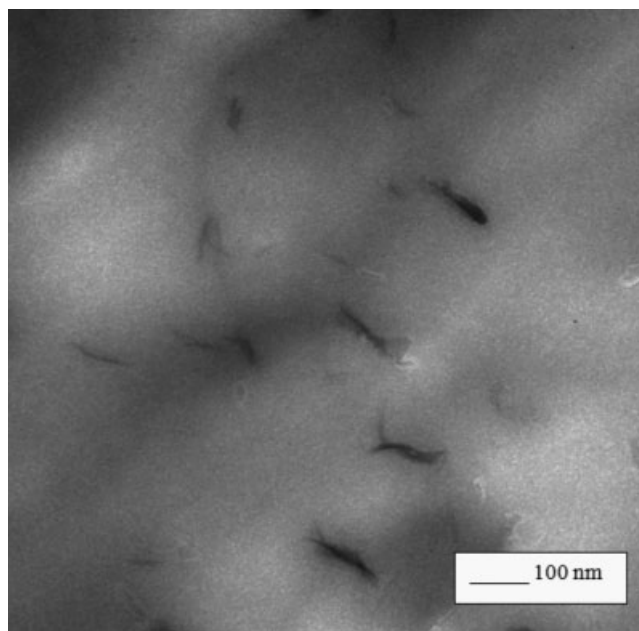


Figure 15 TEM micrograph of nylon 6 nanocomposite containing 2.5% PS clay.

food polymers, as provided by Sealed Air Corporation. The polymers studied include linear low density polyethylene, isotactic polypropylene, ethylene vinyl acetate, and nylon 6. The concentration 95 mequiv/100 g clay was determined from previous organoclay X-ray diffraction to be the minimum needed to provide large gallery spacing.

There are many noteworthy things about the X-ray diffraction patterns of Radiasurf 7174 PS organoclays in these common trade polymers. Most notable is the compatibility of organoclay with polymer material. High compatibility is verified by a diminishing RPSC primary peaks in the patterns. All of the poly-

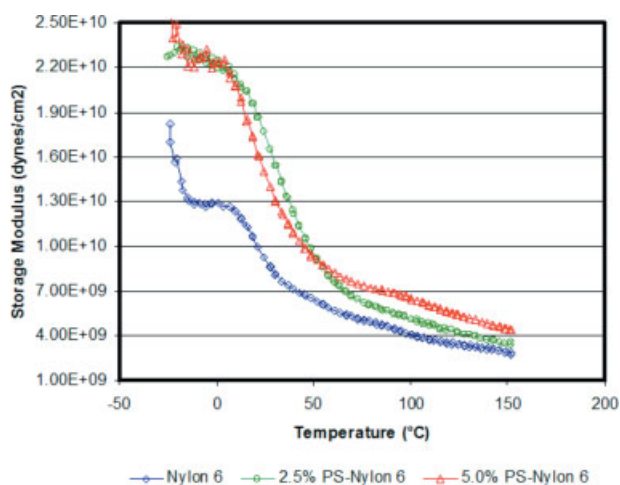


Figure 16 Storage modulus for Nylon 6 and Nylon 6 PES composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mers except nylon 6 showed that the polymers had intercalated into the clay gallery. The only system that appeared to potentially be exfoliated was the nylon 6 composite. It was therefore the only composite that was studied more extensively. The X-ray diffraction pattern of the nylon 6 composite can be seen in Figure 14. The Nylon 6/RPSC nanocomposite system was investigated in more detail. TEM on nylon 6 nanocomposites containing 2.5% dispersed RPSC confirmed that the organoclay was highly dispersed. A representative TEM micrograph is provided in Figure 15. The dispersed clay is substantially exfoliated, with lamellae present primarily as single sheets or very small tactoids comprising a few sheets.

DMA of nylon 6 composites containing 2.5 and 5% PS clay suggested high levels of clay exfoliation and a significant impact on the composite's mechanical properties. Storage modulus is plotted against temperature for the composites and unfilled nylon 6 in Figure 16. Comparing the modulus increase observed in this study to *in situ*-polymerized nylon 6 utilizing clay modified with 12 aminolauric acid⁹ yields a 112 and 91%, respectively. This is very promising that the observed modulus increase in a compounded nylon 6 composite compares very well to an *in situ*-polymerized composite of this study.

CONCLUSIONS

The culmination of data indicates that there are number of very interesting conclusions that can be drawn. There now exist, a readily available, low cost, chemical treatment for nanoclays that exceeds the performance of conventional organoclay in areas such as gallery spacing and thermal stability. X-ray diffraction patterns showed a fivefold increase in basal *d*-spacing for Radiansurf 7174 PS organoclay over dry Cloisite Na⁺. Both PS organoclays showed over twice the *d*-spacing of Cloisite 20A. The implications of such a large *d*-spacing are evident in that the larger the spacing, the more likely individual clay platelets can separate and become part of a polymer matrix. This is evidenced by the ease of exfoliation seen in the nylon 6 nanocomposite. The compatibility in nylon and EVA is a good sign for

the food packaging industry as well as the polymer industry in general.

Implications of the large decomposition temperature observed for the PS organoclays are vast. This study shows about 1% decomposition of the Radiansurf 7174 PS clay composite and ~ 5% decomposition for the Chem Service PS at 250°C, well into the range of nylon processability. One of the limitations to using quaternary amines as a clay intercalate is the difficulties in processing well in nylon, which typically has a processing temperature of >210°C.

The synthesis of an extremely thermally stable organoclay with well modeled and experimentally proven *d*-spacing has been established. This study has indicated that PS-modified montmorillonite has the ability to exfoliate well in Nylon-6, as well as marginally well in vinyl acetate, and polyolefins such as LLDPE and PP.

It has been further demonstrated that commercially available material, that is, labeled as monoester is actually a mixture of all four esters with the mono not being the majority. Separation studies and molecular modeling suggest that the di- and monoesters are the most important components for large *d*-spacings. It is therefore important to maximize the level of the mono- and diesters in commercial products. This could potentially lead to a whole new family of intercalated clays for applications in the food packaging area. However, the commercially available mixture of esters appears to work sufficiently well.

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