

**A SURVEY OF GENERALLY RECOGNIZED AS SAFE (GRAS) CHEMICAL
MODIFICATIONS FOR MONTMORILLONITE CLAY**

THESIS

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ABSTRACT

A SURVEY OF GENERALLY RECOGNIZED AS SAFE (GRAS) CHEMICAL MODIFICATIONS FOR MONTMORILLONITE CLAY

by

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A study was conducted investigating food safe intercalates for montmorillonite clay. The GRAS chemicals used in the study were chosen based on the presence of an oxygenated head group or other similar functionality, as well as compatibility with polymeric media. The synthesized organoclays were examined via X-ray diffraction to ascertain d-spacing. Subsequent organoclays with large gallery spacing were then subjected to thermogravimetric analysis and polymer compounding tests. Pentaerythritol stearate and glyceryl stearate organoclays performed well, with d-spacings approximately six times that of dry montmorillonite. Pentaerythritol stearate organoclays showed high thermal stability, approximately 88°C above that of modern quaternary ammonium organoclay Cloisite 20A. There is also evidence of high intercalation ability in poly(ethylene-co-vinyl acetate) (EVA) and Nylon-6 for the pentaerythritol stearate organoclays.

1.0 INTRODUCTION

1.1 Background

The first attempt to chemically alter clay galleries with various organic molecules was first reported in the late 1940's. 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 NR_4^+ site could cation exchange with the sodium or other alkali metal ions on the surface of the clay. The hydrophobic tallow tails of these quaternary amine species help organophilize the clay platelets for potential exfoliation in solvents, or polymers as first noted in 1950.¹ The mechanistic aspects and physical structure of these platelets has also been widely studied for non-polymeric media, such as aromatic systems,² 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 cousins.³

These initial experiments and observations sparked the growth of the nanoclay field, where engineering processes can break down the modified clay platelets to $<5 \mu\text{m}$. This greatly enhances exfoliation benefits. The culmination of the research thus far has grown immensely, as more and more businesses have started researching the potential benefits of these nanoclays. Products containing these surface modified clays are used in fields relating to the polymer, agriculture, and petroleum/oil industries, among others.

Successful commercial products have been developed from this technology in the polymer field, including various high temperature under-the-hood applications in vehicles not possible with unmodified polymer. The ever widening and broadening field of nanoclays is only recently having direct repercussions on the world of the consumer.

Several nanofillers exist in modern industry, with a large variability of cost, from cheap naturally mined clays and chemically modified organoclays to extremely expensive single wall carbon nanotubes. Organoclays are starting to become a popular choice in industry, driving their cost down as they increase as a viable commodity. These clays disperse in a variety of polymeric media and are becoming more useful with modern polymer industry. However, while quaternary ammonium modified clays are efficient and useful in modern polymer industry, there are drawbacks in the realm of food packaging polymers. The main drawback, and the source of alternative investigation contained herein, is the fact that these chemicals and subsequent organoclays cannot be in contact with food, as regulated by the Food and Drug Administration (FDA), due to toxicity issues with the quaternary ammonium compounds.

1.2. Clay: A Historical Perspective and Modern View

Humans have been using clay as a tool for as far back as recorded human history can show. Recorded human history, in fact, was first written in cuneiform upon clay tablets in ancient Mesopotamia by the Sumerians. There is intense scientific debate over the origins of life, where amino acids were catalyzed by clays to form oligomeric pre-protein like structures. Clays themselves are widely varied chemically from site to site, and have extremely complex structures for naturally occurring compounds.

Using clays for broad scientific advancement did not come, however, until thousands of years later in the early 1900s, with the discovery and use of Bentonite, a natural clay deposit found in the plains of the United States. The name Bentonite comes from W.C. Knight, who named it after Fort Benton, Montana, where it was first discovered. A scanning electron microscope (SEM) image of Bentonite is shown in Figure 1.⁴ Early travelers across the plains used this clay in aqueous solution as a wagon

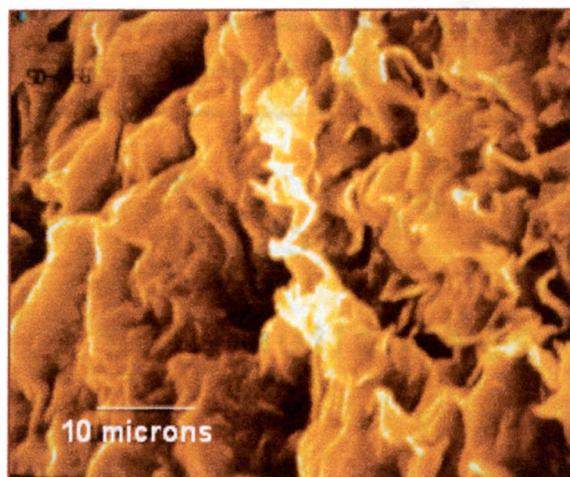


Figure 1. SEM image of Bentonite Clay.

wheel lubricant, while American Indians, indigenous to this region, used the clay as soap. Modern uses for bentonite include sorption of water pollutants and various other health-related detoxificant.⁵

Montmorillonite is obtained from refining natural bentonite deposits. A typical deposit of bentonite contains 75% or more montmorillonite, along with small amounts of other smectic clays such as feldspar. Quartz, ash, and trace minerals are also present in small amounts.⁶ Montmorillonite clays have a long industrial history. Millions of years ago, during the Cretaceous Era, volcanic eruptions spewed billions of tons of ash into the air which settled into salt water beds in the western United States, from Wyoming through the Dakotas. Ash that would settle in the beds of water would, over millions of

years and with the aid of mineral deposits available in this media, transform into the clays we have today. In 1917, D.F. Hewitt was the first scientist to extend the theory that the clay forms from volcanic ash and water beds in-situ.⁷ The most extensive site of concentration of montmorillonite in the modern world is in Wyoming, where over one billion pounds of mineable clay is estimated to reside.⁸

The structure of montmorillonite was deduced in 1933 by Hofmann, Endell and Wilm in Berlin.^{9,10,11} They also deduced how the clay swelled with water based on the structure. Montmorillonite clays are arranged in a monoclinic lattice formation,¹² following the general equation of $(\text{Na})_x(\text{Al}_{2-x}\text{Mg}_x)\text{Si}_4\text{O}_{10}(\text{OH})_{2-x}(\text{H}_2\text{O})$. Every site of magnesium substitution (x) for aluminum ($2-x$) results in one sodium surface cation (x). It isn't possible to quantify how many cations there are per unit area, nor is it possible to know the exact sites of the substitution, as this varies from site to site. Clay chemists designate active cation site composition by using the milliequivalents designation per weight unit (in montmorillonite and similar smectites, values are given in n milliequivalents/100g clay, where n can differ from geographical site to site). The lattice consists of tetrahedral coordinated silicon sheets sandwiching an edge-shared octahedral layer consisting of aluminum, magnesium, or iron (cross section shown in Figure 2).

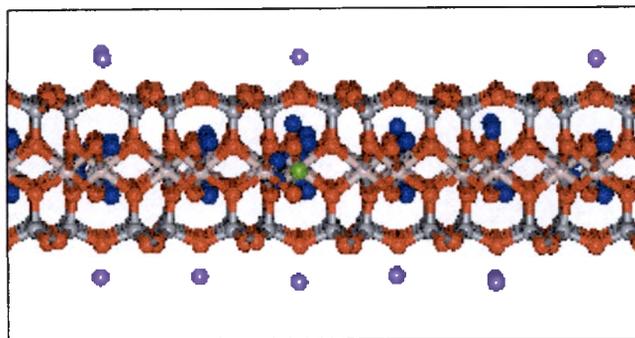


Figure 2. Cross section of a Montmorillonite Sheet¹³

The clay surfaces are the silicon bonded oxygens. The total thickness of this three part lattice is generally around 1 nm, with lateral dimensions varying from 200 Å to several microns. The partially negative charge arises on the clay surface through isomorphous substitution of Al^{3+} by Mg^{2+} . Sodium is the most abundant alkali metal in earth's crust,¹⁴ and tends to associate with the surface more so than other alkali species, calcium being the second most likely ion to associate. The volume between any two sheets of clay, where two tetrahedral layers pocketed by sodium ions come into near direct contact, is called the "gallery." The physical distance between these two sheets can be measured via X-Ray diffraction, and is known as basal d-spacing, as according to Bragg's Law, shown in Equation 1.

$$n\lambda = 2d \sin\theta$$

Equation 1. Bragg's Law

The montmorillonite clay we chose to study was a highly refined and purified clay called Cloisite Na^+ , from Southern Clay Products, Inc, located in Gonzales, Texas. Cloisite Na^+ is essentially purified and processed montmorillonite that is of a particular

size (50% less than $6\mu\text{m}$) without any chemical surface modification, the Na^+ referring to the fact that sodium ions are by far the most populous ion on the surface of the clay.

Refined Cloisite clays are much like its parent montmorillonite in that it is chemically and mineralogically the same yet have been optimized for particle size and purity. The optimum available surface area of Cloisite Na^+ is in excess of $750\text{ m}^2/\text{gram}$ of material. The clays also exhibit a high aspect ratio (ratio of platelet length to thickness) of 200+. Cloisite Na^+ has an available exchange capacity of 92.6 meq/100g clay, and in traditional applications (without chemical modification) it is used to moderately improve various plastic properties, such as barrier and reinforcement. The typical aggregate particle size of Cloisite Na^+ is anywhere from 2-13 μm , with a median particle size of approximately 6 μm . The Cloisite Na^+ clay itself is an off-white, slightly tan powder. "Dry," (as given by the manufacturer it contains <2% H_2O) it shows a XRD (X-ray diffraction) peak showing a d-spacing of 11.7 \AA .¹⁵

Serious scientific research into the uses of clays as pertains to chemical methods started in the 1940's after clay mineralogy was accepted as a legitimate branch of geology. Jordan was one of the frontier scientists to research with montmorillonite (in bentonite form), as evidenced in his work pertaining to organic solvent swelling.^{16,17,18} Research in clays flourished, and technology and testing eventually showed the benefits of having nanoparticulate intercalates inserted into systems like polymers.

Nanocompositing involves insertion of a particulate matter that has dimensions on the nanometer ($1 \times 10^{-9}\text{ m}$) level into a greater bulk media. This type of research was first reported on polymers as far back as 1961, when Blumstein polymerized vinyl monomers with nanoparticulated (unmodified) montmorillonite.¹⁹ Early work over in-situ

polymerization of polyamides over layered silicates was reported in 1976 in Japan,²⁰ which eventually culminated to work in the 1990's from Toyota, who first showed an exfoliated in-situ nylon-12 nanocomposite^{21,22} and in recent years from the University of Texas²³ involving the study of nylon-6 degradation. Thermoset polymer nanocomposites have also been extensively studied,²⁴ as have various other trade polymers, including polycarbonates²⁵ and polyesters.²⁶ Results from these tests all confirm the many properties and abilities nanocomposites have in a polymer matrix.

There are several levels of exfoliation that designate the level of mixing clays into polymeric systems (see Figure 3). "Exfoliation," or delamination, of clay involves a completely randomized and separated clay medium with polymer coating the surface of the clay and interdispersed between the platelets in a random fashion. There are no aggregates of clay platelets, as evidence from x-ray diffraction: no peaks of crystallinity (other than from polymer crystallization) appear from 0 through 20 degrees 2θ . Polymer crystallization peaks are normally sharp and defined, as well as typically found below basal spacings of the clay platelets ($< 11.7 \text{ \AA}$), which are characteristically broad. If these clay platelets are readily aligned and arranged (as opposed to random), but separated by the polymer, this is distinguished as "intercalated."

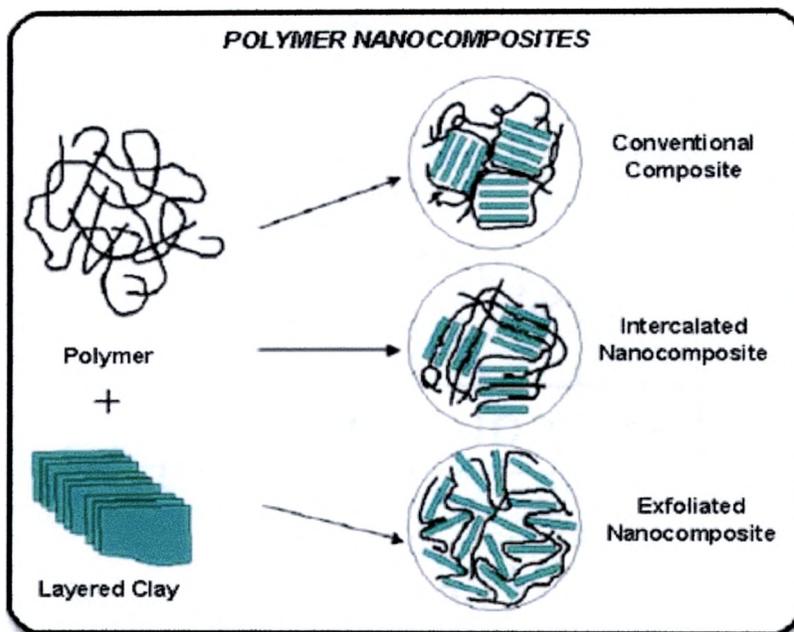


Figure 3. Different phases of clays in polymer media.²⁷

A system that cannot separate clay platelets is designated as a micro or macro (depending on domain size) composite, or “aggregate.” This can be caused from a strong attraction between clay platelets, or a non-affinity between the modifier of the clay and the polymer. A system that shows some evidence of exfoliation (light area) and aggregation (dark area) can be seen in the TEM shown in Figure 4.

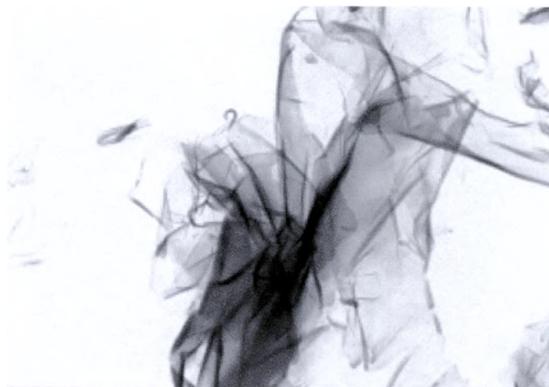


Figure 4. TEM of Cloisite Na⁺ (Montmorillonite).²⁸

Cation-exchanging quaternary ammonium salts onto a clay surface can help achieve a large d-spacing, spreading the gallery, making potential exfoliation into polymers easier than pure unmodified clay. Quaternary ammonium species readily intercalate and sometimes exfoliate clays. Just about any physical parameter can influence exfoliation. These include modifier amount, processing temperature, processing style (melt compounding versus twin screw extruder, etc), chemical properties such as pH, reactive group modification, etc. Careful adjustment and experimentation can define an optimum system.

1.3 GRAS: A History and Choosing a List

Due to industrial demand, there is a growing need to find a better surface treatment for these clays that is both food safe and that would produce similar results as other modified organoclays currently being tested or on the market. There are four legal categories of substances added to food, as passed in the Food Additives Amendment to the Federal Food, Drug, and Cosmetic Act (FD&C Act) in 1958. There are *food additives*, which are additives not yet approved by the FDA but are currently in trials. The category *prior-sanctioned* applies to substances approved before the 1958 passage of the FD&C Act. As an example of this, nitrates were approved for use in meats before 1958 and are still legal to do so, but their use in vegetables is restricted because they were not approved before 1958. The *color additives* category applies to dyes and their use and moderation in foods, drugs and various other classes. Since 1958, all approved chemicals and substances safe to use in food fall under the *Generally Recognized As Safe*, or *GRAS*, category. A substance is deemed GRAS if a common scientific opinion in the safety of the particular additive is positive in relation to ingestion, contact, implantation, etc. This

does not necessarily give a true measure of the safety of any compound, as chemical amounts are regulated as well. For example, chemicals such as hydrogen peroxide have *conditional* GRAS status, and are to be used with “good manufacturing practice.” GRAS status can, albeit rare, be revoked if new evidence to the contrary of a GRAS claim is presented and approved by the FDA.²⁹

All four categories deemed in the FD&C Act of 1958 are under the grand heading of *Everything Added to Food in the United States*, or *EAFUS*.³⁰ This database of chemical compounds is sustained and updated by the FDA’s Center for Food Safety and Applied Nutrition (CFSAN), in the program of Priority-based Assessment of Food Additives (PAFA). The EAFUS list is exceedingly complex, in that it contains many common items, such as herbs and spices, as well as a wide range of complex biomolecules such as enzymes, or plant/animal derived substances and extracts. It also contains many familiar basic organic compounds, such as acetic acid, urea, carbon dioxide, etc.

1.4 Nanocomposites and the Search for Food Safe Alternative Intercalates

The majority of modern nanocomposite research is looking into polymer-nanocomposite interactions. Nanocomposites comprise a large field of substances, including fibers, clays and other silicates, inorganic powders, etc, with at least one dimension on the nanometer scale. Modern clay/polymer nanocomposite research is broad, ranging from non-food applications, such as rubber, wiring insulation, and car parts to food applications such as meat and produce packaging. There is high scientific interest in the use of clay nanocomposites in food packaging due to requirements such as barrier and strength.

There are two general reasons for the banning of certain polymers from use in food packaging. Degradation to monomer can cause serious side effects, as evidenced in polyvinyl chloride (PVC). Vinyl chloride monomer has been proven to cause the liver cancer angiosarcomas in humans.^{31,32,33} This was a loss to the food packaging industry, as PVC has an excellent barrier and would have been an ideal meat packaging material. The second (and related, to an extent) aspect is production of toxic gases when burning. Polymers like polystyrene and PVC emit very toxic off gases when burned. If used on a large scale, accumulation in a landfill that burns trash would pollute the environment and surrounding neighborhoods and cities.

These two aspects limit polymer choice in the food packaging industry to just a few polymers, which may or may not have terrific barrier properties. The weaknesses of modern food packaging polymers can therefore be overcome with the addition of nanocomposites. A commonly used food packaging polymer (polypropylene, PET, LLDPE, etc) can be turned into one of greater strength, with higher barrier properties and potentially higher impact resistance and resistance to modulus changes. The highly debated “torturous pathway” model, as shown in Figure 5, of a clay/polymer nanocomposite illustrates how barrier is improved with the addition of nanocomposites.³⁴

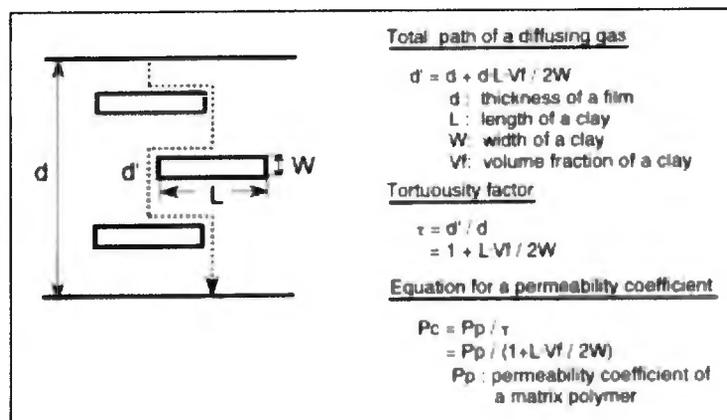


Figure 5. Torturous Pathway in a Polymer/Nanocomposite Matrix

Molecules of air, particularly oxygen due to its involvement in food spoilage, must diffuse through a matrix of clay platelets with a large surface area instead of normal unimpeded polymer. However concise the torturous pathway claims to be, there is evidence that nanocomposite imparted barrier relies on three regions around the clay.³⁵ The first region is the *surface modifier zone*, and its size is dependent on surface modifier type. The zone can be readily measured with X-ray diffraction. The next region is not as physically defined as the surface modifier zone: The *constrained polymer region*. This polymer region is directly interacting with the surface modifier, and can differ in amount of constraint depending on degree of intermolecular bonding. Polymers such as nylon-6, with high amounts of hydrogen bonding, have a larger constrained region. Polyolefins, which have only weak Van der Waals interactions, have a small constrained polymer region. The third region, *unconstrained polymer*, is essentially like unmodified polymer. This zone is unaffected by clay. The culmination of these three zones gives a different shape to the original tortuous pathway model. There is evidence that factors such as constrained polymer region work into the reasoning for such a high barrier. As of

publications, experiments are underway to determine experimental values for the parameters.

Food packaging polymers are of great interest to this study. Four polymers actually used in the food packaging industry were selected to compound for this study: *EVA (Ethylene Vinyl Acetate)* is polyvinyl acetate (PVA) co-polymerized with ethylene to give it a more aliphatic character. It is commonly used in sheeting, coatings, tubing and food packaging. Its soft, tacky nature lends to its use as shrink wrapping used in the market today.

The polyethylene family is the most popular type of food packaging on the market today. Different processing conditions/catalysts/etc can produce different amounts of branching and chain length, giving rise to different density varieties. *Linear Low Density Polyethylene (LLDPE)* is used in food polymer applications such as sandwich bags, as well as in coatings and non food films. It can be injection molded for parts and blow-molded as bottles among thousands of other products.

Polypropylene (PP) is used in similar products that polyethylene is used in, but it has a higher melting point and is typically more rigid (crystalline) than polyethylene. As in polyethylene, a large variety of structures are possible to make using processing and catalysis. Since the monomer propylene is prochiral, there are three basic types of polypropylene. *Isotactic polypropylene (iPP)* has the pendant methyl group all on one side, from unit to unit. *Syndiotactic polypropylene (sPP)* has alternating chirality for its methyl groups, and *Atactic polypropylene (aPP)* has random stereochemistry. Typically, iPP, the polypropylene used in this study, is not as clear as sPP due to higher crystallinity, but it has a better gas barrier and is more suited for food packaging.

Nylon-6 is a strong and proven meat packaging polymer. It has excellent clarity and extremely high barrier compared to all other food packaging films. It is made via an ionically catalyzed ring opening polymerization of ζ -caprolactam. It is possible (though not investigated in these studies) that nanocompositing organically modified clays can be inserted into Nylon-6 via in-situ polymerization, which is easily controlled compared to the conditions and equipment need for polymerizing polyolefins via in-situ. Nylon-6 has similar applications to polypropylene but has the advantage of higher strength and temperature stability.

There are three main ways to mix polymers into clays: in situ, melt compounding, and extrusion. In situ requires initiators and monomer preparation to actually grow the polymer on the clay surface, but that method is not suited for the procedures and chemicals we are working with. In situ preparation is, however, a very reliable method of intercalating and possibly exfoliating these modified clays,³⁶ but small sample size and preparation problems tend to leave the method to mainly non-industrial applications. Of these techniques, melt compounding best suits the current needs and qualifications for the studies to be completed. Melt processing using bowl mixing is in general a preemptive mode of preparation done before scaling up to an extruder. The method involves mixing solid pellets or flakes of polymer with a small (generally <5%) amount of nanocomposite material in an industrial bowl mixer environment. The shear generated by the paddles is typically similar to a single screw extruder. The shear, coupled with the heat, will readily mix in the clay into the polymer matrix.³⁷ Certain precautions of attention include keeping processing temperature below decomposition/reaction temperatures of the GRAS chemical on the clay surface. Methodology of the

melt compounding technique is very well known and prescribed in industrial application. Extrusion methods are the logical “next step” extension of the melt compounding work, as is done in industry. If melt compounding proves successful, a more exfoliated product can generally be achieved using extrusion, where shear is very high and run time is minimized, lowering the chance of the chemicals leaving the clay surface.

The polymer-nanocomposite species made are tested for intercalation via Wide angle X-ray powder diffraction, or WAXRD. X-ray diffraction gives an idea of the extent of platelet separation. Theoretically, a more “exfoliatable” organoclay would have a larger platelet separation, as platelets would rather easily shear apart rather than aggregate. A more exfoliated clay/polymer system would also tend to be clearer as random nanoparticles generally are too small to refract light and less clumping provides a less opaque media. Clarity is also a major concern of modern food consumers.

There are more than 3,000 chemicals with the title of EAFUS. GRAS chemicals make up a large portion of the EAFUS list (2,000+) and include commonly used polymer additives and organic compounds of interest. The selection of GRAS chemicals for intercalation had to be narrowed down to meet several criteria. Foremost, there was interest in a predominately chemical approach, not in investigating plant extracts/herbs/proteins. More specifically, the molecules of interest were species containing a partially negative head group, typically composed of N, S, or O in some form (amine, alcohol, carboxylic acid, etc). This polar head would, according to preemptive molecular modeling work, associate with the alkali ions on the surface of these clays via ion-dipole bonding. Organic oxygenated species such as alcohols, esters, carbonyls, and carboxylic acids were sought out more aggressively as they typically were

more common than sulfur or nitrogen-containing molecules on the GRAS list (typically because most sulfur/nitrogen containing compounds have some degree of toxicity). In order to imitate the benefits of quaternary ammonium species, we would need long R-group tail functionality on our molecule. It is possible, however, that small molecules bound to a clay surface can have some similar functionality with a particular polymer, providing exfoliation benefits without a long R-group. Biomolecules such as vitamins and amino acids were looked into as well, for potential nutritional enforcing of a product wrapped in a polymer containing modified clay.

Of those species, we then refined our choices down to more commonly attainable and widely used compounds. We eliminated compounds with stability issues (ex: peroxides) and large amounts of chain saturation, as they would both be unstable at high temperatures. The research at hand will act as a survey study for further future projects in the field of alternative organic modifiers for montmorillonite organoclays. The culmination of this work and future studies can help determine a way to produce these next generation food safe packaging.

2.0 EXPERIMENTAL

2.1 Materials

The Montmorillonite clay used, Cloisite Na⁺, was supplied by Southern Clay Products (SCP) in dry powder form. No further purifications or modifications were made to the clay before use. Some properties of the clay as provided by the manufacturer are outlined in Table 1.³⁸

Table 1. Properties of Cloisite Na⁺

Name	Cation Exchange Capacity	% Moisture	% Weight Loss on Ignition	X-Ray Basal d-spacing
Cloisite Na ⁺	92.6 meq/100g clay	<2%	7%	11.7 Å

The GRAS chemicals used in our study were obtained from a variety of sources. The chemical names and sources are listed in **Appendix 1**. All chemicals used were used as purchased without further modification or adjustment. Part of our study involved using a variety of esters of multifunctional molecules, including: glycerol, citric acid, and pentaerythritol. During the synthesis of these compounds, it is often prohibitively expensive or unnecessary to separate monoesters from diesters, triesters, etc. Therefore any ester mentioned in these studies should be assumed to be a mixed ester unless specifically stated as a mono-, di-, etc ester, for example glyceryl stearate should be understood to be a mixture of glyceryl monostearate, distearate, and tristearate. All ratios

of esters given by the manufacturer are listed in **Appendix 1**. There is concern over the purity of one of the supposed “monoesters,” Oleon’s Radiesurf 7174 Pentaerythritol Monostearate. Consult Experimental section 2.6 and Results/Discussion section 3.5 for details involving purity assessment of this ester.

Several polymers were used in compounding studies involving attempted exfoliation of our organoclays. The polymers are all commonly used in the modern packaging industry. The polymers used in the study are tabulated in Table 2, along with source, approximate melting point, and other physical data. Consult Results and Discussion section 3.4 for complete uses of the polymers in industry.

Table 2. Complete list of polymers used in the study

Common Name	Industrial Name & Source	Approx. Industrial Processing Temp, °C	Comment*
EVA (Ethylene Vinyl Acetate copolymer)	Escorene LD-761, ExxonMobil ³⁹	155	28% vinyl
LLDPE	Dowlex 2045, Dow Corp ⁴⁰	145	Density = 0.92 g/cc
Polypropylene, Isotactic	Escorene PP-4792, ExxonMobil ⁴¹	170	Density = 0.90 g/cc
Nylon-6	Ultramid B35, BASF ⁴²	210	
Industrial name, source, approximate melting point and other useful information about the polymers are included.			

2.2 Organoclay Preparation

2.2.1 Bulk Method

Ten organoclay blends were prepared via bulk processing on a Hobart single screw processing mixer, model 4522. The shear generated from the Hobart is powered by a 1725 RPM 15 horsepower electric engine. The machine generates an ambient processing temperature of 40°C. The rotor operates at approximately 210 PRM, giving a

strong mixing environment. The bulk method was used to process and generate >250g samples of organoclay, that, with the addition of mechanized shear, generate a highly mixed compound. This method provides optimal working conditions, but was not the most used method of organoclay preparation due to various size issues (see 2.2.2). The Hobart Processor is located in the Polymer Processing Lab at Texas State University - San Marcos.

Prior to any mixing, the weight of the GRAS chemical was calculated initially via a 2:1 chemical: clay by weight ratio and, if not in a liquid state, molten via a double boiler system utilizing boiling water in an outer beaker and an inner beaker in which to melt the compound. Any secondary studies into compounds typically involved changing the amount of chemical in a ladder series based on milliequivalents, the point being to find an optimal minimal amount of chemical needed to swell the clay gallery completely. A 95 meq/100g clay ratio, reflecting a 1:1 chemical: clay *molar* ratio of chemical to mole surface cation, was the center point of any secondary study, from which 50 millequivalent intervals were subtracted or added to form a concentration series. A typical study would have 45, 95, 145, and 195 meq per 100g clay. The clay (always 250 grams to ensure proper loading in the Hobart extruder) would be wetted with 70% water by clay weight and mixed in a common Kitchen Aid mixing bowl. This pre-wetted clay was then treated with the liquid (or solvated) form GRAS chemical in the mixing bowl and mixed for several minutes. The organoclay would then be added to the Hobart Processor and extruded several times over to ensure proper mixing. After the processing, the organoclay would be collected and set upon aluminum foil in an 80°C oven to dry overnight. Any clays still showing “wetness” after an overnight sitting were allowed

longer sit times, but generally no longer than five days. Typical yields were above 300 grams. A complete list of all GRAS chemicals compounded into Cloisite Na⁺ using this method is listed in **Appendix 2**. Dried clays were ground in a mortar and sieved through 200 or 325 mesh screens to achieve a fine powder.

2.2.2 Small Scale (Mortar and Pestle) Method

Over sixty five compoundings of GRAS chemicals into Cloisite Na⁺ were completed using the mortar and pestle method (number of compoundings actually tested is approximately 50). Due to cost and availability issues, several chemicals had to be prepared at a small scale. The methodology of mortar and pestle mixing is very similar to the bulk method, replacing mechanical mixing via machine with mechanical mixing via human work. The drawback to this method is that it does not compare well to mechanical processing in terms of amount of shear. GRAS chemicals were introduced in a liquid stage (molten or solubilized) if possible. A majority of GRAS chemicals were introduced using water or ethanol as a solubilizing agent, which, when dried, would leave our chemical of interest in the clay gallery. Clays were initially prepared on a 2:1 by weight (chemical: clay) ratio to ensure enough chemical was introduced to the gallery. Similar to bulk method, if x-ray data showed compelling results, a ladder series of different chemical concentration to clay weight would be prepared to find a minimal effective concentration for the particular combination. See **Appendix 3** for the full annotated list.

Preparation closely follows that of the bulk method. The GRAS chemical of choice was either molten or solubilized if not in liquid phase. The clay (typically 10 grams) was pre-swelled with 100% by clay weight with water (on a few compoundings,

water amount was varied, see **Appendix 3, 5**). The liquid phase GRAS material would then be added to the swelled clay and mixed for ten minutes. The resultant organoclay would be left to dry in an 80°C oven overnight on aluminum foil. Dried clays were ground in a mortar and sieved through 200 or 325 mesh screens (75 and 40 μm , respectively) to achieve a fine powder.

Various theories were tested using the small scale approach, and experiments were designed to confirm questions that arose during preparation. A strong question brought up when dealing with amino acids was whether or not chirality had a strong effect on binding and/or d-spacing. This experiment was run on DL-Phenylalanine and L-Phenylalanine clay batches (hence the reasoning for having two entries of the same chemical). Another experiment was based on our observations of the chemical Urea, and our want to question whether it's binding mode was based on % water, as well as determining a minimum amount of water needed to provide binding. The results of such tests are in Results and Discussion 3.1 as well as **Appendix 5**.

2.3 Organoclay Testing Methods

2.3.1 X-ray Diffraction

Bragg's Law shows how the d-spacing between any two consecutive clay layers can be calculated via $n\lambda = 2d \sin \theta$, derived from Figure 6. The wavelength of the x-ray, λ , is determined from the source, and n is an integer ($n = 1, 2, 3, \dots$ typically we are only interested when $n = 1$) that indicates the order of the x-rays when they are constructively in phase. Theta (θ) is the acute angle between the entering incident x-ray and the clay platelet. Trigonometry solves all the other relationships listed in Figure 6.

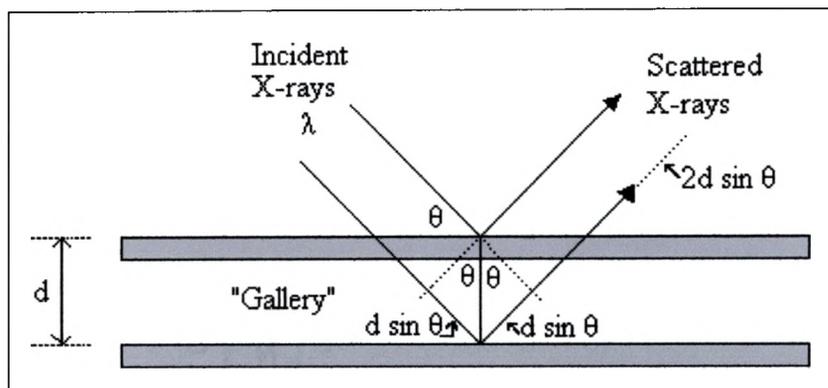


Figure 6. Diagram explaining X-ray diffraction.

Dry (<2% H₂O) Cloisite Na⁺ only shows a d-spacing of 11.7 Å. Any additional intercalated agents *must* increase the clay gallery. A truly exfoliated system would not show a d-spacing (other than high angle A/B plane crystallinity of the montmorillonite itself which details crystallinity and molecular distances in the $hk0$ plane, from 20-25 Å), indicating that individual clay platelets are randomly oriented in a matrix so that no long range crystallinity is intact in the sample. Transmission Electron Microscopy (TEM) imaging would need to be completed to verify any X-ray diffraction patterns that potentially shows exfoliation as a check.

All X-ray studies were performed on a BEDE-D1 X-ray diffractometer in powder mode using a copper source ($\lambda = 1.541838$ Å). The scans were performed in the Physics Department of Texas State University - San Marcos.

2.3.2 Thermogravimetric Testing

Thermogravimetric Analysis, or TGA, was performed on a variety of samples that were proven to have large d-spacings via from X-ray analysis: Urea, glyceryl behenate mixed ester, myristic acid, lecithin, glyceryl monostearate, glyceryl stearate mixed ester, and pentaerythritol monostearate organoclays. All samples were prepared at a 2:1 chemical: clay ratio, except PEMS organoclay, which was 95 meq/100g clay

concentration, and lecithin, which was at a 1:1 ratio by weight. The analysis would help determine and quantify thermal stability a particular intercalate/clay complex.

TGA measures mass loss as a function of temperature, either in an inert Argon atmosphere or in air (methods used in this study used argon). Samples are weighed on a platinum pan (which will not melt, change phase/shape, or react in our temperature range) and heated from room temperature to 800°C on a 20°/min temperature ramp while constantly being weighed. There is generally a small water loss peak for every sample at 60-80°C, typically unavoidable due to humidity and water still in clay gallery. Then samples undergo a large degradation loss curve as the intercalated chemical decomposes. This change is important, as the loss of chemical surface modifier at these higher temperatures can effect d-spacing negatively because of the chemical being boiled or reacted off of the surface. Tied to this value is the 10% loss value, indicating that at this point, 10% of the original weight of the sample is now gone. A final relatively minor loss peak occurs around 600+°C, the loss of the hydroxyl groups (as water) on the tetrahedral outer layer. After this loss, the clay is a char, generally the leftover interior octahedral layer coated with silicon oxide tetrahedral layer.

The original mass loss peak is essentially unimportant as is. One must perform a first derivative scan on the mass loss curve to bring attention to areas of change. Peaks resulting from a first derivative scan show the areas of highest mass loss. First derivative mass loss peaks are produced electronically using a computer program provided with the thermal equipment.

TGA scans were performed on a TA Instruments, Inc. TGA Q50 at a scan rate of 20°/minute from room temperature (generally 20-25°C) to 800°C. The TGA was

operated at the Department of Chemistry and Biochemistry at Texas State University - San Marcos by technician Stewart Harris.

2.4 Polymer / Organoclay Compounding

Primary investigation was attempted using Fortiflex HDPE A60-70-162 from Solvay Polymers, and Polypropylene. The investigation was for general visual qualitative inspection under microscope magnification on the following organoclays at a 5% loading: 2:1 (chemical: clay) Radiesurf 7174 pentaerythritol monostearate blend, 2:1 glyceryl stearate, 2:1 glyceryl monostearate, 2:1 glyceryl behenate, 2:1 urea and 1:1 lecithin. The top performing organoclay out of these preliminary trials, Radiesurf 7174 PEMS blend, was chosen for optimization tests. It was made in 95 meq concentration and compounded at a 5% loading into the polymers listed in Table 2.

All compounding was accomplished via a Haake driven Rheomix 600 bowl mixer. The bowl mixer could adequately allow up to 65 grams of polymer at a time. All compoundings were run at a 5% organoclay by weight of a 50 grams polymer sample, which still allowed for maximum mixing. Initially, the machine's three heating stages would be set to industrially used processing temperatures (see Table 2). Then the polymer would be introduced in pellet form at a low RPM paddle setting, generally 10 or lower. The polymer was allowed several minutes to reach its melt point while at this low RPM setting, turning the once solid polymer to a viscous fluid. To this molten polymer the organoclay was added carefully and slowly, typically 1 gram per minute, 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 minutes at 50 RPM. After the allotted time, the vent would be opened, the paddles slowed to a stop, and the temperature

would be lowered to stiffen the polymer for ease of removal. Compounded polymer was collected and cooled on aluminum foil, then bagged to lock out contaminants and minimize reactions with air.

2.5 Polymer Organoclay Intercalate Testing Methods

2.5.1 X-ray Diffraction of Polymer Organoclay Intercalates

X-ray diffraction can be used for determining extent of intercalation of organoclays in polymeric media. Amorphous polymers have extremely small amounts crystallinity, and therefore no appreciable 2θ peaks are observed due to polymer alone (polypropylene (iPP) and polyethylene-co-vinyl acetate (EVA) are exceptions as pertaining to this study, as they have respective peaks reflecting crystalline domains). In an X-ray of an exfoliated nanoclay/polymer system, there should be little to no peaks due to the original nanoclay itself. The ability of a polymer to organophilize with the organoclay will be directly evident in an X-ray scan; the primary peak of the nanoclay will lower or spread out more. If there appears to be peaks around 6.00-8.00 degrees 2θ , there is evidence of collapsed organoclay (dry montmorillonite has an 11.7 Å d-spacing).

The scans were completed on melt compounded blends of 5% by polymer weight pentaerythritol monostearate organoclay with the polymers listed in Table 2.

Pentaerythritol monostearate organoclay showed the most promise as an intercalate, as it had the highest d-spacing of the 40+ chemicals reviewed. Due to availability of the X-ray machine, a complete array of polymer compoundings with various GRAS modified clays could not be performed. Scans were performed on the same X-ray instrument as used for the organoclays, a BEDE-D1 X-ray diffractometer in powder mode using a

copper source The scans were performed in the Physics Department of Texas State University - San Marcos.

2.6 Purity Assessment of pentaerythritol monostearate

Radiasurf 7174 received from Oleon is sold as “pentaerythritol monostearate.” The chemical, however, is not pure monostearate, as the manufacturer has brought to our attention. Several tests were run to determine the ester percentage of the blend. Using solubility tests across a broad range of solvents, including: hexane, ethyl acetate, dimethyl sulfoxide, tetrahydrofuran, benzene, chloroform, isopropyl alcohol, and methanol, a TLC strategy was developed and implemented. After optimization on TLC, a silica column chromatography column was set up to attempt separation that would yield usable amounts of individual esters. The column was approximately 1.5” in diameter and 3’ long. 1kg of silica gel was poured into the column and topped by a layer of sand. The silica gel was pre-wet with a 50/50 toluene/ethyl acetate mixture, taking careful measure not to disturb the sand. After completely wet, the thick slurry of toluene and the Radiasurf 7174 PEMS blend was added at the top and solvent was added to start the column. Due to the nature of pentaerythritol stearate esters (not UV/Vis active), there is no definitive way to track progress other than make note of amount of solvent added. Once we had estimated the first product had reached the bottom, we took 25 ml aliquots for the first 100 ml of solvent, than 50 ml aliquots for a remaining 200 ml of solvent. A final 100 ml aliquot was taken at the end.

Samples were collected and boiled down using a Rotovac to minimal volume, and allowed to evaporate on a 100°C hotplate. Aliquots 1-3 contained sample (shown by a white waxy material) believed to be monoester, aliquot 4 contained a very minimal

amount, showing a break in the esters. Aliquots 5-9 all contained appreciable amounts of product, likely a mixture of diester and triester. All aliquots were tested via TLC to determine purity.

As an alternative measure of Radasurf 7174 PEMS blend composition, a ^1H NMR was performed by post-doc Anathanarayanan Iyer on a 400-MHz Oxford NMR 400 spectrometer in Texas State University's Chemistry Department. The Radasurf 7174 PEMS blend was dissolved in d-benzene for the run.

3.0 RESULTS AND DISCUSSION

3.1 Organoclay Composite Study

All organoclays made were surveyed via X-ray diffraction to search for high d-spacing. The higher the d-spacing, the more potential the organoclay has for intercalation in polymers, in that a more exfoliated platelet can individually break off. The more random and spread out an organoclay species is, the more it can potentially fortify a polymer. Additional effects of having successfully exfoliated nanoclay include lowering gas permeability and increasing modulus.

The data compiled shows a small amount of species have over a 20 Å d-spacing. Four species show an improvement over a common major cation exchanged quaternary ammonium modified organoclay (Cloisite 20A). There is a large amount of variety in the species; most have one or more long alkyl R-group, typical of established large d-spacing moieties, hooked to an oxygen-containing functional group. Others have an altogether different approach as to how they spread the clay gallery.

X-ray studies can determine how well our GRAS organic species is intercalated into our parent clay, as well as how well the GRAS organoclay intercalates into polymer systems. Using TGA, we can assess how thermally stable a GRAS organoclay is by looking at the organic decomposition peak.

3.1.1 GRAS Organoclays

The vast majority of organoclays produced using either large or small scale methods underwent drying and labeling procedures without incident. There was a slight difference in color from organoclay to organoclay, mostly ranging from a slight tan (Cloisite Na⁺ being a slight tan) through various brown shades. There were a few exceptions to this (See section 3.2.7).

Various chemicals did not survive the rigors of initial processing, particularly the drying step. These species are listed in **Appendix 4**. Most of the molecules in this section succumbed to oxidation due to conjugation or openly reactive sites. From this original compounding work it was learned very quickly that there is little stability for most vitamins above 80°C (most vitamins are complex biomolecules not tolerant to harsh temperatures). The one exception in our study was Vitamin C (a simple organic molecule, ascorbic acid). Other compounds that proved nutritious to bacteria/fungi (sugars, amino acids, etc) had to be carefully watched and thoroughly dried to prevent microbial growth, while in some cases it was unavoidable no matter what the precaution (ex-inositol, which had microbe growth in a dry sealed container).

3.2 X-ray Diffraction Studies of GRAS Organoclays

The large amounts of chemicals intercalated into Cloisite Na⁺ montmorillonite were diverse functionally and chemically. The one tie line to all species, in addition to GRAS status, was the presence of some sort of functional group that ion dipole bonds to the positive alkali metal cations on the surface. Only one GRAS chemical (lecithin) contained a site of quaternary ammonium capable of cation exchanging with surface sodium cations.

X-ray diffraction proved to be quite a useful tool in determining basal d-spacing for our organoclays. The resulting charts of GRAS chemical d-spacings, as well as the patterns themselves, are available in **APPENDIX 5**. Of all the chemicals we intercalated into Cloisite Na⁺, ten species showed a d-spacing above that of 20 Å. These species are listed in Table 3. As a point of clarification, an additional peak at 13.87 degrees 2θ, corresponding to a d-spacing of 6.42 Å, appears on a few X-ray spectra listed in **Appendix 5**. This peak is from inherent polymer crystallinity in the tape used to affix the samples to the x-ray plate. The x-ray for tape alone (labeled “Background Tape”) is available in **Appendix 5**.

Table 3. List of top performing GRAS organoclays as compared to Cloisite 20A

Chemical*	d-spacing (Å)
Glyceryl Stearate, mixed ester	78.20
Radiasurf 7174 (Pentaerythritol stearate, mixed ester)	72.00
Glyceryl monostearate	54.00
Lecithin	52.76
Pentaerythritol Monostearate	50.43
Myristic Acid	32.02
L-Proline	26.80
<i>CLOISITE 20A</i>	26.20
Urea	24.78
Glyceryl Behenate	23.00
Urea 25% H ₂ O	21.13
Propyl Gallate	20.54
*For full data on the organoclays, see Appendices 1, 5	

3.2.1 X-ray results and discussion for organoclays below 20 Å

While the vast majority of the organoclays did not have a large d-spacing (considered over 20 Å), this does still not rule them out as a good potential intercalate for polymers. Various chemicals that are polymer additives, such as anti-fogging agents, anti-static chemicals, neutralizers, plasticizers and lubricants are also on the GRAS list. Typical of these polymer additives (but not always the case) are the oxygenated head group and/or long R-group tails discussed earlier as high priority to our studies. Even if the proposed intercalate did not separate the clay gallery well, there could still be potential exfoliation of the clay if the polymer is attracted enough to the intercalating chemical agent, providing atypical results. These follow up procedures were not undertaken in this study, but research would point that the likelihood is good enough to continue future alternative investigation.

Typical polymer additives or derivatives thereof that were studied with a d-spacing below 20 Å are listed in Table 4. The presence of a glycerol unit or carboxylic acid (such as citric acid and lactic acid) head group is a common generality. The highly oxygenated groups can ion-dipole around surface cations with a high degree of sophistication (to be discussed in a later section).

Table 4. Common polymer additives/derivatives used in industry with <20 Å d-spacing.

Chemical*	d-spacing[†]
Propylene Glycol	18.91
Triethyl citrate	17.34
Stearyl Citrate	17.32
Lactic acid	16.37
Citric acid	15.50
Benzoic acid	15.25
Oleic acid	13.08
*For full data on the organoclays, see Appendices 1, 5 †in Angstroms	

A trend noticed in the below 20 Å group was an expected/predicted one: the shorter the chain, the lower its place on the list, with some exception. Oleic acid has a long R-group, C-18, but the addition of a double bond on the C-18 tail adds in reactivity to the molecule. It is likely that while in the oven oxygenation reactions occurred to degrade the molecule down to smaller pieces. Oleic acid will not degrade at 80°C by itself, as it is a common appendage to various polymer additives used at much higher temperatures. Montmorillonite clays are known to catalyze a wide variety of oxidation reactions, but it is unclear whether or not this is the culprit for the degradation.

3.2.2 X-ray results and discussion for Amino Acid Organoclays

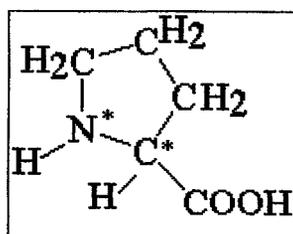
Also of note is discussion for amino acid organoclays. The typical amino acid had a very low d-spacing, as shown in Table 5.

Table 5. Amino acid organoclays d-spacings.

Chemical*	d-spacing (Å)
L-Proline	26.80
L-Tryptophan	17.97
DL-Phenylalanine	15.87
L-Phenylalanine	15.83
L-Methionine	15.32
L-Isoleucine	14.04
L-Asparagine	13.89
DL-Lysine	13.68

* For full data on the organoclays, see Appendices 1, 5

Most amino acids gave modest spacings, except in the case of proline. Proline is the only cyclic amino acid, and is one of the twenty naturally occurring amino acids among most of living organisms in the known world. Figure 7 shows the structure. As an aside, the proline used in this study is 100% L-conformation (as it is in nature).

**Figure 7. The cyclic amino acid proline.** * denotes a chiral site.

Proline is odd in that there is no long R-group to provide the d-spacing observed (as there is in every molecule above 26.4 Å). It is unclear as to why such a large d-spacing occurred. It is possible that some sort of intermolecular stacking is occurring, or some sort of gallery packing is stable enough to provide the d-spacing shown.

A question raised in the experimental section asked whether chirality makes a difference in d-spacing. That question was answered with the compounding of DL-Phenylalanine and L-Phenylalanine organoclays and the subsequent x-ray diffraction results. From our diffraction data, there is no statistical difference between the two as far as d-spacing. This could be cautiously applied throughout to every one of the essential amino acids, as they all have the same type of chiral site, where an NH_3 is joined to the same central chiral carbon that a COOH group is attached to. Also bonded to that central carbon are hydrogen and an R group that is the only site of variation. Regardless of R group, the proximity of the NH_3 and COOH to one another should always bind in a particular way, regardless of chirality.

3.2.3 X-ray results and discussion for Lecithin Organoclays

Lecithin is the only chemical on the GRAS list that we chose to study that contains a quaternary ammonium site. The site is choline linked through a phosphate bond to a glycerol unit with 2 long R-groups joined by ester bonds to the glycerol unit. The R-groups can be different fatty acid residues (C-14, 16, 18 with varying conjugation), and they differ in percentage and type from animal to animal/plant to plant, even from cell system to cell system. Biomolecules such as phospholipids that have conjugation are all *cis* across the double bond as they appear in nature. The site of conjugation is typically at the 9th carbon from the ester linkage if conjugated once (ex-oleic acid), or at the 9th and 12th carbon if there is double conjugation (ex-linoleic acid). A molecular model of one type of lecithin is shown in Figure 8.

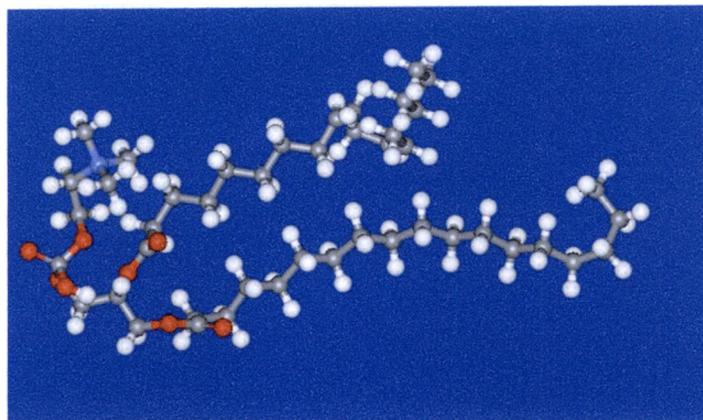


Figure 8. Molecular model of lecithin. The blue site is the choline unit; the middle chain is kinked, showing a site of conjugation.

Molecular modeling evidence shows that the quaternary ammonium site on the lecithin cation exchanges with sodium ions on the clay surface. Experimentally we observe a large d-spacing corresponding to two full lecithin molecules stacked end to end, so there is little or no evidence of interdigitation of the R-groups. While the lecithin organoclays were made and dried at 80°C, there is evidence that lecithin itself cannot withstand higher temperatures (similar to oleic acid), as evidenced in later sections detailing polymer compounding results.

3.2.4 X-ray results and discussion for Glyceryl Stearate Organoclays

Glyceryl stearate esters provided some of the largest d-spacings shown in our study. A glycerol unit has three hydroxyl sites available for esterification. Esterification with long fatty acids leads to compounds commonly known as mono-, di- and triglycerides (the most commonly known of the “saturated fats” group). Stearyl groups are C-18 carboxylic acid groups that are completely saturated. Examples of the different types of glyceryl stearate along with isomers can be seen in Figure 9.

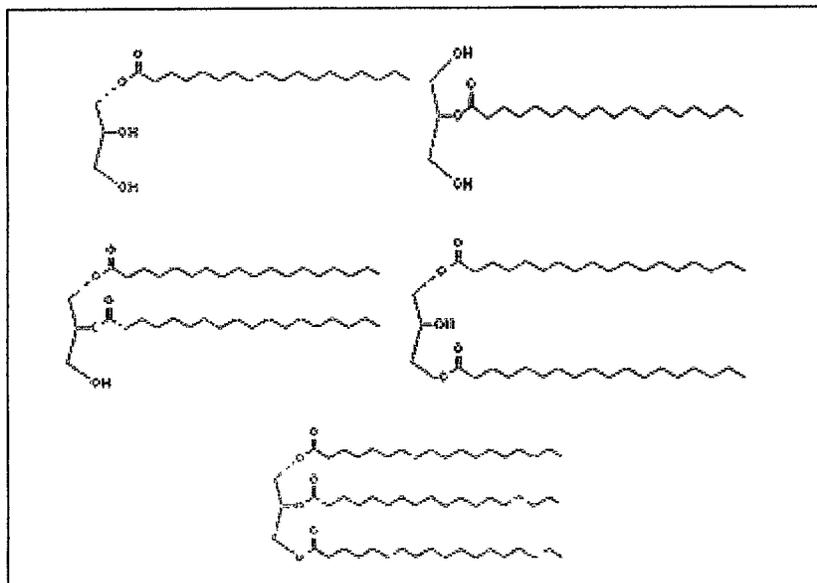


Figure 9. Glyceryl monostearate (top two isomers), glyceryl distearate (middle) esters, and glyceryl tristearate (bottom).

Figure 9 shows the two isomers of the monostearyl ester (Glyceryl Monostearate, or GMS). Alone, the d-spacing of the mixed isomer monoester was not as high as a mixed mono-, di-, and triester compound. Reasons for this discrepancy have arisen from molecular modeling. There is strong evidence the ester with the “middle” linked (secondary hydroxyl) monostearate group (top right molecule in Figure 9) has a strong ion-dipole bonding affinity for surface sodium cations as compared to an ester with the stearate group on a primary hydroxyl (top left molecule in Figure 9). Molecular modeling has shown the primary hydroxyl case to have the stearate group leaning down or angled, giving a much reduced d-spacing (most likely attributed to the 17.8 Å peak (5.00 degrees 2θ) noticed in the X-ray pattern, see Figure 10). Modeling has also shown the secondary linked ester to have the stearate group sticking straight up, providing us with the large primary peak observed via X-ray analysis.

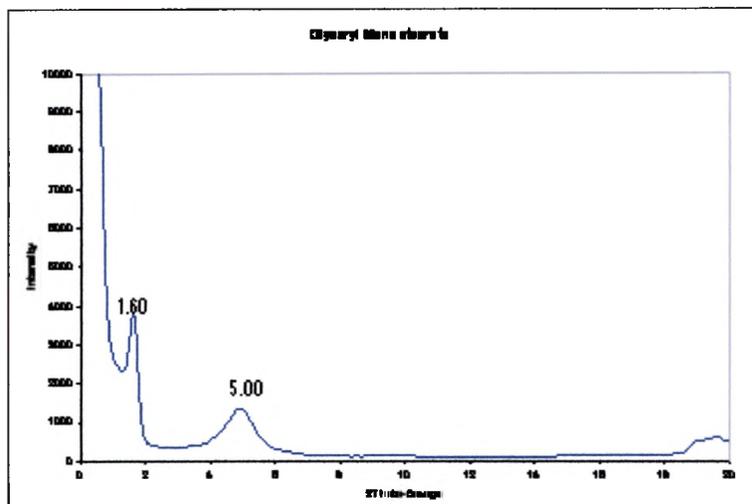


Figure 10. Glyceryl monostearate organoclay x-ray diffraction peaks.

Note the sharp peak at around 1.60 2θ ($d=54.00 \text{ \AA}$) and a secondary peak at 5.0 2θ ($d=17.8 \text{ \AA}$).

For our mixed ester (approximately 40% mono, 30% di and 30% tri-ester) case we see a d-spacing 15.54 \AA larger than in pure monoester. This discrepancy cannot be proven using molecular modeling, but evidence provides for a synergistic effect from unbound di- and tristearate molecules interdigitating, via the long stearate tails, with surface cation bound monostearate and distearate molecules. From Figure 11, we can see

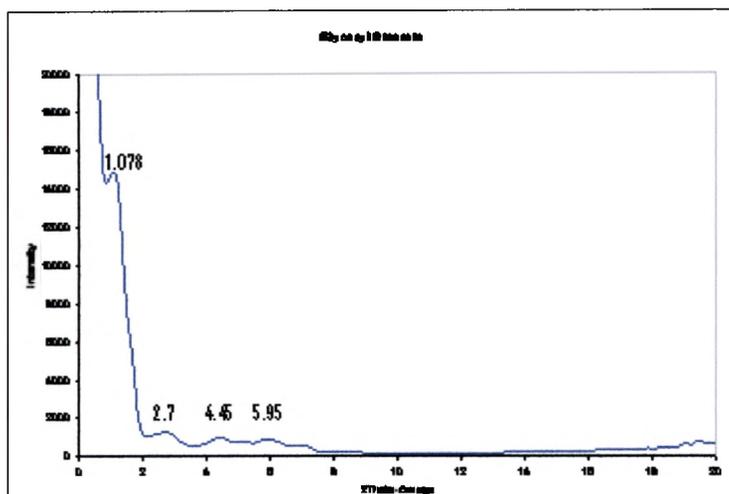


Figure 11. Glyceryl Stearate mixed ester x-ray diffraction peaks.

Peaks shown are: 1.078 2.7, 4.45, and 5.95 2Theta-Omega ($d=81.91, 32.24, 19.98$ and 14.83 \AA respectively).

the larger primary peak along with the appearance of several new peaks. These peaks are a conglomeration of phases of the glyceryl stearate esters form in the clay gallery.

As the size of our study was so vast and was primarily a survey study, we were limited in optimization studies. Although we obtained the highest d-spacing from glyceryl stearate, there was no attempt to optimize surface concentration (milliequivalents) due to the timing of our study.

3.2.5 X-ray results and discussion for Pentaerythritol Stearate Organoclays

Pentaerythritol Stearate, mixed ester, modified organoclay proved to have one of the highest basal d-spacing, with a d-spacing of approximately 72.00 \AA at concentrations higher than 95 meq. The pentaerythritol stearate used and tested for all procedures was the Radiesurf 7174 brand Pentaerythritol Monostearate (PEMS, actually a blend of pentaerythritol stearate esters). Radiesurf 7174 PEMS organoclay was the most studied of our compounds due to its outstanding X-ray results even at low concentration.

The binding mode of the molecule pentaerythritol monostearate is complex, but very efficient for separating clay galleries. Consider the precursor molecule pentaerythritol, shown in Figure 12. Its method of binding is efficient: the quaternary

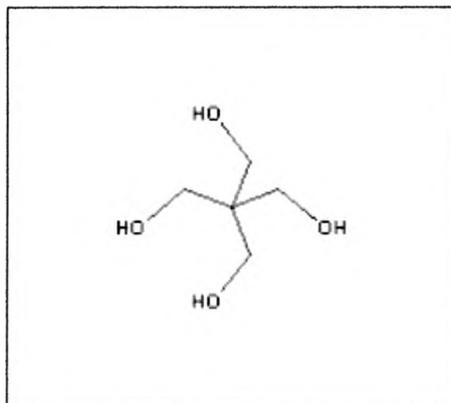


Figure 12. Stick model of Pentaerythritol.

carbon's tetrahedral geometry allows three hydroxymethyl's to ion-dipole bind to surface cations, leaving the fourth hydroxyl perpendicular to the clay surface. When this fourth hydroxyl is esterified with stearic acid, this leaves a long C-18 tail essentially straight up from the surface, in the primary binding mode for the monostearyl pentaerythritol. The X-ray diffraction pattern for 95 meq/100g clay pentaerythritol monostearate (obtained from ChemService) is shown Figure 13.

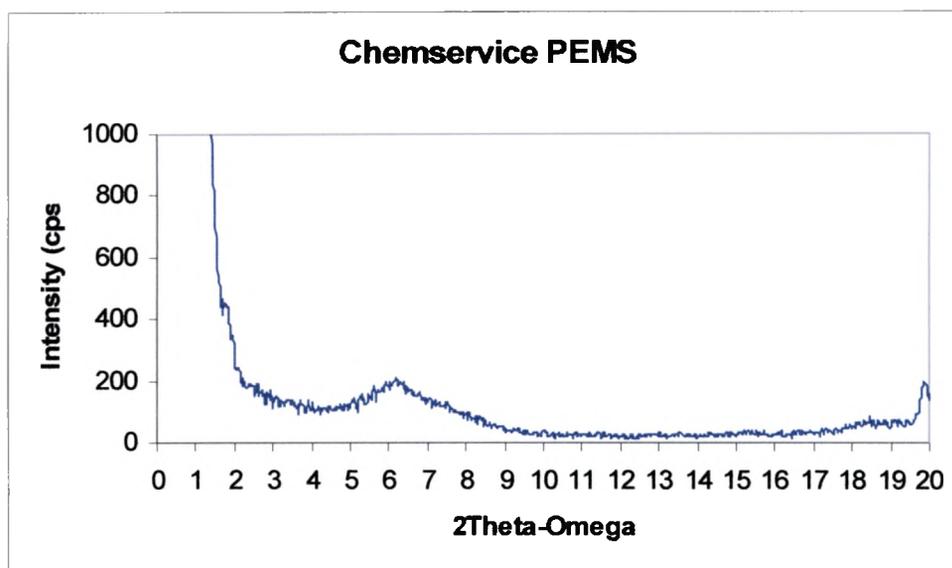


Figure 13. Pentaerythritol Monostearate diffraction pattern

What was discovered in the molecular model of how PEMS binds to montmorillonite is that the three open hydroxyl groups of the pentaerythritol form a strongly ordered casing around the cation with the alcohol hydrogens pointing away. This is confirmed by molecular modeling in Figure 14. The ion-dipole connection formed between the hydroxyl groups and surface cation is strong (see Section 3.3).

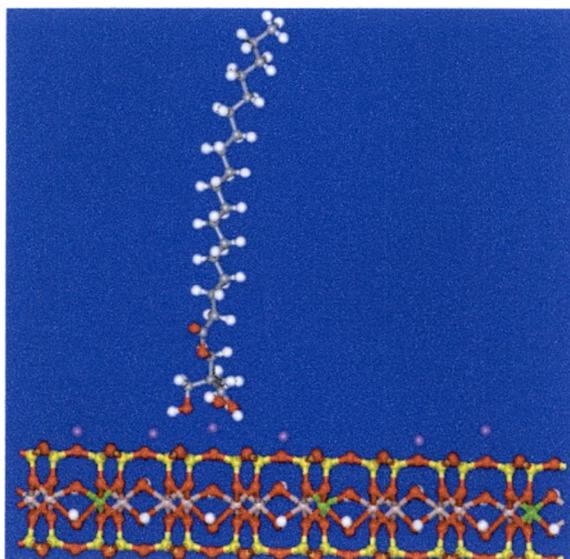


Figure 14. Molecular model of PEMS coordinating with surface alkali cation.

In the Radiesurf 7174 Pentaerythritol stearate mixed ester blend, excess molecules that are not surface bound, with varying degrees of esterification, can interdigitate in a similar manner to the glyceryl stearate molecules. These aspects give a d-spacing 21.57 Å larger than pure monostearate. The mixed ester diffraction pattern is shown in Figure 15).

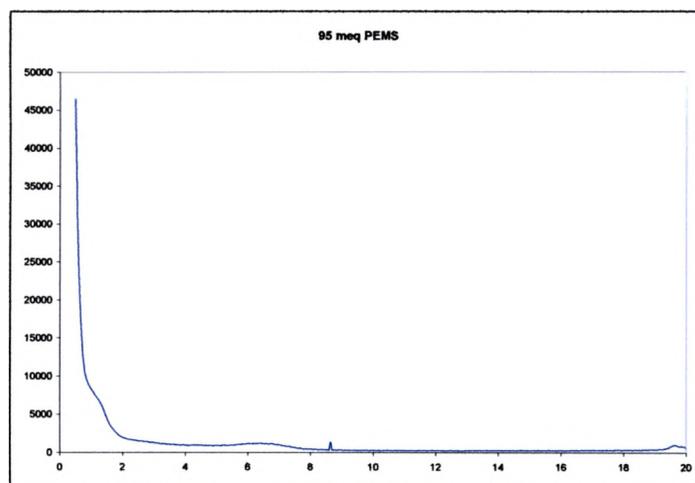


Figure 15. 95 meq Radiesurf Pentaerythritol Stearate mixed ester organoclay.

The region of scattering in the X-ray pattern is somewhat broad, and seems to run from ~1.00-1.90 degrees 2θ . There is evidence the other multi-esters contribute to this large spacing. Molecular modeling evidences shows the distearate ester can also ion-dipole bind to surface cations similar to monostearate moieties, but the additional stearate arm is now approximately 90° to the initial one that is pointing straight up. A model of pentaerythritol distearate complexed with a sodium cation is shown in Figure 16. With the monostearate and distearate molecules bound to the surface, tri- and tetra-ester molecules interdigitated 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.

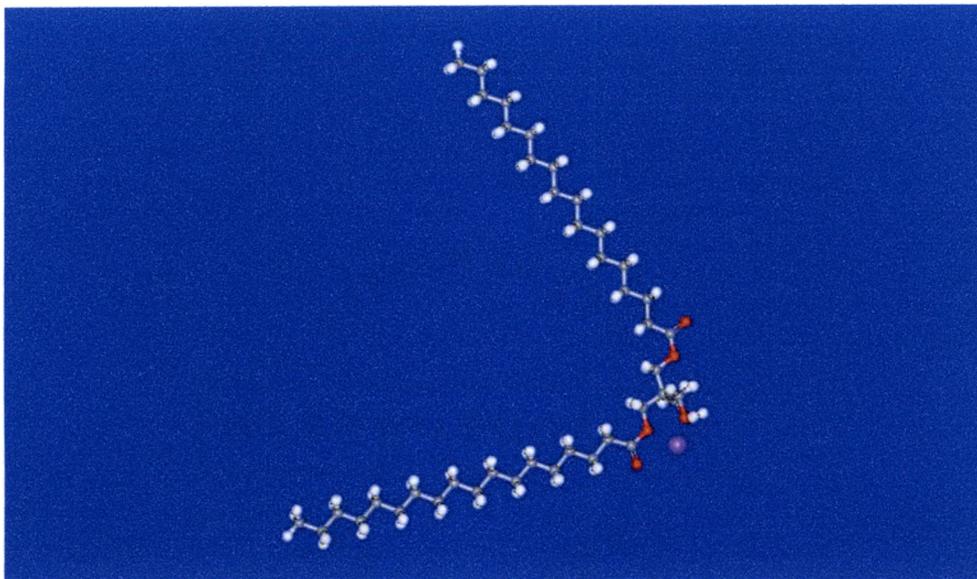


Figure 16. Pentaerythritol distearate complexed with a sodium cation.

Due to the large spacing compared to other GRAS organoclays (along with thermal data results), optimization studies into the concentration of the Radasurf 7174 PEMS modifier needed to provide d-spacing were also performed. From a study of 45, 95, 145, and 195 meq/100g clay, it was determined that 95 meq/100g clay provided the 72.00 Å peaks shown earlier but at a highly reduced concentration (2:1 chemical to clay ratio is approximately 250 meq/100g clay, whereas 95 meq/100g clay corresponds to 0.383:1 chemical: clay ratio). The X-ray of the series is shown in Figure 17.

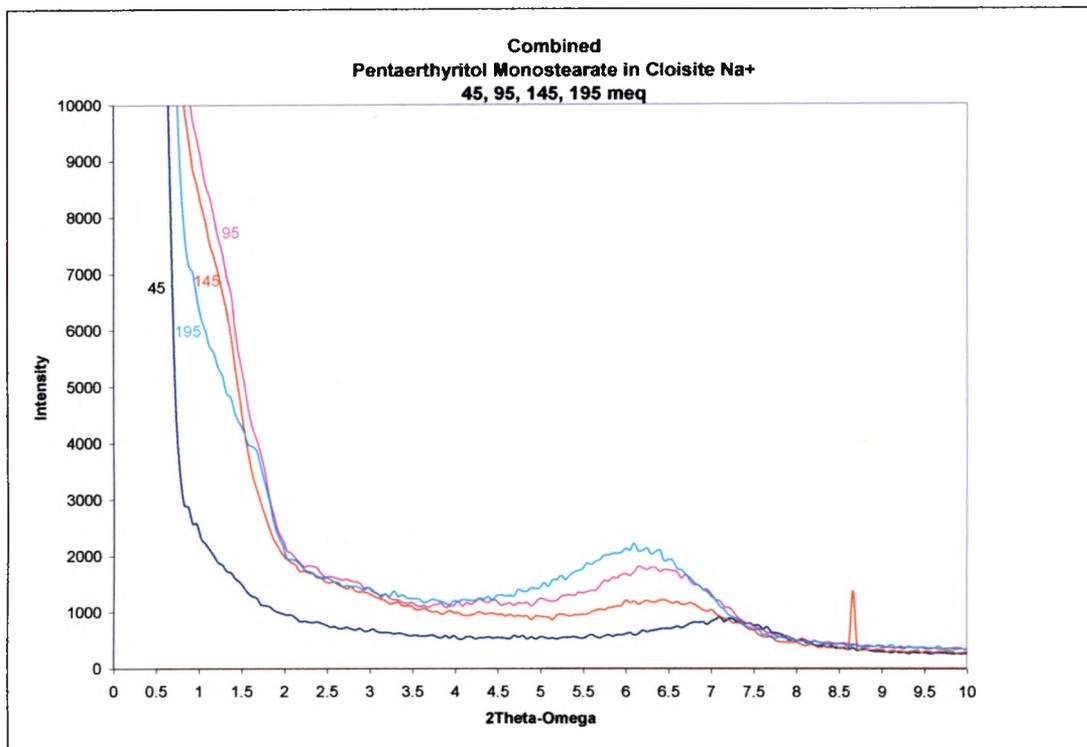


Figure 17. X-ray diffraction data on the ladder series of PEMS organoclays.

Unfortunately, since it was learned late into the study that the organoclays made with Radasurf 7174 Pentaerythritol Monostearate were not made of pure pentaerythritol monostearate, but rather a mixture of di-, tri-, and tetraesters, the numeric milliequivalent values are not correct. To solve for amount of surface modifier, a study of the Radasurf 7174 was needed. After consultation with Oleon, the producer of Radasurf blends, the 7174 Pentaerythritol Monostearate compound was reported as containing 6% monoester, 27% diester, 48% triester, and 29% tetraester. These values were obtained from Oleon via capillary GC, reference method AOCS Cd 11b-91. This would alter the values for what we thought were 45, 95, 145, etc milliequivalents considerably. Alternative testing methods were conducted that concluded different results, as discussed in Section 3.5.

3.2.6 Other observations with Organoclays

While the crux of the research undertaken was to survey GRAS species which would give a large d-spacing, several atypical reactions occurred worthy of note. In the case of propyl gallate organoclay, made via small scale procedures as described in Experiment section 2.2.2, a color change was noted. Upon addition of a 50/50 mixture of ethanol and water to solubilize the propyl gallate with the Cloisite Na⁺, a deep purple color flushed throughout. The reason for this most likely has to deal with propyl gallate stacking with itself using the clay as a template, creating a conjugated enough system to absorb visible light. The color change persisted, subsiding slightly upon drying.

A similar result happened to the Vanillin organoclay, prepared small scale as well (but with absolute ethanol), although the color change was not observed while processing the clay. After the typical preparation, the vanillin organoclay was set to dry overnight. During the drying process the organoclay took on a light purple color. This color has continuously persisted. Chemically, the reasons for the color change are likely similar to propyl gallate, due to their similar aromatic structure.

3.3 Thermogravimetric Analysis of Organoclays

Thermogravimetric analysis (TGA) of the high d-spacing organoclays provides some insight into the strength of the ion-dipole bond between surface onium ions and the GRAS chemical in question. In the graphs of first derivative weight percent versus temperature, several important results can be obtained. The original onset of degradation of the major peak tells us when the chemical is starting to break down, either chemically reacting (dehydration, decarboxylation, etc) or physically coming off the clay surface (boiling). The major peak can tell us a multitude of information. **Table 6** contains the

information on the onset and peak temperature of degradation for the organoclays tested.

The resultant graphs of the compounds can be viewed in **Appendix 6**.

Table 6. Organoclays with their onset of degradation and peak degradation

Organoclay component	Onset of Degradation (°C)	Peak (°C)
Myristic Acid	130.24	223.44
Urea	137.17	237.46
Cloisite 20A (2H2T)	205.14	317.42
Lecithin*	180.39	361.26
Glyceryl Behenate, mixed	211.19	393.21
Glyceryl Stearate, mixed	177.67	395.37
Glyceryl Monostearate	154.97	409.19
ChemService Pentaerythritol Monostearate†	201.66	431.71
Radiasurf 7174 blend Pentaerythritol Monostearate†	254.41	402.11
*1:1 chemical: clay by weight. † 95 meq/100g clay.		

3.3.1 Thermogravimetric Analysis Results and Discussion

In table form, the results can be misleading. Each individual TGA says something about the individual components. An ideal combination would be a late onset of degradation and a late peak. Only four organoclays that we tested have an onset degradation past 200°C: Cloisite 20A, glyceryl behenate mixed ester, Radiasurf 7174 PEMS and ChemService PEMS.

3.3.2 Thermogravimetric Analysis Results and Discussion for a Carboxylic Acid

The poorest performing organoclay that we ran a Thermogravimetric scan of was a C-14 carboxylic acid, myristic acid. The low temperature peak indicates that there is not a large binding affinity for the carboxylic acid and the surface cations. This is likely due to a poor chelation of the surface cations (compared to strong binding moieties like pentaerythritol or glycerol) as well as charge disparities between the carboxylic acid head group and the surface cations.

3.3.3 Thermogravimetric Analysis Results and Discussion for Top Performing Organoclays

The two GRAS organoclays that begin degradation above 200°C are an exciting find. They perform just as well as or better than Cloisite 20A, the quaternary ammonium modified organoclay that was tested as a comparison to the GRAS organoclays.

Southern Clay, Inc has already proven Cloisite 20A's resistance to degradation (one of the reasons it is such a successful product), and our test agreed with their results: onset of degradation does not begin until after 200°C. Radasurf 7174 PEMS blend organoclay in particular has a very late onset of degradation, into the region of Nylon processing (>220°C). ChemService PEMS has a slow rate of degradation until approximately 350°C, when it begins to rapidly degrade. Both pentaerythritol stearate esters have extremely high degradation peaks. This is exciting from an industrial processing standpoint, as organoclay nanocomposites are limited by hundreds of important factors, including the modifier's breakdown temperature, tending to char if mixed with Nylon. Radasurf 7174 PEMS blend begins to degrade at 250°C, whereas Cloisite 20A and

ChemService PEMS are already >10% degraded. Figure 18 contains a graph of the first derivative weight percent versus temperature of PEMS organoclay versus Cloisite 20A.

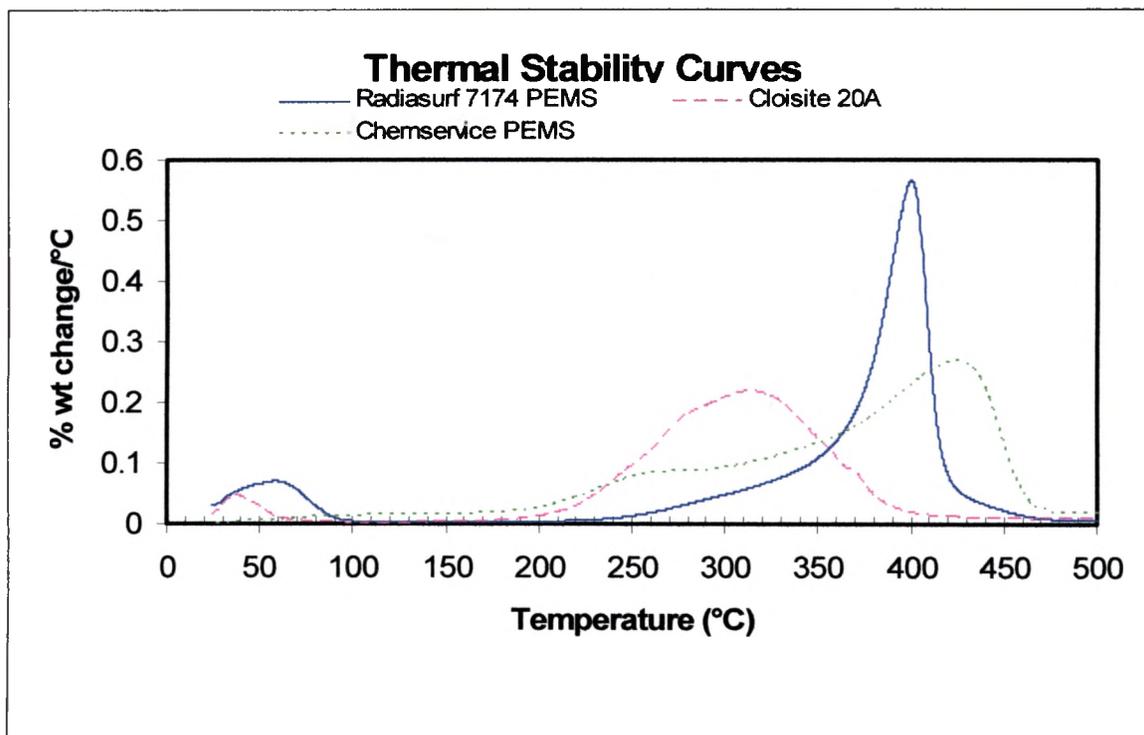


Figure 18. First derivative TGA mass loss plot of Radasurf 7174 PEMS blend, ChemService PEMS and Cloisite 20A.

The rounded low hump of Cloisite 20A shows that there is a constant strong affinity of the quaternary ammonium site for the clay surface. There is little change over the large temperature range it takes to dissociate the quaternary ammonium. Radasurf 7174 PEMS blend and ChemService PEMS on the other hand slowly degrade, slower than Cloisite 20A, but around 350°C both begin to rapidly degrade and come off en-mass. This would indicate a stronger bonding energy between the pentaerythritol moiety and surface cations; as energy is increased there is a rather sharp “breaking point” for the

PEMS molecule to dissociate off the surface. Radiansurf 7174 pentaerythritol stearate degrades approximately 30°C before ChemService PEMS, further proving the existence of extra-gallery tri- and tetraester compounds, which would degrade from the gallery faster than ion-dipole bound mono- and diesters. Cloisite 20A's mass loss on the other hand is even in loss/degradation of modifier, not showing a definitive point of dissociation.

Another aspect of thermal mass loss to consider is the formation of noxious byproducts. Quaternary ammonium organoclays, when heated, will give off tertiary amine complexes which have a smell similar to decomposing fish, in addition to alkenes which also are known for their foul odors. This degradation is accomplished in a method similar to Hoffman elimination, and only occurs at temperatures above 180°C.⁴³ This further limits quaternary ammonium organoclay use in food packaging. Pentaerythritol esters on the other hand do not produce any detectable off odors during high temperature polymer compounding, however it should be noted that chemical separation/mass spectrometry methods to determine degradation products have not been performed as of publication.

3.4 Polymer Compounding

Several GRAS organoclays gave significant enough x-ray results to warrant investigation into polymer compounding. The compounding method is listed in Experimental section 2.4. Extent of exfoliation would be quantifiable through x-ray diffraction methods. Visual inspection would add any justification to these results. An exfoliated polymer/clay nanocomposite system would 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. Visually, there should be no solid clumps. The appearance of such clumps (aggregates, see Figure 3 in Introduction Section) would show the clay could not exfoliate well.

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 harsh processing conditions the chemical treatment would be mechanically 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. A probable fix to this situation would use industrial methods such as a single or twin screw extruder, which have extremely short compounding residency, reducing the surface chemical stripping.

Six different polymers were used to conduct compounding tests. At first qualitative testing (as a visual guide) was done with generic in-house HDPE and Polypropylene. Final higher quality tests were completed on four food-grade polymers commonly used in modern industry shown in Table 2 in the Experimental Section.

3.4.1 Results and visual qualitative analysis of polymer composites

The organoclays listed in Experimental section 2.4 were compounded in HDPE and PP as a general visual test. No X-ray diffraction data was carried out on these samples; they were a simple generic microscope “test” to check viability in polymeric media. There was no implicit evidence of complete exfoliation in any of the samples, just varying shades of intercalation. There were macroscopic clumps in each polymer

sample, with a minimal amount present in the PEMS organoclay. Lecithin organoclay charred in both HDPE and PP, showing that it decomposes in open air processing conditions above 145°C. The charred lecithin organoclay looked like millimeter wide black flakes in the polymers. There is evidence from our findings that lecithin is catalytically degraded by montmorillonite in the presence of oxygen. As yet unpublished studies from Cryovac-Sealed Air have shown successfully lecithin organoclay intercalating into various trade polymers without the degree of degradation observed by our studies. Different equipment and processing conditions are likely to blame for the disparities.

3.4.2 Results and Discussion of PEMS Organoclay in Commercial Food Polymers

Of the various polymer compoundings made, only 95 meq/100g clay Radasurf 7174 PEMS was extensively studied in a good cross section of common commercially used food polymers (see Table 2 in Experimental section), as provided by Cryovac-Sealed Air, a major producer of meat and produce packaging in the United States. The concentration 95 meq/100g clay was determined from previous organoclay x-ray diffraction (see Figure 17) to be the minimum needed to provide large gallery spacing. The results of the compounding are shown in Figures 19, 20, 21 & 22, as compared to dry 95 meq Radasurf 7174 PEMS organoclay. The low intensity peak in all of the X-ray diffraction patterns around 8.5 degrees 2θ is typical of a metal (likely the background plate used in X-ray studies) and is not considered a valid peak related to our studies.

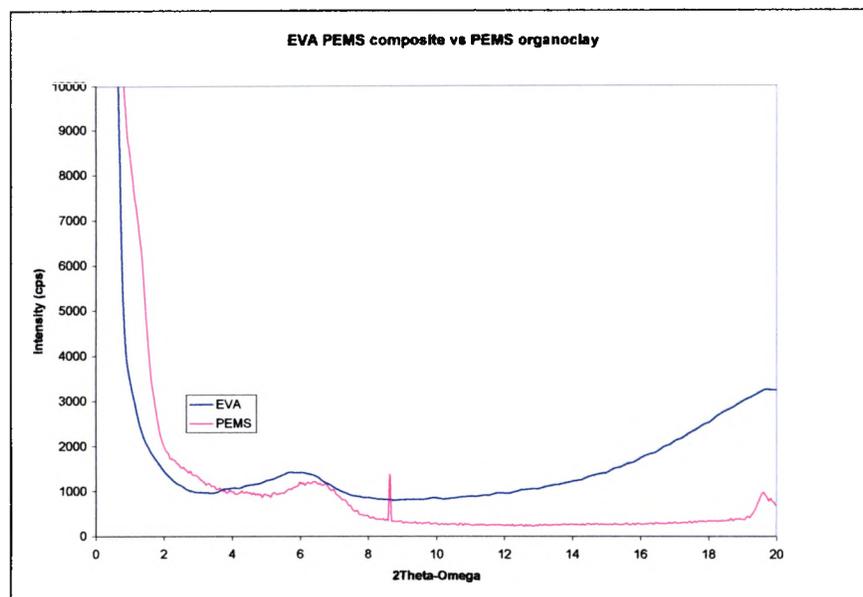


Figure 19. X-ray diffraction of 5% PEMS organoclay in EVA copolymer vs that of 95meq/100g clay Radiansurf 7174 PEMS organoclay.

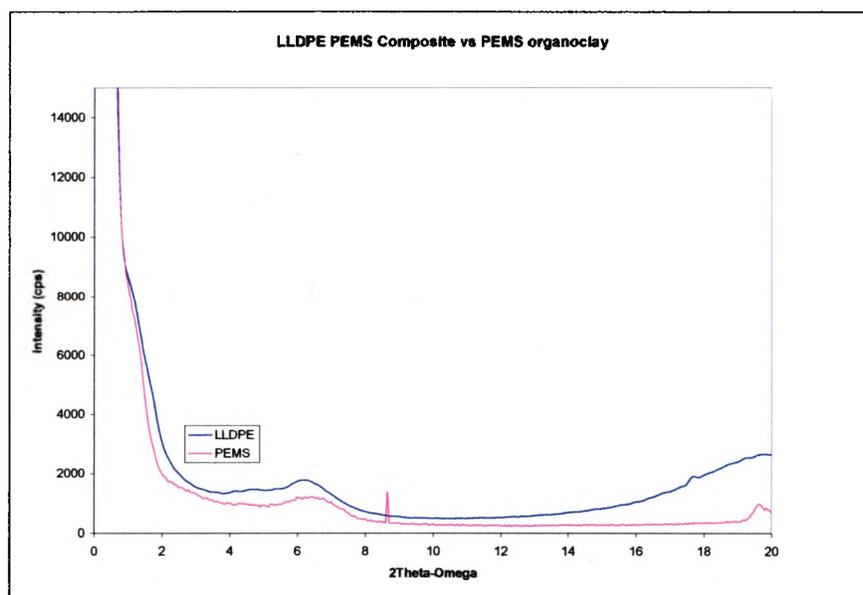


Figure 20. X-ray diffraction of 5% PEMS organoclay in LLDPE vs that of 95meq/100g clay Radiansurf 7174 PEMS organoclay.

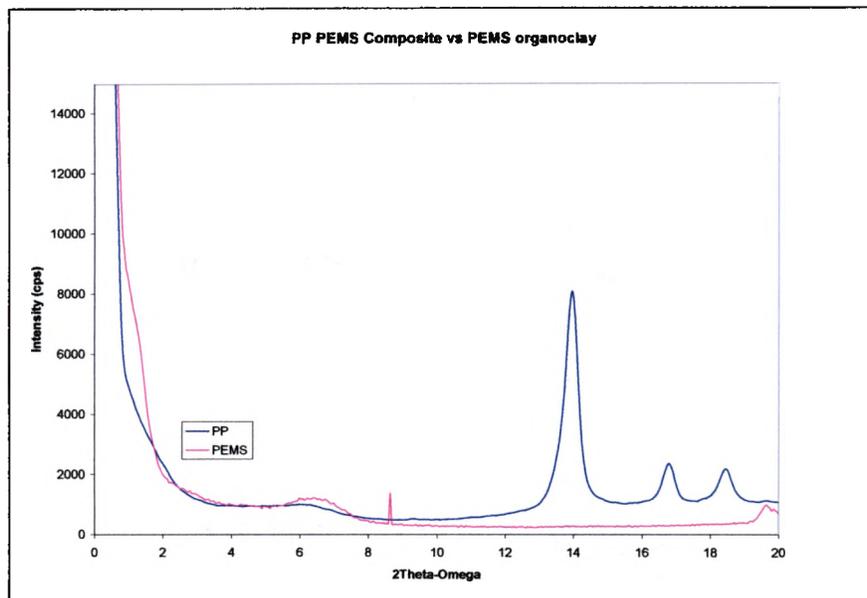


Figure 21. X-ray diffraction of 5% PEMS organoclay in Isotactic Polypropylene vs. that of 95meq/100g clay Radasurf 7174 PEMS organoclay. The three peaks at 14, 17, and 19 degrees 2θ are characteristic to Polypropylene's crystallinity and unrelated to organoclay modification.

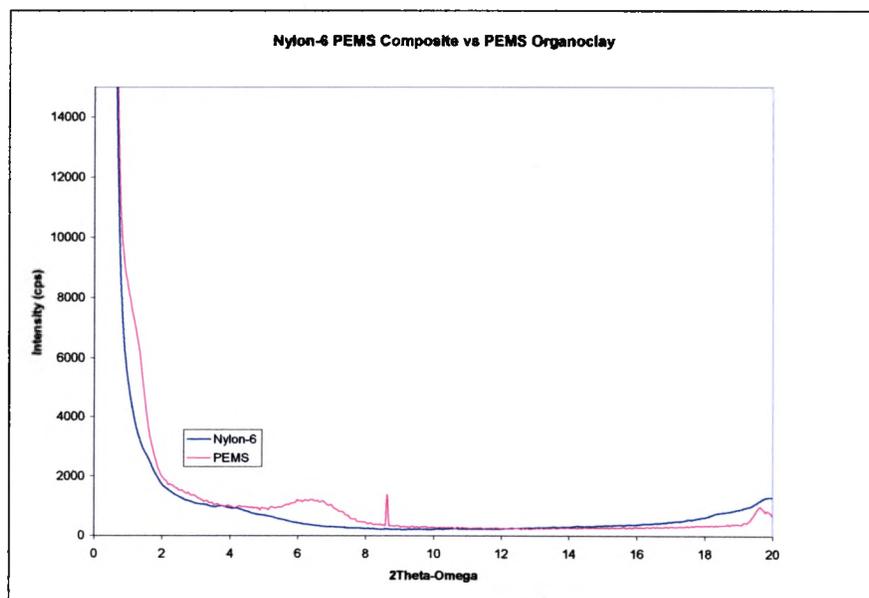


Figure 22. X-ray diffraction of 5% PEMS organoclay in Nylon-6 vs. that of 95meq/100g clay Radasurf 7174 PEMS organoclay.

There are many noteworthy things about the X-ray diffraction patterns of Radasurf 7174 PEMS organoclays in these common trade polymers. Most notable is the compatibility of organoclay with polymer material. High compatibility is verified by a diminishing Radasurf 7174 PEMS organoclay spectrum (the marked shoulder around 1-2 degrees 2θ , as well as the peak around 6.0 degrees 2θ that denotes any unmodified clay). Good intercalation capability could then be inferred from these X-ray characteristics. All of the four polymer blends show slight areas of compatibility; however EVA and Nylon-6 (Figures 19 & 22) show a slightly more diminished Radasurf 7174 PEMS patterns than LLDPE and PP, indicating a more compatible clay/polymer system.

3.5 Results and Discussion of Radasurf 7174 Pentaerythritol Monostearate

Separation

Radasurf 7174 Pentaerythritol “monostearate,” actually a blend of mono-, di-, tri- and tetraesters of pentaerythritol, underwent a series of in house tests to determine percent composition, ultimately leading up to an attempted separation of the individual components. Attempts to solvate the ester mixture were mildly successful: It was soluble at 0.1g to 1.0 ml loadings in benzene, DMSO, and THF. It was sparingly soluble in isopropyl alcohol and it emulsified in hexane. In all other solvents it was not noticeably soluble.

Of the three solvents that PEMS is soluble in, benzene was considered the best choice. However, due to toxicity and availability, benzene was not used. Toluene, from the same family of solvents with similar solubility properties as benzene, was therefore selected. Toluene is also cheap, readily available and far less cancerous/health hazardous than benzene. For the TLC experiment, different amounts of hexane and ethyl acetate

were mixed with toluene to find a good separating mixture. Due to a hazy mixture forming from emulsification, hexane was not considered as a mobile phase. 50/50 (by volume) Toluene/Ethyl Acetate turned out to be the best mixture, giving 4 distinct peaks. The manufacturer listed no presence of either pentaerythritol or stearic acid.

Column chromatography was attempted to separate pentaerythritol esters from the parent Riasurf 7174 moiety, but a large amount of solvent was needed to completely separate. Two liters of solvent were needed to separate the first two bands of solvent. A commercial source of pure pentaerythritol monostearate was instead purchased.

As an alternative testing method, ^1H NMR was performed on the Riasurf 7174 blend to attempt to ascertain the percent composition. The NMR spectrum is shown in

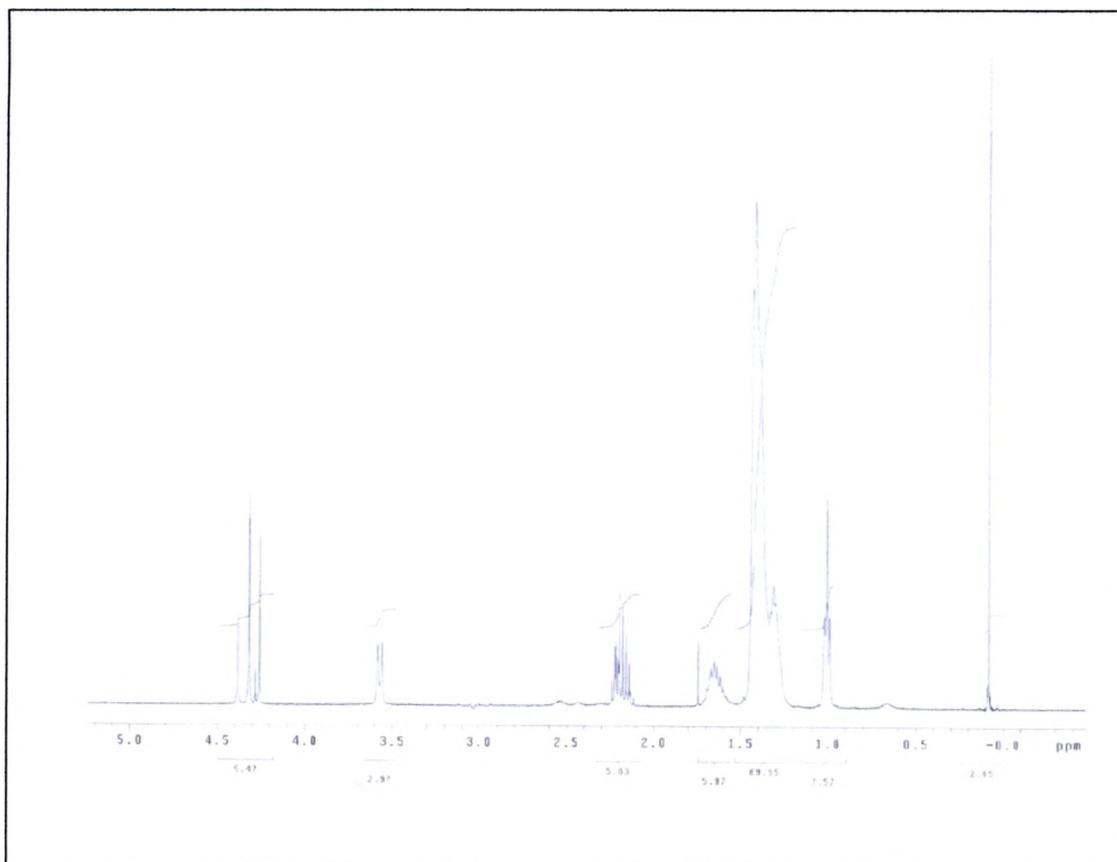


Figure 23. NMR of Riasurf 7174 Penterythritol Monostearate

Figure 23. A high % proton in the stearate peak can lean the argument that there is a large amount of stearate groups compared to hydroxyl protons, proving a mixed system. Calculations show an approximate 50% mono ester composition, a value that was in disagreement with the manufacturer, Oleon. They performed a capillary GC method of separation and yielded a 6% mono, 27% di, 48% tri, and 29% tetra ester. Disparities arise from the low concentration of what molecular modeling determined to be the surface binding molecules (mono- and diester). Such low concentration of bind-able molecules (6% monoester, 27% diester) would not yield the high d-spacings shown experimentally, as there would be no preferential attraction to the surface. There is likely a middle ground between manufacturer values and NMR determined values. Regardless of ester percentage of the Radiesurf 7174 blend, there is believed to be a synergy between the mono and diesters, which bond to surface cations, and the tri and tetra esters, which further interdigitate with the R-groups of the mono and diesters sticking out from the clay surface.

4.0 CONCLUSION

A myriad of generally recognized as safe (GRAS) compounds were intercalated to montmorillonite clays in hopes of finding an ideal candidate for further study investigating alternatives to quaternary ammonium modified organoclays. This survey of GRAS species has identified a number of future food safe alternatives to quaternary ammonium organoclays, information which is of valuable interest to the food packaging industry, where exfoliation of montmorillonite nanocomposites would give benefits such as strength and barrier. A series of additional tests of the GRAS organoclays would begin once a large d-spacing was obtained on x-ray analysis, including concentration optimization, molecular modeling, thermogravimetric analysis, and polymer blending. The results of the tests are summarized and highlighted below.

X-ray diffraction was, as stated, the primary tool in identification of what would be considered a good candidate for potential work. The resultant diffraction patterns provided evidence of whether an organoclay could potentially disperse well in polymeric media. A large basal d-spacing, combined with a chemical attraction to a particular polymer, are the ingredients for potential exfoliation of the modified clay platelets. Once exfoliated in a polymer, these platelets can provide outstanding strength, stability and barrier.

There were eight organoclays produced that had a d-spacing twice or more than that of dry unmodified Cloisite Na⁺, and of those, seven organoclays performed better

than a top industrial quaternary ammonium modified organoclay, Cloisite 20A. Notable attributes of a large d-spacing were long R-group chain(s) attached to a source of ion-dipole formation. The best chain length tended to be C-18, or stearyl, groups. The best head group that bound to surface cations was glycerol or pentaerythritol based moieties. Due to the heat from oven drying and the tendencies of montmorillonite clay to catalyze oxidation, R-groups bearing any carbon-carbon double bonds did not perform as well as saturated molecules.

Among the esters that produced such large d-spacings, it was typical that a mixed ester system provided a higher d-spacing than a pure monoester. This runs contrary to speculation and molecular modeling evidence. There is, no doubt, a synergistic effect of having amounts of multi-esters present along with the primary binding monoester in the case of glycerol stearate esters and having amounts of multi-ester along with mono- and diester in the case of pentaerythritol stearate. The evidence is obtained directly from organoclay d-spacing: glyceryl monostearate yielded a 54.00 Å d-spacing while glyceryl stearate mixed ester yielded a 78.20 Å d-spacing. This is also evident in pentaerythritol stearate esters, where ChemService pentaerythritol monostearate (100% monoester) gave a d-spacing of 50.43 Å while Radiansurf 7174 PEMS mixed ester gave a d-spacing of 72.00 Å.

Concentration optimization was attempted, but not completed. What is understood is that finding (via X-ray diffraction) and using a minimal surface modifier concentration is complicated from the viewpoint of processing conditions and temperatures. A minimal concentration may be partially stripped in higher temperatures and not provide ample d-spacing. Future studies into optimizing and perfecting the

concentration would need to be undertaken to truly understand the complexity of the large amount of variables responsible for an optimized system.

Thermogravimetric analysis of the organoclays provided a wealth of data. The affinity a GRAS chemical has for the clay surface can be quantifiably inferred from the TGA data. Molecular modeling indicated a strong interaction between the pentaerythritol moiety and a surface Na^+ cation, and this was indicated in our results. The ability for pentaerythritol stearate mixed ester organoclay to have a high temperature onset and peak of degradation is a bonus to its high d-spacing. ChemService PEMS doesn't have as good an onset degradation temperature, but it has a far greater peak of degradation, proving that there is a strong affinity for the monoester for the clay surface. Binding strengths for other moieties were also examined, and evidence shows a progression for binding affinity with pentaerythritol being strongest, then glycerol, citric acid, and then carboxylic acids.

Future thermal studies involving GRAS organoclays should include TGA experiments conducted in this experiment, but under air. To become industrially significant, TGA studies in air need to be conducted to simulate real world processing conditions. The reactive oxygen in air tends to speed degradation, but the extent of this difference is what is important. TGA run in air of saturated moieties like Cloisite 20A and both pentaerythritol stearate should not show a large depression when compared to argon studies.

Thermal studies into the binding strength of Radiesurf 7174 PEMS would provide great insight into the true effect the tri- and tetraesters have upon gallery spacing. One such experiment could ramp up a series of 0.5:1 chemical: clay by weight (what we

erroneously labeled 145 meq/100g clay) organoclays to a series of temperatures (one organoclay per temperature setting): 100°C, 200°C, 300°C, and 400°C. Once the temperature setting is reached, the clay would be allowed to cool down. Once cool, the clays would then be subjected to powder X-ray tests to determine if extraneous gallery components have volatilized off, leaving an essentially pure mono- and diester layer on the clay. There will likely be no change in X-ray pattern at 100°C, but beginning with 200°C there should be a shift towards decreasing d-spacing. If the 400°C organoclay shows an approximate 50 Å d-spacing, then there would be assurance that multi-esters help extend the gallery. A similar experiment could also be run for the glyceryl stearate ester series.

Polymer/organoclay interactions were not extensively studied, but preliminary results have promise for future projects. The study of a surface modifying group's ability to "organophilize" clay platelets to achieve the desired effects from polymer intercalation is a widely researched field. There are hundreds of modifications that can be made to any given organic molecule to tweak organophilicity. Pentaerythritol stearate esters were studied more at length, interactions between surface modifier and polymer were limited to the organophilic alkyl stearate R-group. The affinity between the stearate R-group and EVA and Nylon-6 was much more intimate than for LLDPE and iPP. This conclusion was shown from X-ray data for pentaerythritol stearate organoclay/polymer compoundings vs. original pentaerythritol stearate organoclay. EVA and Nylon-6 showed a clearer, less aggregated system while LLDPE and iPP had more clumps and opaqueness. This would indicate a more intimate pairing between the long chain esters and slightly polar polymers (EVA and Nylon-6) compared to strict non-polar polyolefins.

In future studies, investigation into potential GRAS chemicals that are commonly used in polymer industry would definitely be worth looking into. Chemicals that have affinity for polymers would likely enhance the ability of a clay coated in such a material to exfoliate. GRAS capable plasticizers, antifogging agents, stabilizers, lubricants and oxygen scavenging molecules should be looked into as future clay intercalates for polymer compounding.

Follow up studies on proline possibly forming oligomers could be tested via GC/MS of surface contents. Proving this mechanistically happens could spark interest into oligimerization of other amino acids perhaps more able to form chains with itself or other amino acids. Also of future interest would be the investigation into the propyl gallate and vanillin color transformation. Solving this issue could provide hints into how exactly these aromatic molecules are binding.

In conclusion, pentaerythritol and glycerol stearate esters were the top surface modification agents by a large degree compared to the rest of the chemicals and agents on the survey. Thermogravimetric analysis and molecular modeling helped bolster pentaerythritol stearate alone as the “top performer” out of all the chemicals surveyed. Work on pentaerythritol stearate esters and their various strengths and attributes as pertaining to clays nanocomposites systems has culminated in a patent pending (as of this writing) and a number of patents are potentially going to be submitted in the future concerning other chemical agents and analogues thereof used in this survey. Due to the sheer size of the study, investigational optimization could not be attempted to as high a degree as originally wished, but future studies mentioned in this text conducted by the

nanocomposite group at Texas State University - San Marcos and collaborations with Cryovac-Sealed Air are sure to clear up the many questions raised by this undertaking.

APPENDICES

Appendix 1: All GRAS chemicals used in the study

-All chemicals acquired from Sigma-Aldrich unless noted.

-All chemicals in pure 98+% form unless noted.

-All chemicals were used as obtained from the manufacturer. No further reactions or purifications were conducted before use.

- 2-heptanone
- 2-octanone
- Acetic Acid¹
- Aconitic acid
- Adipic Acid²
- Alginic acid
- L-Asparagine
- Benzoic acid
- Caprylic Acid
- Cinnamaldehyde
- Citric acid
- L-Cysteine
- d-gluconolactone
- Diacetyl
- Ethyl Formate
- Glyceryl Behenate, mixed ester³
- Glyceryl monostearate⁴
- Glyceryl Stearate, mixed ester⁵ (continued.....)

¹ Obtained from stockroom, glacial

² Obtained as a sample from Solutia

³ Obtained as a sample from Gattefosse, trade name Compritol 888 ATO. Composition: monoester: 13-21%, diester: 40-60%, triester: 21-35%. Values were obtained from manufacturer.

⁴ Purchased from Alfa Aesar, 100% mono ester

- Gum Guar
- Inositol
- L-Isoleucine
- Lactic acid⁶
- Lauric acid
- Lecithin⁷
- L-Leucine
- DL-Lysine
- Malic acid
- L-Methionine
- Methylparaben
- Myristic Acid
- Nicotinamide
- Nicotinic acid
- Oleic acid
- Radiesurf 7174 Pentaerythritol Monostearate⁸
- ChemService Pentaerythritol Monostearate⁹
- L-Phenylalanine
- DL-Phenylalanine
- L-Proline
- Propionic acid
- Propyl Gallate
- Propylene Glycol (continued ..)

⁵ Obtained as a sample from Lipo Chemicals, trade name LIPO GMS-450 ~40% mono, 30% di, 30% triester.

⁶ Obtained as a 85% solution (Sigma Aldrich)

⁷ Purchased from Alfa Aesar

⁸ Obtained as a sample from Oleon, trade name Radiesurf 7174. Composition: mono: 6%, di: 27%, tri: 48%, tetra: 29%. Values were obtained from manufacturer via Capillary GC, reference method AOCS Cd 11b-91.

⁹ Obtained from ChemService. 100% monoester.

- Propylparaben
- Pyridoxine
- Sorbitol¹⁰
- Stearyl Citrate¹¹
- Succinic acid
- Sucrose
- Tartaric Acid
- Triacetin
- Triethyl citrate
- L-Tryptophan
- Urea
- Vanillin

¹⁰ Obtained as a sample from Lipo Chemicals

¹¹ Predominantly monoester

Appendix 2: Clays run on a large scale (250g) via Hobart extruder

-All clays listed were processed under procedure listed in Experimental section.

- Adipic Acid
- Citric acid
- Ethyl Formate
- Glycerol Stearate, mixed ester*
- Lauric acid
- Lecithin*
- Nicotinamide
- Pentaerythritol Monostearate*
- Sorbitol
- Sucrose

* denotes clay was remade on a small scale as well

Appendix 3: Clays run small scale (10-20g) via mortar/pestle methods

-All clays listed were processed under procedure listed in Experimental section.

-Notes relay if anything happened to clay while processing or after.

- 2-heptanone
- 2-octanone
- Acetic Acid
- Aconitic acid
- L-Asparagine
- Benzoic acid
- Caprylic Acid
- Cinnamaldehyde
- L-Cysteine[†]
- d-gluconolactone
- Diacetyl¹²
- Glyceryl Behenate
- Glyceryl monostearate
- Glyceryl Stearate, mixed ester
- Gum Guar
- Inositol¹³
- L-Isoleucine
- Lactic acid
- Lecithin
- L-Leucine (Continued.....)

¹² Clay was very wet in addition to smelling strongly. It was never dried fully.

¹³ Bacterial growth on clay prohibited further study.

- DL-Lysine
- Malic acid
- L-Methionine
- Methylparaben
- Myristic Acid
- Nicotinic acid
- Oleic acid¹⁴
- Radiesurf 7174 Pentaerythritol Monostearate
- ChemService Pentaerythritol Monostearate
- L-Phenylalanine
- DL-Phenylalanine
- L-Proline
- Propionic acid
- Propyl Gallate
- Propylene Glycol
- Propylparaben
- Pyridoxine[†]
- Sorbitol[†]
- Stearyl Citrate
- Succinic acid
- Sucrose
- Tartaric Acid
- Triacetin[†]
- Triethyl citrate (Continued.....)

¹⁴ Clay was a strong dark brown after oven drying, probably due to conjugation.
[†]Denotes clay was charred after drying overnight in an 80°C oven

- L-Tryptophan
- Urea
- Vanillin

APPENDIX 4: Organoclays that did not survive to trial.

-Method of decomposition is noted for each compound.

- L-Cysteine: Amino acid, charred in oven overnight.
- Inositol: Precursor to lecithin, experienced rapid bacterial growth.
- Pyridoxine: Vitamin B6, charred in oven overnight
- Sorbitol: Low calorie sweetener, clay was unusable after production.
- Triacetin: Glyceryl triacetate, clay charred and adhered to aluminum foil in oven

Appendix 5: Complete list of x-ray diffraction peaks obtained from organoclays.

-Order is from highest to lowest d-spacing. Included on the chart are x-rays run on

Cloisite 20A and Cloisite Na⁺ so a comparative basis could be ascertained.

-Urea/%water series was not used in thesis survey results, but x-ray data is given as a supplement.

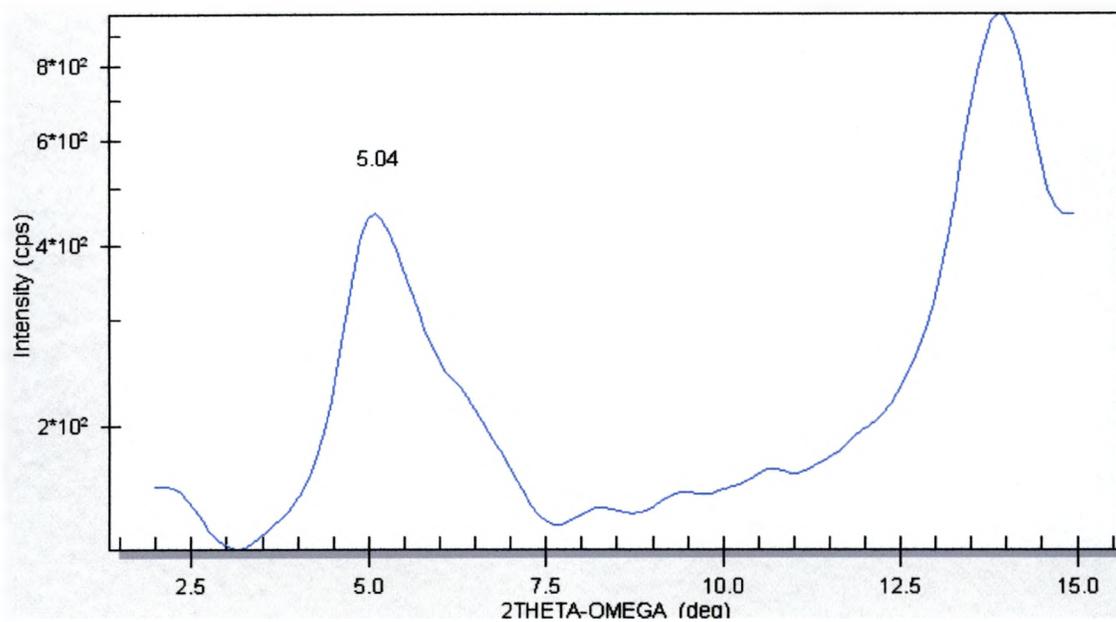
Chemical	d-spacing (Angstroms)
Glyceryl Stearate	78.20
Radiasurf 7174 PEMS	72.00
Glyceryl monostearate	54.00
Lecithin	52.76
ChemService PEMS	50.43
Myristic Acid	32.02
L-Proline	26.80
CLOISITE 20A	26.20
Urea	24.78
Glyceryl Behenate	23.00
Urea 25% H ₂ O	21.13
Propyl Gallate	20.54
Propylene Glycol	18.91
d-gluconolactone	18.79
Urea 0% H ₂ O	18.73
Urea 50% H ₂ O	18.70

Urea 10% H ₂ O	18.50
Tartaric Acid	18.13
Sucrose	18.08
L-Tryptophan	17.97
Vanillin	17.70
2-heptanone	17.41
Malic acid	17.40
Triethyl citrate	17.34
Stearyl Citrate	17.32
Aconitic acid	17.01
Nicotinamide	16.43
Lactic acid	16.37
2-octanone	16.07
DL-Phenylalanine	15.87
L-Phenylalanine	15.83
Cinnamaldehyde	15.83
Alginate acid	15.82
Methylparaben	15.78
Citric acid	15.50
L-Methionine	15.32
Benzoic acid	15.25
L-Leucine	14.82
Diacetyl	14.33
Gum Guar	14.29
L-Isoleucine	14.04
L-Asparagine	13.89

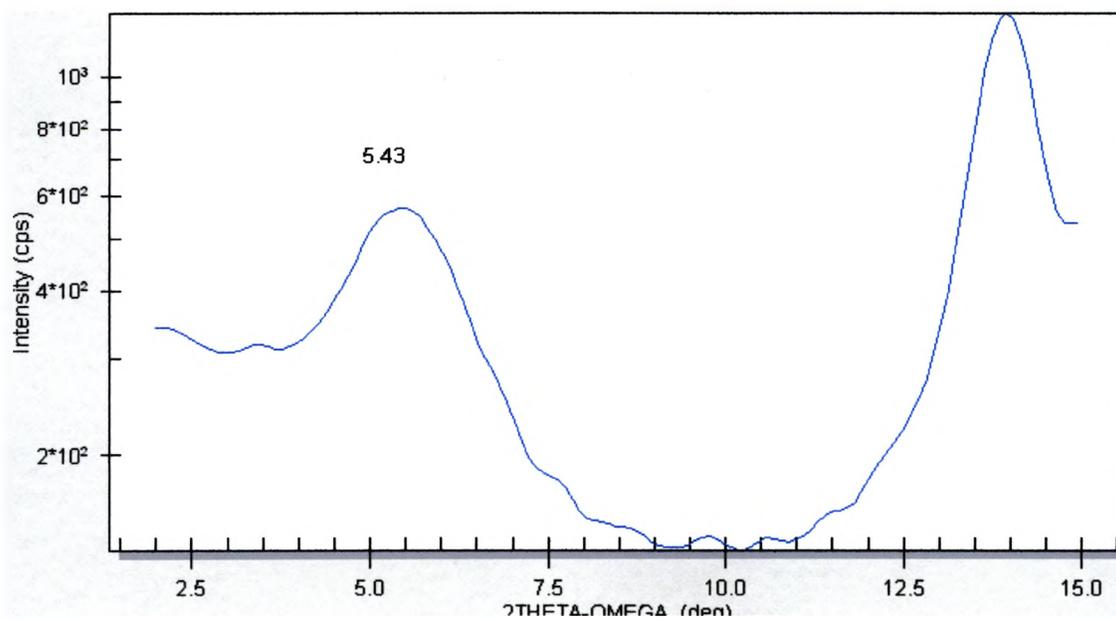
DL-Lysine	13.68
Propylparaben	13.62
Caprylic Acid	13.41
Adipic Acid, Na ⁺ clay	13.21
Lauric acid	13.17
Oleic acid	13.08
Adipic Acid, Ca ²⁺ clay	13.02
Succinic acid	13.02
Propionic acid	12.96
Acetic Acid	12.83
Nicotinic acid	12.82
Ethyl Formate	12.3
Cloisite Na ⁺	12.3

Complete X-ray spectrum in alphabetical order, w/ amino acid organoclays thereafter. Spectra appear as they do in the Bede x-ray program Quickdraw, used to manipulate and work with X-ray spectra.

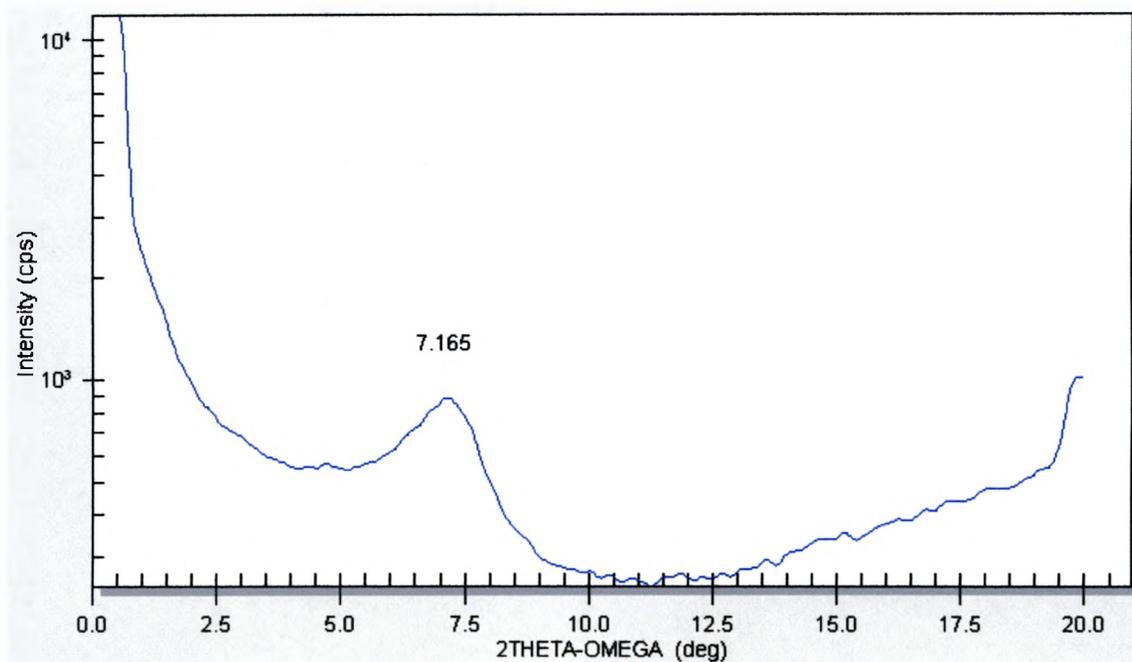
2-heptanone



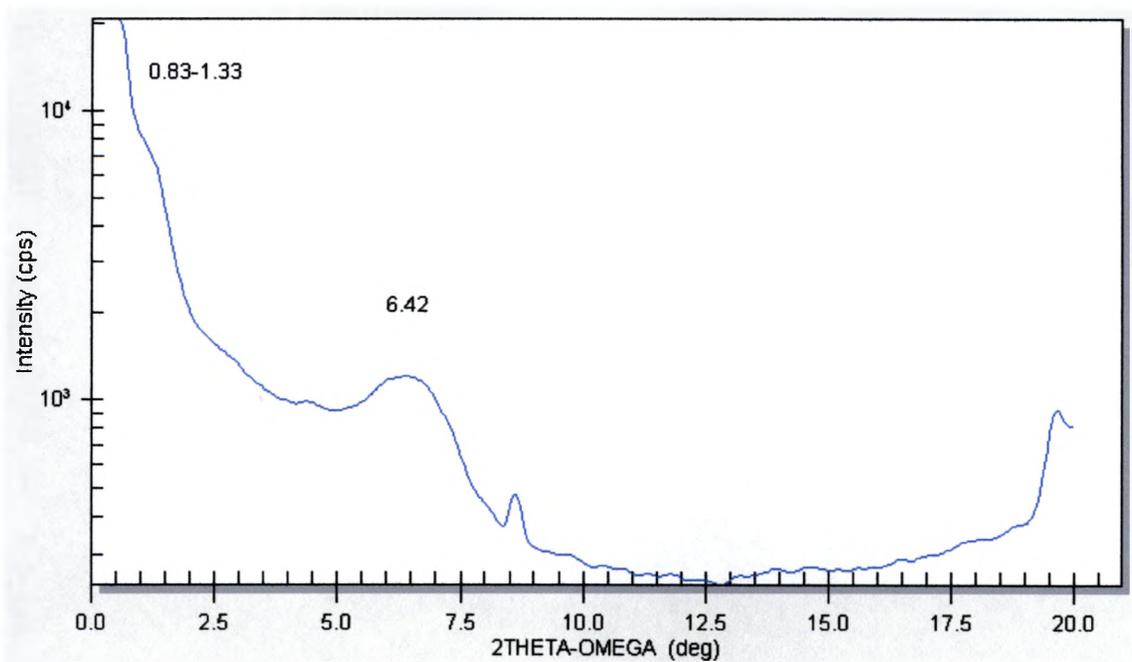
2-octanone



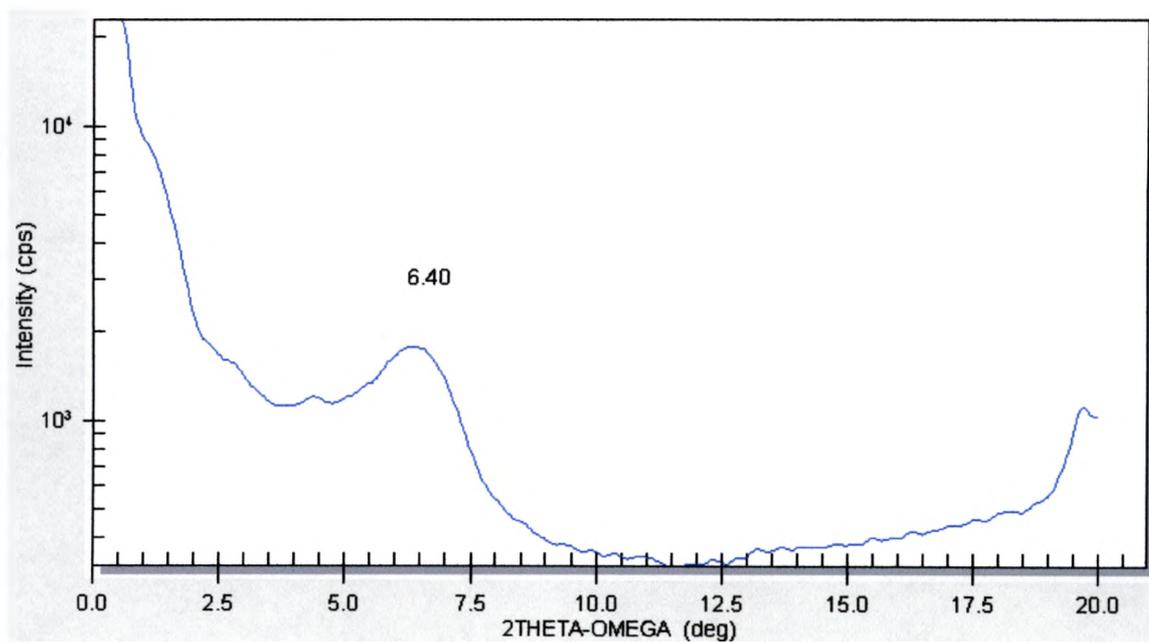
45 meq Radasurf 7174 PEMS



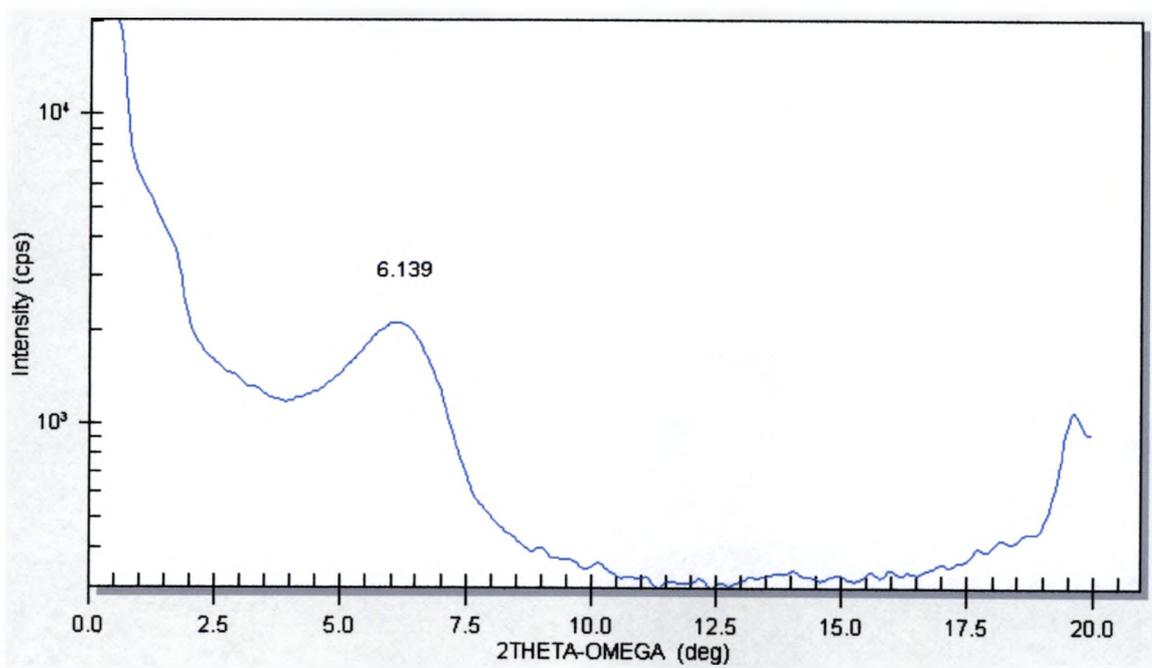
95 meq Radasurf 7174 PEMS



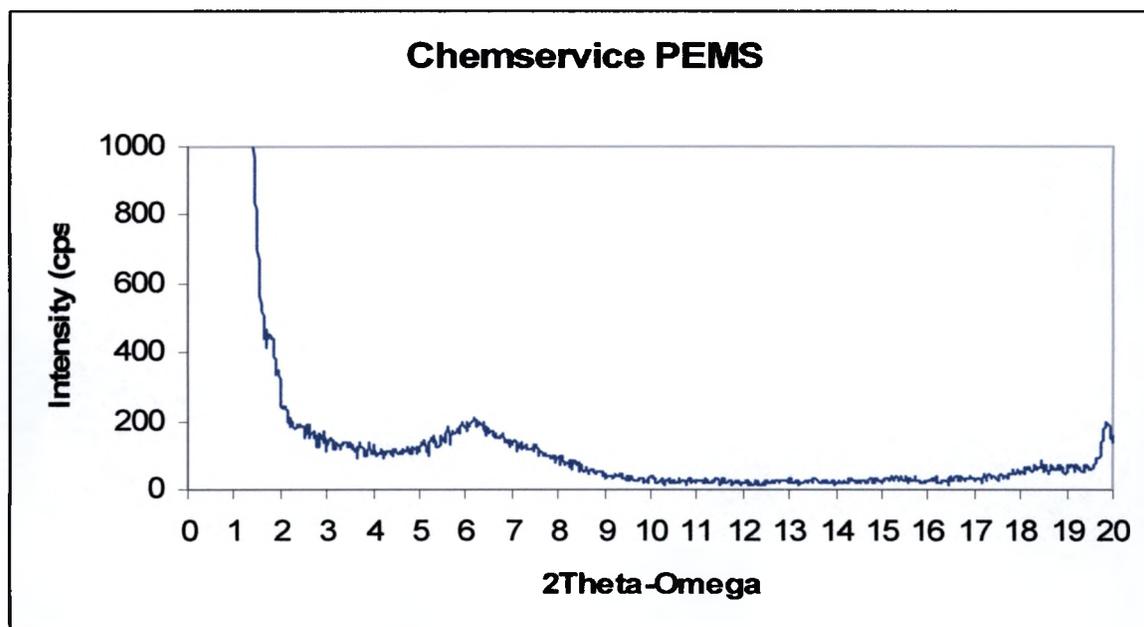
145 meq Radasurf 7174 PEMS



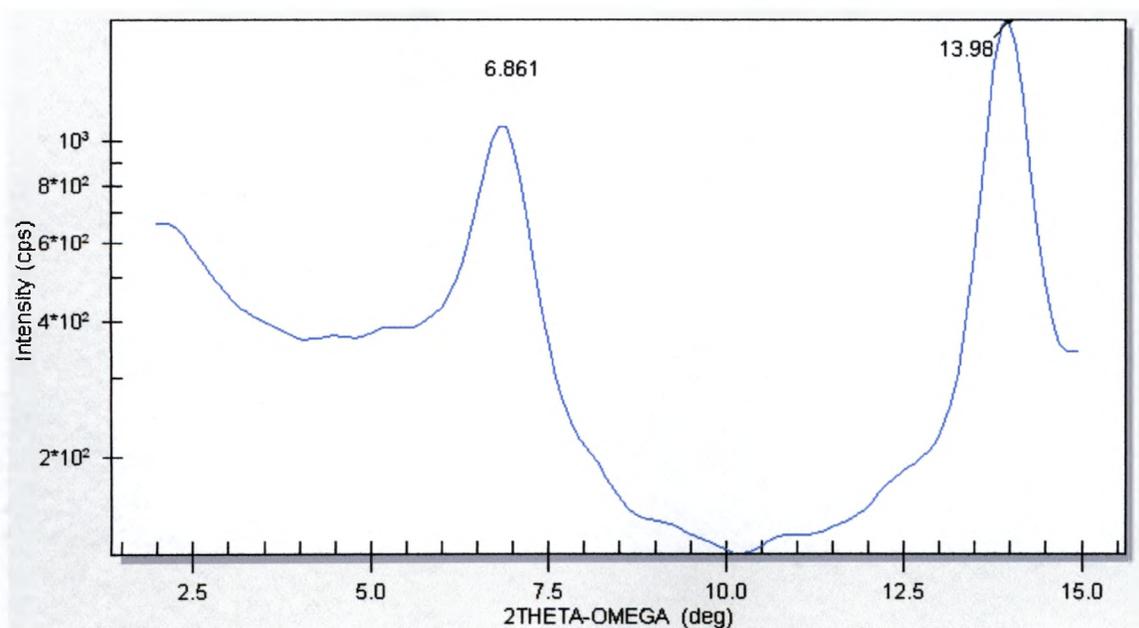
195 meq Radasurf 7174 PEMS



95 Meq ChemService Pentaerythritol Monostearate¹⁵

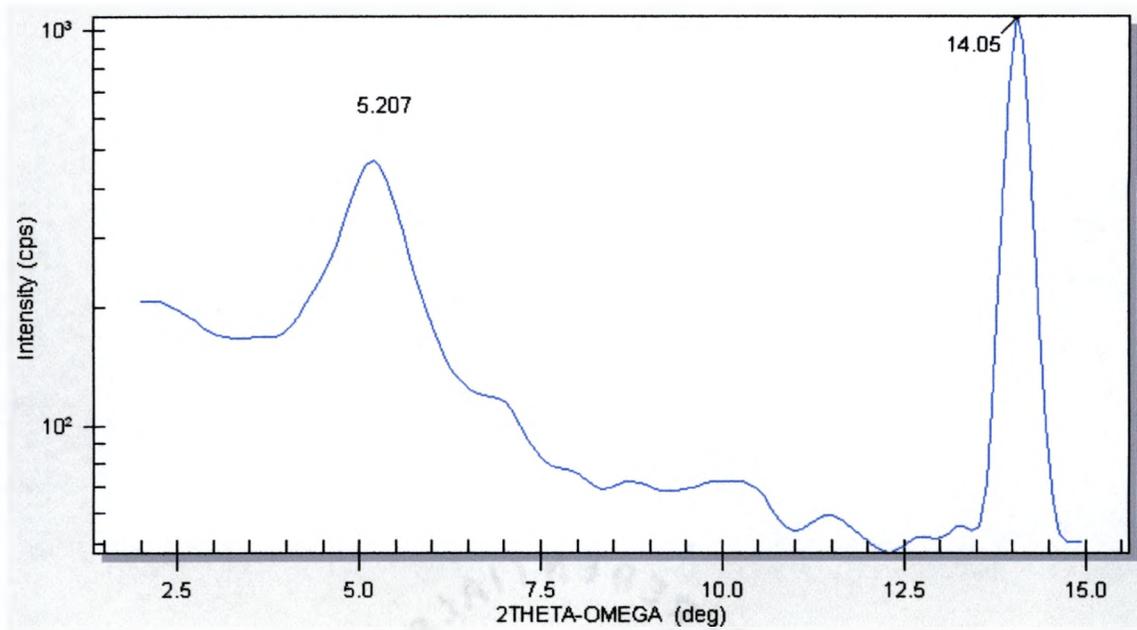
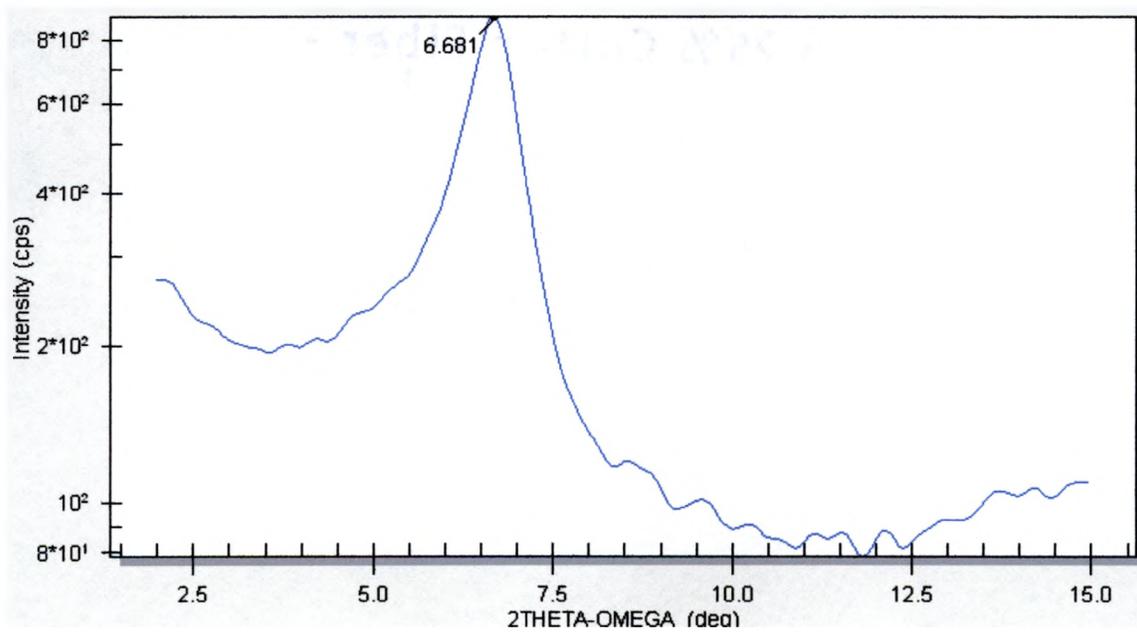


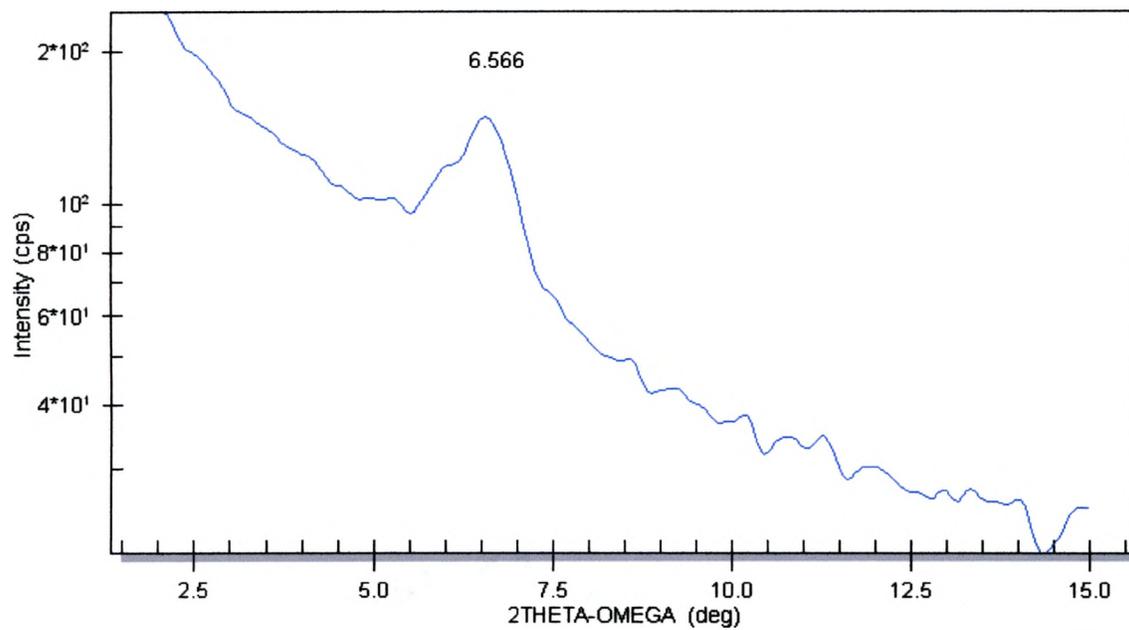
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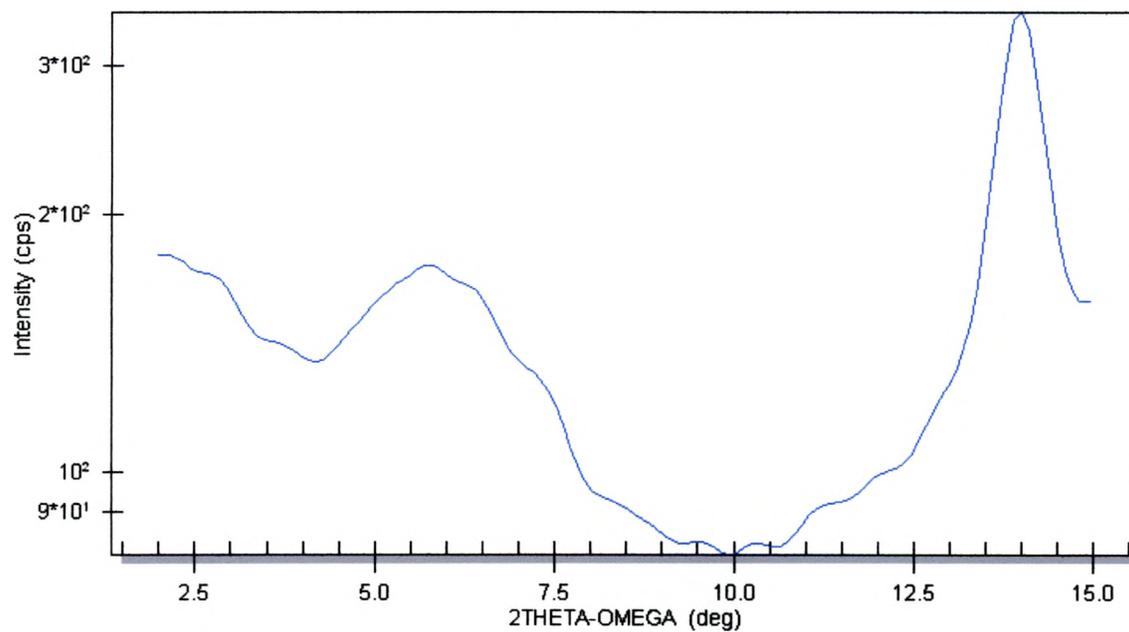
¹⁵ Run by Southern Clay Products staff from 1.2 – 20.2 2 θ on April 11th, 2005. Copper K α X-ray source.

Aconitic Acid

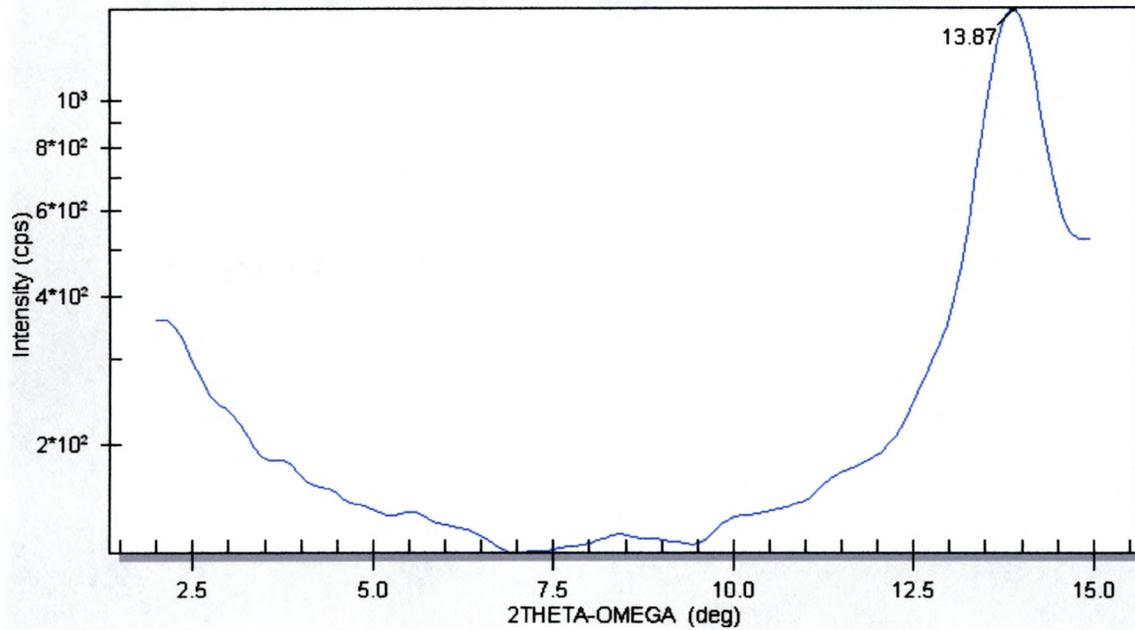
Adipic Acid Ca^{2+} 

Adipic Acid Na⁺

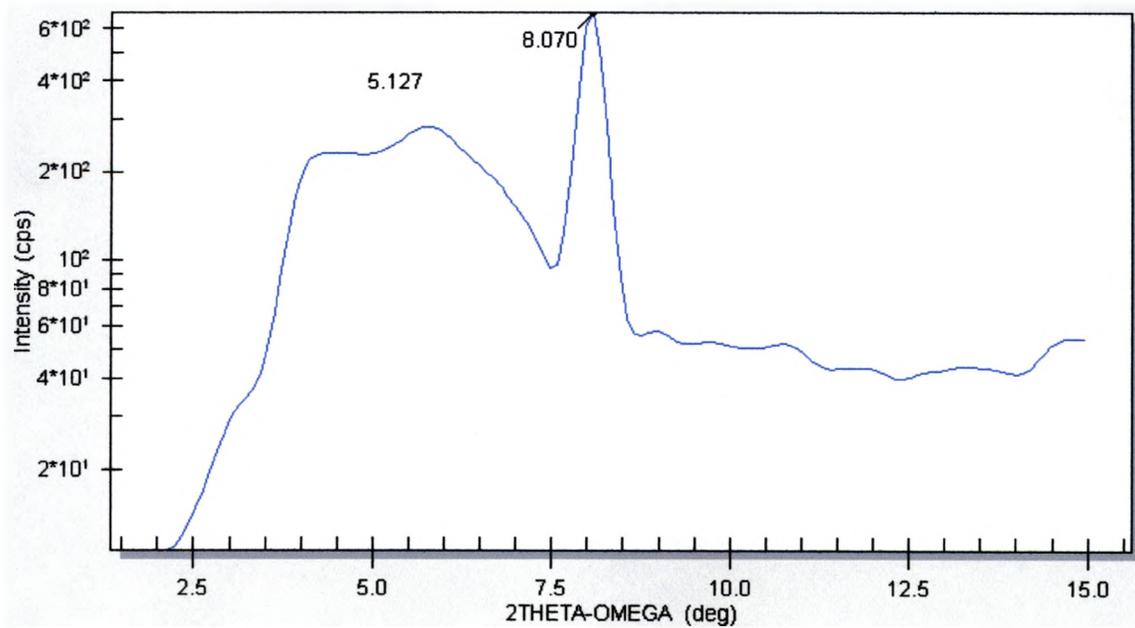
Alginic Acid



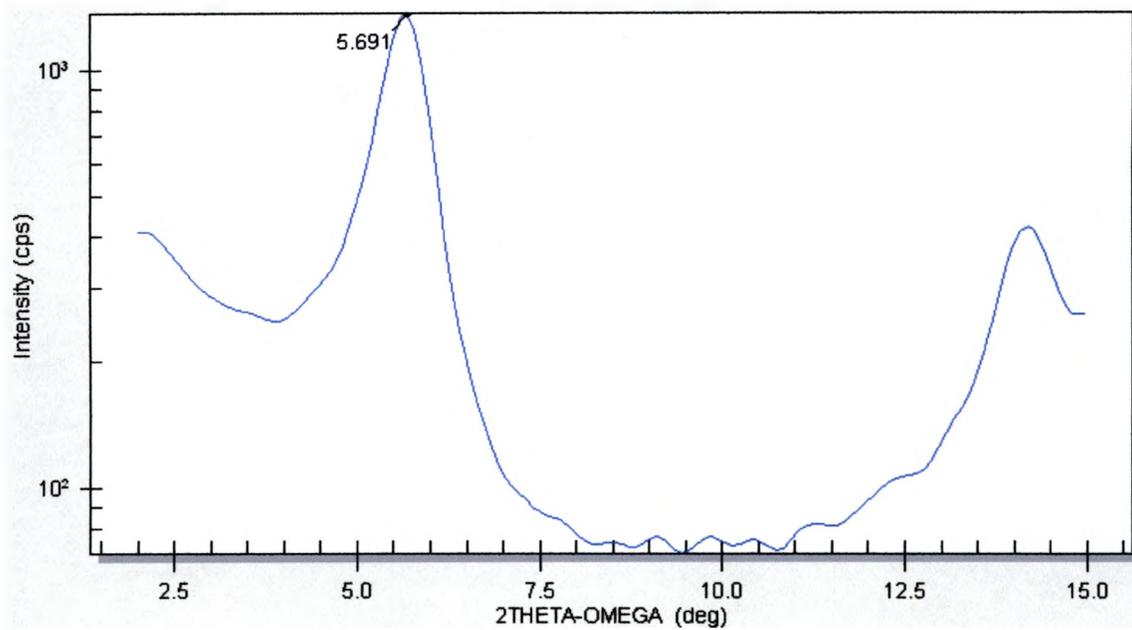
Background tape (proves the large peak is a crystallinity peak in the tape used to secure clays to scan board).



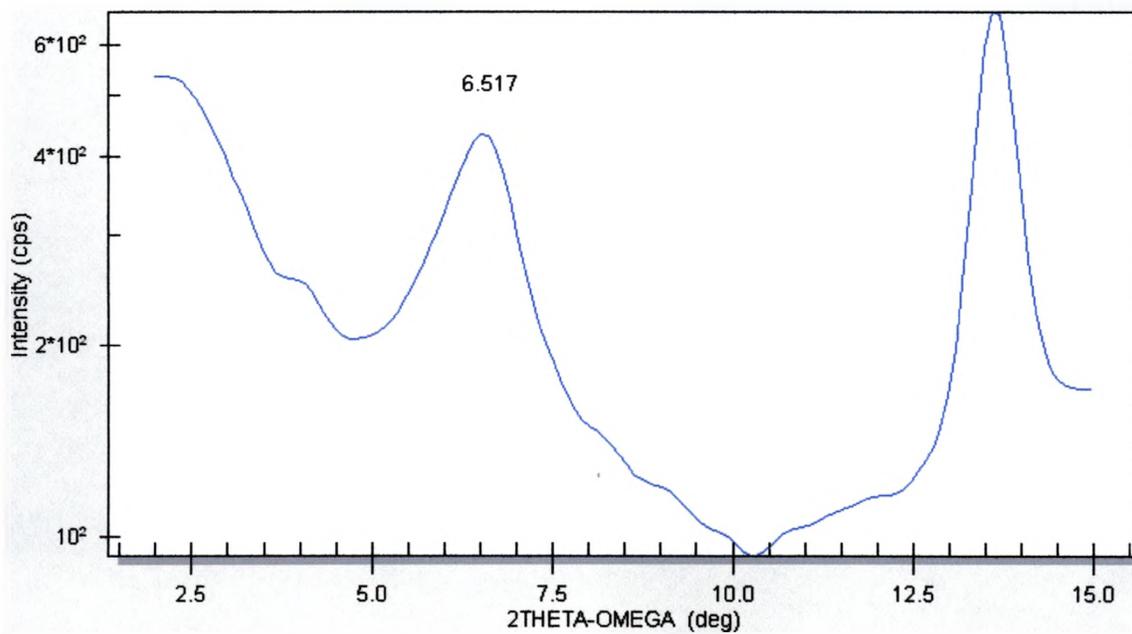
Benzoic Acid



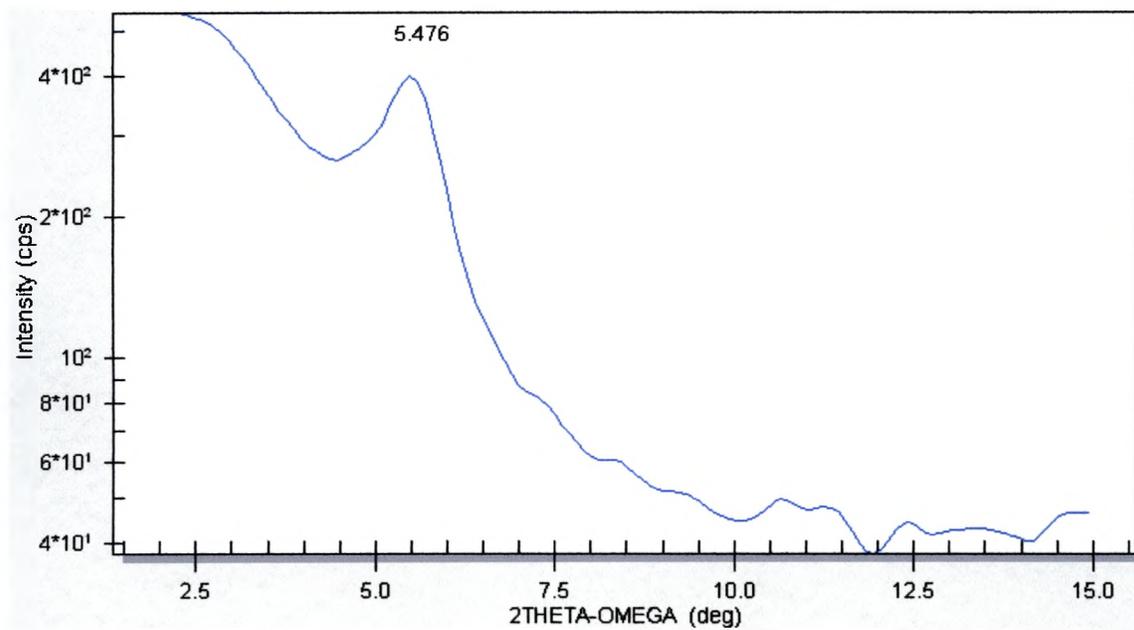
Canola Oil Esterification (Side project)



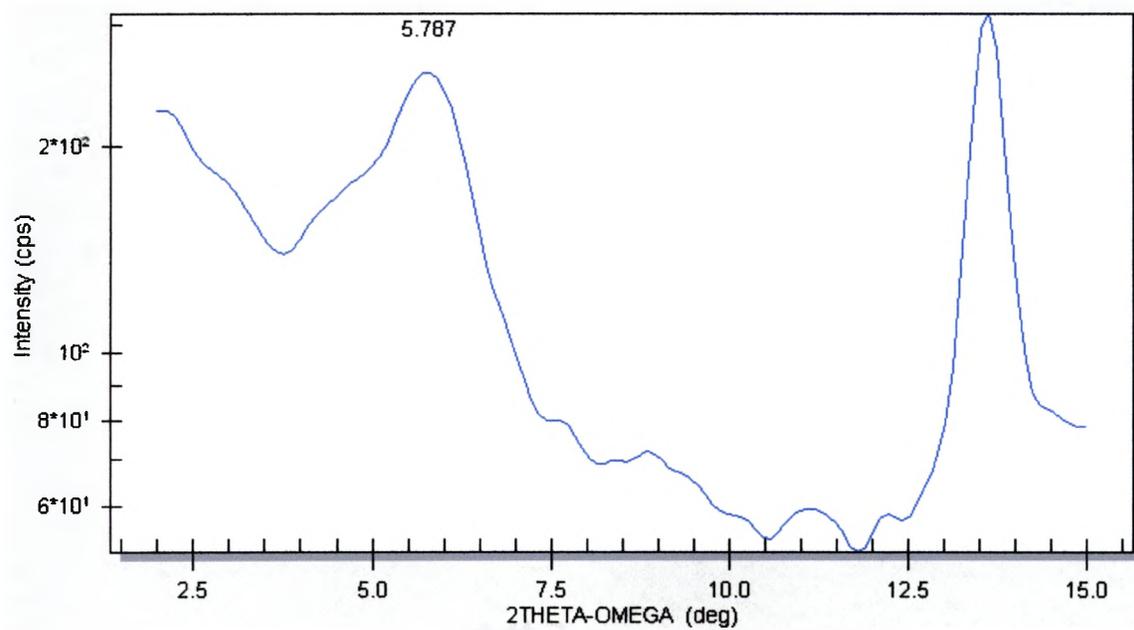
Caprylic Acid



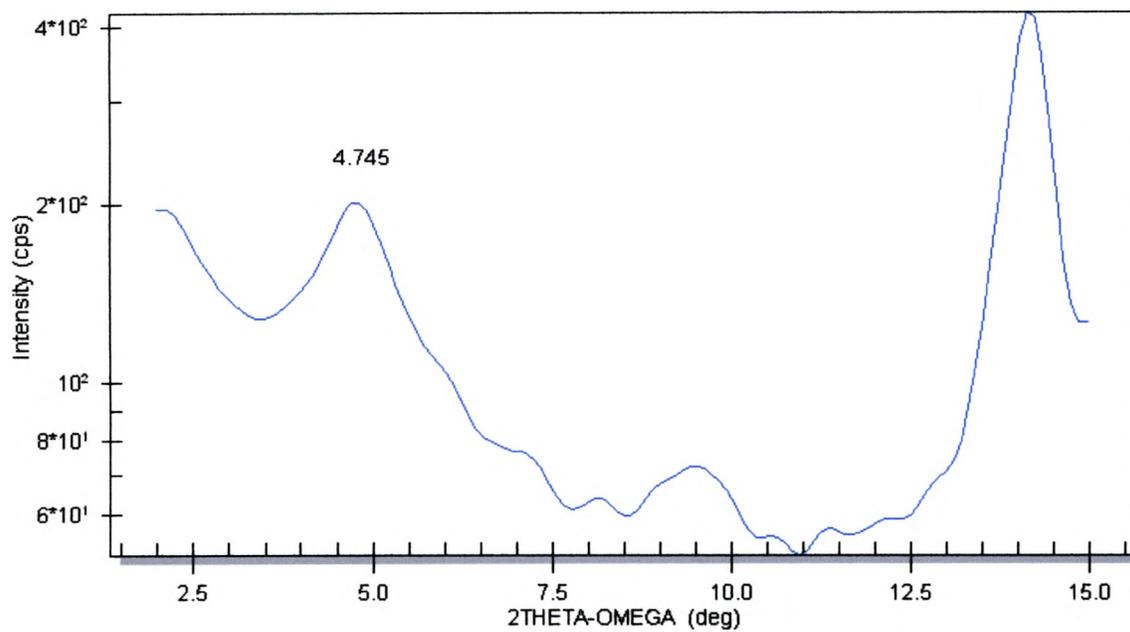
Cinnamaldehyde



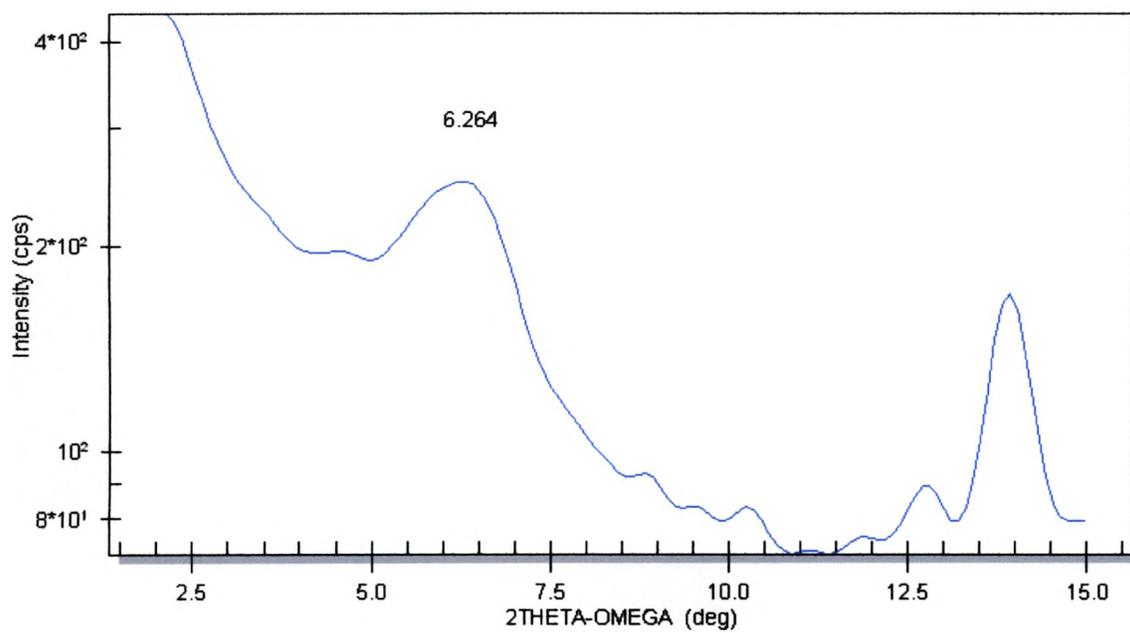
Citric Acid



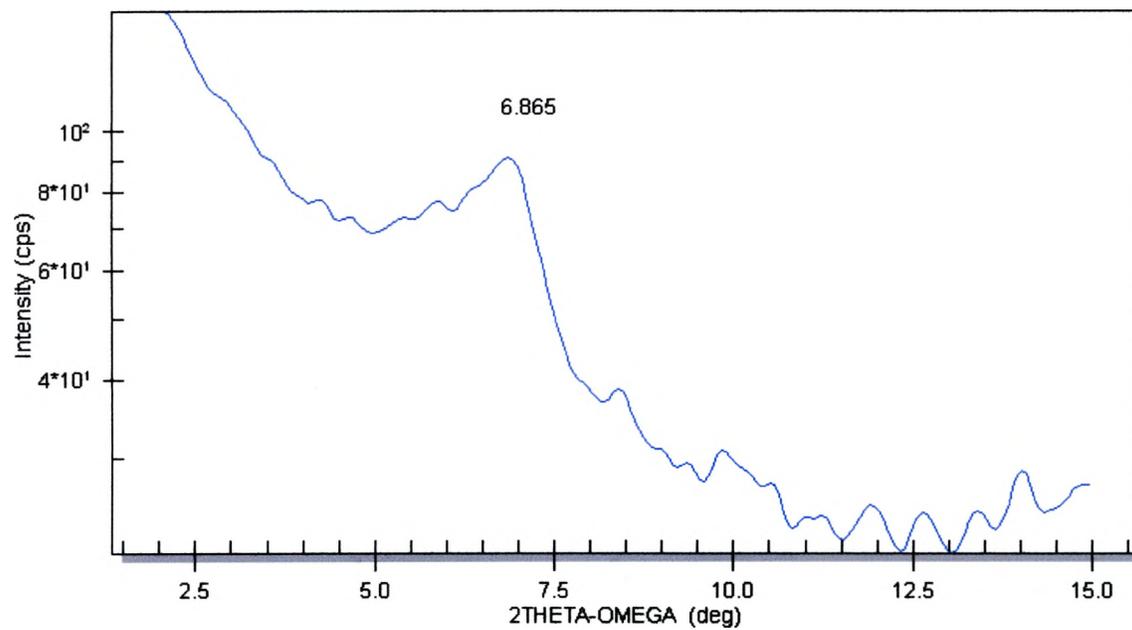
d-gluconolactone



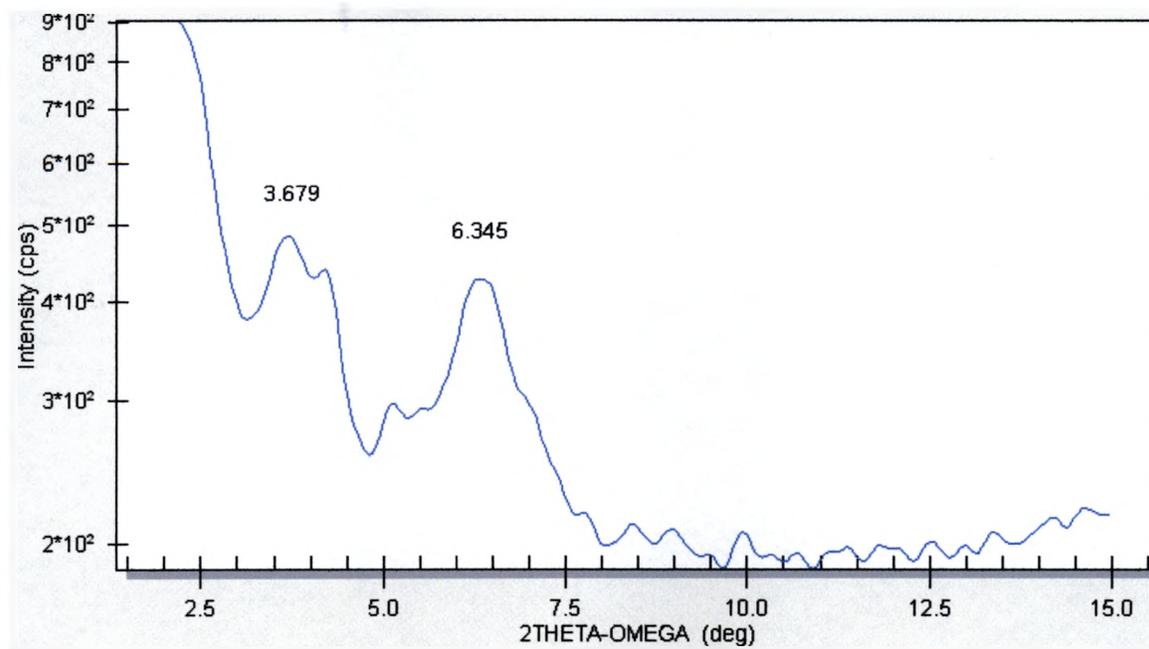
Diacetyl (2, 3 butadione)



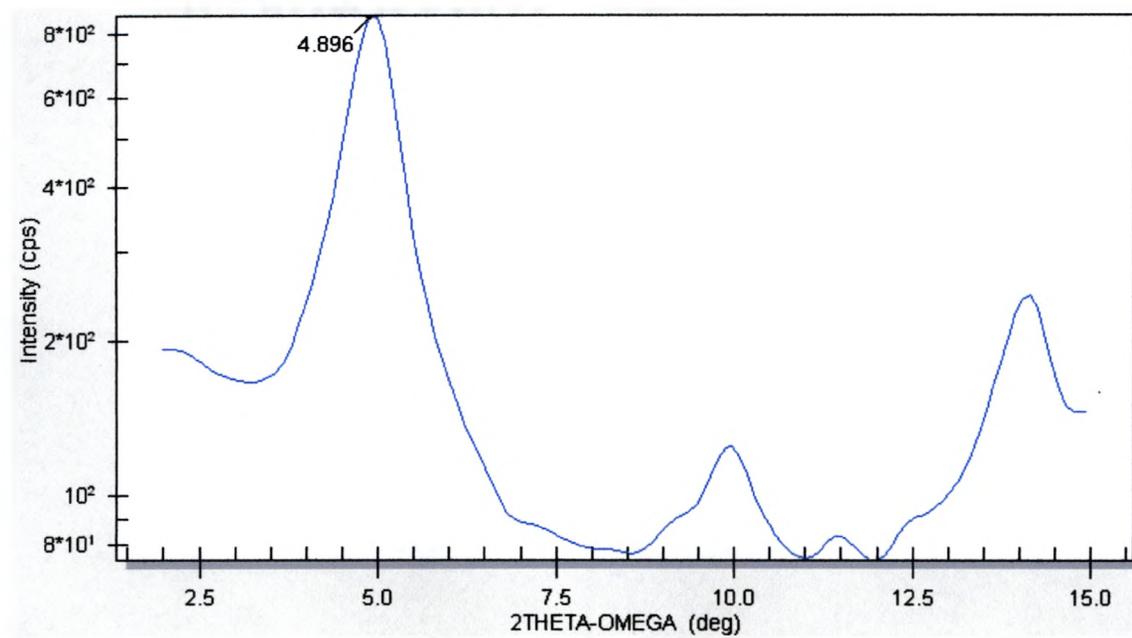
Ethyl Formate



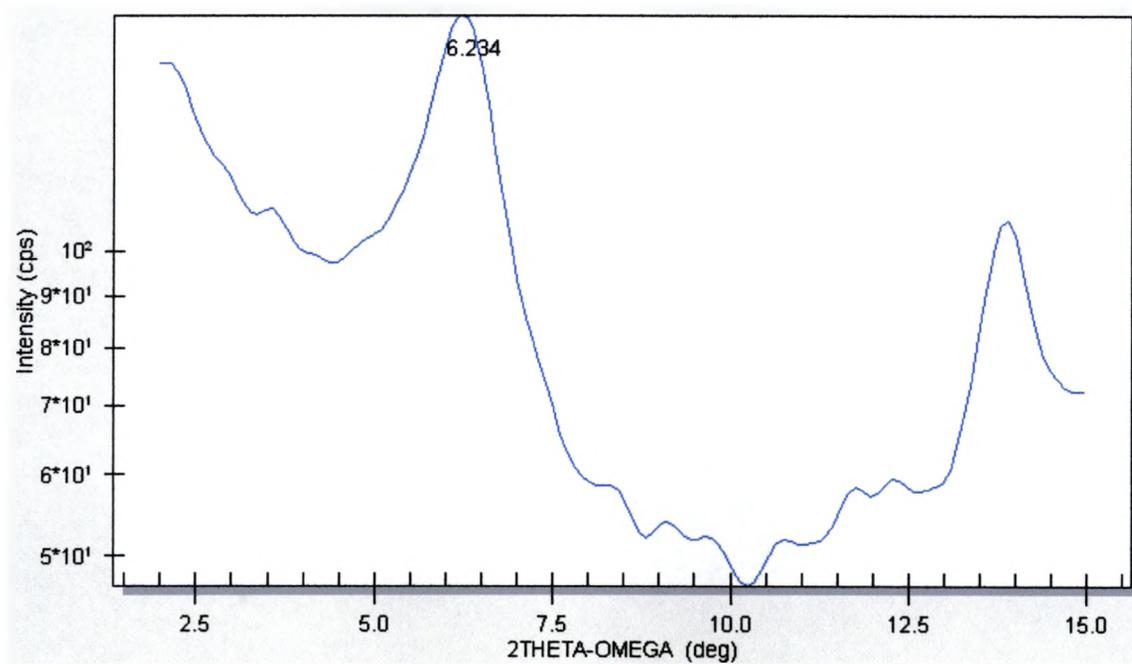
Glyceryl Behenate



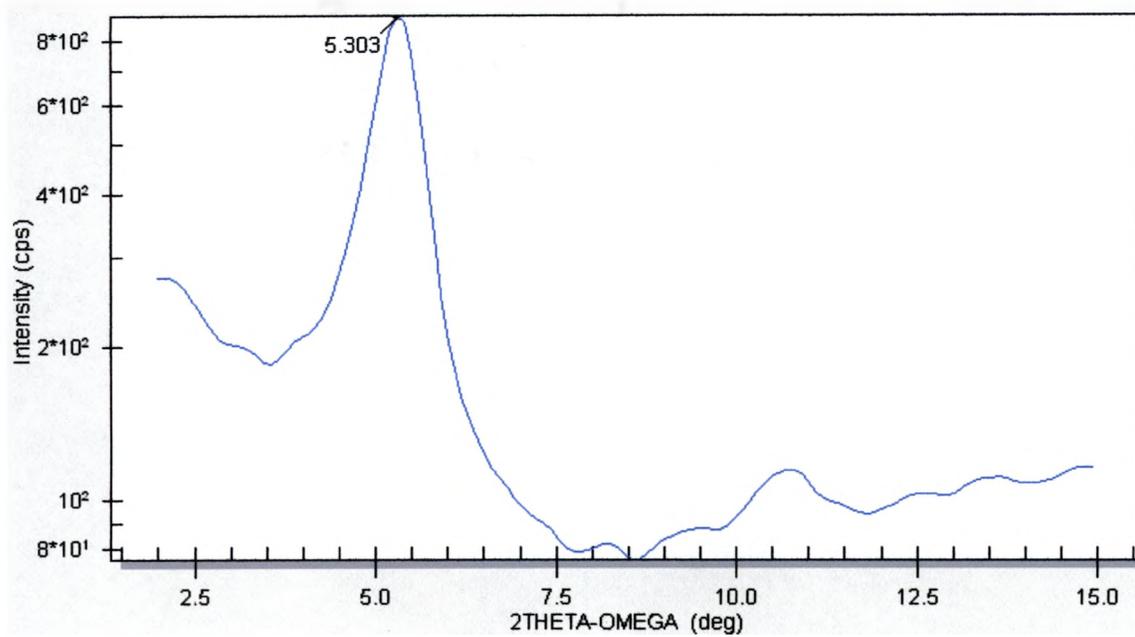
Glyceryl Monostearate



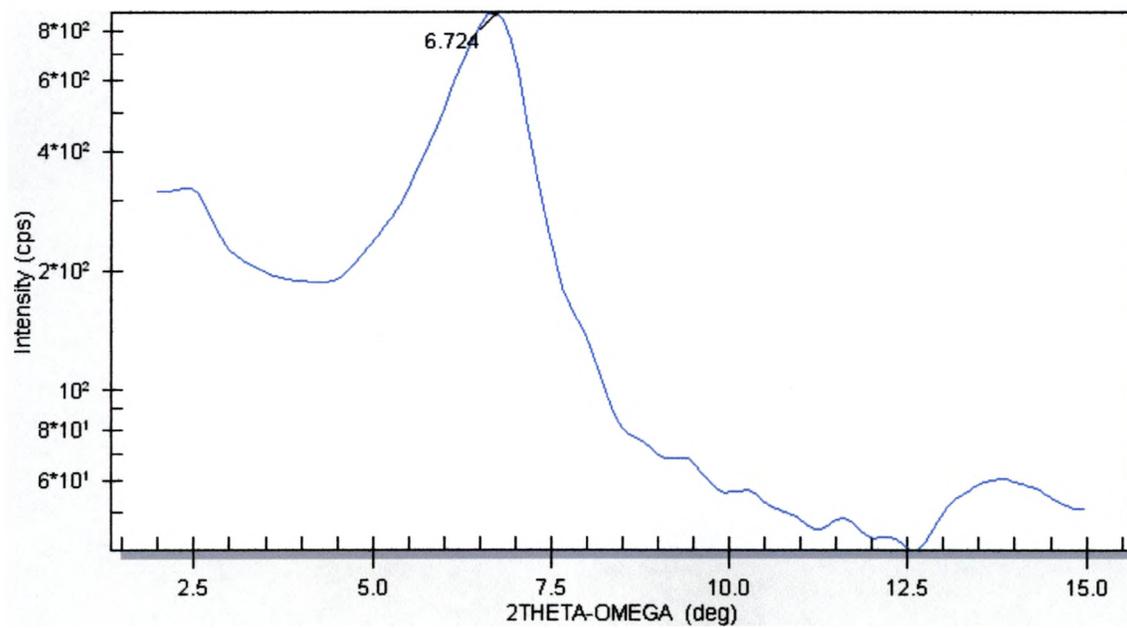
Gum Guar



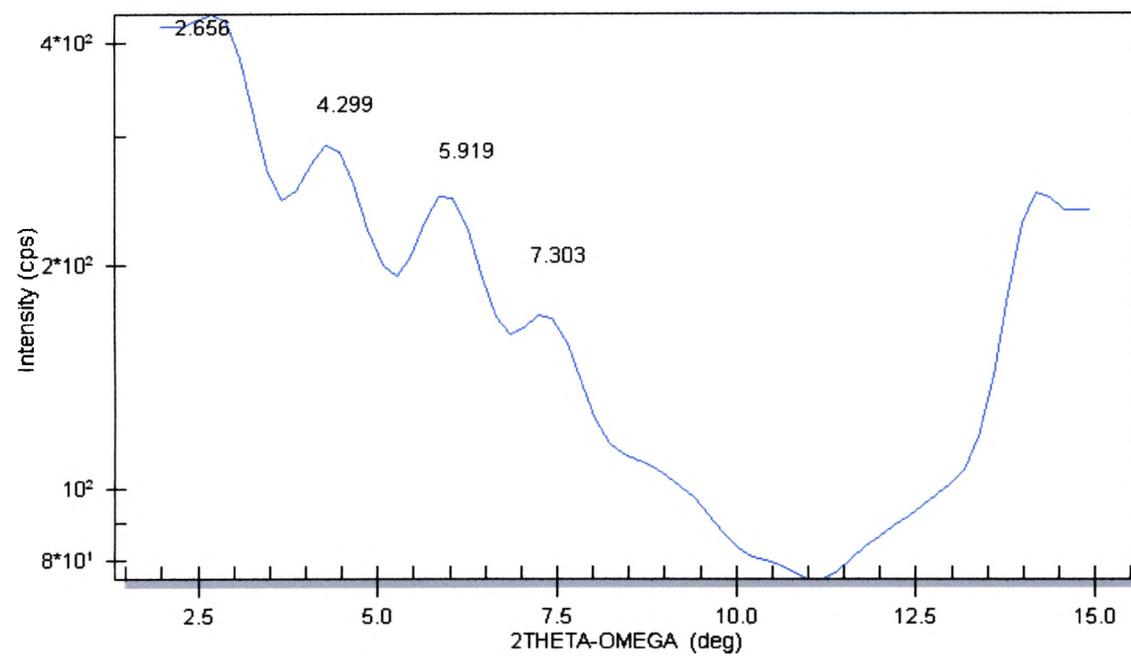
Lactic Acid



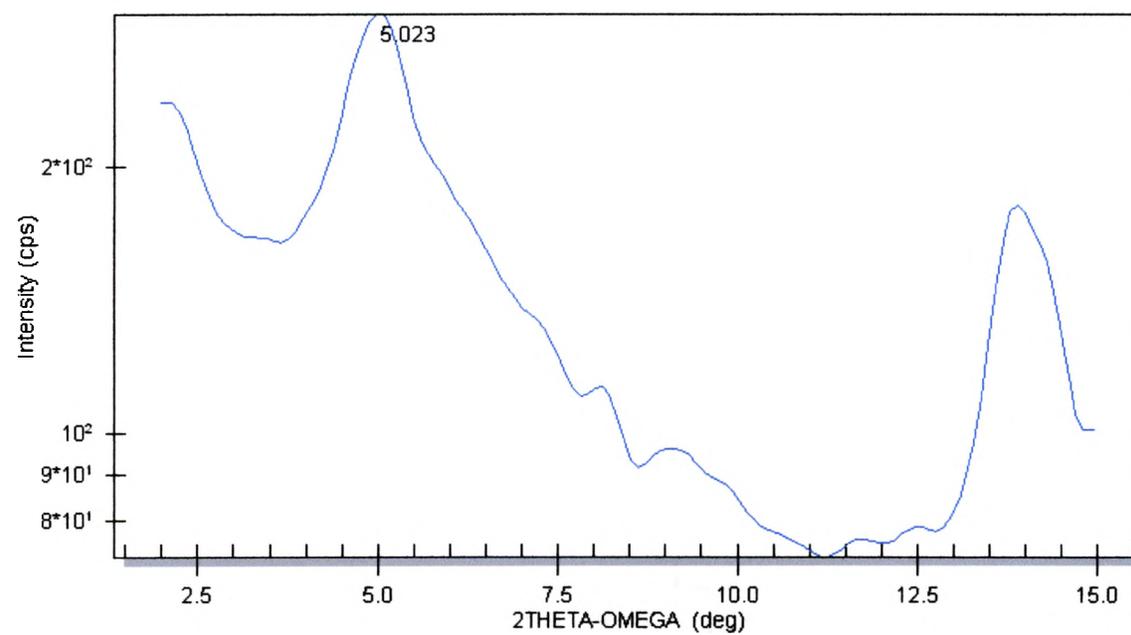
Lauric Acid



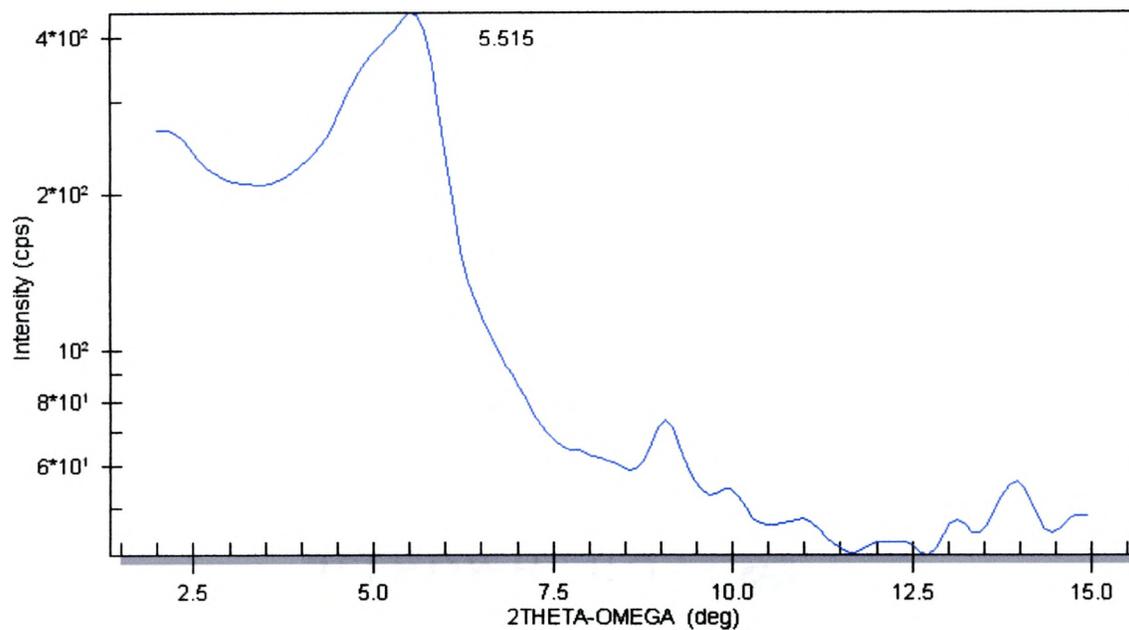
Lecithin



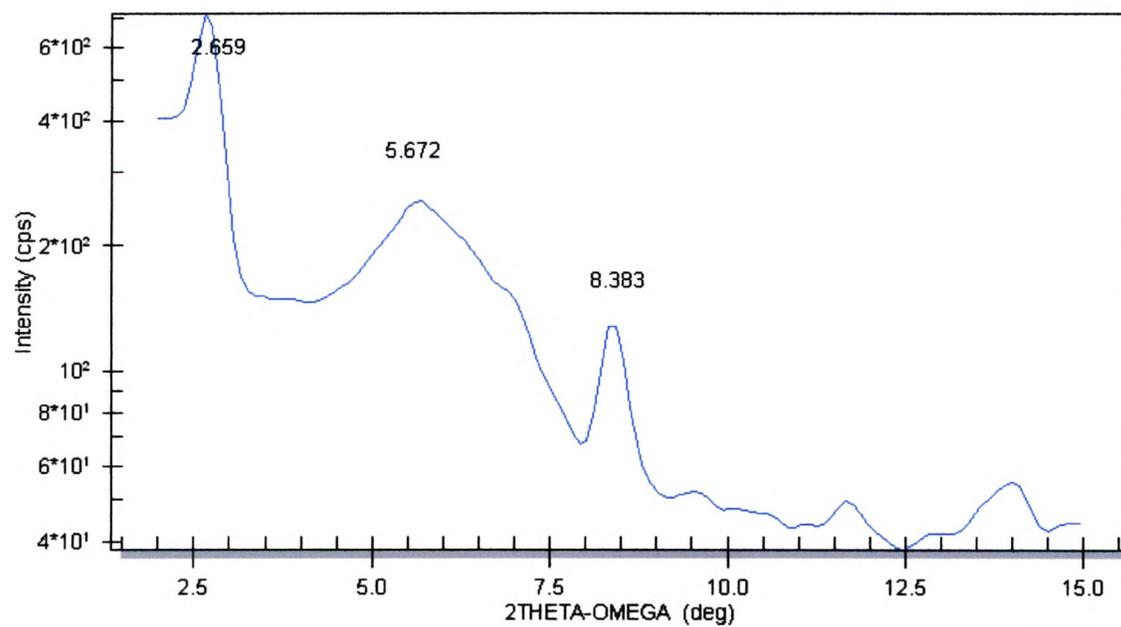
Malic Acid



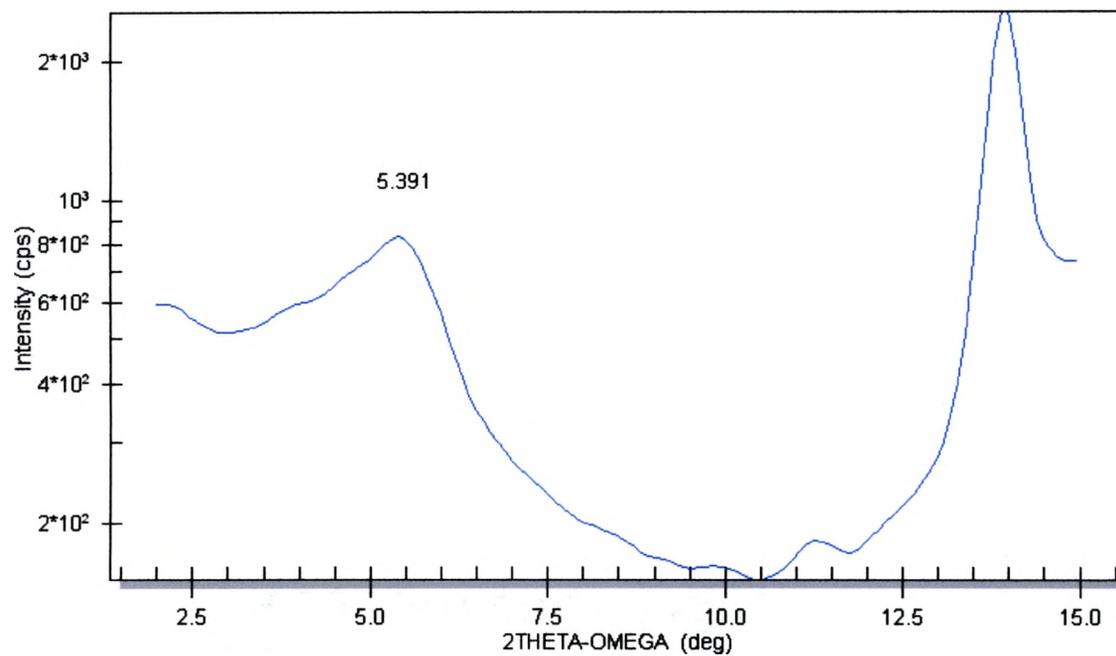
Methylparaben



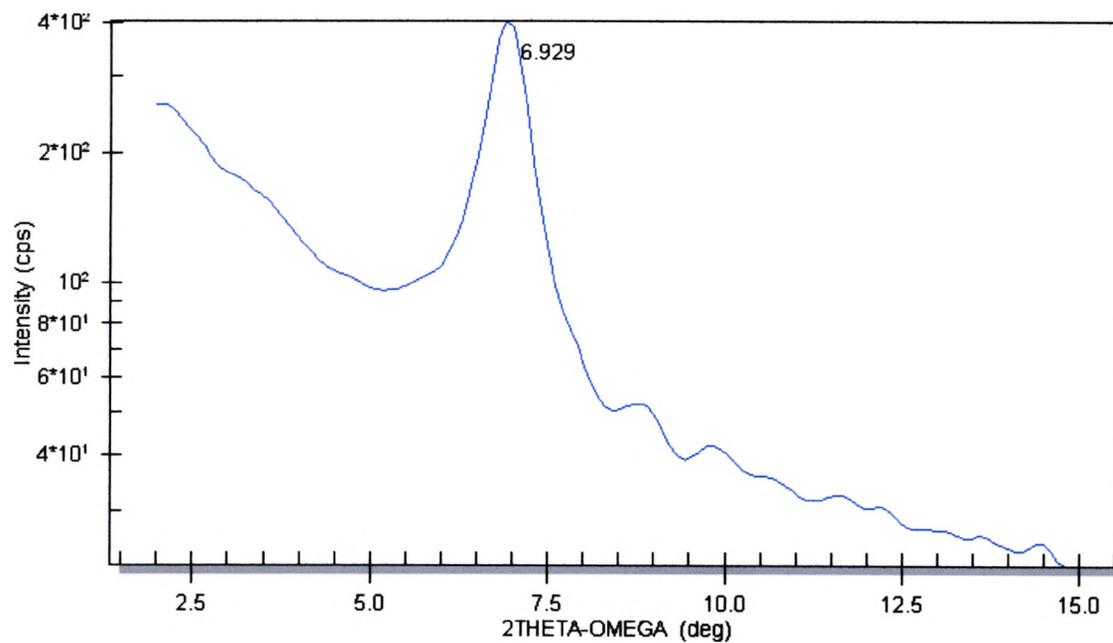
Myristic Acid



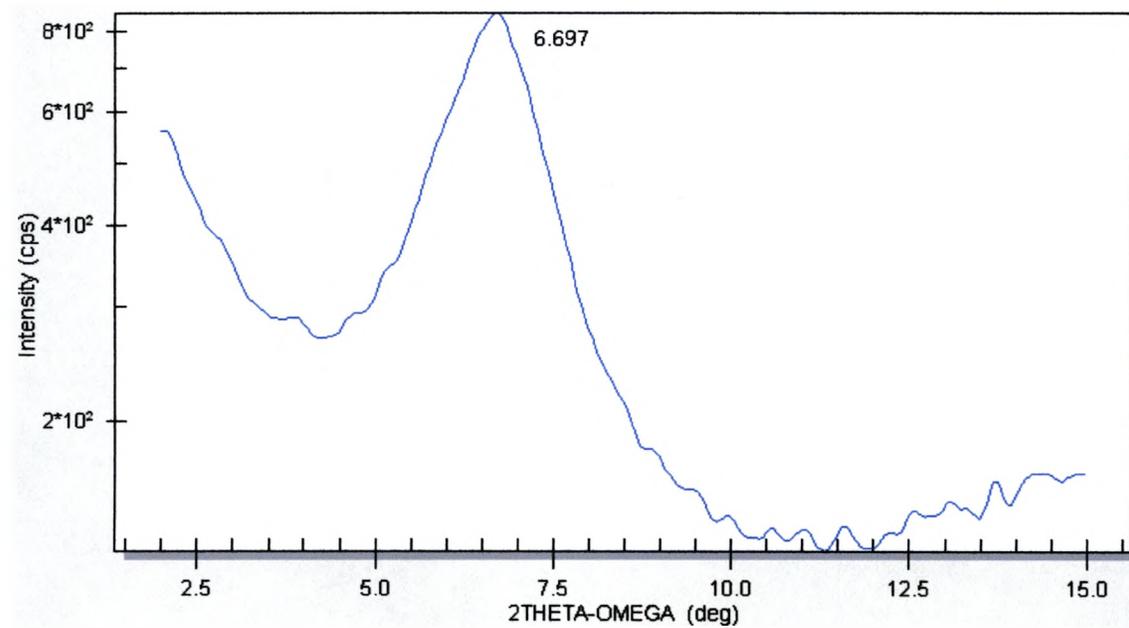
Nicotinamide



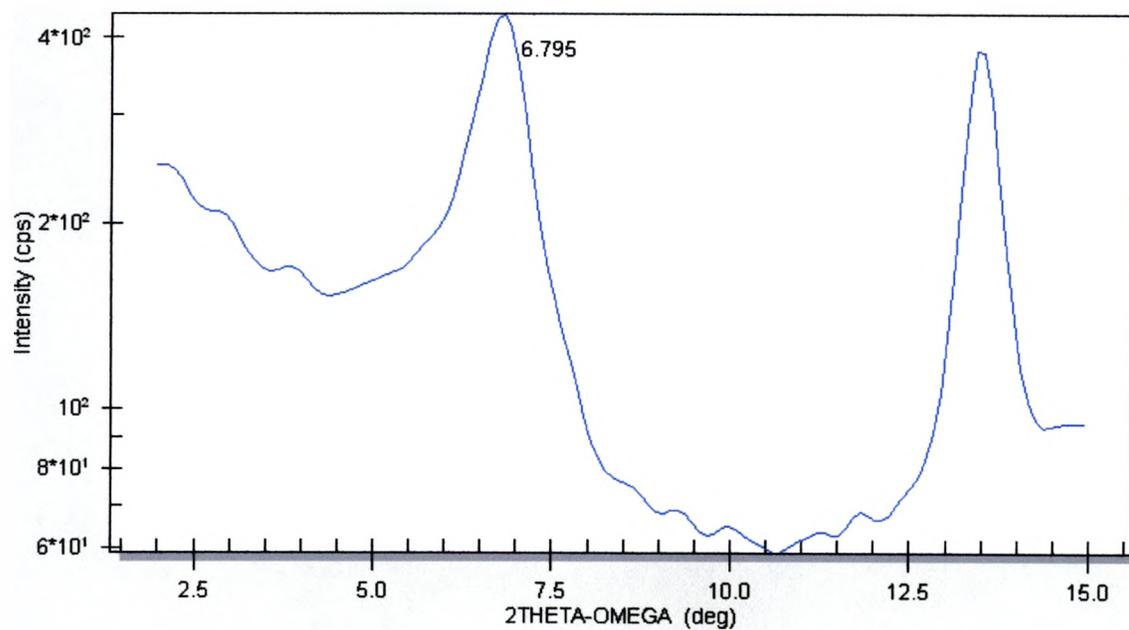
Nicotinic Acid



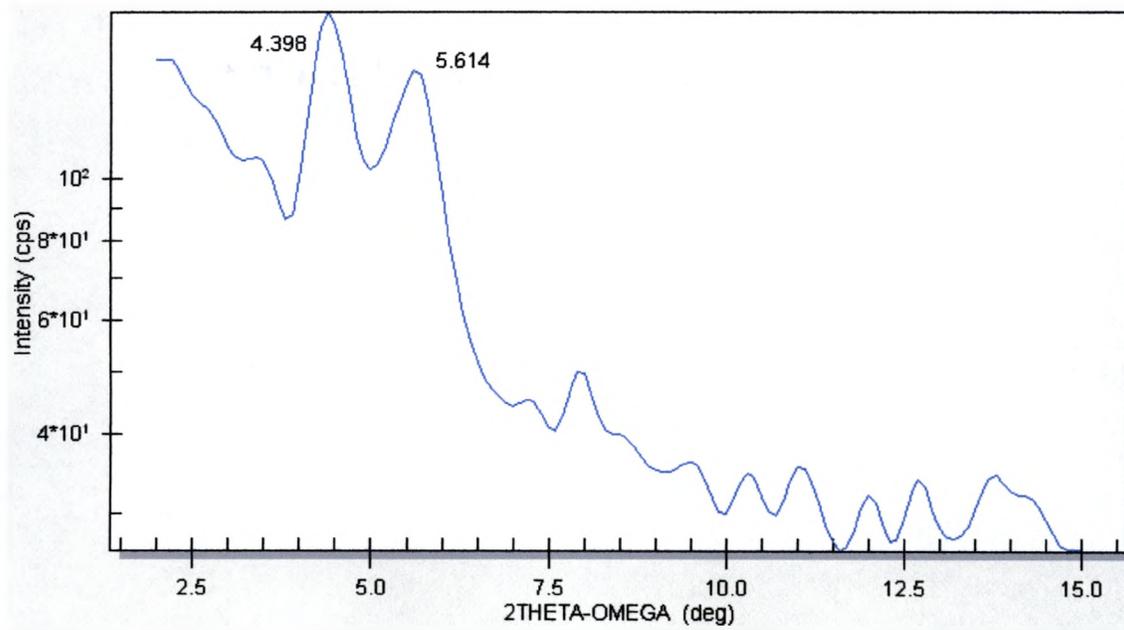
Oleic Acid



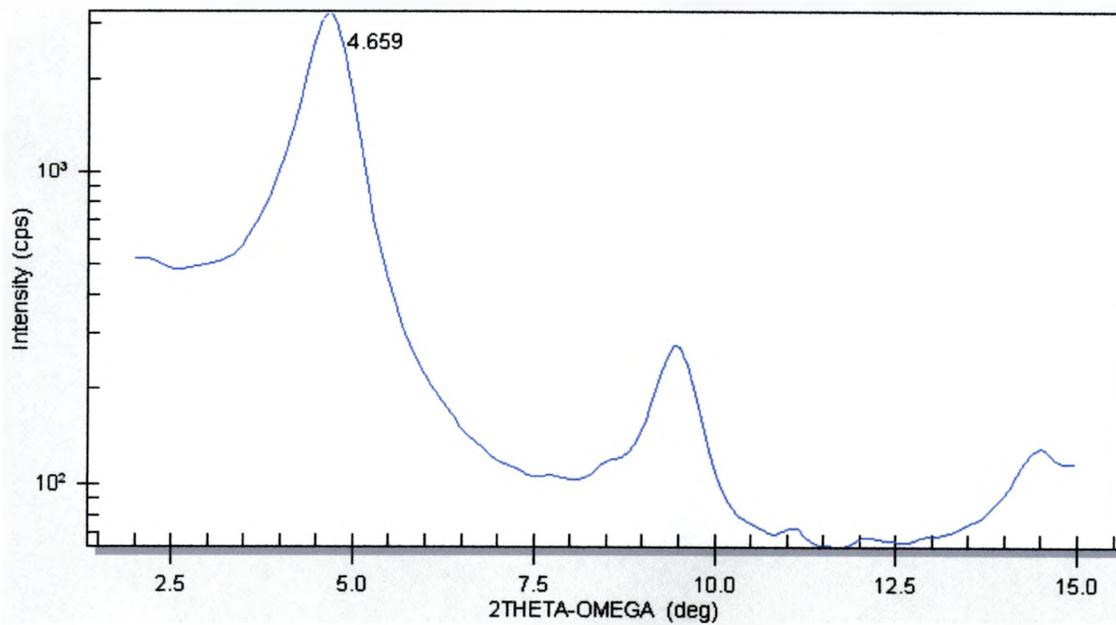
Propionic Acid



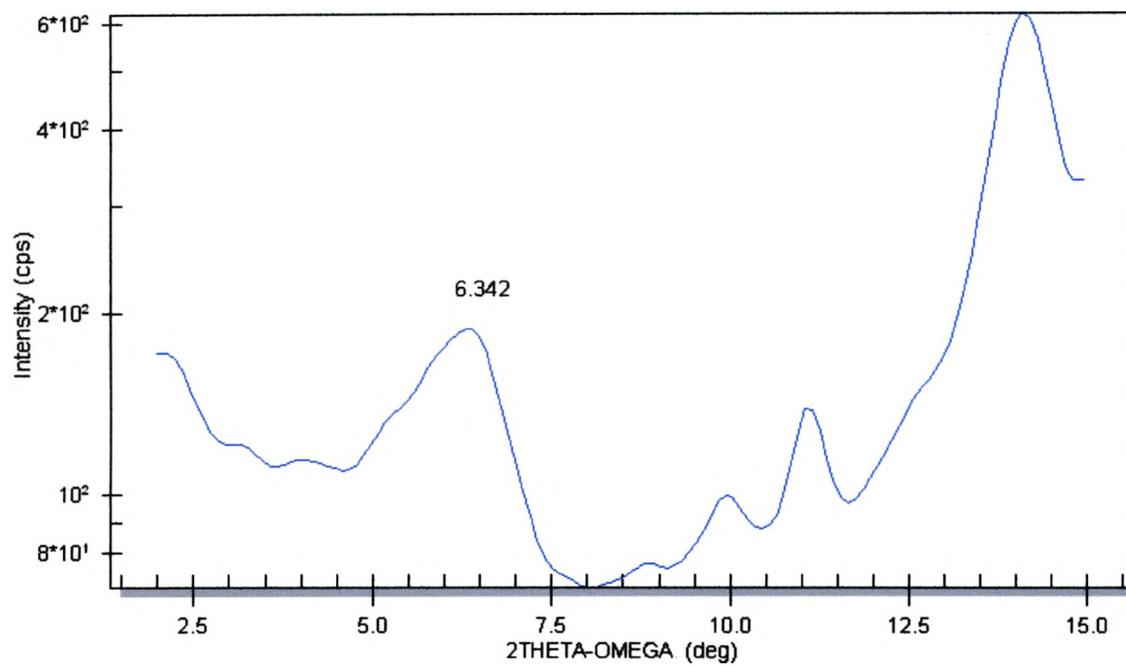
Propyl Gallate



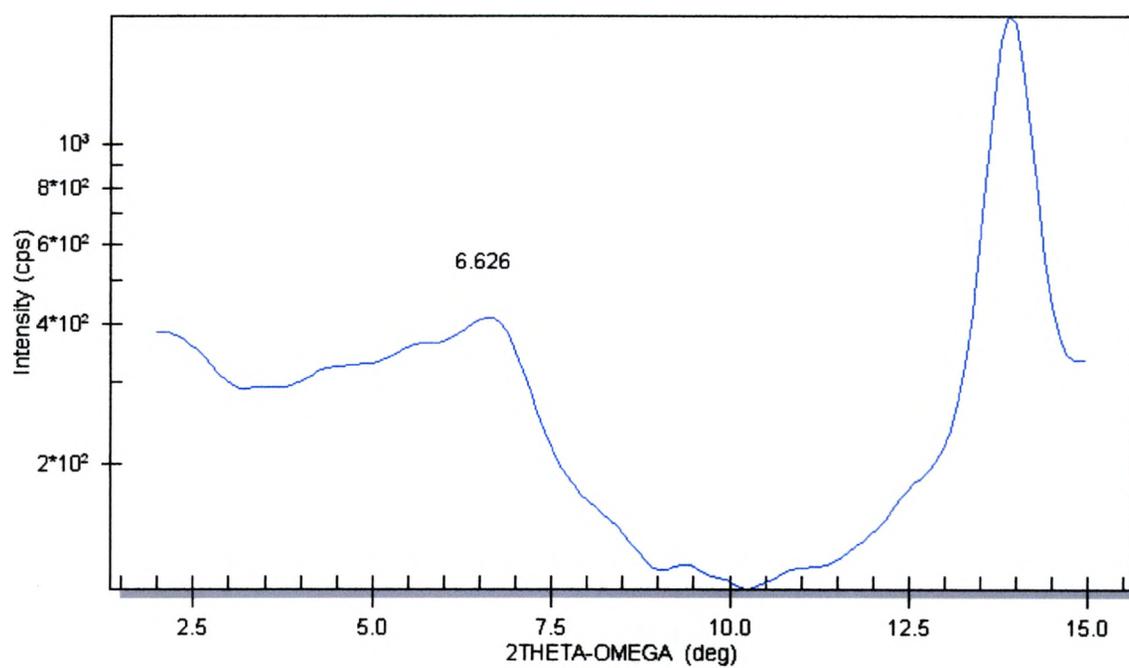
Propylene Glycol



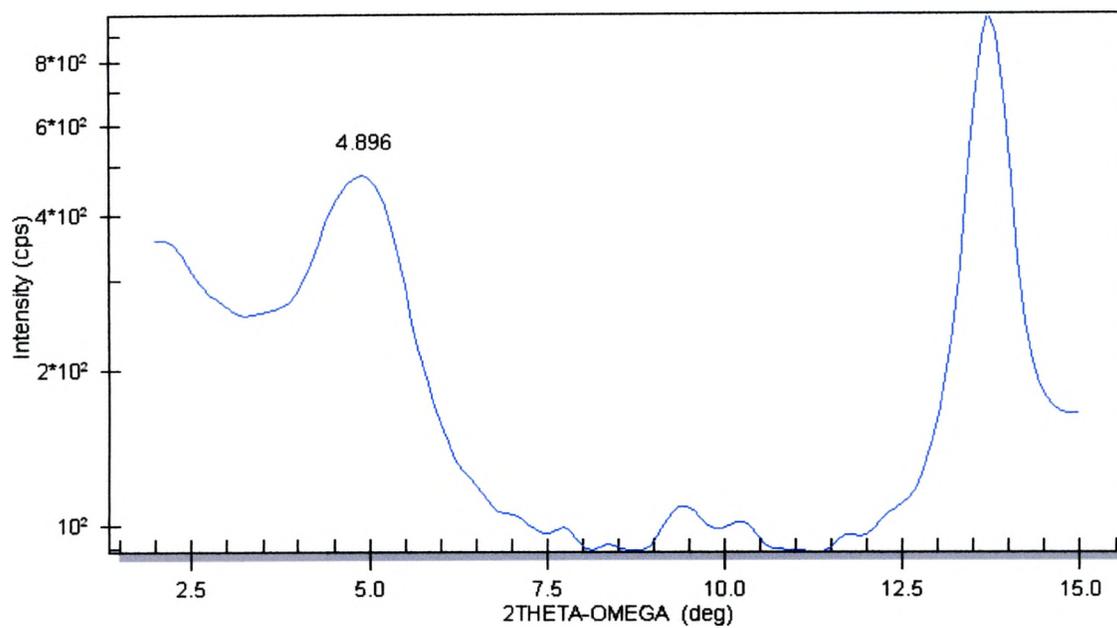
Propylparaben



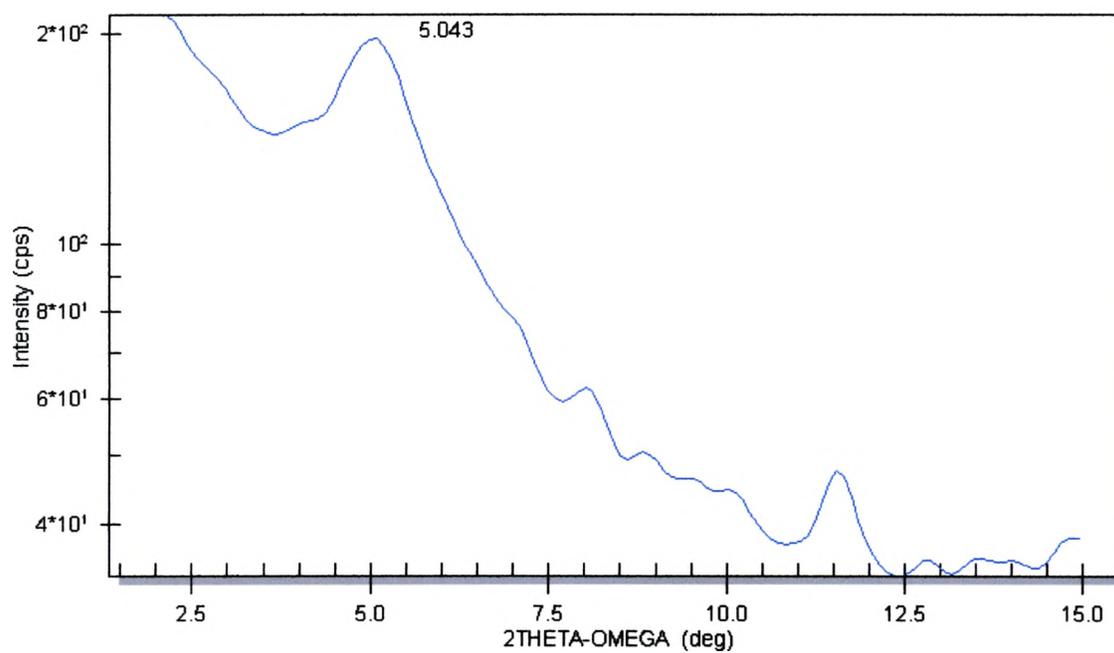
Succinic Acid



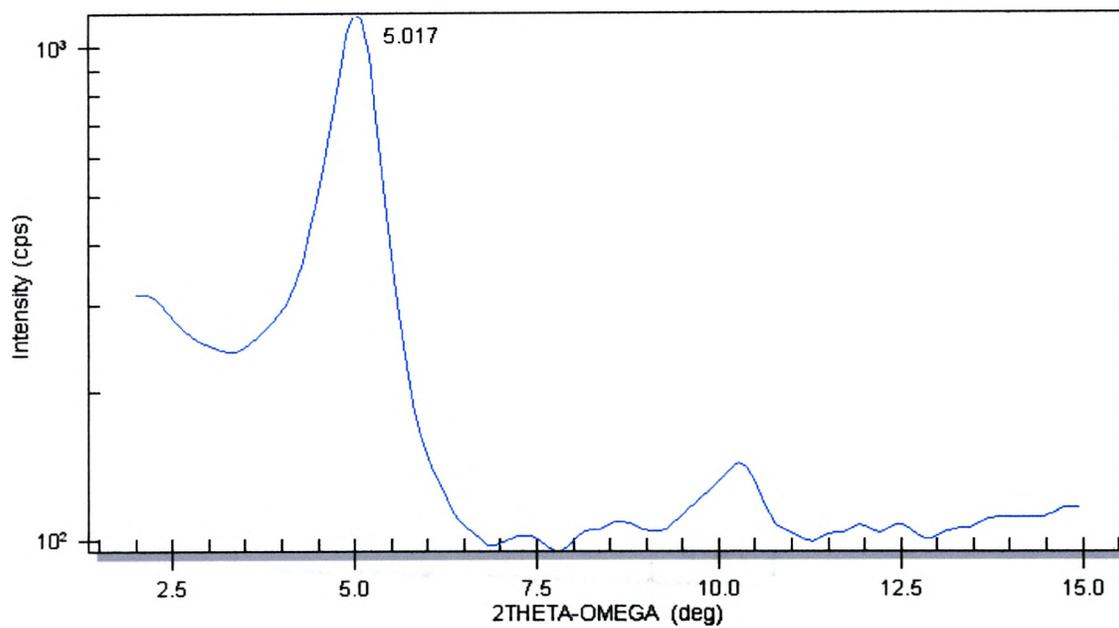
Sucrose



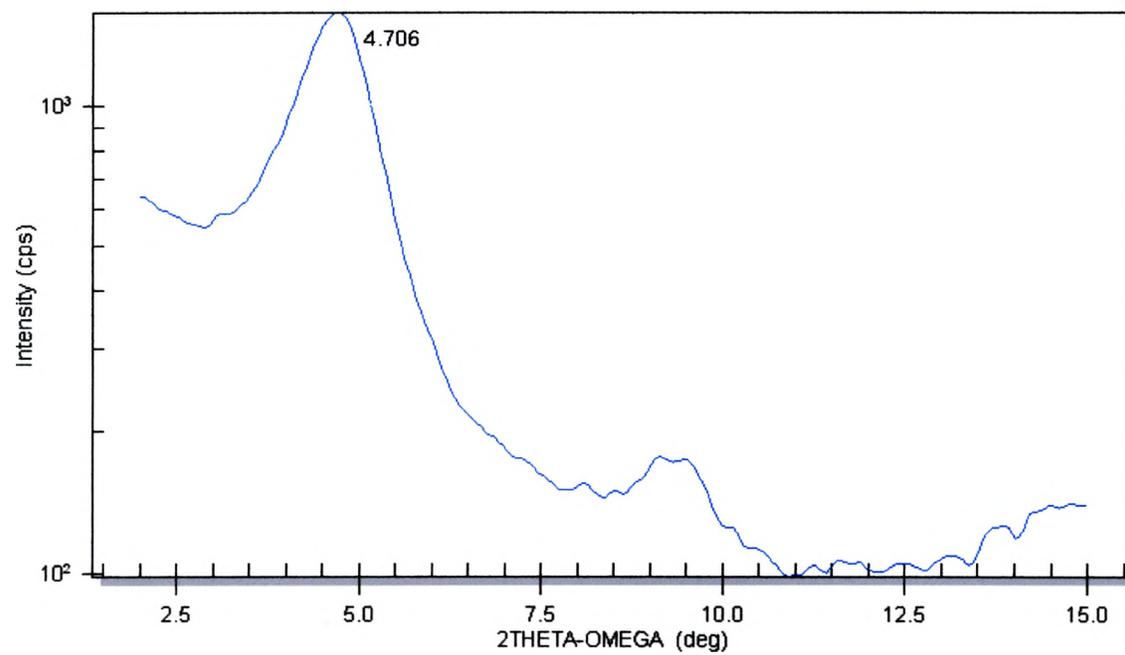
Tartaric Acid



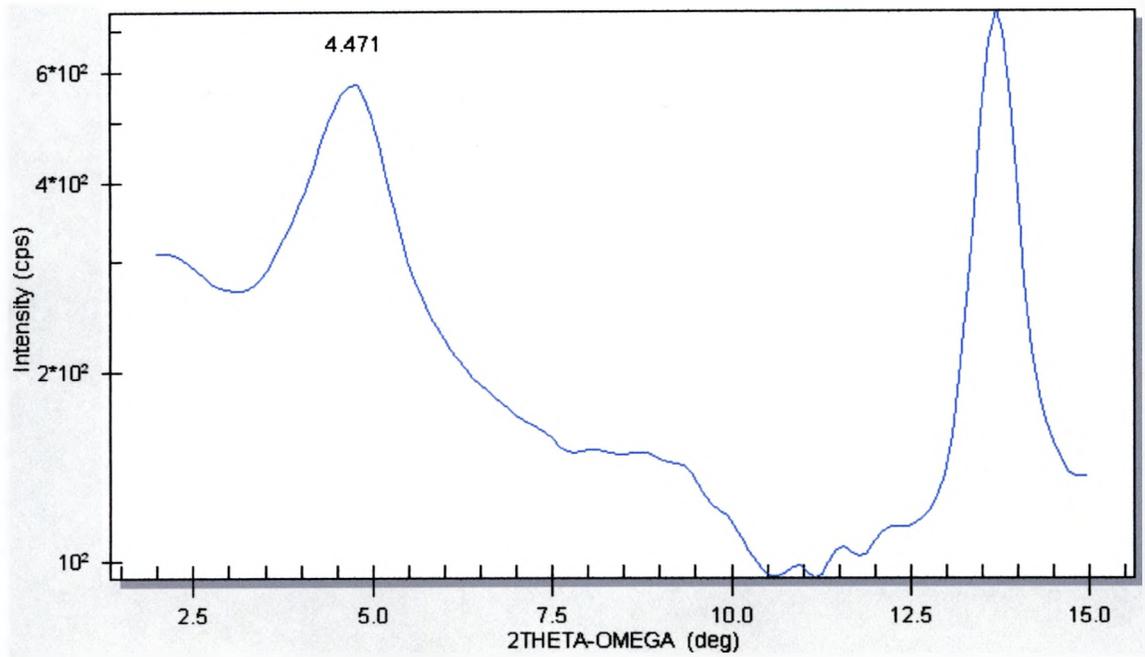
Triethyl Citrate



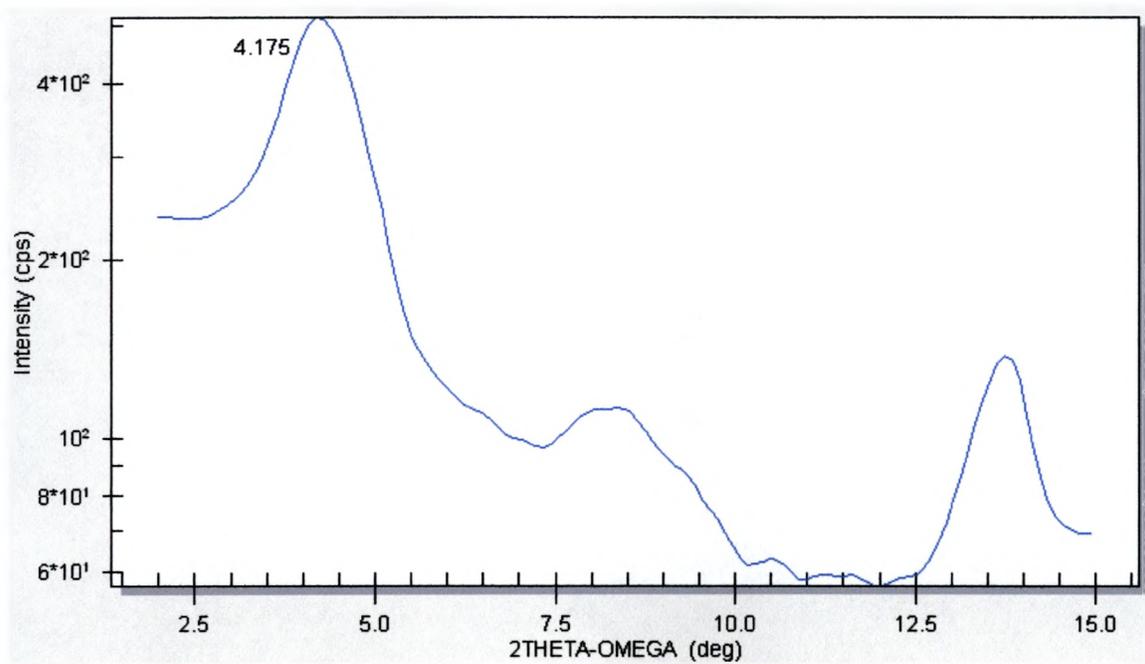
Urea 0% water



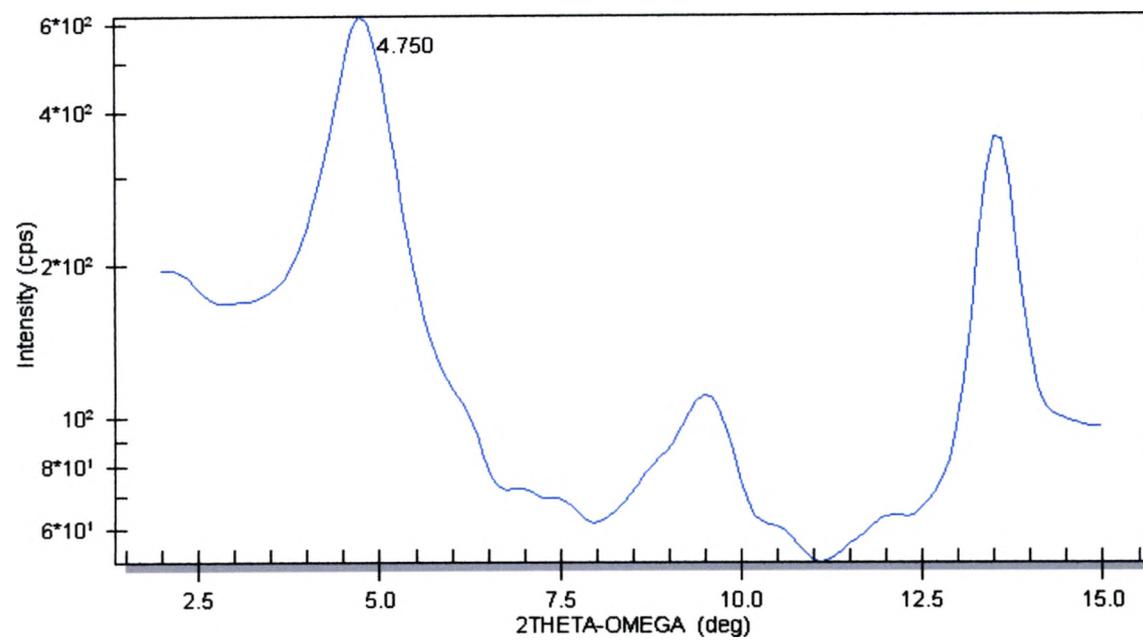
Urea 10%



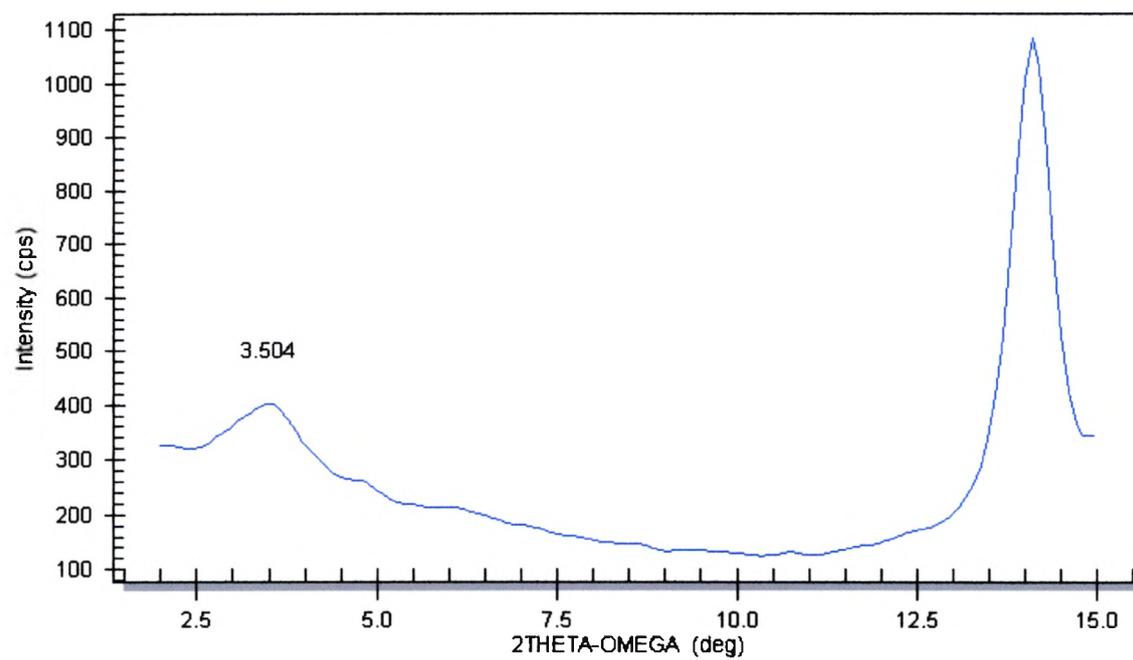
Urea 25%



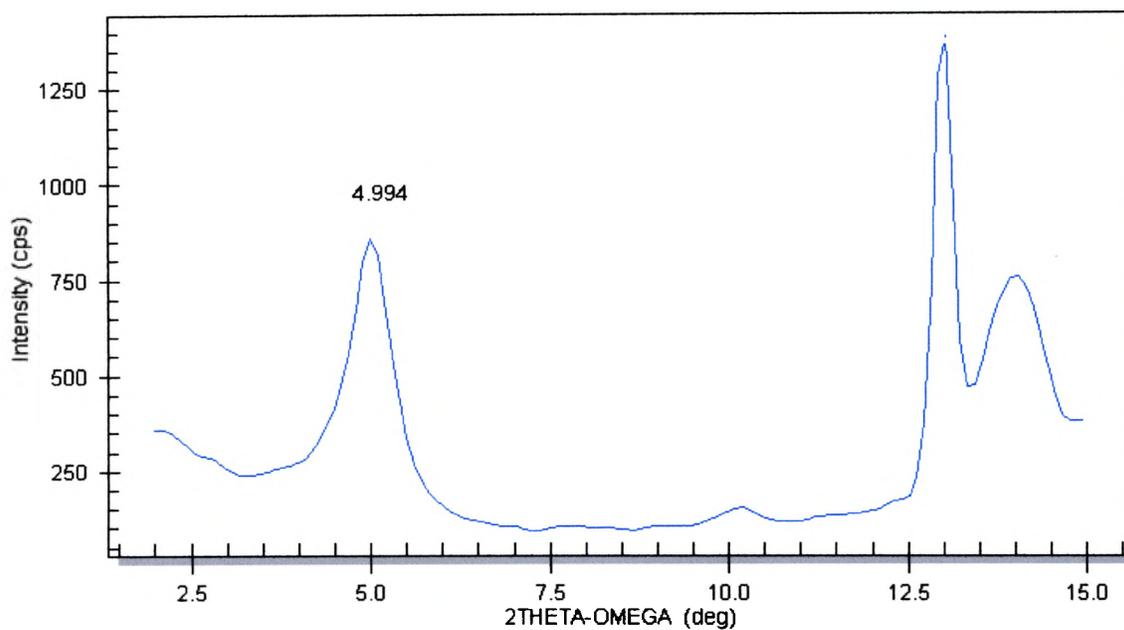
Urea 50%



Urea

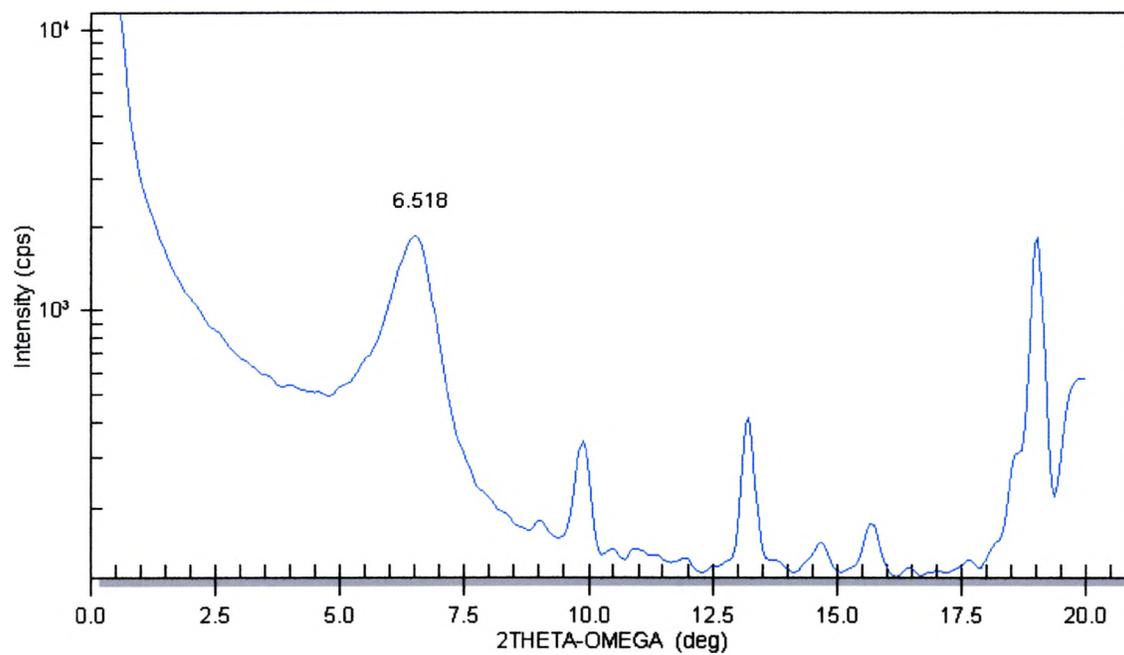


Vanillin

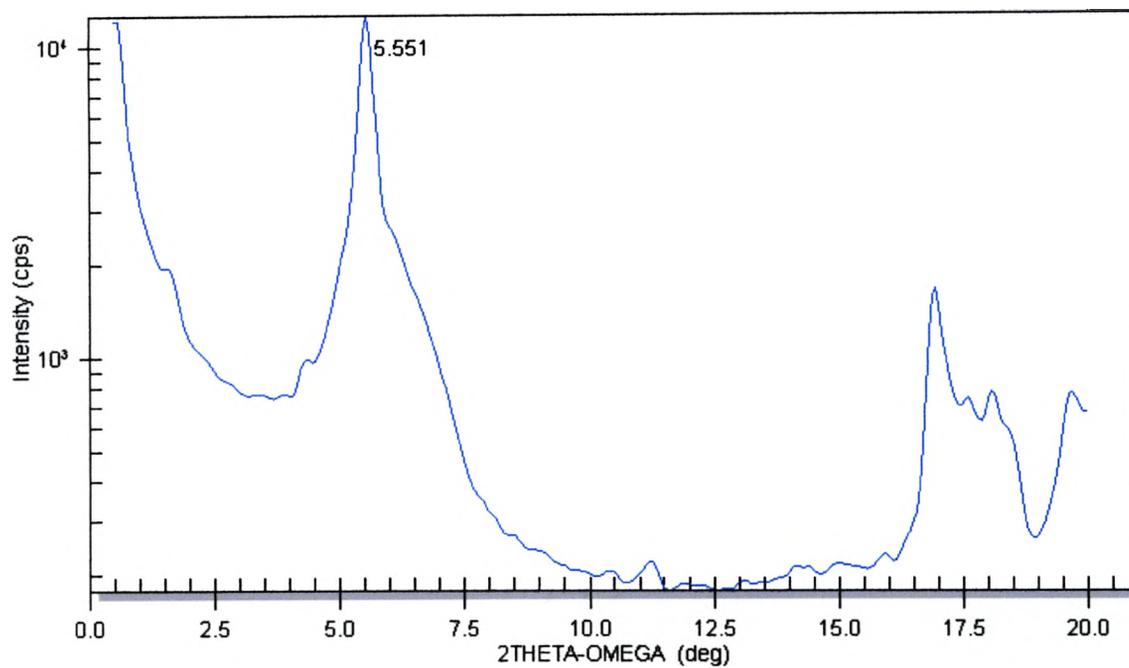


AMINO ACIDS

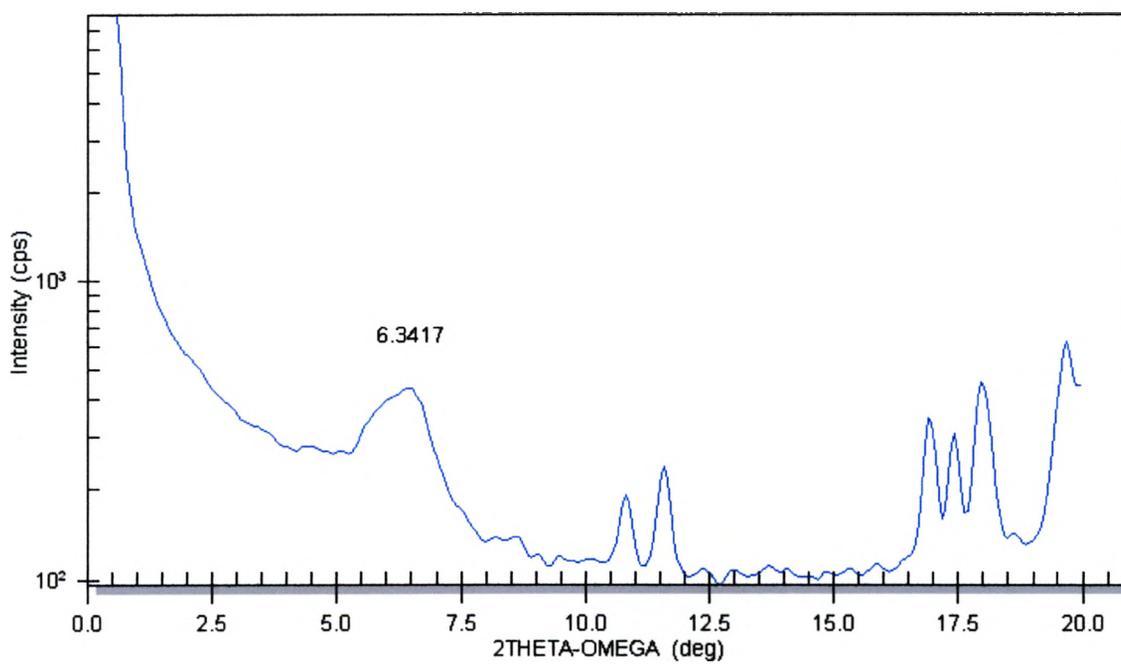
DL Lysine



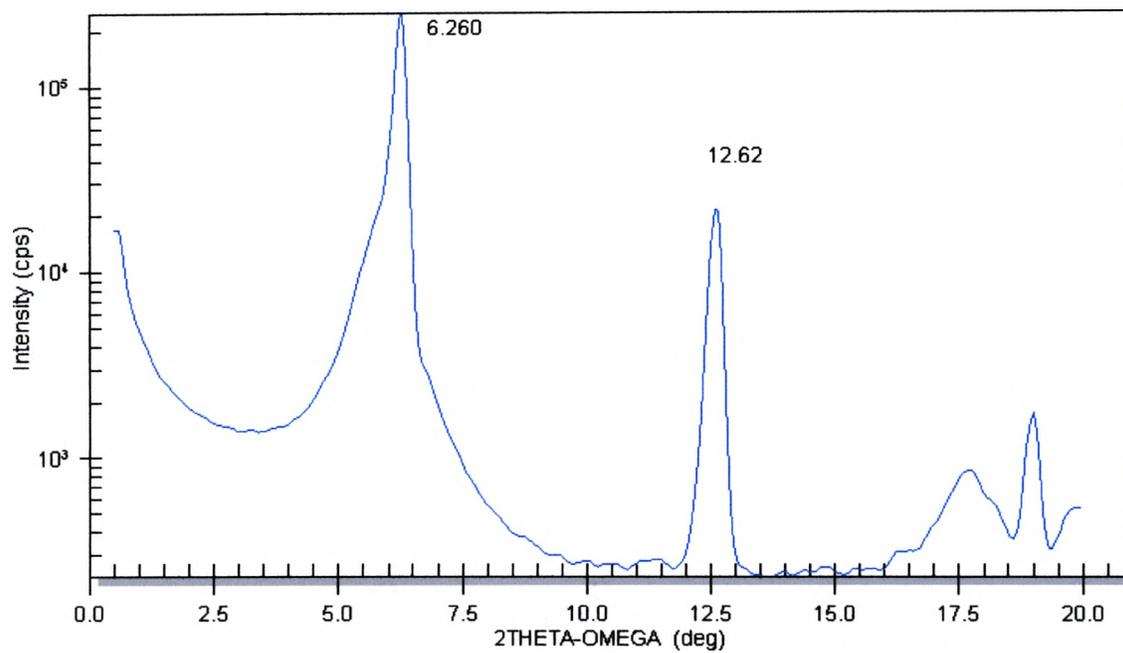
DL Phenylalanine



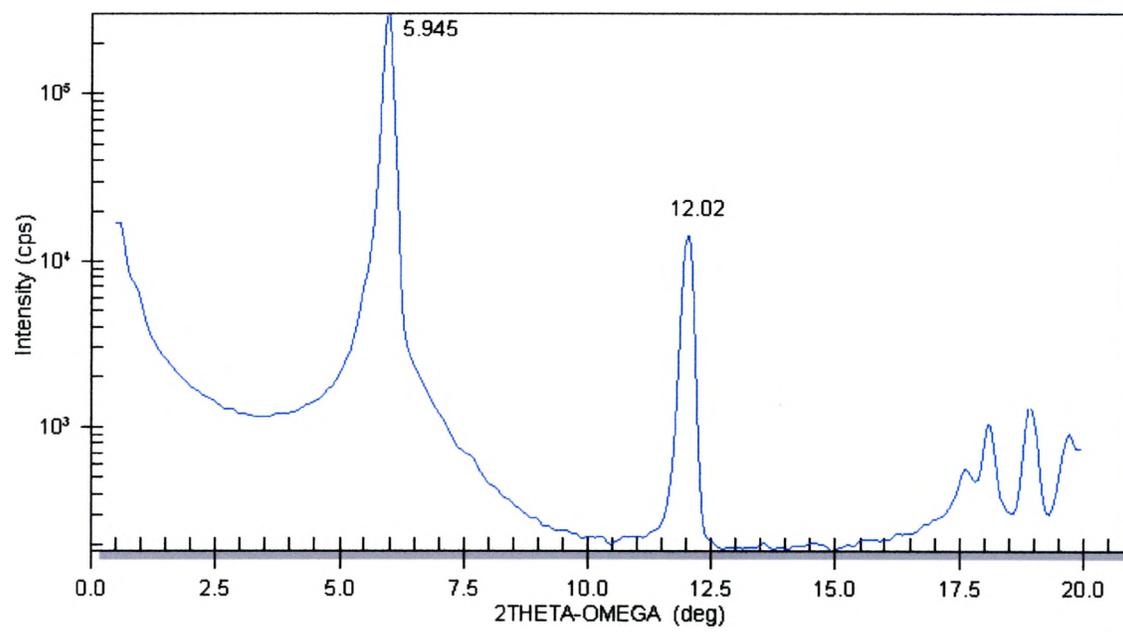
L Asparagine



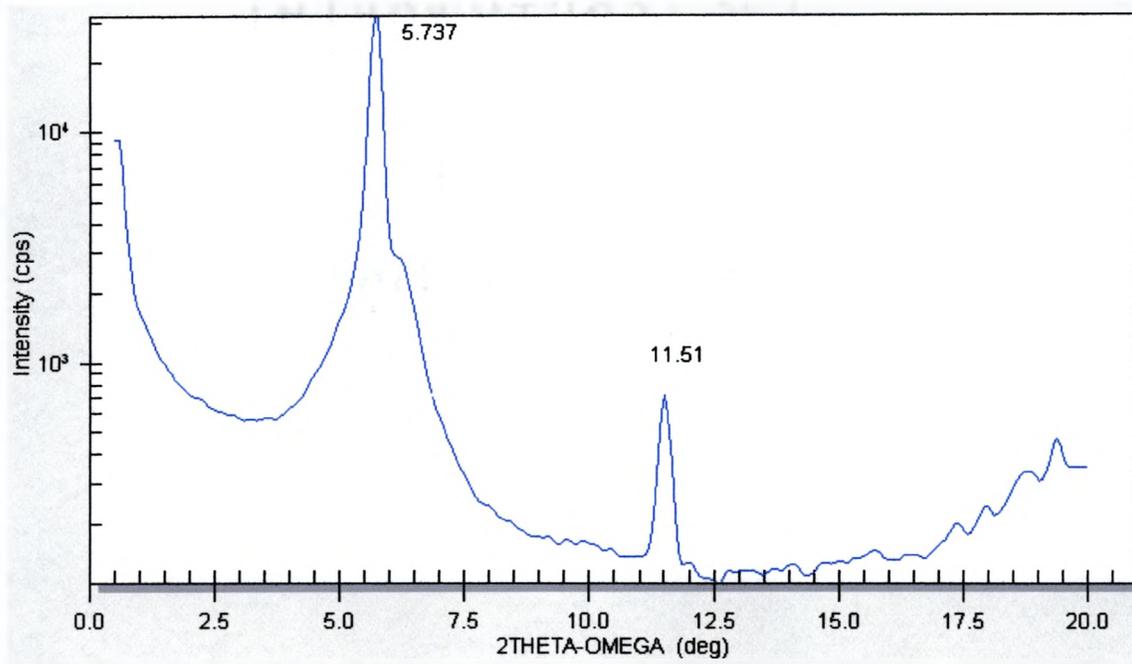
L Isoleucine



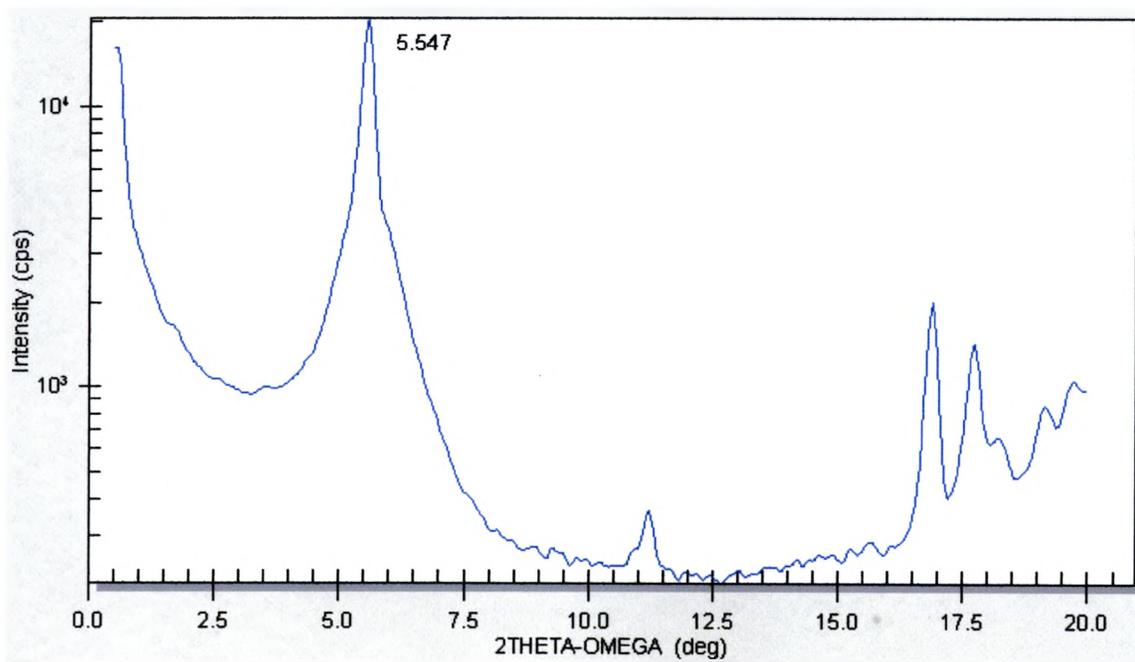
L Leucine



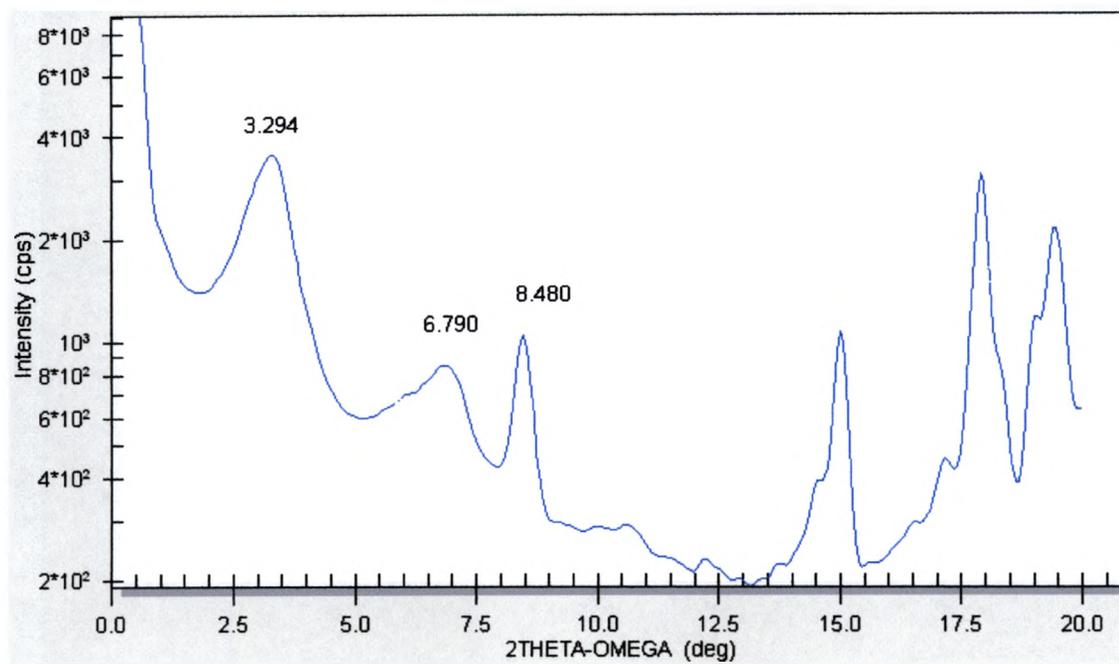
L Methionine



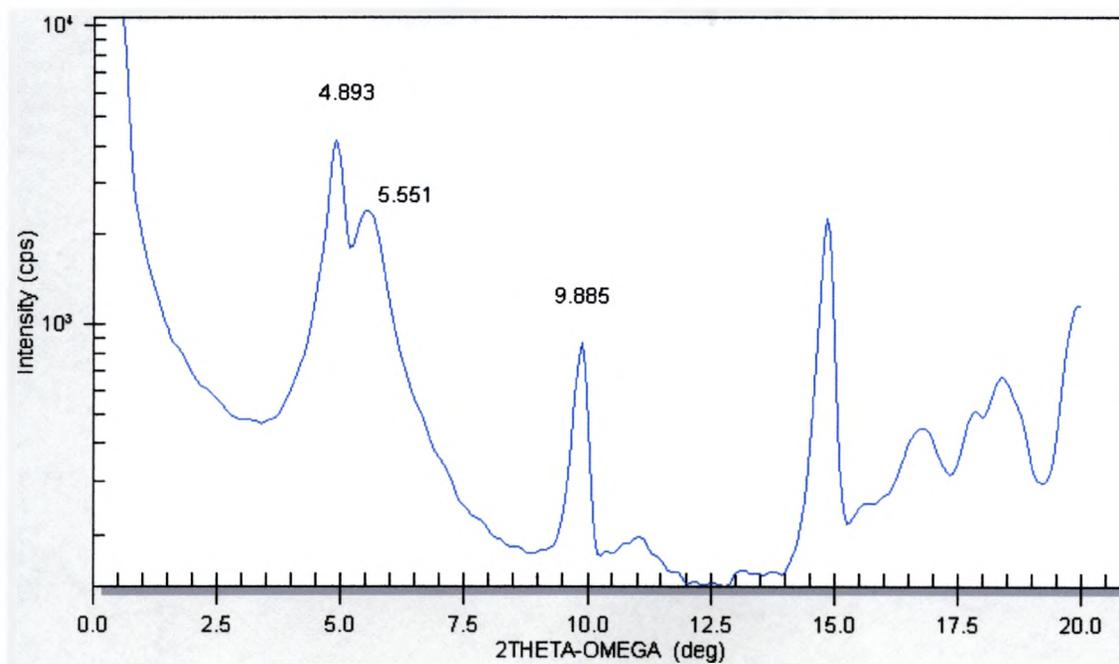
L Phenylalanine



L Proline

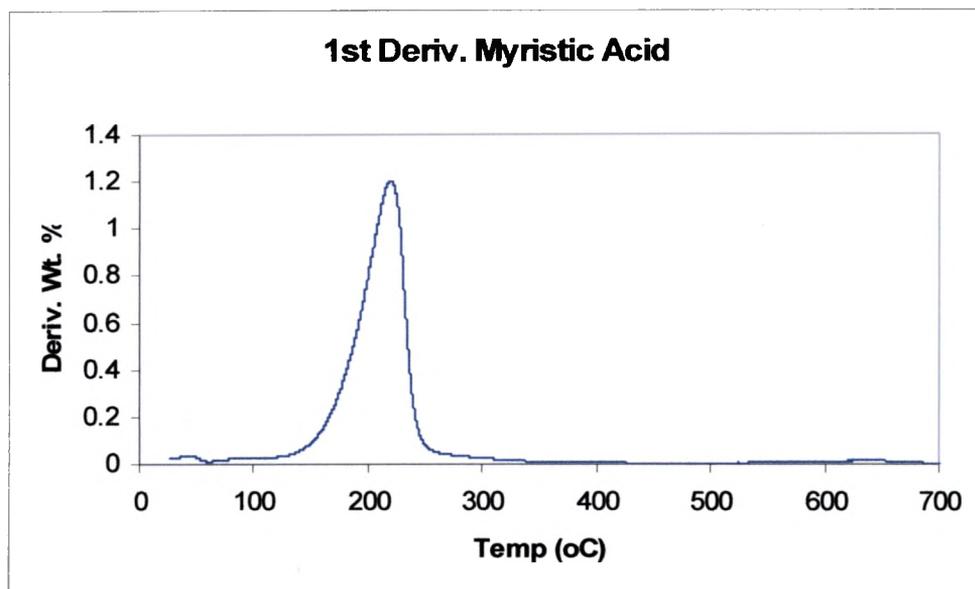
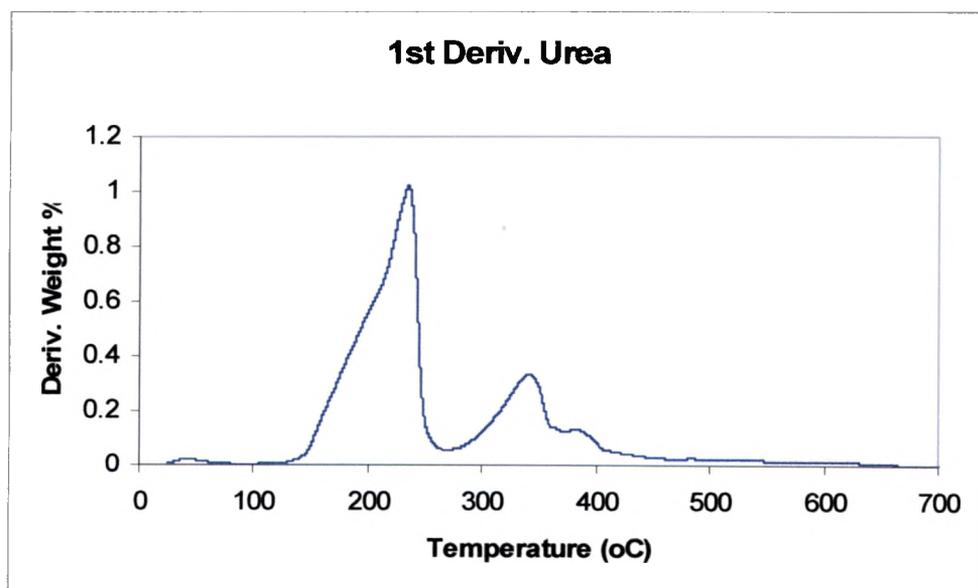


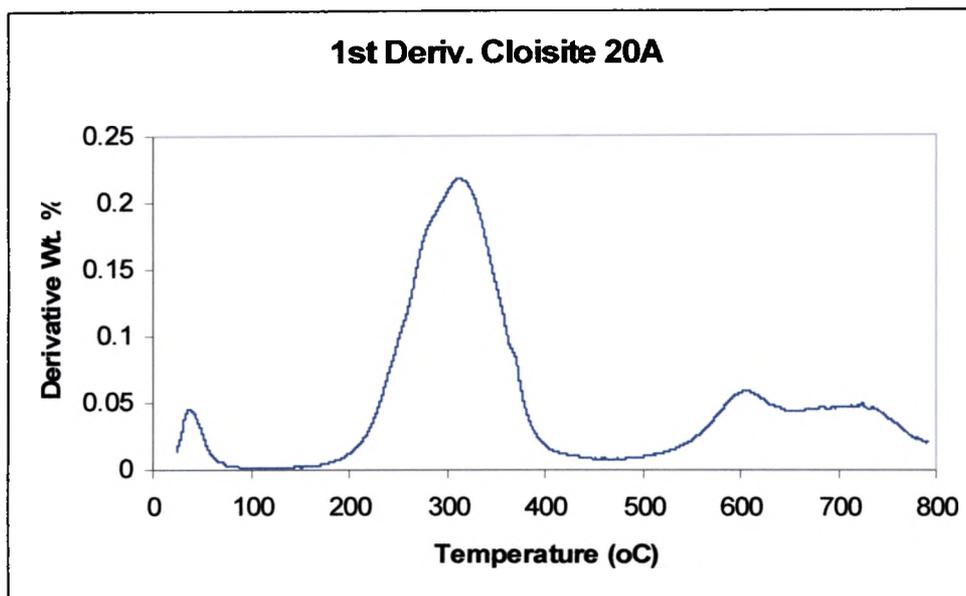
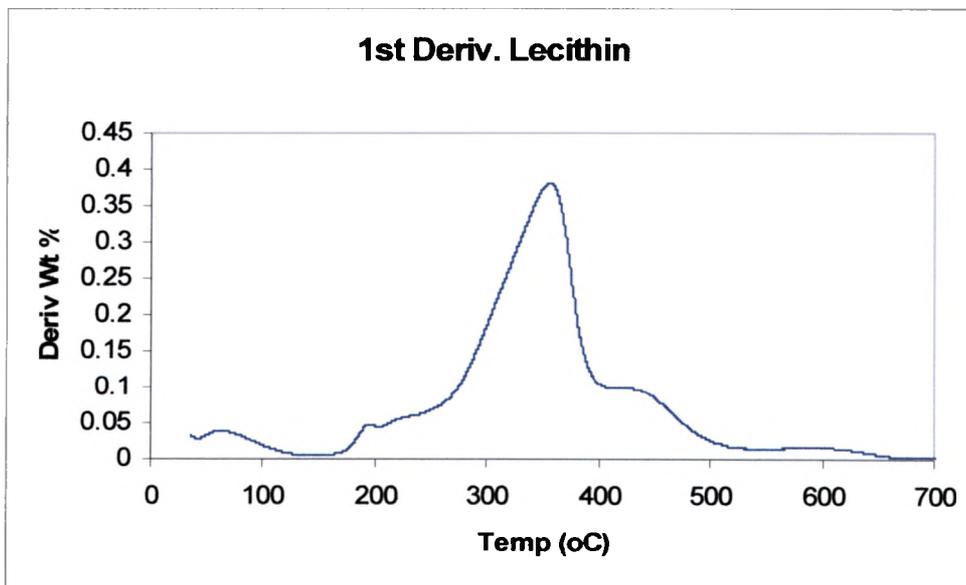
L Tryptophan



Appendix 6: TGA 1st derivative graphs.

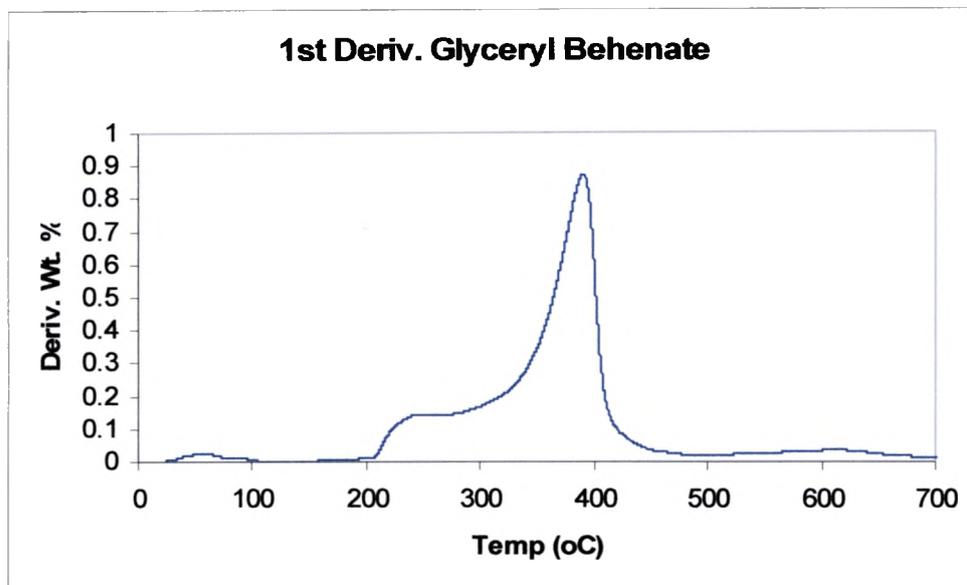
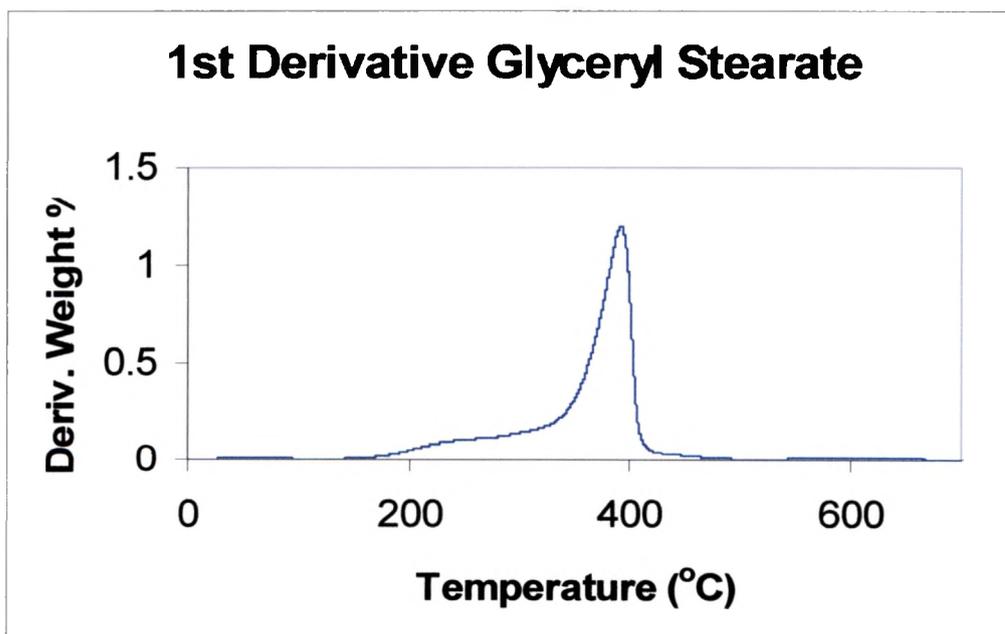
- All scans run under Argon atmosphere from room temperature to 800°C.
- All scans run by technician Stewart Harris (except for ChemService PEMS run by technician Jessie Hancock) at Texas State University - San Marcos IEIS department.
- All organoclays were 2:1 chemical: clay wt ratio, unless otherwise noted.

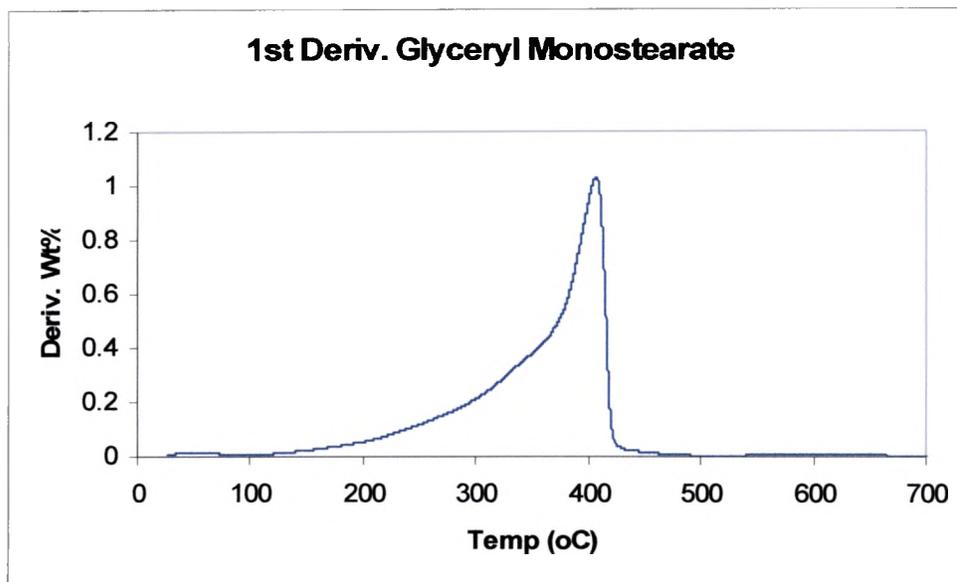
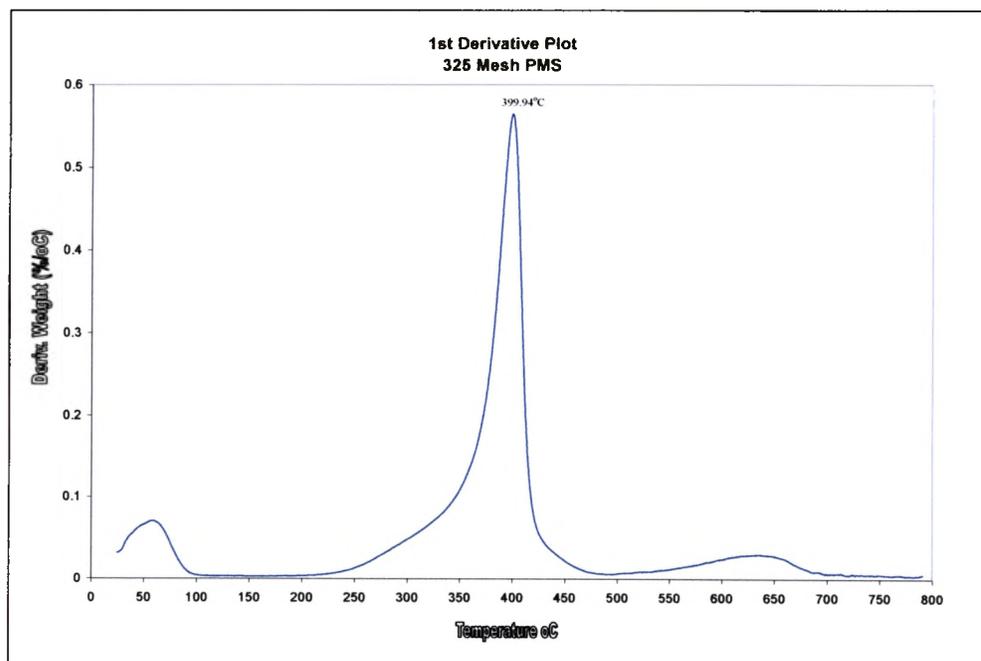
Myristic Acid**Urea**

Cloisite 20A (Dimethyl dehydrogenated tallow ammonium chloride)¹⁶**Lecithin¹⁷**

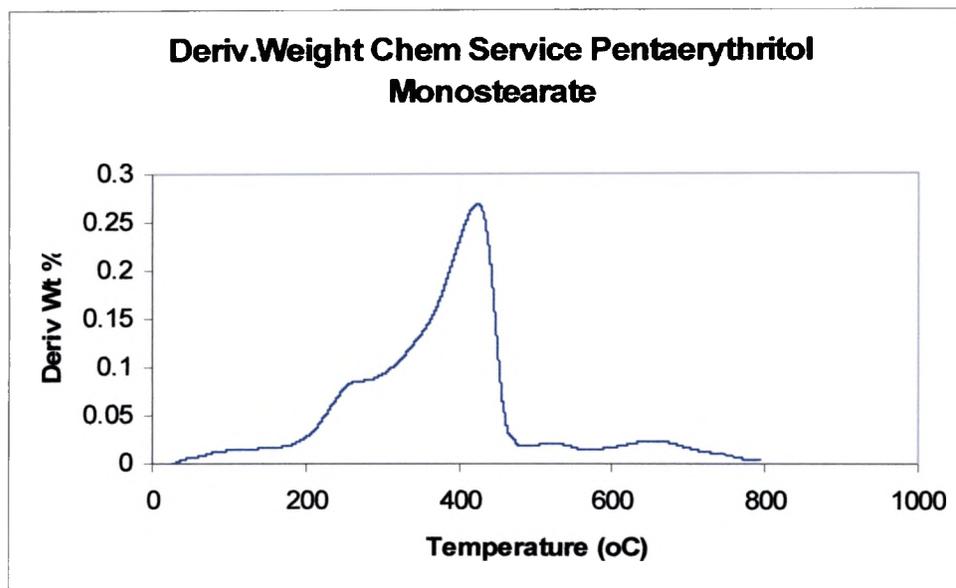
¹⁶ Cloisite 20A was tested as obtained from Southern Clay. No chemical or physical alterations were made to the clay before testing. Modifier (dimethyl dehydrogenated tallow) concentration is 95 meq/100g clay.

¹⁷ Organoclay was tested as 1:1 chemical: clay ratio, approximately 100 meq/100g clay.

Glyceryl Behenate, mixed ester**Glyceryl Stearate, mixed ester**

Glyceryl Monostearate**Radiasurf 7174 Pentaerythritol Monostearate¹⁸**

¹⁸ Organoclay was tested as 95 meq/100g clay.

ChemService Pentaerythritol Monostearate¹⁹

¹⁹ Organoclay was tested as 95 meq/100g clay.

REFERENCES

- ¹ Carter L. W., Hendricks J. G., Bolley D.S. US Patent 2,531,396, November, 1950.
- ² Moraru, V.N. "Structure Formation of Alkylammonium Montmorillonites in Organic Media." *Applied Clay Scienc.*, **19**, 11-26, (2001).
- ³ Pozsgay, A., Fráter T., Százdi, L., Müller, P., Sajó, I., Pukánszky, B., "Gallery Structure and Exfoliation of Organophilized Montmorillonite: Effect on Composite Properties." *European Polymer Journal*. (2003).
- ⁴ Hunter, D. Nanocomposite Extrusion - ANTEC 2000 presentation. – [Website] 2000; <http://www.nanoclay.com/antec2000/>. [Accessed March 1st, 2005]. Slide 4.
- ⁵ Zhu, L., Zi, Y., Zhang, J. "Sorption of Organobentonites to some Organic Pollutants in Water." *Environ. Sci. Technol*, **33**, 1407-1410, (1999).
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VITA

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