

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

**PREPARATION OF POLYACRYLAMIDE-CLAY
NANOCOMPOSITES BY REDOX POLYMERIZATION**

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Department : Advanced Technologies in Engineering

Programme: Materials Science and Engineering

JULY 2006

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Date of submission : 12 July 2006

Date of defence examination: 25 July 2006

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**POLİAKRİLAMİD-KİL NANOKOMPOZİTLERİNİN
REDOKS POLİMERİZASYONU İLE HAZIRLANMASI**

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**Tezin Enstitüye Verildiği Tarih : 12 Temmuz 2006
Tezin Savunulduğu Tarih : 25 Temmuz 2006**

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TEMMUZ 2006

ACKNOWLEDGEMENT

I would like to express my deep gratitude to my advisors; Prof. Dr. A. Tuncer ERCİYES and Prof. Dr. Mehmet Ali TAŞDEMİR, for their guidance, support and encouragement toward the completion of this thesis. I am also grateful to Prof. Dr. Yusuf YAĞCI, for his advice and suggestions.

I would like to thank Osman EKSİK and Neslihan ALEMDAR for their friendly and helpful attitude during my laboratory works.

I would also thank to Esra ENGİN for XRD measurements and want to acknowledge the TÜBİTAK-MAM for SEM analysis.

I have been also indebted to the TÜBİTAK-BİDEB for their financial support through M. Sc. Scholarship.

Finally I want to dedicate this thesis to my family who always supported and trusted me during my whole life and this thesis.

JULY 2006

Mustafa Serdar ÖNSES

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ABBREVIATIONS

PCN	: Polymer-clay nanocomposites
NC	: Nanocomposites
HDTMA	: Hexadecyltrimethylammonium chloride
XRD	: X-ray diffraction
FTIR	: Fourier Transform Infrared Spectroscopy
TEM	: Transmission Electron Microscopy
SEM	: Scanning Electron Microscopy
PAAM	: Polyacrylamide
OCLAY	: Pristine clay modified with HDTMA
ACLAY	: Pristine clay modified with acrylamide
PAAM-ACLAY	: Polyacrylamide-clay nanocomposites prepared with acrylamide as a surfactant
PAAM-OCLAY	: Polyacrylamide-clay nanocomposites prepared with HDTMA as a surfactant
DSC	: Differential Scanning Calorimetry
MMT	: Montmorillonite

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PREPARATION OF POLYACRYLAMIDE-CLAY NANOCOMPOSITES BY REDOX POLYMERIZATION

SUMMARY

Polymer-clay nanocomposites (PCNs) have received much attention in the last decade, due to their enhanced mechanical, thermal stability, gas barrier and flame retardancy properties in comparison to pure polymers, provided with the addition of low volume (1-5 %) of clays. Main principle of PCNs is well dispersion of clay layers which naturally exist together in stacked forms. Dispersion of these clay layers having thickness of about 1 nm and aspect ratios of 100-1000 provides large interfacial areas which are suitable for the interaction of organic and inorganic constituents and result in dramatic enhancements in the properties stated above.

Mostly used method for synthesis of PCNs has been in-situ polymerization in which polymerization takes place in the clay gallery. Main difficulty in obtaining well dispersions is, clays and polymers having different natures called as hydrophilic and organophilic (hydrophobic) respectively. Therefore first step of synthesis is making these two constituents compatible with each other. This so called organically modification of clays is done with cation exchange reaction between organic cations (surfactants) and inorganic cations of the clay gallery. By the reaction, clay is made organophilic and expanding of layers is provided.

Redox polymerization provides short reaction times, capability of polymerization at low temperatures and high conversions. Ce(IV) is one of the widely used and efficient redox initiator for vinyl polymerization in aqueous solutions with suitable reducing agents such as alcohols, aldehydes and amines. In spite of their advantages, use of redox polymerization and in particular Ce(IV) in the synthesis of polymer-clay nanocomposites were not much investigated.

In this study, polyacrylamide-clay nanocomposites were prepared by in-situ polymerization of acrylamide initiated by redox pair of Ce(IV)-glycerine. Two types of surfactants; a commercial long alkyl chained hexadecyltrimethylammonium chloride (HDTMA) and acrylamide monomer itself were used in the organically modification of clay. Two series of polyacrylamide-clay nanocomposites with each surfactant were prepared by varying the clay loading between 1 % and 5 %.

Organophilic clays modified with HDTMA and acrylamide, were characterized by X-ray diffraction (XRD). It was shown that, while HDTMA results in a considerable increase in the interlayer distances, acrylamide has limited effect on expanding of the clay gallery. Effect of mixing time before initiation of polymerization, on expanding of layers was also investigated with XRD. Swelling of clays was found almost independent of mixing time after two hours.

Prepared polyacrylamide-clay nanocomposites were characterized by XRD, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). XRD results suggested exfoliated type structure for all clay loadings in polyacrylamide-clay (PAAM-ACLAY) nanocomposites prepared with the acrylamide as an intercalating agent. Polyacrylamide-clay nanocomposites (PAAM-OCLAY) synthesized with the organophilic clay modified with HDTMA, also showed exfoliated structure, but with the increase of clay loading above 1 %, some intercalated structure was evidenced by XRD. SEM images did not indicate any aggregation of clays and an intercalated structure. FTIR also verified the incorporation of clay into the polymer matrix.

Glass transition temperatures of polyacrylamide-clay nanocomposites were measured with differential scanning calorimetry (DSC). All nanocomposites displayed higher glass transition temperatures than the pure polyacrylamide. Increments were higher for PAAM-OCLAY nanocomposites. Conversions were also calculated on the basis of dry weights of products. For PAAM-ACLAY nanocomposites conversion was found to increase with the clay loading, while relation is in an opposite manner for PAAM-OCLAY nanocomposites.

POLİAKRİLAMİD-KİL NANOKOMPOZİTLERİNİN REDOKS POLİMERİZASYONU İLE HAZIRLANMASI

ÖZET

Polimer-kil nanokompozitleri (PCNs), polimerlere az miktarda (% 3-5) kil ilave edilmesiyle sahip oldukları üstün mekanik, ısıl dayanıklılık, gaz bariyer ve alev geciktirici özellikleri ile geçtiğimiz on yıl içinde oldukça ilgi görmüştür. PCN'lerin ana prensibi doğal olarak istiflenmiş halde bulunan kil tabakalarının iyi bir şekilde disperse edilmesidir. Yaklaşık kalınlıkları 1 nm ve görünüm oranları 100-1000 olan killerin disperse edilmesi, organik ve inorganik bileşenlerin etkileşimi için uygun, geniş ara yüzey alanları sağlamak ve bu da yukarıda sayılan özelliklerde oldukça büyük iyileşmelerle sonuçlanmaktadır.

PCN'lerin sentezlenmesinde en sık kullanılan yöntem, polimerizasyonun kil galerisi içinde meydana geldiği, yerinde polimerizasyondur. İyi dispersiyonların elde edilmesindeki temel zorluk, kilin ve polimerin sırasıyla hidrofilik ve organofilik (hidrofobik) olarak adlandırılan farklı yapılarda bulunmalarıdır. Bu nedenle, sentezin ilk adımı bu iki bileşimi birbiriyle uyumlu hale getirmektir. Killerin organik olarak modifiye edilmesi olarak adlandırılan bu işlem, organik katyonların (yüzey aktif maddelerin) kil galerisi içindeki inorganik katyonlarla verdiği katyon değiştirme reaksiyonu ile olmaktadır. Bu reaksiyon ile kil hem organofilik yapılmakta hem de tabakaların arasının açılması sağlanmaktadır.

Redoks polimerizasyonu kısa reaksiyon süresi, düşük sıcaklıklarda polimerizasyon imkanı ve yüksek verim sağlamaktadır. Ce(IV), alkoller, aldehitler ve aminler gibi uygun indirgeyicilerle beraber, sulu çözeltilerdeki vinil polimerizasyonunda sıklıkla ve etkin bir şekilde kullanılan redoks başlatıcılarından. Avantajlarına rağmen, redoks polimerizasyonunun ve özel olarak Ce(IV)'ün, polimer-kil nanokompozitlerin sentezlenmesinde kullanımı fazla incelenmemiştir.

Bu çalışmada poliakrilamid-kil nanokompozitleri, akrilamidin Ce(IV)-gliserin redoks çifti ile başlatılan yerinde polimerizasyonu ile hazırlanmıştır. Kilin organik olarak modifiye edilmesinde; biri ticari, uzun alkil zincirli heksadesiltrimetilamonyum klorür (HDTMA) ve diğeri monomerin kendisi, akrilamid, olmak üzere iki farklı tip yüzey aktif madde kullanılmıştır. Kil içeriği % 1 ile % 5 arasında değiştirilerek her bir yüzey aktif madde ile iki seri poliakrilamid-kil nanokompoziti hazırlanmıştır.

HDTMA ve akrilamid ile organik olarak modifiye edilmiş killer X-ışını difraksiyonu (XRD) ile karakterize edilmiştir. HDTMA'nın tabakalar arasındaki mesafede ciddi bir artış sağladığı, akrilamidin ise tabakaların açılmasındaki etkisinin sınırlı olduğu gösterilmiştir. Polimerizasyonun başlaması öncesi karıştırma süresinin, kil tabakalarının açılması üzerindeki etkisi de XRD ile incelenmiştir. Killerin arasının açılması iki saatten sonra hemen hemen zamandan bağımsız bulunmuştur.

Hazırlanan poliakrilamid-kil nanokompozitleri; XRD, Fourier Transform İnfrared Spektroskopisi (FTIR) ve Taramalı Elektron Mikroskobu (SEM) ile karakterize edilmiştir. XRD sonuçları; akrilamidin “intercalating” ajanı olarak kullanılmasıyla hazırlanan poliakrilamid-kil nanokompozitlerinde (PAAM-ACLAY), tüm kil yüzdeleri için, “exfoliated” tipi bir yapıya işaret etmektedir. HDTMA ile modifiye edilen organofilik kille üretilen poliakrilamid-kil nanokompozitleri (PAAM-OCLAY) de yine “exfoliated” tipi bir yapı göstermektedir, fakat kil miktarı % 1’i aştığında kısmi “intercalated” yapıların varlığı XRD ile ortaya konmuştur. SEM görüntüleri killerin topaklanmasına ve “intercalated” bir yapıya ilişkin herhangi bir işaret göstermemiştir. Yine FTIR ile de kilin polimer matrisi içine dahil olması doğrulanmıştır.

Poliakrilamid-kil nanokompozitlerinin camsı geçiş sıcaklıkları Diferansiyel Taramalı Kalorimetre (DSC) ile ölçülmüştür. Bütün nanokompozitler, saf polimerden daha yüksek camsı geçiş sıcaklıkları göstermiştir. Artışlar PAAM-OCLAY nanokompozitleri için daha yüksek bulunmuştur. Ürünlerin kuru ağırlıkları baz alınarak dönüşümler de hesaplanmıştır. PAAM-ACLAY nanokompozitleri için dönüşümün kil miktarıyla arttığı bulunurken, PAAM-OCLAY nanokompozitleri için ilişkinin tam tersine olduğu görülmüştür.

1. INTRODUCTION AND OBJECTIVE

Research on nanoscale materials exploded in the last decade [1]. Among these, one of the major focuses has been on polymers which have various applications in daily life [2]. The pioneering work of Toyota on polymer-clay nanocomposites (PCNs) stimulated the research in both academia and industry [3-5]. Their Nylon-6/clay nanocomposite showed dramatic enhancements in mechanical and thermal properties with only addition of 1-3 % silicate layers [6]. Following this, many PCNs were reported with superior mechanical, thermal stability, flame retardancy, gas barrier and solvent resistance properties in comparison to pure polymer and conventional polymer-clay composites [3-5, 7, 8].

The unique properties of nanocomposites are mainly attributed to the strong interactions between the dispersed phase and the matrix, provided with the larger interfacial area per weight of the dispersed constituent in comparison to the conventional composites [2]. Clays (especially montmorillonite of the smectit family) are suitable materials for reinforcing polymer matrix that they consist of small crystalline layers of aluminosilicates having thickness of ~1 nm and aspect ratios of 100-1000, which are also called as clay nanolayers. But these aluminosilicate layers originally exist in stacked forms called tactoids maintained by electrostatic forces which is not possible to overcome by simple shear [1, 8, 9]. Another main difficulty dispersing these clay nanolayers in the polymer matrix is incompatibility between the hydrophilic clay and the hydrophobic organic polymer. Therefore clay should be modified via a typical cation exchange reaction between inorganic cations (Na^+ , Ca^{++}) of the clay gallery and the organic cations, mostly alkylammonium ions. This treatment provides both the pristine clay to be organophilic and expanding of the clay nanolayers by the insertion of long chained molecules into the clay gallery [8, 10].

Polymer-clay nanocomposites are classified into two main groups called as exfoliated and intercalated. Exfoliated structure is obtained when clay nanolayers are completely dispersed in the polymer matrix [1, 10]. On the other hand intercalated structure is formed as a result of penetration of polymer chains into the gallery.

Ordered structure of clay layers are retained, but an increase in the interlayer distance is observed in intercalated nanocomposites [4, 11]. As the property enhancements are mostly provided with exfoliated structures, it has been general objective of the researchers [4, 10, 12, 13].

Among the various methods, in-situ polymerization has been the mostly utilized one in which polymerization is carried out in the presence of organically modified clays. Successive exfoliated structures were obtained by different research groups using this technique [9, 13, 14]. Also improvement of dispersion was reported with the use of functional surfactants for the modification of clays: Qutubuddin et al. [12] used a polymerizable cationic surfactant, Yeh et al. [15] studied acrylamide, monomer itself, in the synthesis of polyacrylamide-clay nanocomposites, Weimer et al. [16] replaced a living free radical initiator into the clay gallery and Yagci & Nugay et al. [7] cation exchanged clay with a photo-initiator.

Although there are some reports [17, 18] on the synthesis of polyacrylamide-clay nanocomposites, these are mostly concentrated on the gel form of polyacrylamide. Only typical polymer-clay nanocomposite study on polyacrylamides was reported from Yeh et al. [15]. They synthesized polyacrylamide-clay nanocomposites via in-situ ultraviolet-radiation polymerization and used acrylamide as both the monomer and intercalating agent. They obtained partially exfoliated and intercalated structures depending on clay loading.

Redox polymerization may be characterized by short times of reaction, ability of carrying the reaction at room temperature and high yields [19, 20]. It has found application especially in low temperature and emulsion polymerizations [21, 22]. Among the redox initiators, Ce(IV) is more efficient and has been widely used in polymerization of vinyl monomers in aqueous solutions with suitable reducing agents such as alcohols, aldehydes and amines [19, 23-25]. There are only few reports on the use of redox initiators in synthesis of polymer-clay nanocomposites: Stadtmueller et al. [26] reported the synthesis of poly(methyl methacrylate) nanocomposites initiated with a benzoyl peroxide/amine redox couple and Chung et al. [27] synthesized nanocomposites using potassium persulfate in the presence of silicate and 2-acrylamide-2-methyl-1-propanesulfonic acid initiated by the catalytic activity of the clay itself without exterior redox co-catalyst. Only report on the use of Ce(IV) in the synthesis of organic-inorganic hybrids was from Qian et al. [28] on the

preparation of modified palygorskite-polyacrylamide ionic hybrids which differ with its inorganic material, palygoskite, and not a typical polymer-clay nanocomposite study.

Objectives of this thesis were synthesis and characterization of polyacrylamide-clay nanocomposites prepared via in-situ polymerization initiated by Ce(IV)-glycerine redox system. Main idea was to utilize the redox initiation to the synthesis of polymer-clay nanocomposites. Study focused mainly on two parameters; clay loading and type of intercalating agent used to modify natural clay. Clay loading was varied between 1 and 5 % of monomer. Two types of surfactants used were a typical and commercial alkyl ammonium ion, hexadecyltrimethylammonium chloride (HDTMA), and monomer itself, acrylamide. Further goals of this study have been to establish a basis for the use of acrylamide and water soluble polyacrylamide in the synthesis of other polymer-clay nanocomposites.

2. LITERATURE REVIEW

2.1 Composite Materials

Field of materials has always been crucial for the development of new technologies that without the discovery and invention of new materials it wouldn't be possible to solve many engineering problems. As the problems were solved, the newer and harder ones came on the scene. This showed the inadequacy of individual materials that each of them had some advantages and limitations. Wood was light and tough, but it would burn. Ceramics and metals were very strong, but heavy [11, 29].

This situation led human kind to combine various materials to obtain better properties. Actually it wasn't so difficult for human to find this idea, since nature is full of examples of wherein the idea of composites is utilized. The coconut palm leaf, for example, is a cantilever using the concept of fiber reinforcement. Wood is a fibrous composite: cellulose fiber in a lignin matrix. Bone is another example of a natural composite that supports the weights of bodies. Human discovered this idea long time ago that they have been putting fibers into a binder or matrix body for more than 3000 years. The Pharaohs of Egypt in Biblical times and the ancient Incan and Mayan societies knew that plant fibers helped strengthen and prevent bricks and pottery from cracking. Later, Eskimos found that moss strengthen ice. Today, one of the mostly used composite is concrete, which is a mixture of sand, gravel, and cement. Structural parts with superior properties have been made by using steel reinforcing bars with high tensile strength and toughness combined with a concrete matrix for rigidity and compressive strength [11, 29].

Increasing demand for stiffer and strong but lighter materials in fields as space research, aeronautics, energy and construction, from the 1960's has been the pushing power of research on composites. As a result today's integral composite materials satisfying user requirements were made inspiring from nature. These materials result in a performance unattainable by the individual constituents and offer great advantages in flexible design. However, development of individual materials is also

very important for the advances in the technology that newly developed organic polymers have added a lot to the design and fabrication of composites [11,29].

Composites are simply defined materials consisting of two or more distinct components. Generally continuous phase is called the matrix, and the discontinuous phase is the filler. Composites can be divided into categories from various aspects. But accordingly to the natures of the matrix and the filler they can be classified as; metal/metal, metal/ceramic, ceramic/ceramic, ceramic/polymer, and polymer/polymer [11, 29].

Also there can be made a distinction with the constituent forms involved: Fibers, particles, laminae, flakes are major reinforcing forms used in composite materials (Figure 2.1). Matrix encloses these reinforcing constituents and provides the bulk form of composite [11, 29].

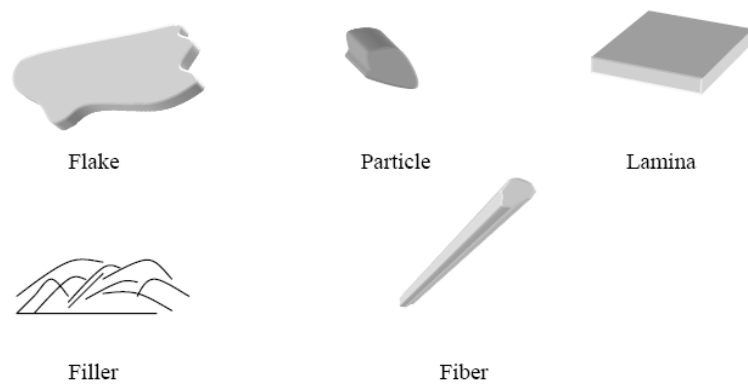


Figure 2.1: General shapes of reinforcing agents [11]

2.1.1 Nanocomposite concept

Nanocomposites are composite materials consisting of building blocks in the nanometer or tens of nanometer size scales. Generally speaking, any composite that contains particles having at least one dimension in 1-100 nm range, can be considered a nanocomposite [29]. Depending on how many dimensions are in the nanometer range, a classification can be made [30]:

- Isodimensional nanoparticles; three dimensions are on the order of nanometers.
- Nanotubes or whiskers; two dimensions are on the order of nanometers.
- Nanolayered composites; only one dimension is on the order of nanometers.

Research at the nanosize is very popular today that there are lots of nanotechnology centers all over the world and considerable funds are devoted to this area. Main reason in this interest is the achievement of superior properties by using nanomaterials and designing at the nanoscale. One interesting point is that new properties are possible, which are not exhibited by the parent constituent materials. Nanocomposite property enhancements can be more than those simply predicted by the rule of mixtures. On the other hand, control of the nanoscale structure is very challenging that the properties of nanocomposites are determined not only by the bulk properties of each of the components, but also by complex interactions between the building blocks and interfaces between them [11]. Also properties of nanocomposites are very dependent on the dispersion of the nanoparticles in the matrix that most of the effort in the nano area is devoted to this problem [31].

Similarly to composites, nanocomposites can be classified into groups according to nature of the materials used: Ceramic/ceramic, metal/ceramic, metal/metal and ceramic/polymer (inorganic/organic). Polymer-clay nanocomposites are included in the organic/inorganic nanocomposites which will be detailed in the next section [29].

2.1.2 Polymer nanocomposites

Polymers are one of the most widely used materials with their unique properties such as light weight, ease of processing, ductile nature and economical value. On the other hand lower modulus and strength are main disadvantages of polymers in comparison to metals or ceramics. Some methods have been proposed to solve these problems: One approach is to synthesize polymers, whose molecular architecture incorporates by rigid units, such as aromatic rings and/or heterocyclic rings into the main polymer chain. Although these polymers have high modulus, strength and thermal stability, use of strong solvents and acids causes difficulties in their processing.

Another approach is addition of inorganic fillers to the polymer matrix, to enhance mechanical and other properties, such as flammability and permeability [32]. Actually inorganic fillers can be classified into two main groups as active and inactive. Inactive fillers have the only function of filling and have no interaction with the media. They are used for decreasing the cost of the products. Particle size, shape, surface characteristics and their distribution in the polymeric matrix is more important rather than their chemical structure. Active fillers on the other hand act as

reinforcement and they interact with the polymer. Here important point for a proper interaction is that inorganic filler and organic polymer matrix must be compatible. Since most inorganic fillers are generally hydrophilic and the organic polymers are hydrophobic, compatibility between them must be provided. Clays, as active fillers of the polymer-clay nanocomposites mentioned in this study, are organically modified for compatibility which will be detailed in the next sections [33].

Use of fillers is not a new topic that there are many applications. Giving popularity to the area is exactly the reflection of the rapid developments in nanotechnology. Because it was seen that decreasing the size of particles from 1-50 μm (conventional fillers) to 1-100 nm resulted in dramatic increases in mechanical, gas barrier and thermal stability properties. This is mainly due to interfacial interactions at the molecular level. Polymer nanocomposite is the general name given to these polymer-based materials with homogeneously dispersed ultra fine organic and/or inorganic materials with sizes in the nanoscale [32].

As all nanosystems, properties of polymer nanocomposites are determined by the dispersion of the nano-fillers in the polymer matrix. This is due to increase in the surface energy with the decrease in the particle size which causes aggregation of nano-particles. Variety of techniques is used to make well dispersion of particles in the polymer matrix [32].

Synthesis of organic-inorganic hybrid materials at the nanoscale has been achieved over the past 10 years. However, there are many examples of organic-inorganic nanocomposites in biological systems (bones, cuticles, shells and teeth). The mechanism of “biomineralization” utilized by nature to efficiently produce well defined nanocomposites is not entirely clear. But it is a templated self-assembly process. There is a great scientific interest on self-assembled structures that examples as the nacre of abalone shell being 1000 times tougher than its constituents show that there is much way to go. Today organic-inorganic nanocomposites are commonly synthesized by one of three strategies: sol-gel processing, host-guest inclusion, use of inorganic nanoparticles [29, 34, 35].

2.2 Polymer-Clay Nanocomposites

Polymer-clay nanocomposites are a good example of the organic/inorganic hybrids which have attracted much attention in the last decades. They are simply low volume of clay layers dispersed in a polymer matrix at nanoscale. Pioneering studies have been carried out at Toyota Central Research Laboratories. Their first report on Nylon-6/clay nanocomposite, in which very small amounts of clay resulted in outstanding mechanical and thermal properties, stimulated the research on the area in both industry and university level. Also the first practical application of PCNs is the use of nylon-clay nanocomposite as a timing belt cover on Toyota Camry automobile [3, 6, 36].

General property enhancements provided with PCNs loaded with 3-5 % clay are in; mechanical properties (tensile strength, modulus), thermal stability, barrier properties (decreased permeability to gases), flame retardance and reduced smoke emissions, chemical resistance, surface appearance, electrical conductivity [11, 33, 37]. Both thermosets and thermoplastics have been incorporated into polymer-clay nanocomposites, including: Nylons, polystyrene, poly(methyl methacrylate), poly(ethylene), poly(propylene), poly(ethylene terephthalate), epoxy resins, polyester, polyimide etc [9, 35, 37].

2.2.1 Structure of clay

Clays originate from the hydrothermal alteration of alkaline volcanic ash and rocks of the Cretaceous period (85-125 million years ago). Mostly clays are crystalline, composed of fine, usually plate-shaped crystals about 1 nm thick with high aspect ratio, and have large specific surface areas. They are classified on the basis of their crystal structure and the amount and locations of charge per basic cell [35].

Actually one can not understand properly the use of “nano” word in these polymer-clay composites, without investigating the clay structure in detail.

Clay minerals consist of small crystalline layers of aluminosilicates in various compositions, with possible iron and magnesium substitutions by alkalis and alkaline earth elements. There are two types of sheets (units) in each aluminosilicate (or phyllosilicate term is used for a more general name) layer: Octahedral and tetrahedral sheets. Silicon-oxygen units form the tetrahedrons where one silicon atom is

surrounded by four oxygen atoms in the corners; three of the four oxygens are simultaneously attached to adjacent tetrahedrons. These tetrahedrons are linked so as to create hexagonal rings. This pattern repeats in two dimensions and forms a tetrahedral sheet. Similarly, Aluminum and oxygen units form the octahedrons where one aluminum atom is surrounded by eight oxygen atoms. These octahedrons also repeat in two dimension and form an octahedral sheet. Also there are hydroxyl groups at the edges of each clay platelet [9, 10].

The tetrahedral and octahedral sheets can be stacked in different manners to form two basic clay structures: 1:1 and 2:1. Kaolinite is a 1:1 type of non-swelling dioctahedral clay in which a sheet of alumina octahedra sitting on top of a sheet of silica tetrahedral. The other type, 2:1, is called smectites; two sheets of silica to one of alumina (or magnesium) [35].

Most of the layered silicates used in polymer-clay composites belong to the smectit family (2:1) in which one octahedral alumina sheet is sandwiched between two tetrahedral silica sheets as shown in Figure 2.2. Montmorillonite, hectorite and saponite are the commonly used members of the smectit family. Among these, Montmorillonite (MMT, name derived from Montmorillon in France where clay was discovered) is the mostly investigated one in PCN applications, with their ion exchange, unusual intercalation and swelling properties. It is important to note here that, some times bentonite term is used for MMT commercially. Actually bentonite is another member of smectites, which is rich in MMT (<80%) [11, 30, 33, 38].

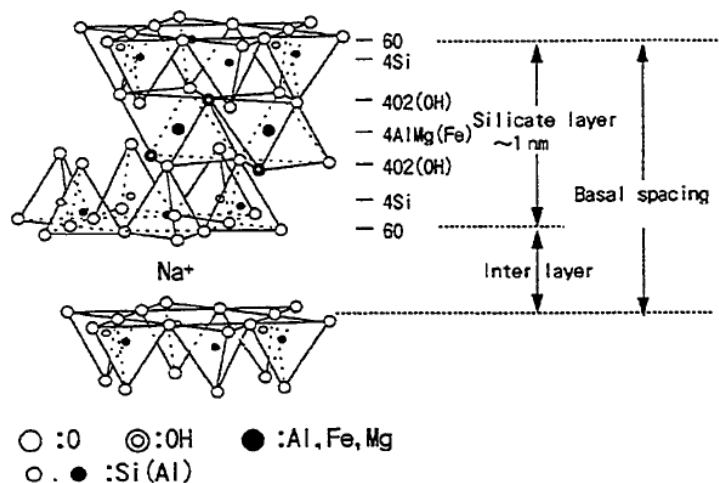


Figure 2.2: Structure of montmorillonite [31]

Crystal structure of montmorillonite is monoclinic with lattice parameters of $a = 5.17 \text{ \AA}$, $b = 8.94 \text{ \AA}$, $c = 9.95 \text{ \AA}$ and $\beta = 99.54^\circ$ [35]. The unit cell is generally written as $(\text{Na}, \text{Ca})_x(\text{Al}_{4-x}\text{Mg}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4 (n\text{xH}_2\text{O})$ [33]. Here x is degree of isomorphous substitution between 0.5 and 1.3. General x takes the value of 0.67 [35]. Reference number of montmorillonite for XRD is 00-002-0009.

In the montmorillonite, thickness of the individual clay platelet is around 1 nm (9.6 \AA) and end to end distance is 100-1000 nm giving an overall aspect ratio about 1000. This morphology results in a very large surface area about $750 \text{ m}^2/\text{g}$. The individual clay platelet is the smallest level of structure of montmorillonite. Individual platelets form stacks called tactoids that have a regular van der Waals gap in between the layers which is called the interlayer space of the gallery. These stacks or tactoids are often called primary particles and are in the range of (8-10) nm thick. The largest structure level is the aggregate and contains many primary particles in different arrangements. The aggregates are generally in the 0.1-10 μm size range [33].

Isomorphous substitution takes place in smectite clays, by ions of lesser charge, Si^{4+} by Al^{3+} in the tetrahedral positions and Al^{3+} or Fe^{3+} by Mg^{2+} or Fe^{2+} in the octahedral positions. In the montmorillonite, substitution occurs in the octahedral sheets, with Al commonly replaced by Mg. Result of this substitution is negative charge on the surface of layers. This negative charge is balanced by alkali and alkaline earth cations as Na^+ , Ca^{++} , K^+ to maintain charge neutrality. MMT is sometimes called with the name of cation in the interlayers; as Na-MMT or Ca-MMT [9, 11, 33].

Amount of isomorphous substitution is not same in all layers, as a result the charge and charge density distribution may be different from layer to layer. Thus, an average measure of negative charges is given for clays with the name of the cation exchange capacity (CEC) which is one of the important characteristics of silicate layers and is expressed in units of milliequivalents per 100 grams of clay (meq) [9, 11, 33].

Two important qualities are required in clay to be considered for polymer nanocomposites. First, the surface chemistry of the clay layers must be changed from hydrophilic to hydrophobic (or organophilic) in order to make it compatible with polymer matrices. Secondly, the clay layers should be able to disperse into individual layers that a nano size could be established. Both of these are achieved through surface modification with surfactants via cation exchange reaction [31].

2.2.1.1 Cation exchange of clay with surfactants

As stated above, between the layers of clay there are inorganic ions (Na^+ , Ca^{2+} , Mg^{2+} , H^+ , K^+ and NH_4^+) which causes the surface to be hydrophilic. An important characteristic of these cations from the view of polymer-clay nanocomposites is that these alkali metal and alkaline earth cations can be replaced by almost any desired cations by treatment in water solution [29, 33]. For a clay placed in a solution of a given electrolyte, a typical cation exchange reaction occurs as shown in the reaction scheme (2.1)



Cation exchange reaction is used to provide two important characteristics: First one is to make clay compatible with polymer matrix. Clay layers are hydrophilic while the most polymers are hydrophobic (organophilic). Thus, pristine layered silicates are not miscible with most polymers (except some hydrophilic polymers as poly(ethylene oxide) and poly(vinyl alcohol)). This problem is solved by modification of clay surface with organic surfactants by ion-exchange of the inorganic cations. This surface modification is achieved by exchanging ammonium or phosphonium cations with the inorganic ones. Generally used surfactants are primary, secondary, tertiary and quaternary alkyl ammonium cations with long chains. This modified clay is generally called organo-clay. Schematic representation of organo-clay synthesis is given Figure 2.3 [30, 38].

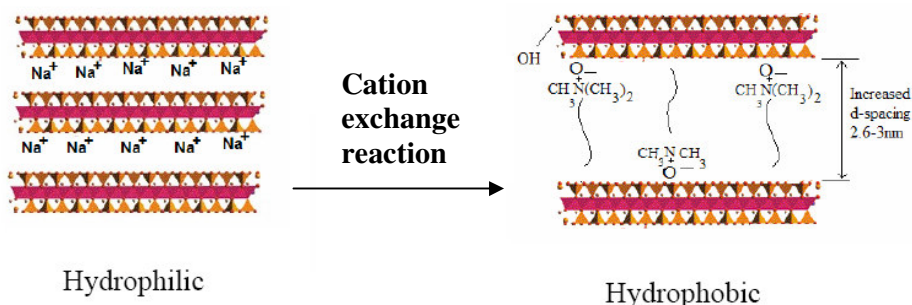


Figure 2.3: Typical process of cation exchange reaction with organic ammonium ions [11]

Second achievement of cation exchange with organic cations is the expanding of the clay galleries and as a result increasing of the d-space with respect to pristine clay. This is due to insertion of large molecules between the silicate layers. Organic cations also lower the surface energy, improve the wetting and intercalation ability of

the polymer matrix. Additionally, some organic cations are reactive that polymerization occurs from the functional groups involved, and it is claimed that better interfacial adhesion is obtained between the nanolayers and polymer matrix [9, 29].

Understanding the ion exchange and adsorption of surfactants into the clay surface and gallery has been an important issue due to industrial applications of organoclays (i.e. thickeners in paints, oil-based glue, grease and cosmetic products) [9, 10]. Diffusion laws govern the cation exchange process, and reactions begin at the edges of the particles and progress towards the center. Electrostatic forces are the main reason of the attraction of the organic cations by the negatively charged clay layers. Complementary effect is due to van der Waals forces between the flat oxygen planes and the organic compounds located in the galleries. Sorption energy, as the van der Waals forces are said to be more effective, with the increase in the size of the organic cation. Clays having high affinity towards long chain organic cations is also result of increase in the van der Waals interactions [30, 33].

As stated above, one of the main functions of surface modification of clays is the expanding the layers and as a result increasing the interlayer spacing. Various investigations showed that this spacing is defined mainly by the chain length of surfactant used [6, 29, 33, 35, 38]. For example; in the study of Usuki and coworkers on the cation exchange of ω -amino-acids with MMT, it was found that there is an increase in the interlayer spacing with the increase of the carbon number in the alkyl chain as seen from Figure 2.4. Also it was found in the study that a critical number of carbons in the alkyl chains of surfactants is 11 to obtain exfoliated type structure when ϵ -caprolactam was in-situ polymerized [33].

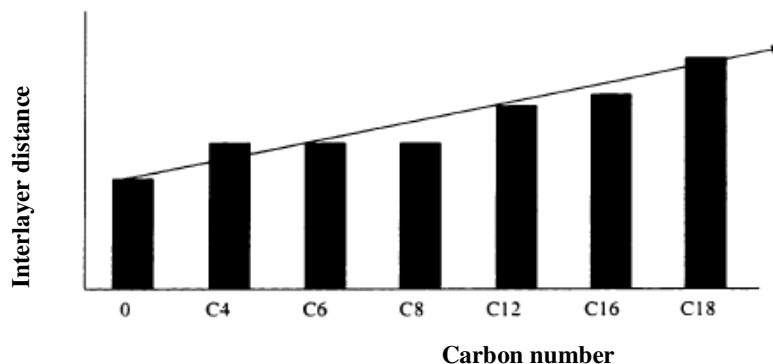


Figure 2.4: Effect of alkyl chain length on interlayer distance after modification of a clay [33]

Investigations also showed that inter gallery structures of organo-clays can take different forms depending on the length of alkyl chains and the charge density. Mainly four different types of assemblies have been considered for smectite clays modified by alkylammonium ions as shown in Figure 2.5: In the monolayer and the bilayer structures long alkyl chains lie parallel to the silicate layers. On the other hand alkyl chains are kinked in the trimolecular structure and alkyl chains are inclined in the paraffin structure. For the lower clay charge densities and shorter alkyl chain lengths, monolayer structure is encountered. With the increase of clay charge density; bilayer, trimolecular and paraffin structures are realized respectively [29, 39].

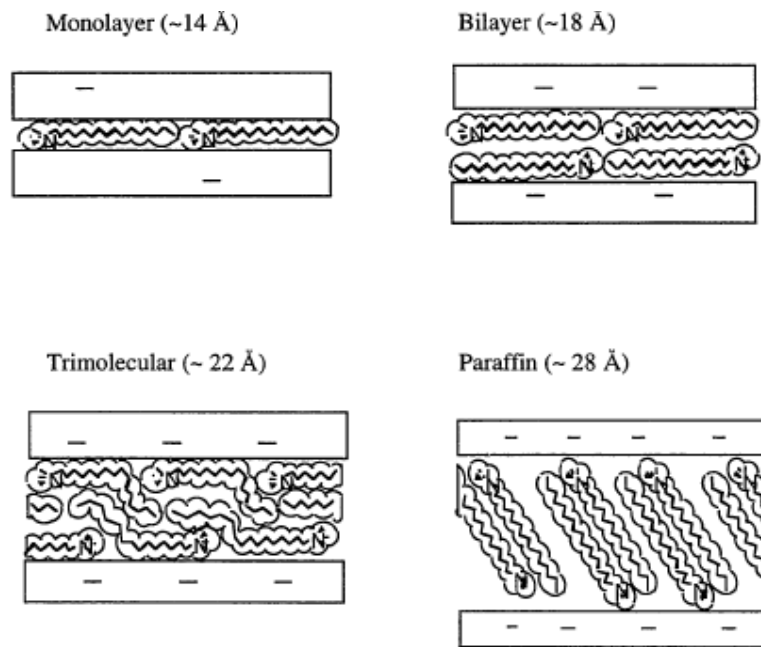


Figure 2.5: Different orientation of alkylammonium ions in the clay gallery [11]

2.2.2 Types of polymer-clay nanocomposites

From a general point of view, polymer-clay composites can be classified into “conventional composites” and “nanocomposites”. In conventional polymer-clay composites, mixing occurs in a micrometer scale and clay tactoids are retained. On the other hand, phase mixing is achieved in nanometer scale in the polymer-clay nanocomposites. Main difference between two groups is that properties of final product is not only determined by constituents, also interactions between them are effective in nanocomposites. Polymer-clay nanocomposites can also be classified

into two groups: Intercalated and exfoliated polymer-clay nanocomposites. General classification of polymer-clay nanocomposites are summarized in Figure 2.6 [11, 39].

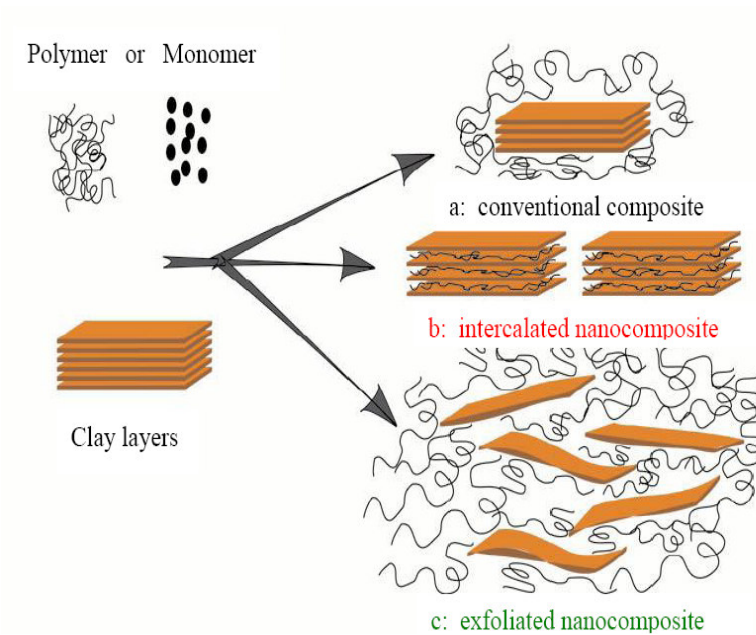


Figure 2.6: Schematic illustrations of different types of polymer-clay nanocomposites [9]

2.2.2.1 Conventional polymer-clay composites

Clay tactoids exist in their original aggregated state with nanolayers stacked face to face and without any polymer intercalation [29]. As a result of this, there is no or little functionality of clay in conventional polymer-clay composites and in most cases inexpensive clay component is used as filler for economical considerations. Generally, an improvement in tensile modulus can be achieved but this is accompanied by a decrease in other mechanical properties such as strength and elasticity [11, 39]. Reason of the structure and the properties is mainly due to lack of miscibility between silicate layers and polymers [37, 38].

Conventional clay composites of polyethylene, polypropylene, ethylene vinyl alcohol, polyester and epoxy resin were synthesized in the past, by mixing the mechanically crushed clay aggregates with the polymer matrix. Also some additives were used to increase binding between clay and polymer. Low aspect ratios about 20-30 are obtained as a result of crushing in comparison to polymer-clay nanocomposites [29]. Processing of these composites is generally difficult due to high percentage of clay loading [11].

2.2.2.2 Intercalated polymer-clay nanocomposites

Intercalated nanocomposites are formed when single or a few polymer chains are inserted between the silicate layers resulting in the arrangement of the silicate layers with a repeat layer distance of a few nanometers (Figure 2.7). In other words, clay layers retain their original structure, but the d-spacing increases [11, 37, 39]. The degree of expansion and intercalation depends on the synthesis method, clay loading, and the miscibility between polymer and clay [38].

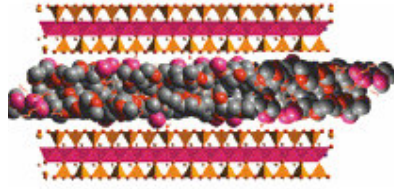


Figure 2.7: Typical intercalated structure [11]

There are mainly two strategies to prepare intercalated polymer-clay nanocomposites: In the first one preformed polymers are directly intercalated into the clay gallery by dissolving polymer and clay in a solvent and mixing them. This strategy was applied to the water soluble polymers such as polyethylene oxide, polyethylene vinyl alcohol, polyvinyl alcohol, and polyvinyl pyrrolidinone. The second approach is in situ (intercalative) polymerization of monomers which have been adsorbed or intercalated into the clay gallery. This approach is more significant, because there are limited polymers which can be directly intercalated [11, 29, 39]. Various intercalated polymer-clay nanocomposites were prepared by using this approach, such as nylon-6, polymethyl methacrylate, polyaniline, polystyrene, poly-ε-caprolactone, polyacrylonitrile, polypropylene [29]. Although the mostly desired type of polymer-clay nanocomposite is the exfoliated, intercalated ones have superior properties to the conventional composites [35].

2.2.2.3 Exfoliated polymer-clay nanocomposites

In the most of the research on polymer-clay nanocomposites, main objective is to obtain exfoliated type nanocomposites which have unique structure and properties [4, 10, 12, 13]. In these types of nanocomposites, alumina silicate layers having thickness of one nanometer are individually dispersed in the polymer matrix as shown in Figure 2.8 [11, 29]. Average distances between the clay layers which

depend on clay loading, is long enough that interaction between the host layers is weak in relation to interactions between polymer chains and layered silicates [9, 37, 39]. In truly exfoliated nanocomposites the clay layers are randomly dispersed throughout the matrix and a greater homogeneity is obtained in comparison to the intercalated type. Generally, the clay loading is also lower in exfoliated nanocomposites. Another important point of exfoliation is great increase of aspect ratios from 20 for stacked crystallites to values of about 2000 which means maximum interfacial area between clay and polymer is provided [29].

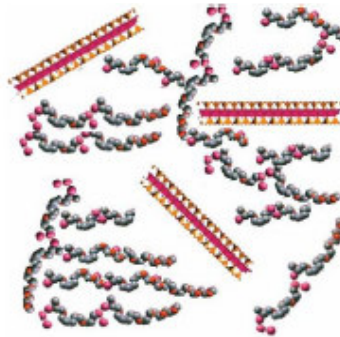


Figure 2.8: Typical exfoliated structure [11]

Homogeneous dispersion of clay nanolayers is very critical for the mechanical behaviors that it provides maximum reinforcement via distribution of stress and deflection of cracks resulting from an applied load. Strong interactions between polymer matrix and exfoliated nanolayers having large interfacial area lead to superior mechanical properties (higher tensile strength and modulus) and higher thermal stability [10]. Performance properties of exfoliated Nylon-6/clay nanocomposite, first PCN developed by Toyota Research Group, was really spectacular that addition of a few percent clay resulted in about 50 % increase in tensile strength and modulus [6]. Exfoliation of silicate nanolayers with high aspect ratio also improves some other properties that are not achievable with conventional composites: The impermeable clay nanolayers provide a tortuous pathway for a gas to diffuse through nanocomposite. Hindered diffusion in these nanocomposites also leads to enhanced barrier property, reduced swelling by solvent and improvements in chemical stability and flame retardance [11, 40].

Although property enhancements are really very exciting for the exfoliated polymer-clay nanocomposites, it is not easy to synthesize truly exfoliated structures. The majority of the reported exfoliated polymer-clay nanocomposites contain a mixture

of platelets and tactoids, and these nanocomposites are called as partially exfoliated or highly delaminated nanocomposites (Figure 2.9).

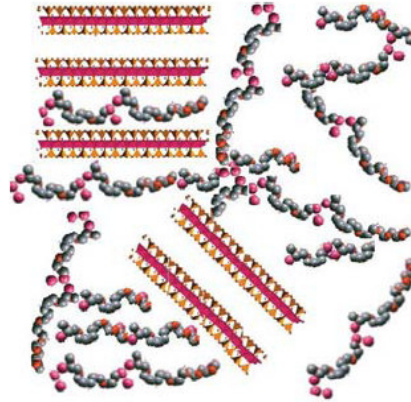


Figure 2.9: Typical partially exfoliated structure [11]

Actually partially exfoliated nanocomposites are a mixture of individual 1 nm clay nanolayers and small tactoids dispersed in the polymer matrix. There can be about 2-20 clay nanolayers in a tactoid. In some examples, there can be a well dispersion locally, but it is not uniformly throughout the matrix [11, 40].

Various exfoliated or partially exfoliated clay nanocomposites of nylon-6, polystyrene, epoxy-resin, polypropylene, polyimide, polymethylmethacrylate were successively synthesized. Research groups used different approaches to reach to the exfoliated structure. For example; exfoliated polystyrene nanocomposites were synthesized by Fu and Qutubuddin via in-situ polymerization of styrene with a reactive organoclay [10].

2.2.3 Characterization of polymer-clay nanocomposites

Characterization of PCNs identifies which of the structures mentioned above best suits to the synthesized product. As the types of structures are mainly classified according to dispersion of silicate layers in the polymer matrix, characterization of nanocomposites deals with the measurement of this dispersion. Common characterization tools used in the polymer-clay nanocomposites are the X-ray diffraction (XRD) and the transmission electron microscopy (TEM). Generally structure is first identified with XRD and then confirmed with TEM. Because XRD measure large areas of sample, they are not sufficient to define the nanocomposite.

On the other hand TEM shows dispersion in small areas of sample. Additionally, recent advances in fourier transform infrared spectroscopy (FTIR), atomic force microscopy, 2D small angle X-ray scattering, solid-state nuclear magnetic resonance spectroscopy and polarized optical microscopy can be used to deeper interpretation of the three dimensional morphology, surface chemistry, and dynamics of structure [31, 37]. As use of these additional techniques are not required for a general characterization, only details of XRD and TEM will be given.

2.2.3.1 X-ray diffraction analysis (XRD)

XRD is the mostly used technique to reveal the nanocomposite structure. It is not only used to determine whether the structure is intercalated or exfoliated, it is also used to measure the expanding of organoclay with respect to pristine montmorillonite.

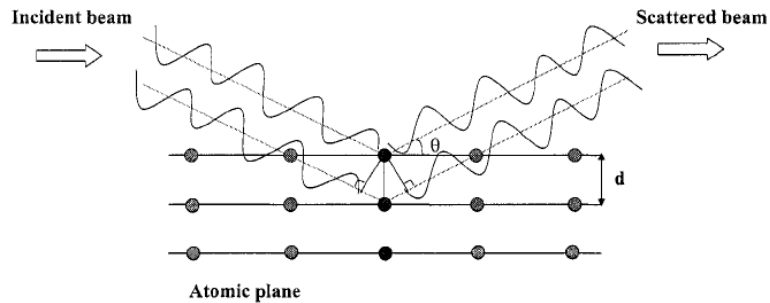


Figure 2.10: Schematic illustration of Bragg's law [37]

Main principal of XRD consists of passing the X-ray beam through the polymer nanocomposite and then measurement of the scattered beam via a detector. The inorganic atoms (Al or Mg) scatter the incident beam to give a regular pattern of arrangement as shown in Figure 2.10 Bragg's law (2.2) is used to interpret the monitored basal reflections or angles of scattering (2θ) to the interlayer distance (d -spacing) between the clay layers:

$$n \cdot \lambda = 2 \cdot d \cdot \sin \theta \quad (2.2)$$

Here n is the order of reflection, λ is the incident wavelength, d is the interlayer distance and θ is the reflection angle. Generally scattering from the d_{001} plane is used in measurements ($n=1$).

Nanocomposite structure is easily determined by the intensity, position and shape of the silicate peak obtained from the basal plane. There are generally three typical

patterns obtained as shown in Figure 2.11. Here initial XRD spectra belong to the pristine or organically modified clay. For the conventional composites, clay and the polymer matrix are not immiscible, as a result no polymer enters into the clay gallery and tactoids exist in their original structure, thus the position of the basal reflection peak corresponding the d-spacing is unchanged and there is no difference between the initial and final X-ray patterns [33].

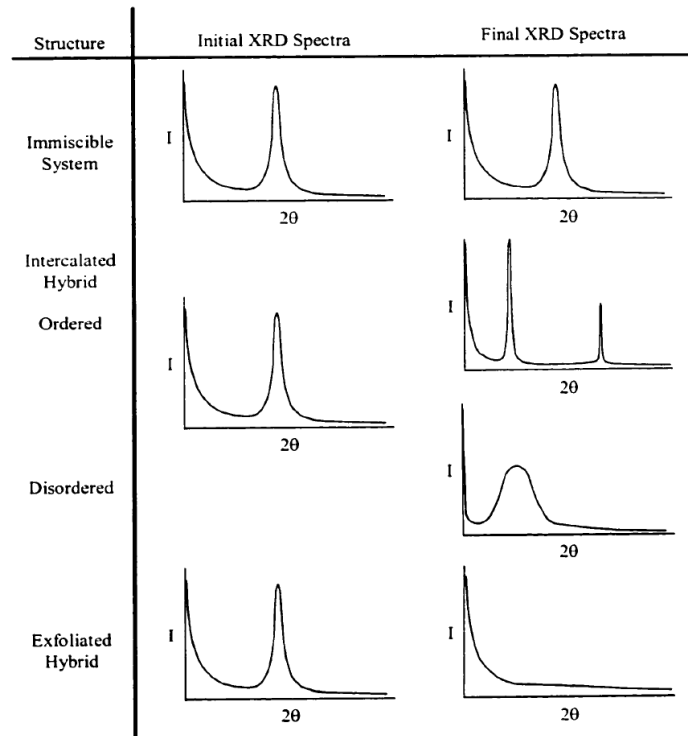


Figure 2.11: Typical X-ray patterns of PCN [33]

In the case of intercalated structure; two general types of profiles are obtained according to level order. For the well-ordered case; reflection peak shifts to a lower 2θ value which shows an additional expansion of clay gallery. But there is an immiscible fraction that intergallery distance has not changed in ordered systems as seen from the XRD spectra having two peaks (Figure 11). It is also significant that peaks are very narrow in comparison to disordered one, due to high degree of registry of the clay platelets. On the other hand disordered system has a one broader peak with an intensity loss, resulting from a larger variation in the d-spacing [33, 37].

As the 1 nm clay nanolayers are randomly dispersed in exfoliated nanocomposites, no regularity remains in the structure. This results in, with a no distinctive reflection peak and a featureless spectrum [33, 37].

Typical X-ray diffraction profiles obtained in the studies are generally similar. XRD spectra from the study of Yeh and coworkers [41] on polymethylmethacrylate-clay nanocomposites are presented in Figure 2.12 as an example. As seen that for the pristine clay d-spacing is the minimum or the peak is in the largest 2θ value. After modification of clay, peak shifts to left indicating the increase of basal spacing. Typically, for the 1% of clay loading there is a lack of any peak showing a possible exfoliated structure. As the clay loading increases to 3 %, there exists a small peak which implies that there is a small amount of clay that cannot be exfoliated. For the 10 % clay loading, position of peak is same with the organoclay's that no further increase of interlayer distance can be reached for this loading.

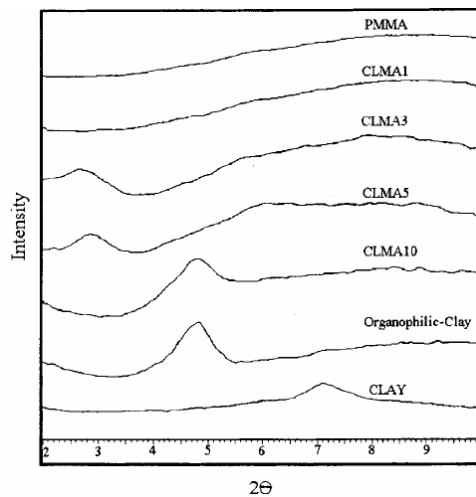


Figure 2.12: Typical XRD pattern of clay, organoclay and a series of PCNs [41]

2.2.3.2 Transmission electron microscopy (TEM)

Although XRD is a very convenient way to investigate the interlayer spacing of silicate layers in the original state and in the intercalated nanocomposite, peak broadening and intensity variation are difficult to analyze by it alone. Also interpretation of spatial distribution or any structural non-homogeneity is limited with XRD. Therefore, XRD should be accompanied by TEM, which provides localized information on the hybrid structure [3, 38].

On the other hand TEM allows a qualitative understanding of the internal structure, spatial distribution and defect structure. But sample preparation for TEM is very time consuming and special care must be given to cross-sectioning the sample. It is important to note that; TEM is only a qualitative technique, while XRD is a

quantitative. Generally both techniques are used together concluding about the structures of nanocomposites [3, 38].

Typical TEM micrographs of an intercalated and exfoliated structure can be seen in Figure 2.13(a) and Figure 2.13(b) respectively. Here dark lines are due to silicate layers and bright regions correspond to polymer matrix.



Figure 2.13(a): Typical TEM image of an intercalated structure [38]

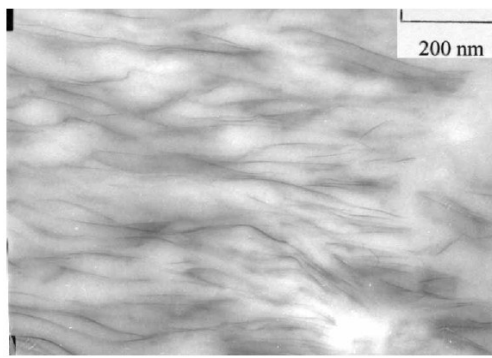


Figure 2.13(b): Typical TEM image of an exfoliated structure [9]

2.2.4 Synthesis methods of polymer-clay nanocomposites

There are various methods for PCN preparation but main three methods are [6, 30]: In-situ polymerization, solution intercalation and melt intercalation. Principles of synthesis of polymer-clay nanocomposites are summarized schematically in Figure 2.14. Actually there are two general strategies for preparation of PCN depending on the starting material is a monomer or a polymer. For the in-situ polymerization there is an additional step of polymerization for the synthesis. On the other hand for the other two techniques polymers are directly intercalated into clay gallery with different approaches.

2.2.4.1 In-situ polymerization

It is the most commonly used method for the synthesis of PCNs. Also it can be concluded from experimental results and thermodynamic considerations that method is the most promising for the synthesis of highly exfoliated nanocomposites. In the method organically modified clay is first swollen within the liquid monomer or the monomer solution and therefore monomer molecules can diffuse and intercalate into clay gallery. This is followed by the polymerization initiated by any of the typical initiators like heat, radiation, chemical, photo or redox. There are also some examples of initiators placed into clay gallery via cation exchange reaction before

swelling. Clay nanolayers are forced to disperse with the ongoing polymerization [3, 6, 10, 30].

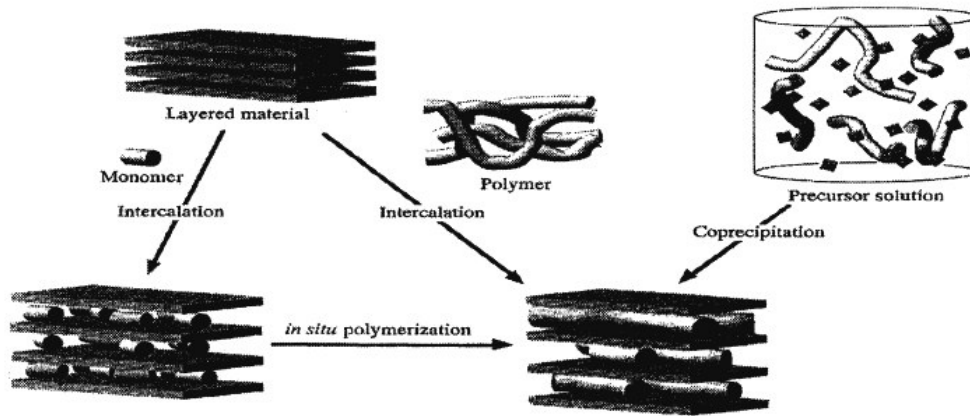


Figure 2.14: Schematic view of general preparation methods of PCNs [6]

Method was first developed by the Toyota group to synthesize Nylon-6 nanocomposite from caprolactam monomer. Variations of the procedure have been utilized for bulk, solution and emulsion polymerizations with polymer systems ranging from thermosets to thermoplastics. Among these emulsion polymerization is considered solely as another method in some sources [9, 10, 37]. Method is again in-situ polymerization in principal, but the only difference is that modification of the clay can be done in the same emulsion where the polymerization occurs rather than functionalizing the clay in a separate stage [9].

2.2.4.2 Solution intercalation

This technique is based on a solvent system in which the polymer or pre-polymer is soluble and the silicate layers are swellable [3]. In the method, a polymer is dissolved in a solvent and then mixed with organophilic clay. After insertion of polymer chains into the clay gallery, solvent is removed by either heat or by evaporation under vacuum and nanocomposite is obtained. Technique was widely applied to the the water soluble polymers such as poly(vinyl alcohol), poly(ethylene oxide), poly(acrylic acid) [10, 30, 33, 37].

2.2.4.3 Melt intercalation

In the melt intercalation method; clay is mixed with the polymer in the molten state. It involves annealing, statically or under shear, a mixture of the polymer and

organically modified layered silicates above the glass transition or melting temperature of the polymer. In the case of sufficient compatibility between the polymer and the clay surface, polymer diffuses into the clay gallery. On the other hand, some compatibilizer agents can be used. The shear profile, residence time, temperature profile and addition sequence can be tailored for optimal clay platelet dispersion. Melt intercalated nanocomposites are processed in equipment like twin screw, one screw extruders and batch mixers [3, 9, 30, 33, 38].

Method is the most suitable and favorable one for the industrial processes to make nanocomposites that it is compatible with the current process such as extrusion and injection molding. Also it does not require use of solvent and therefore it can be said to be environment friendly. A wide range of thermoplastics were synthesized with melt intercalation including of polymers which are not suitable for in-situ polymerization and solution intercalation [3, 9, 33, 38].

2.3 Polymerization Reactions

By the definition; polymers are large molecules made up of simple repeating units. They are synthesized by linking of many simple molecules called monomers with a process called polymerization. Characteristic feature of polymers is their long chain nature constituted of repeating units [21, 22].

There are mainly two types of polymerization mechanisms called as step-growth and chain-growth processes. In the chain-growth polymerization, the reaction is initiated by a free radical which is formed via an external source called initiator. Monomer molecules link to the end of a growing free radical chain successively and high molecular weight polymers can be formed with chain growth mechanism. On the other hand, in step-growth polymerization polymer chains are built in a stepwise fashion by random union of two polyfunctional molecules to produce one larger polyfunctional molecule generally elimination of a small molecule such as water. High molecular weights can only be achieved in long reaction times in this scheme [21, 22, 42].

Polymers can be categorized in different manners depending on their various characteristics [21, 42]:

- Chain structure: linear, branched or cross-linked

- Polymer architecture: star, comb, ladder, semi-ladder, dendrimer
- Composition: homopolymer, copolymer, terpolymer
- Use in polymer industry: plastics, fibers, rubber, adhesives, coatings
- Behavior to temperature: thermoplastics, thermosets

There is a lot to say about physics, chemistry and engineering properties of polymers which are deeply investigated in detailed references [21, 22, 43, 44] on polymers.

2.3.1 Free radical polymerization

Free radical polymerization is the most widely used system for the synthesis of polymers. As commercially vinyl monomers are the most important ones much research has been accomplished in the area of free radical polymerization. Vinyl polymerizations are a kind of chain reactions as the majority of the addition polymerizations. An initiator is required for generating a free radical and therefore polymerization to begin. As can be understood from the name, polymerization undergoes from free radicals and it occurs only from the reactive end group of a growing chain that is the characteristic which results in high molecular weights to be reached at short times and at low conversions. Also there is a significant amount of monomers available in the reaction media during polymerization [21, 22].

A typical free radical polymerization consists of three stages called; initiation, propagation and termination. As stated above, in the first stage, a free radical is generated by initiation. It is considered to involve two reaction steps; decomposition of initiator (I) to yield radicals ($R\cdot$), followed by addition of ($R\cdot$) to monomer (M), to give a new radical $M_1\cdot$ as shown in Equation (2.3) and (2.4) [21, 22].



In the propagation step, monomers are added to the $M_1\cdot$ successively and generate new monomers continuously.



Final step is termination in which propagation of polymer chain stops principally by radical coupling or disproportionation as shown in Equation (2.8) and (2.9) respectively.



2.3.1.1 Methods of free radical generation

There are various methods of producing free radicals. But except some monomers (styrene, methyl methacrylate etc.) which can undergo polymerization with heat in the absence of an external species, most of them need an initiator for polymerization. Initiators may be classified under four major types: peroxides and hydroperoxides, azo compounds, redox initiators and photoinitiators. Also electrochemical, high energy radiation and plasma polymerization has some applications [21].

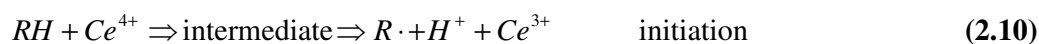
Only redox initiators, which synthesis of polymer-clay nanocomposites in this study is achieved through, will be investigated in detail.

2.3.1.2 Redox initiators

Generation of free radicals by means of a redox reaction has especially found application in initiation of low temperature and emulsion polymerization. Mainly, an electron transfer occurs from reducing agent to oxidant and this is accompanied by the scission of an intermediate to produce an active free radical [21, 22, 45]. While, generally oxidant is called as initiator or catalyst, reducing agent is called as activator or accelerator [46]. Main characteristics of redox polymerization are very short induction time, ability to carry the polymerization below or at room temperature (low activation energy), high yield in a short time and easy control of reaction due to limited side reactions at low temperatures [19, 20].

Use of many redox initiators -both organic and inorganic- has been reported in the literature. Generally used oxidants are; peroxides, peresters, persulfates, permanganates, hydrogen peroxide, other peroxides and the salts of transition metals. Also there are various reducing agents forming redox systems as; alcohols, aldehydes, amines, amides, ketones, acids thiols etc. for aqueous polymerization and metal ions (Co^{2+} , Fe^{2+} , Cr^{2+}) for non-aqueous polymerization [20, 22].

The ceric ion, Ce(IV) has been widely used in polymerization of vinyl monomers in aqueous solution with its strong oxidation power. It is used in the form of cerium(IV) ammonium nitrate, cerium(IV) ammonium sulfate, cerium(IV) sulfate and ceric perchlorate, and forms a very effective initiator system with suitable reducing agents such as alcohols, aldehydes and amines [20, 23, 24]. A free radical is formed in the reductant groups through an electron transfer as seen from a typical reaction scheme:



Use of Ce(IV) is also suitable for preparation of graft and block copolymers by producing radical sites on macromolecules. This approach is applied to the many substrates having labile protons such as alcohols, amides and urethanes [24, 46, 47].

2.4 Polyacrylamides

Polacrylamide (PAAM) is a product of free radical polymerization of acrylamide which is a white, crystalline solid having a chemical formula of $H_2C=CHCONH_2$ as seen in Figure 2.15(a). Acrylamide has two reactive groups consisting of the amide group ($CONH_2$) and the electron deficient double bond. Aqueous solutions of acrylamide can be polymerized with the use of all free radical initiators (peroxides, persulfates, redox pairs, azo compounds, UV light), resulting in chain structures as shown in Figure 2.15(b) [46].

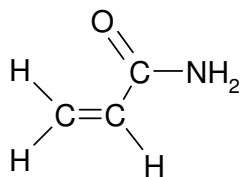


Figure 2.15(a): Acrylamide

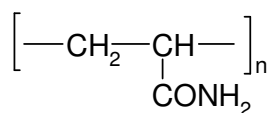


Figure 2.15(b): Polyacrylamide

Polyacrylamide is a brittle, white, odorless polymer. One of the main properties of it is being water soluble at all concentrations, temperatures and pH values. As a water soluble polymer, less is known on their mechanical and electrical properties. The average molecular weight of commercial polyacrylamide ranges approximately from 2×10^3 to 15×10^6 . This high molecular weight determines their product activity as a flocculant and a rheology control agent [48].

Polyacrylamide is one of the widely used polymers. One of their areas of use is as flocculating agents in the treatment of various aqueous suspensions of solids as a liquid-solid separator [47, 48]. With this property they are used in the processing of minerals in mining and waste treatment. Also it has a significant application in paper industry as a chemical additive to improve the various strengths. Another important area of use is in enhanced oil recovery [46, 48].

2.5 Polymerization Of Acrylamide Initiated By Cerium(IV)-Glycerin Redox System

Use of Cerium(IV)-glycerin system for the initiation of acrylamide polymerization has been investigated by Erciyes, Yagci et al. [47, 49] previously. They used this system to extend the chains of polyacrylamide which was initiated by azo initiators and obtained high molecular weights.

In this thesis, polymerization of acrylamide will be directly initiated by the Ce(IV)-glycerine redox pair. Polymerization is expected to occur according to scheme given in Figure 2.16. First Ce(IV) and glycerine form a complex and this is followed by the generation of an initiator radical on the carbon atom which is bonded to oxygen. Then this initiator radical reacts with acrylamide and a new radical on acrylamide is formed. Polymerization propagates from this radical and terminates by disproportionation or combination [20, 47, 48].

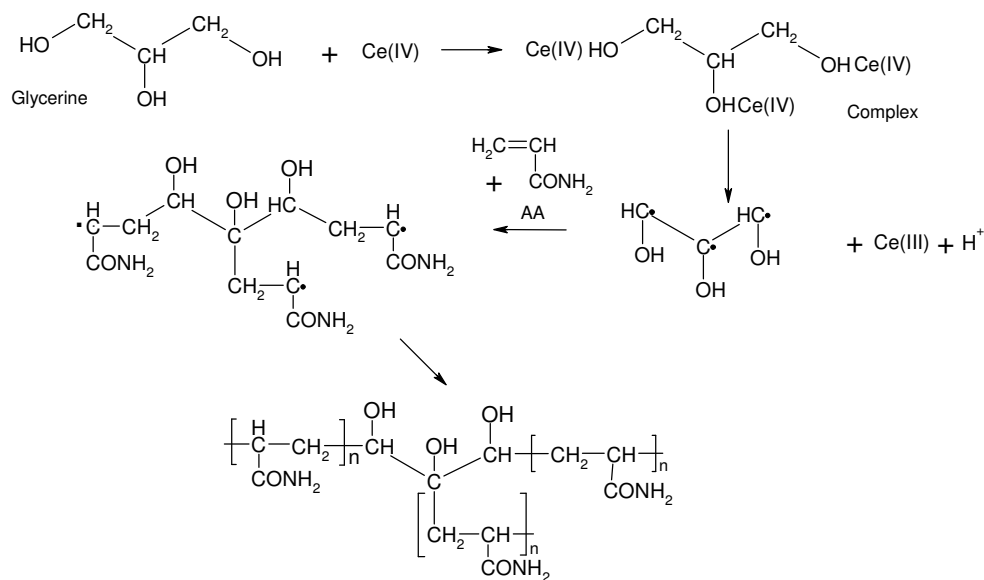


Figure 2.16: Polymerization of acrylamide initiated by Ce(IV)-glycerine redox pair

2.6 Studies On Polyacrylamide-Clay Nanocomposites

In spite of various studies [15, 17, 18, 50-56] on incorporation of clays in polyacrylamide, most of them can not be classified as polymer-clay nanocomposites. Also majority of the researchers interested on polyacrylamide gels, due their great capacity to absorb water, rather than polyacrylamide itself.

Rheological properties [51], swelling and collapse [52], development of a sensor based on superabsorbency [54], use of starch in the synthesis [55], of polyacrylamide gels containing clays were investigated. Another concern was on interactions of polyacrylamide and clay in applications such as potable and waste water treatment, mineral processing, drilling fluids, soil stabilization, oil recovery, irrigation erosion control [50, 53, 56].

Reports on so called nanocomposite of polyacrylamide and clay also focus on the gel form. Zolfaghar et al. [17] studied the preparation and characterization of nanocomposite hydrogels based on polyacrylamide for oil recovery applications. However, their study mainly differ from this study by the use of polyacrylamide in the gel form, that they concentrated more on gelation parameters, and their XRD results showed great difference due to gel form in comparison to the typical polymer-clay nanocomposites. Starodoubtsev et al. [18] reported the mechanism of smectit arrangement of montmorillonite and bentonite clay platelets incorporated in gels of poly(acrylamide) induced by the interaction with cationic surfactants. Similarly their study differs from typical polymer-clay nanocomposites with the incorporation of the gel form.

On the other hand, report of Yeh et al. [15] on polyacrylamide-clay nanocomposite materials prepared by photopolymerization with acrylamide as an intercalating agent is a completely an example to typical polymer-clay nanocomposites that they did not study with the gel form. They obtained intercalated and exfoliated nanocomposites depending on clay loading. Also use of acrylamide as both the monomer and the intercalating agent made the study attractive and contributed to this study.

3. EXPERIMENTAL

3.1 Materials

Montmorillonite (MMT) was purchased from Aldrich Chemical Company under the trade name of Bentonite. It is a purified and fine powder with a surface area of 750 m²/g. It mainly contains exchangeable cations of Na⁺. Acrylamide (99%), C₃H₅NO, and glycerine (99 %), C₃H₈O₃, was purchased from Merck. Cationic surfactant hexadecyltrimethylammonium chloride (HDTMA) (25 %), C₁₉H₄₂ClN and cerium ammonium nitrate, Ce(NH₄)₂(NO₃)₆, (99.99 %) were also purchased from Alrich Chemical Company. All the materials were used as received without further purification. Structures of chemicals are shown in Figure 3.1

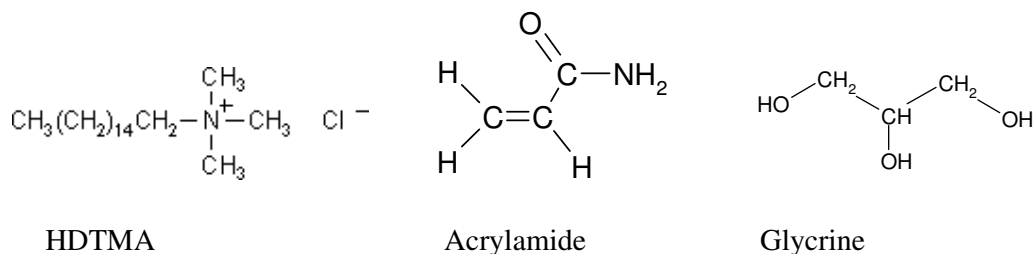


Figure 3.1: Structures of chemicals used

3.2 Instrumentation

X-ray diffraction measurements were made using a PANalytical X-ray generator/diffractometer with a nickel filtered Cu KR source ($\lambda=1.5417 \text{ \AA}$) at a scanning rate of 3.3 °/min in the range of 2 θ of 1° to 10° operating at 40 kV and 40 mA. Fourier transform infrared (FTIR) spectra of the samples were obtained on powders with a Perkin-Elmer FTIR spectrometer. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC7 from 100 °C to 200 °C at a heating rate of 20 °C/min. Scanning electron microscopy (SEM) images were obtained from both the bulk and powder samples using Jeol Jsm 6335f field emission scanning electron microscope. Samples were covered with a thin layer of gold to obtain a conductive surface.

3.3 Synthesis

3.3.1 Preparation of organophilic clay with HDTMA

Organophilic clay (OCLAY) was prepared by a typical cation exchange reaction between the sodium ions of MMT and alkyl ammonium ions of HDTMA. 6.25 g of MMT, 9.3 g of HDTMA was mixed in 120 ml distilled water. Then the suspension was mechanically stirred at 75 °C for 2 h and at room temperature for an additional 22 h. The exchanged clays were filtered and washed with distilled water several times until no chloride ion was detected (white color) with 0.1 M AgNO₃ solution. After drying the OCLAY in an oven for 24 h at 60 °C, it was ground to powder with a mortar and pestle.

3.3.2 Preparation of organophilic clay with acrylamide

MMT was organically modified by the use of acrylamide in place of a commercial surfactant. This second type organophilic clay (ACLAY) was again prepared by a typical cation exchange reaction between the sodium cations of MMT and the alkyl ammonium ions of the intercalating agent, acrylamide [15, 41]. Firstly, 2.5 g MMT was mixed in 300 mL of distilled water with a mechanical stirrer at room temperature overnight (A). At a separate beaker (B), 0.21 g of acrylamide was mixed in 30 mL of distilled water with a magnetical stirring. Then 1-2 drops of 1.0 M HCl aqueous solution was added to acrylamide solution (B) to make the pH value to about 3-4 and is mixed for 1 h. This protoned amino acid solution (B) was added at a rate of approximately 10 mL/min with vigorous mixing to the MMT suspension (A). This final suspension was mixed overnight at room temperature. The exchanged clays were filtered and washed with distilled water several times until no chloride ion was detected (white color) with 0.1 M AgNO₃ solution. This washing is also important for the removal of any excess ammonium ions. After drying the ACLAY in an oven for 24 h at 60 °C, it was ground to powder with a mortar and pestle.

3.3.3 Intercalation of precursors into organophilic clays

For the investigation of mixing time effect, organophilic clays were treated as follows: 5 g of acrylamide, 0.75 g of glycerine and 0.3 g of organically modified clay were mixed in 20 ml of distilled water. This mixture was stirred vigorously with magnetic stirring for different times (2 h, 4 h, 8 h). Then the organophilic clay was

filtered and washed with distilled water. After drying the organophilic clay in an oven for 24 h at 60 °C, it was ground to powder with a mortar and pestle.

3.3.4 Synthesis of PAAM by redox polymerization

Polymerization reactions were made in three necked flask covered with a thick foil, in a water bath. 2.5 g of acrylamide and 0.375 g of glycerine were dissolved in 10 ml of distilled water. The system was degassed with nitrogen and thermostated to 30 °C. Then 1.2 mL of 8×10^{-2} M Ce(IV) in 1 N HNO₃ aqueous solution was added to the reaction mixture under nitrogen atmosphere. Polymerization was carried out in the absence of light with magnetic stirring at 30 °C for 4 h. At the end of 4 h, reaction mixture was poured into 50 mL acetone and precipitated polymers were filtered and dried in an oven at 40 °C for 24 h.

3.3.5 Synthesis of PAAM-clay nanocomposites by redox polymerization

Polymerization reactions were made in three necked flask covered with a thick foil, in a water bath. Typical procedure for 1% of clay loading is as follows: 2.5 g of acrylamide, 0.375 g of glycerine and 0.025 g of organically modified clay were mixed in 10 ml of distilled water. This mixture was stirred vigorously with magnetic stirring for 2h. Then system was degassed with nitrogen and thermostated to 30 °C. This was followed by addition of 1.2 mL 8×10^{-2} M Ce(IV) in 1 N HNO₃ aqueous solution to the reaction mixture under nitrogen atmosphere. Polymerization was carried out in the absence of light with vigorous magnetic stirring at 30 °C for 4 h. At the end of 4 h, reaction mixture was poured into 50 mL acetone and precipitated polymer-clay nanocomposites were filtered and dried in an oven at 40 °C for 24 h.

4. RESULTS AND DISCUSSION

Polyacrylamide-clay nanocomposites were prepared by first intercalating the acrylamide monomers and glycerine into the clay gallery and then initiation of in-situ polymerization by the addition of Ce(IV) through redox polymerization. In the synthesis, two different types of organically modified clays were used: OCLAY (section 3.3.1) and ACLAY (section 3.3.2). For each type of clay, loading was varied between 1 % and 5 %.

4.1 Characterization of Organically Modified Clays

XRD is the most commonly used technique for investigation of the surfactant intercalation and expanding of the clay layers. As the interlayer distance increases, d_{001} reflection of XRD shifts to left. By the use of Bragg's law, XRD results can be interpreted to the interlayer spacings.

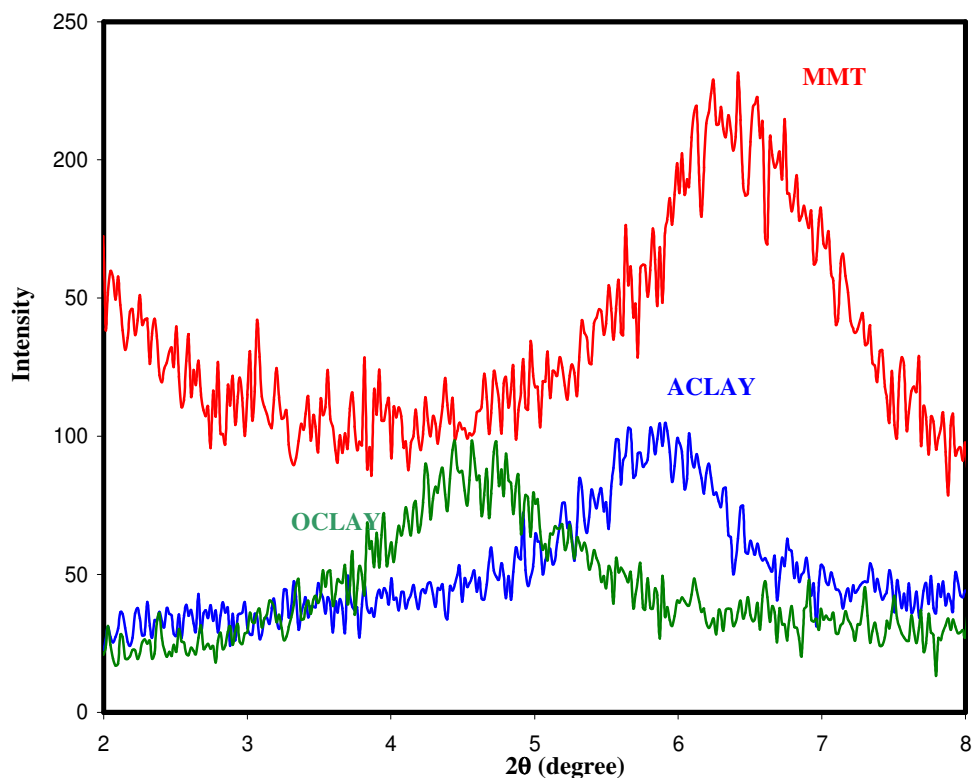


Figure 4.1: XRD diffractograms of MMT, OCLAY and ACLAY

Figure 4.1 shows the XRD diffractograms of pristine MMT clay and organically modified clays ACLAY and OCLAY, which were ion exchanged with acrylamide and a typical commercial surfactant HDTMA respectively. Position of the peak shifts to left for both of the cation exchanged clays, as a result of penetration of organic cations to the clay gallery.

Table 4.1: d_{001} spacings of clays

Clay	d_{001} spacing (Å)
MMT	14.3
ACLAY	15.0
OCLAY	19.4

As also can be seen from Table 4.1, there is an increase in basal spacings (d_{001}) of both organophilic clays in comparison to MMT having a basal spacing of 14.3 Å. However, expanding of layer is significantly greater for OCLAY (19.4 Å) than ACLAY (15.0 Å). This is an expected result that while HDTMA, used in modification of OCLAY, has a long alkyl chain, acrylamide used in modification of ACLAY is a small molecule. Dependence of interlayer spacing to alkyl chain length was also reported by other researchers [13, 29]. As the increase of interlayer distance for ACLAY is so small (0.7 Å), it can be concluded that main function of acrylamide is make to surface organophilic rather than expanding.

4.2 Mixing Time Effect

One of the important parameters in the preparation of polymer-clay nanocomposites by in-situ polymerization is the time of mixing before the initiation of polymerization. Aim of this mixing is the intercalation of monomers and initiators into the clay gallery, and therefore provide the polymerization to be there. There is no doubt on necessity of such a mixing, but different applications were reported as; ultrasonication for 15 min, [57], 24 h magnetic stirring [15], ultrasonication for 3 h [14], stirring for 4h [30] etc. In none of the studies, there is an explanation on chosen time of mixing.

Therefore effect of mixing time, before initiation of polymerization, on swelling of clays was studied. Basal spacings obtained from XRD measurements were used as a parameter. For this purposes, a series of samples were prepared according to section 3.3.3. Mixing time was varied as 2 h, 4 h and 8 h for each type of organophilic clay.

XRD diffractograms obtained for organophilic clays after different mixing times are given in Figure 4.2 and Figure 4.3 for ACLAY and OCLAY respectively.

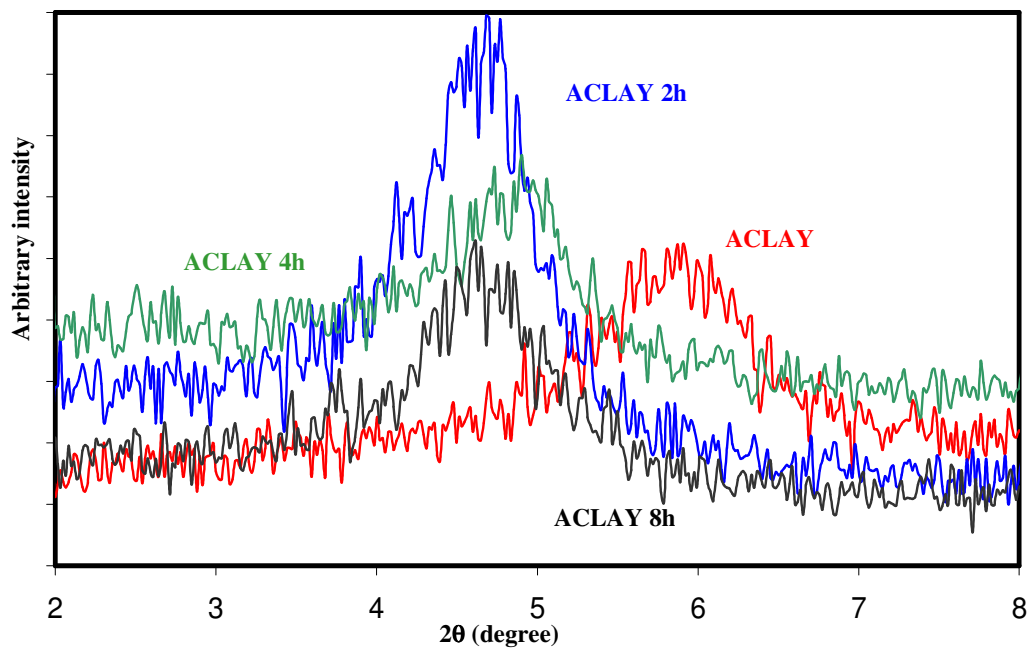


Figure 4.2: XRD diffractograms for different mixing times of ACLAY

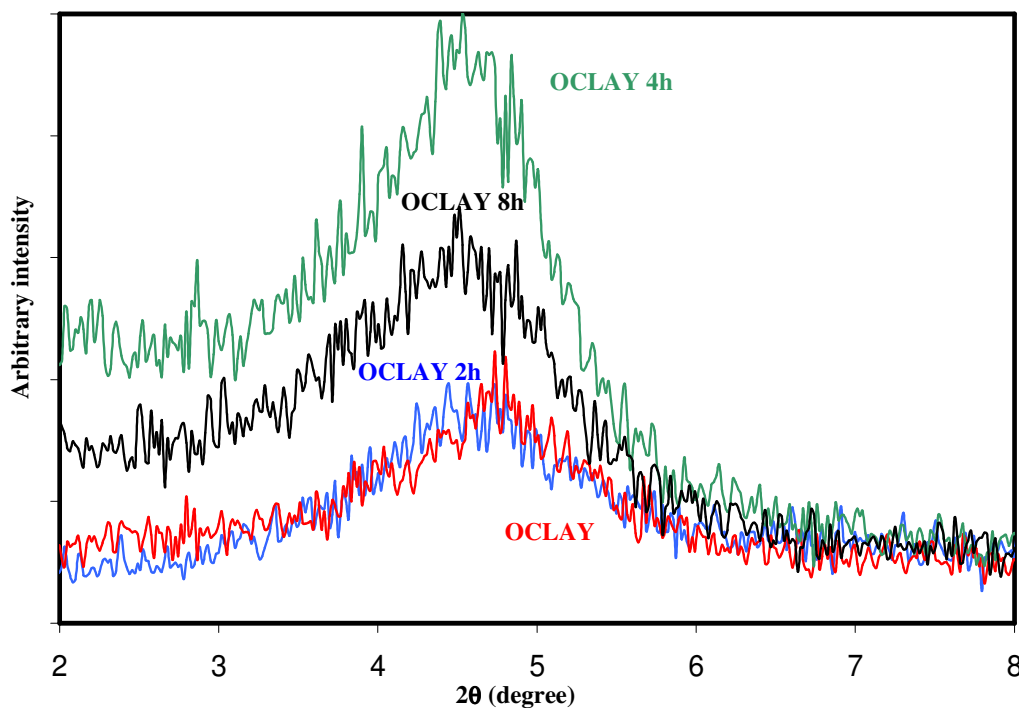


Figure 4.3: XRD diffractograms for different mixing times of OCLAY

Interestingly swelling behavior was found to be almost independent of mixing time after 2 h for both clays. As also can be seen in Table 4.2, d-spacings of organophilic

clays does not vary with the time of mixing. Similar results were also reported on intercalation of epoxy monomers into organophilic clays [29]. As a result of this investigation mixing time before polymerization was chosen as 2h.

Table 4.2: Effect of mixing on d_{001} spacings of clays

Clay	Time of mixing (h)	d_{001} spacings (Å)
ACLAY	No mixing	14.95
	2	18.68
	4	18.01
	8	18.63
OCLAY	No mixing	19.38
	2	19.05
	4	19.50
	8	19.61

There is a significant difference between the behaviors of two clays that while there is an increase in d-spacing of ACLAY with mixing, no expanding was seen upon mixing for OCLAY. This can be attributed to the differences in sizes of molecules used to modify the pristine clay. As the OCLAY was cation exchanged with HDTMA having long alkyl chains, it cannot be further expanded by the intercalation of monomer acrylamide and glycerine. On the other hand, ACLAY was modified with a small sized molecule, acrylamide, and as a result it can be expanded by the penetration of glycerine and more acrylamide monomers.

4.3 Characterization of Polyacrylamide-Clay Nanocomposites

Prepared polyacrylamide-clay nanocomposites were characterized by XRD, FTIR and SEM. While XRD and SEM were used to identify the dispersion of clay layers and structure, FTIR was used to identify the molecular components in the structure.

4.3.1 XRD measurements

In revealing the structure of polymer-clay nanocomposites, XRD forms the first step, that it provides information about the dispersion of clay layers in the polymer matrix. Figure 4.4 shows the XRD patterns of ACLAY, polyacrylamide (PAAM) and series of polyacrylamide-clay nanocomposites with ACLAY loadings of 1 % (PAAM A1), 3 % (PAAM A3) and 5% (PAAM A5).

As it is seen from Figure 4.4, there is only a very small and broad diffraction peak at about 2θ of 2.5° for the nanocomposites while a peak exists at 2θ of 5.9° for ACLAY. The same peak obtained for nanocomposites also exist for the polyacrylamide itself. Therefore this peak can be attributed to the reflection of some beams due to working in small angle scan and it shouldn't be taken into consideration in evaluation of the structure. Therefore, these XRD data suggest a possible exfoliated structure for all clay loadings. Independency of structure from clay loading was also reported by some groups [3, 57].

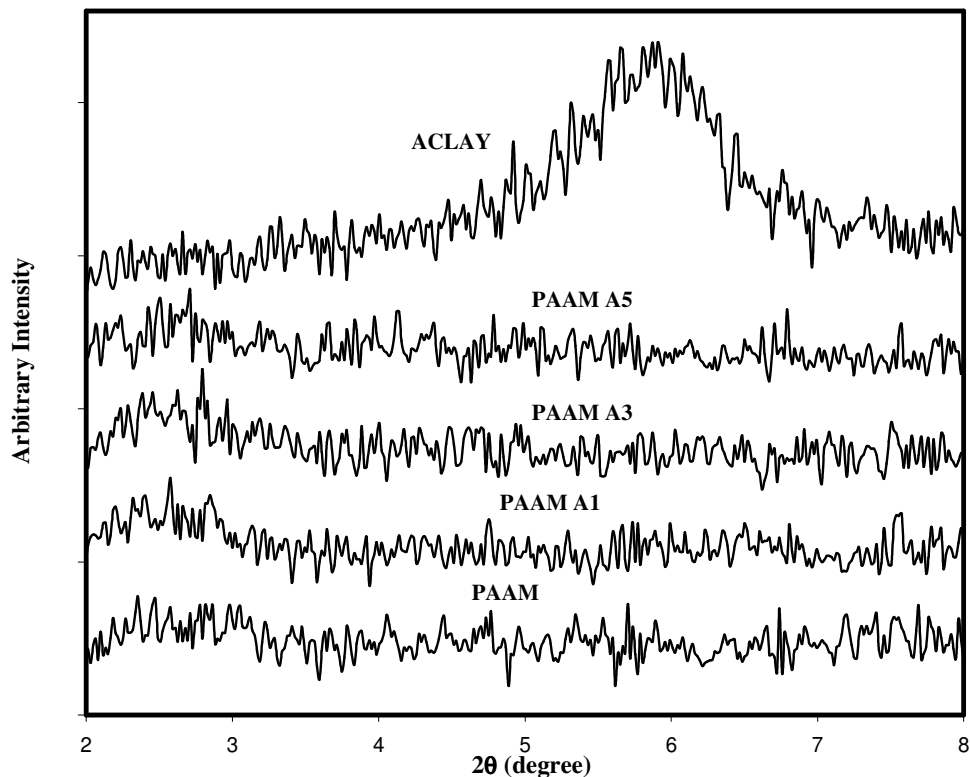


Figure 4.4: XRD patterns of the ACLAY, PAAM and NCs with different clay loadings

XRD patterns of the polyacrylamide-clay nanocomposites synthesized with the use of organophilic clay modified with a typical surfactant HDTMA, are given in Figure 4.4 in the same manner. For the PAAM O1 (1 % clay loading), pattern is similar to PAAM A1, and it can be inferred as a possible exfoliated structure. In contrast to series of nanocomposites with ACLAY, a different behavior was observed as the clay loading increased to the 3 %: For the PAAM O3 and PAAM O5 a very small and very broad peak exists about 2θ of 4° (d-spacing = 20.1 \AA). This can be attributed to the partially intercalated and partially exfoliated structure. But as the peak is very weak it can be suggested that structure is mostly exfoliated.

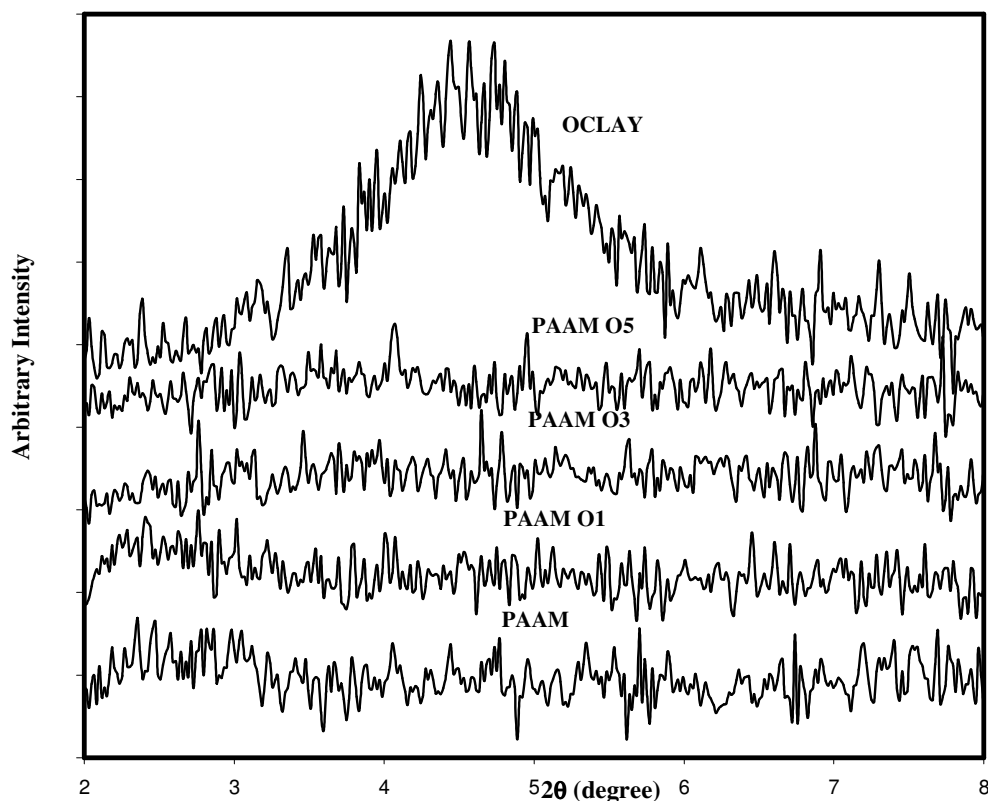


Figure 4.5: XRD patterns of the OCLAY, PAAM and NCs with different clay loadings

Although d-spacing of ACLAY was lower than OCLAY, polyacrylamide-clay nanocomposites synthesized with ACLAY showed better dispersion of clay nanolayers, especially in high clay loadings. Therefore, according to the XRD results, it can be concluded that use of acrylamide as an interlayer agent is more effective in obtaining exfoliated structures in comparison to the typical surfactant HDTMA.

4.3.2 Fourier transform infrared spectra (FTIR)

FTIR spectra have also found many applications in the characterization of polymer-clay nanocomposites [15, 29, 41, 58]. FTIR spectra of the organophilic clays, polyacrylamide and polyacrylamide-clay nanocomposites with different clay loadings are given in the Figure 4.6 and Figure 4.7 for series of ACLAY and OCLAY respectively. The characteristic peaks of PAAM appear at 1630-1680 cm^{-1} (C=O stretching), 3190 and 3350 cm^{-1} (-NH₂ stretching) [15, 59]. On the other hand, characteristic absorption band of montmorillonite is found at 1030-1040 cm^{-1} due to Si-O-Si stretching [15, 41]. For OCLAY, representative peaks include CH₂

asymmetric stretching at 2920 cm^{-1} , CH_2 symmetric stretching at 2849 cm^{-1} , CH_2 plane scissoring at 1434 cm^{-1} and CH out of plane bending at 797 cm^{-1} [15, 41, 58].

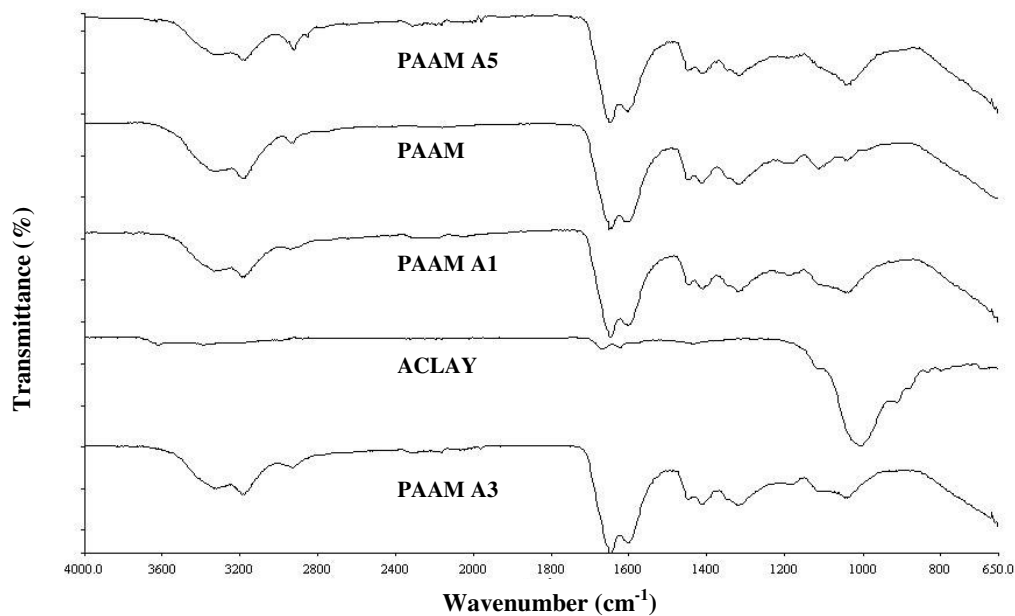


Figure 4.6: FTIR spectra of ACLAY, PAAM and PAAM-ACLAY nanocomposites

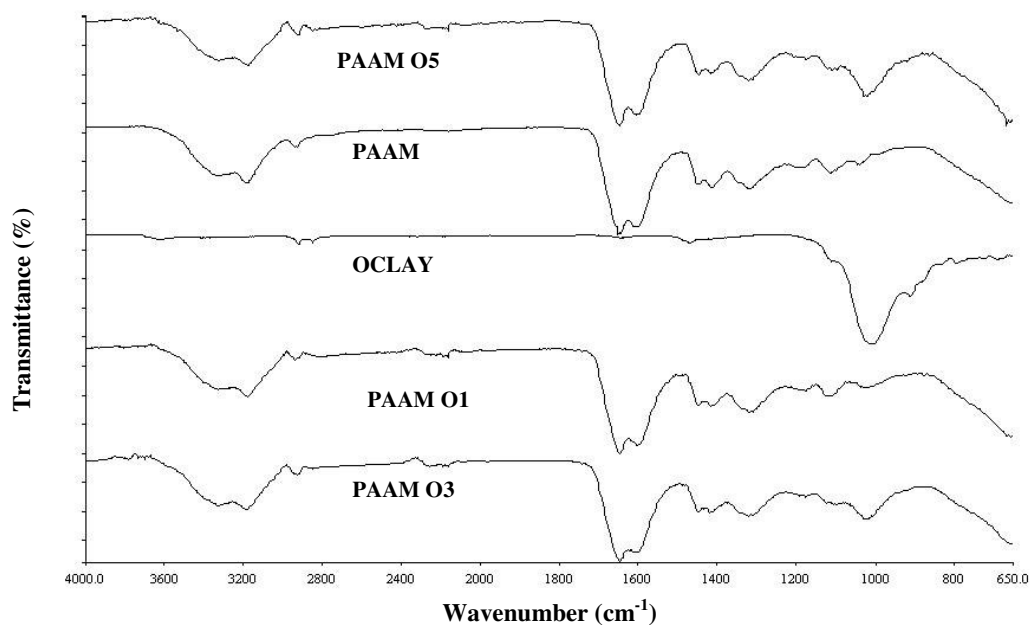


Figure 4.7: FTIR spectra of OCLAY, PAAM and PAAM-OCLAY nanocomposites

Existence of characteristics peaks of both silicate and PAAM in nanocomposites confirm the incorporation of clay layers into polymer matrix. Also intensity of the Si-O-Si peak gets stronger as the clay loading increases for both series with ACLAY and OCLAY.

4.3.3 Scanning electron microscopy (SEM) images

Concluding the type of polymer-clay nanocomposites solely on the basis of XRD results is not possible and it has to be accompanied with images of the internal structure. Although mainly used imaging technique is TEM in polymer-clay nanocomposites, SEM can also provide some information about the dispersion of clay nanolayers in the polymer matrix.

Bright regions are said to correspond clay layers in a previous study [7]. SEM images of pure polyacrylamide are shown in Figure 4.8 at lower and higher magnification. The bright regions seen at the lower magnification are due to reflections from regions having different depths.

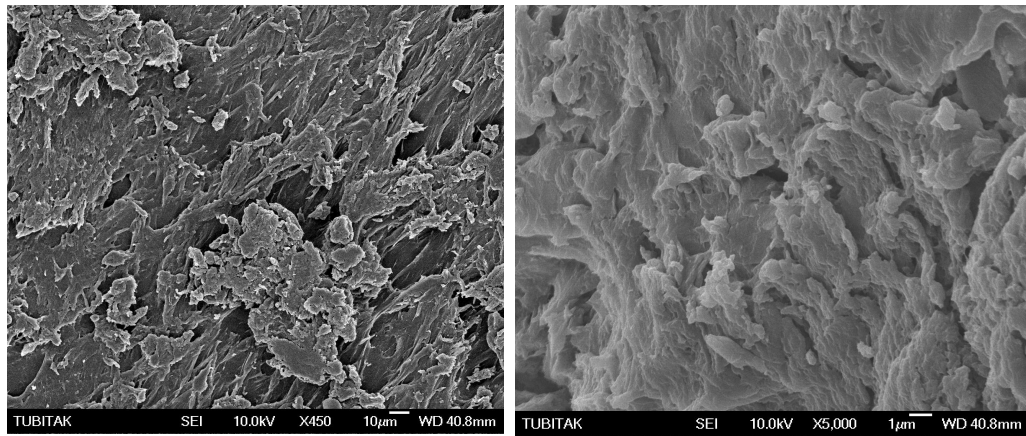


Figure 4.8: SEM images of pure PAAM at 450 and 5,000 magnifications

SEM images of nanocomposites having 1 % ACLAY and 1 % OCLAY are also given in Figure 4.9 and Figure 4.10 respectively for lower and higher magnifications.

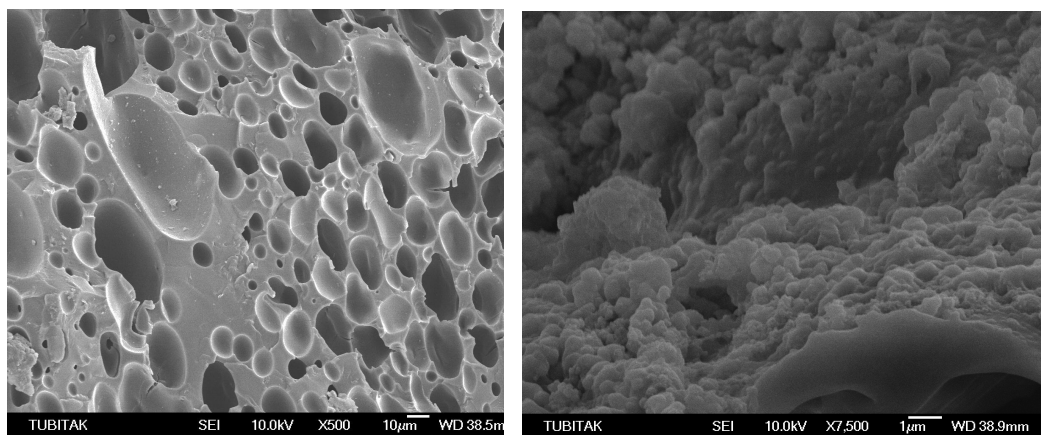


Figure 4.9: SEM images of PAAM A1 at 500 and 7,500 magnifications

As the images of PAAM A1 nanocomposite at lower magnification was taken from bulk samples, a porous structure is seen. Although some changes in morphologies are observed with the incorporation of 1 % clay, silicate layers can not be seen in both Figure 4.9 and in Figure 4.10

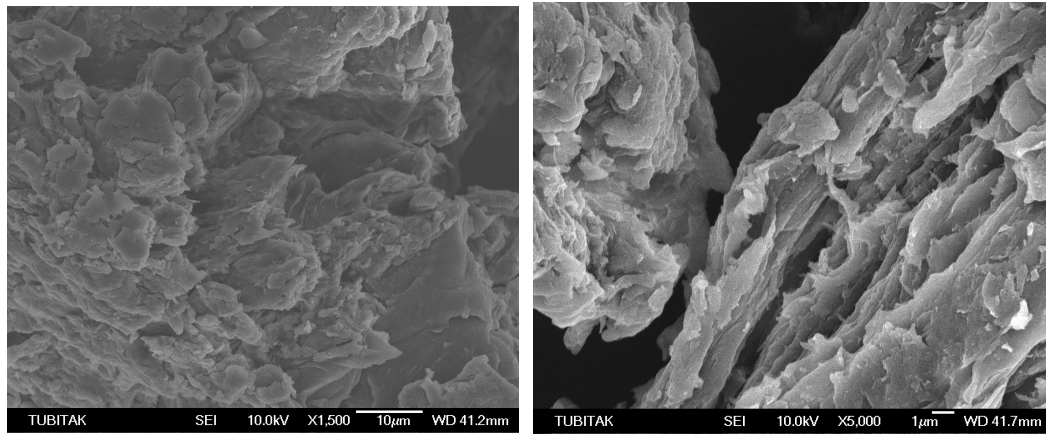


Figure 4.10: SEM images of PAAM O1 at 1,500 and 5,000 magnifications

SEM images of PAAM A3 and PAAM O3 can also be seen in Figure 4.11 and 4.12 respectively at lower and higher magnifications.

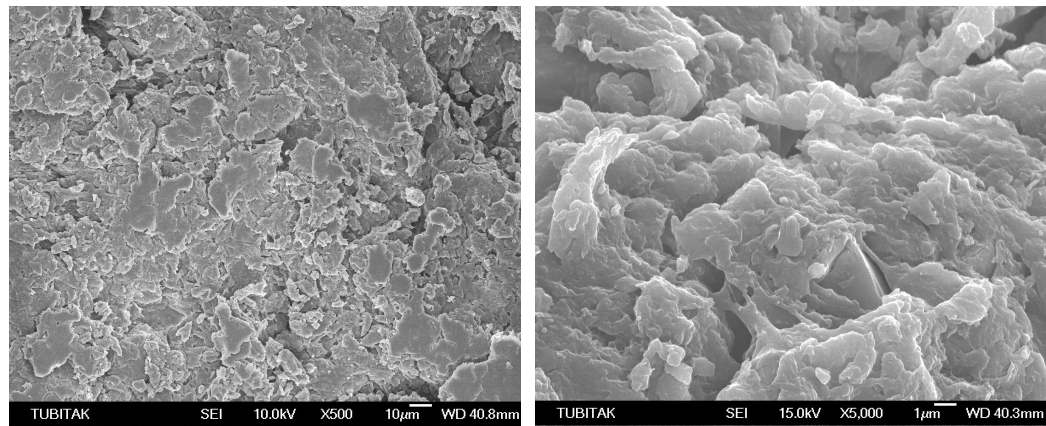


Figure 4.11: SEM images of PAAM A3 at 500 and 5,000 magnifications

As the clay loading increases some changes in fracture surfaces and morphologies are observed, but silicate layers again can not be seen even for 3 % clay loading.

Internal structure of the pure polymer and two series of nanocomposites are not quite distinguishable from each other. Also silicate layers can not be seen clearly in images. This may be probably due to the exfoliation of the clay nanolayers, as their thickness is about 1 nm, they cannot be seen with the SEM.

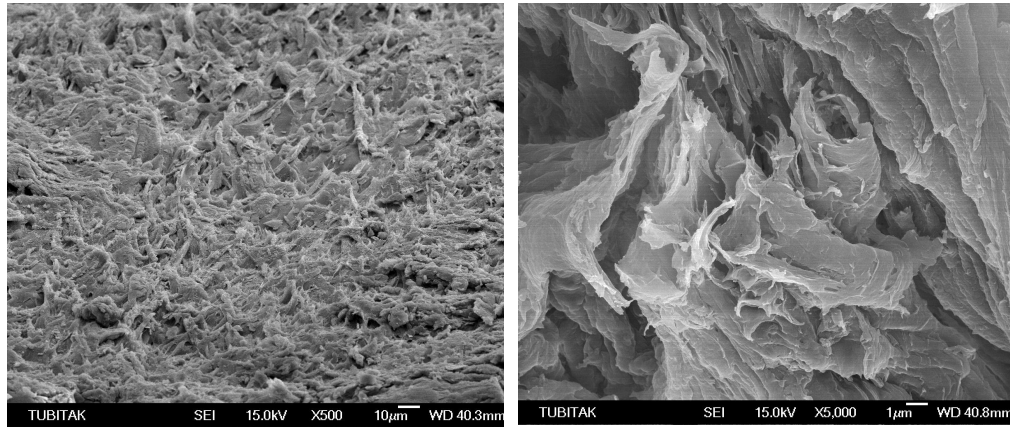


Figure 4.12: SEM images of PAAM O3 at 500 and 5,000 magnifications

For concluding about the type of polymer-clay nanocomposite and understanding the internal structure properly, silicate layers should be seen clearly in images. Therefore TEM imaging technique must also be utilized, thus micrographs with higher resolution and magnification could be taken. By this way, dispersion level of clay nanolayers can be seen and XRD results can be confirmed.

4.4 Effect of Surfactant Type On Conversion

Various researchers reported on restrictive effect of clay loading on polymerization. They generally measured molecular weights of polymers extracted from nanocomposites and found a decrease with the increase of clay loading [10, 15, 41, 60]. They concentrated on possible chain transfer effect of montmorillonite.

In this study, conversion was used as a parameter on restriction of polymerization. Conversions were calculated on the basis of dry weights of precipitated polymers according to equation (4.1):

$$X = \frac{P - C}{M} \times 100 \quad (4.1)$$

X: Conversion

P: Dry weight of product (g)

M: Weight of monomer (g)

C: Weight of clay loading (g)

Variation of conversion with the clay loading is given in Figure 4.13 for polyacrylamide-clay nanocomposites synthesized with ACLAY and OCLAY. Conversion values are also given in Table 4.3.

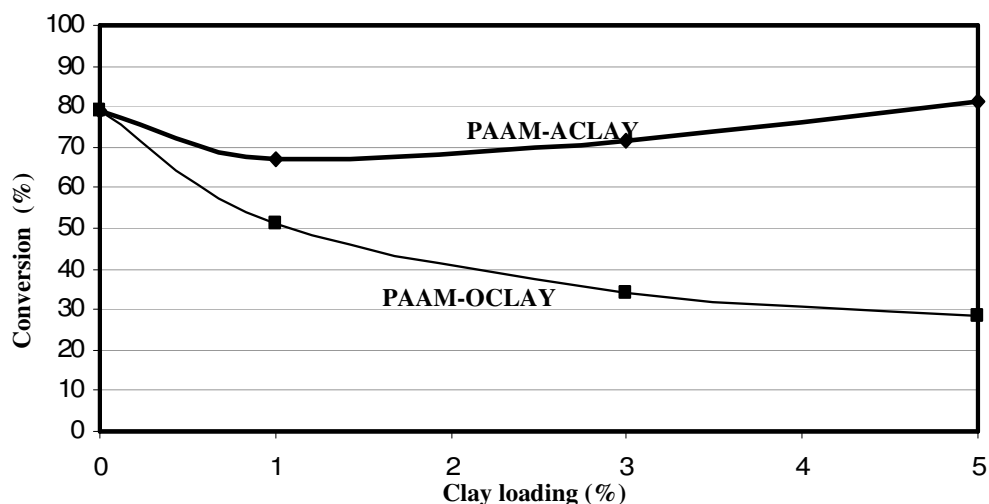


Figure 4.13: Variation of conversion with clay loading for ACLAY and OCLAY

Results are quite interesting that two types of surfactants behave in opposite manner that with the increase of clay loading while conversion decreases for the nanocomposites synthesized with OCLAY, an increase is seen in conversion for the PAAM-ACLAY nanocomposites. The only common point is the decrease of the conversion with the incorporation of clay for both types of surfactants in comparison to pure polymer.

Table 4.3: Conversions of PAAM-ACLAY and PAAM-OCLAY nanocomposites

Clay loading (%)	Conversion (%)	
	PAAM-ACLAY	PAAM-OCLAY
0	79.2	79.2
1	67	51.0
3	71.8	34.2
5	81.4	28.6

Behavior of ACLAY can be attributed to the better interaction of the monomer (acrylamide) with the surfactant, itself, (acrylamide) and possible polymerization reactions initiated by the free radicals generated in the acrylamide of surfactant which is bound to the clay layers. The decrease of conversion for the 1% loading in comparison to the polymer itself, shows the restrictive effect of clay. However, as the clay loading increases more acrylamide of surfactant is present and effect of compatibility surpass the restrictive effect of silicate layers.

On the other hand, significant decrease of conversion with the clay loading for PAAM-OCLAY nanocomposites is not only due to effect of montmorillonite and lack of compatibility. HDTMA has also negative effect on polymerization in this system. This was confirmed with two experiments: Conversion of monomers was quite well when polymerization was carried out with the untreated pristine clay (but, as they are immiscible, clays were aggregated). In a second experiment, an attempt was made to synthesize pure polyacrylamide in the presence of HDTMA (not clay) and there were no polymers at the end of the reaction. But here as chloride was not removed from the media, it can have a possible inhibiting effect on polymerization.

4.5 Glass Transition Temperatures by Differential Scanning Calorimetry (DSC)

Among the thermal properties, mostly used one is glass transition temperature (T_g) for polymer-clay nanocomposites. Almost every study utilized the DSC for determination of T_g and they generally found higher values in comparison to pure polymer with the addition of silicate layers [2, 6, 7, 15].

DSC measures the difference in energy input of a substance and a reference material as a function of temperature. DSC scans of pure PAAM and PAAM-clay nanocomposites with different loadings of ACLAY and OCLAY are given in Figure 4.14 and in Figure 4.15, respectively. Values of T_g are also given in Table 4.4

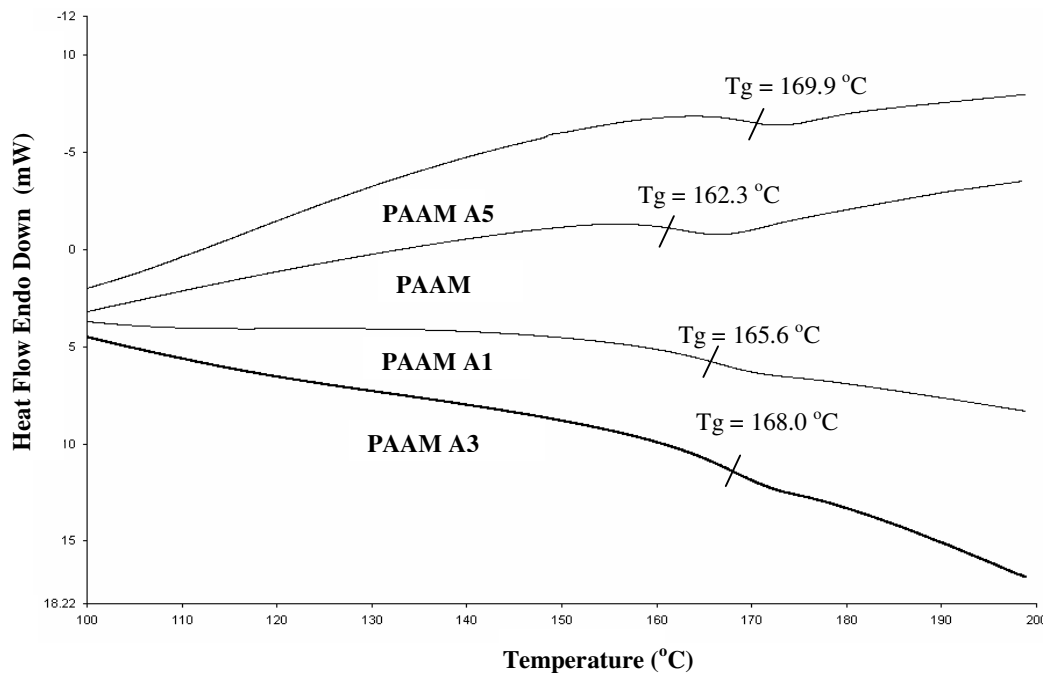


Figure 4.14: DSC scans of pure PAAM, series of PAAM-ACLAY nanocomposites

Glass transition temperatures of the nanocomposites are higher than the pure polyacrylamide for both series. This shows that incorporation of clay results in an increase in glass transition temperatures. This is mainly due to the confinement of the polymer chains within the clay galleries, leading to limited segmental motions of polymers especially near organic-inorganic interfaces [15, 41, 61].

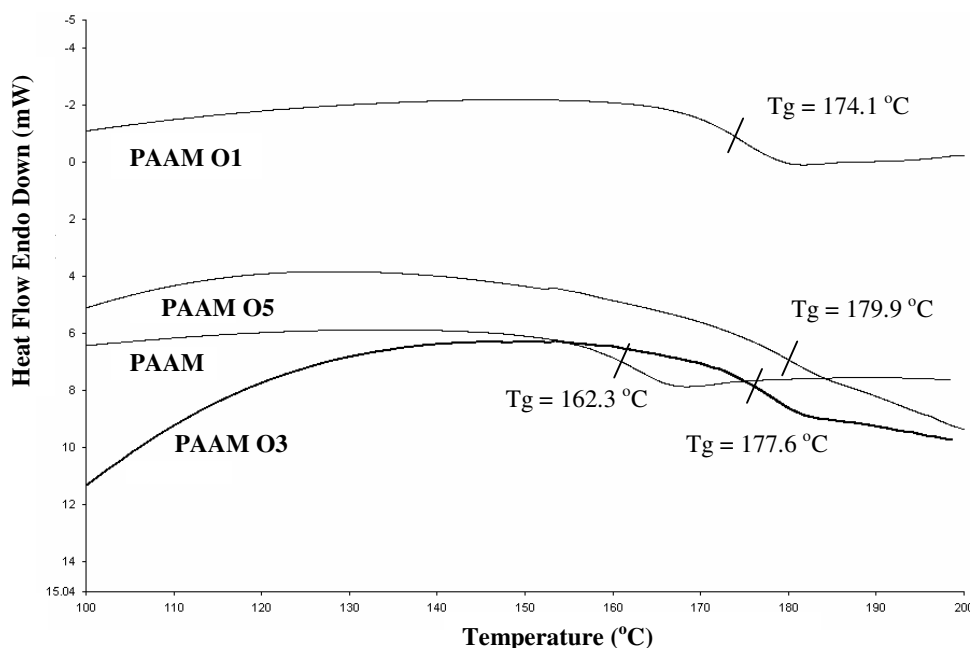


Figure 4.15: DSC scans of pure PAAM, series of PAAM-ACLAY nanocomposites

As seen from Table 4.4 clearly, increments in T_g of nanocomposites synthesized with ACLAY and OCLAY are quite different. PAAM-OCLAY nanocomposites have higher increments for all clay loadings. This can be attributed to the lower conversion of nanocomposites with O-CLAY, that lesser polymers are in the same clay gallery and as a result their motions are more restricted.

Table 4.4: Glass transition temperatures for PAAM-ACLAY and PAAM-OCLAY series

Clay loading (%)	Glass transition temperature (°C)		Increment (°C)	
	PAAM-ACLAY	PAAM-OCLAY	PAAM-ACLAY	PAAM-OCLAY
0	162.3	162.3	-	-
1	165.6	174.1	3.3	11.8
3	168.0	177.6	5.7	15.3
5	169.9	179.9	7.6	17.6

Larger increments for series of nanocomposites with OCLAY due to lower conversion, can be seen easier when actual clay loadings are considered. Table 4.5 shows the actual clay loadings and reduced increments. Here actual clay loadings were calculated by division of the dry weight of precipitated product to the amount of clay present at the beginning. Reduced increments were also obtained by dividing the increment values to the actual clay loading values.

Table 4.5: Reduced increments of T_g's with respect to actual conversions

Clay loading (%)	Actual clay loading (%)		Reduced increment (°C)	
	PAAM-ACLAY	PAAM-OCLAY	PAAM-ACLAY	PAAM-OCLAY
1	1.5	1.9	2.2	6.1
3	4.0	8.1	1.4	1.9
5	5.8	14.9	1.3	1.2

As seen from the table above, reduced increments in T_g's of two series are close to each other showing the effect of conversion. There is an exception for the 1 % clay loading, that some additional effects may exist.

Also application of Fox Approach to the polymer-clay nanocomposite can explain the same effect of conversion. According to Fox equation (4.2), glass transition temperature of a uniform mixed blend of two polymers is described as [62]:

$$\frac{1}{T_g} = \frac{m_1}{T_{g1}} + \frac{m_2}{T_{g2}} \quad (4.2)$$

Here; m_i denotes the mass fraction of polymer "i".

If glass transition temperature of the clay is considered as infinity, then T_g of the nanocomposite will increase with the increase of clay loading (or with the decrease of percentage of polymer).

5. CONCLUSION

Polyacrylamide-clay nanocomposites were synthesized by in-situ polymerization of acrylamide initiated by redox system Ce(IV)-glycerine. Two types of intercalating agents were used in organically modification of clays: a typical long alkyl chained HDTMA and acrylamide, monomer itself. In each case, polymer-clay nanocomposites were successively synthesized for the clay loadings between 1 % and 5 %, as evidenced by XRD, SEM, DSC and FTIR.

ACLAY showed very little increase (0.7 \AA) in d-spacing with respect to the MMT, indicating that acrylamide mainly makes surface organophilic rather than expanding. On the other hand HDTMA provided a considerable expanding (5.1 \AA) of clay layers for OCLAY.

XRD results suggested exfoliated structures for all range of clay loadings in PAAM-ACLAY nanocomposites. Also PAAM-OCLAY nanocomposites exhibited possible exfoliated structures, but with the increase of clay loading above 1 %, some partially intercalated structures were revealed in XRD. SEM images did not indicate any aggregation of clays and an intercalated structure.

Polymer-clay nanocomposite structure was also confirmed with the increase of glass transition temperature, even with 1 % clay incorporation. This was mainly due to fixation of polymer chains into clay gallery. Increments were higher for the PAAM-OCLAY nanocomposites which is a result of lower conversion.

One of the most significant effects of surfactant type was found to be on conversion. While there was a decrease in the conversion by addition of both organophilic clays, a regular increase was seen with the increase of clay loading for ACLAY in contrast to a regular decrease for OCLAY. This was attributed to the stronger interaction of ACLAY with the polymer in comparison to OCLAY.

In conclusion, it was seen that ACLAY has a better compatibility than OCLAY with the polymerization system studied, since acrylamide, monomer itself was used to modify pristine clay. By this application, acrylamides penetrated into the clay

gallery also formed polymerization sites. Also it was shown that restricted polymerization in the clay gallery is mainly due to surfactant used rather than MMT.

With the light of these results, it can be inferred that use of acrylamide as an intercalating agent removes the restrictive effects of known surfactants like HDTMA on the polymerization reaction. Consequently, use of acrylamide as an intercalating agent will probably be efficient in the synthesis of other polymer-clay nanocomposites. Also it will be worthy to investigate the use of other water soluble monomers in the organically modification of clays. Copolymers of water soluble polyacrylamide can also be introduced into the polymer-clay nanocomposites.

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