ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

IN-SITU POLYMERIZATION OF POLYSTYRENE-CLAY NANOCOMPOSITES

M.Sc. Thesis by
Merve ÇETİNTAŞ

Department : Polymer Science and Technology

Programme : Polymer Science and Technology

JANUARY 2011

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

IN-SITU YÖNTEMLE HAZIRLANAN POLİSTİREN-KİL NANOKOMPOZİTLERİ

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OCAK 2011

FOREWORD

This M.Sc. study has been done in Polymer Science and Technology Graduate Program of Institute of Science and Technology at Istanbul Technical University.

First and foremost I would like to express my indebtedness to my advisor Prof. Dr. Nurseli UYANIK who has supported and encouraged me from the beginning of this study and shared her deep knowledge and experience.

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I would like to thank to my friends in our laboratory group for their contribution during my study.

Last, but not least, I am so grateful to my family, without them I could not be able to finish this thesis. I would like to express my deep gratitude; to my parents, Nurten and A. Samim MOCAN who raised me with their love and who never get tired to support me for every subject in my life, even in this thesis, as material and as spiritual; and to my husband M.Cenap ÇETİNTAŞ for his tender care, support and love for me.

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Polymer Science and Technology

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ABBREVIATIONS

PCN : Polymer-Clay Nanocomposite
PLS : Polymer-Layered Silicate
PS : Polystyrene
CEC : Cation Exchange Capacity
MMT : Montmorillonite
XRD : X-ray Diffraction
WAXS : Wide angle X-ray Scattering
SAXS : Small angle X-ray Scattering
TEM : Transmission Electron Microscopy
TGA : Termogravimetric Analysis
DTA : Differential Thermal Analysis
DSC : Differential Scanning Calorimeter
FT-IR : Fourier-Transform Infrared Spectrometer
UV : Ultraviolet
DMA : Dynamic Mechanical Analysis
NMR : Nuclear Magnetic Resonance
HDT : Heat Distortion Temperature
CTE : Coefficient of Thermal Expansion
PHRR : Peak Heat Release Rate
SIP : Surface Initiated Polymerization
Tg : Glass Transition Temperature
GPPS : General Purpose Polystyrene
EPS : Expanded Polystyrene
HIPS : High-Impact Polystyrene
SAN : Styrene-Acrylonitrile
ABS : Acrylonitrile-Butadiene-Styrene
CSTR : Controlled Stirred Tank Reactor
iPS : Isotactic Polystyrene
sPS : Syndiotactic Polystyrene
AIBN : 2,2'-Azodiisobutyronitrile
PVA : Polyvinyl Alcohol
ODA : n-Octadecylamine
DDA : n-Dodecylamine
THF : Tetrahydrofuran
VDAC : Vinylbenzyldimethyldodecyl Ammonium Chloride
VBTACl : Vinylbenzyl Trimethyl Ammonium Chloride
VBDEAC : Vinylbenzyldimethylethanol Ammonium Chloride
CPC : Cetylpyridinium Chloride
ABTBA : 2,2-Azobis[2-methyl-N-(2-hydroxyethyl) Propionamide
MHAB : 2-Methacryloyloxyethylhexadecyldimethyl Ammonium Bromide
POSS : Aminopropyl-Isobutyl Polyhedral Oligomeric Silsesquioxane
CD : Cyclodextrin
VBC : Vinylbenzyl Chloride

PS/20A **:** Dimethyl Dehydrogenated Tallow Ammonium Montmorillonite

LIST OF SYMBOLS

λ = Wavelength

δ = Phase angle

υ = Wavenumber

θ = Diffraction angle

d_{001} = Layer distance of clay platelets

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IN-SITU POLYMERIZATION OF POLYSTYRENE-CLAY NANOCOMPOSITES

SUMMARY

Polystyrene (PS) is one of the most widely used polymers in industry because of its many advantages like low cost and flexibility for various kinds of end uses. On the other hand polystyrene has some deficiencies like brittleness, low thermal and dimensional stability, high flammability; which permits to use this polymer in more technical areas. To able to have polystyrene with better properties some modifications are performed physically or chemically like adding additives or modification with rubber, copolymerization of styrene with different monomers, synthesizing in the presence of special catalysts to obtain the polymer with different tacticities etc.

Adding layered silicate to the system is another way to improve the properties of polystyrene like mechanical, thermal, dimensional, inflammability properties. This can be achieved by molecular-level incorporation of the layered silicate in the polymer matrix by addition of a modified silicate either to a polymerization reaction (in situ method), to a solvent-swollen polymer (solution dispersion), or to a polymer melt (melt blending). Except solution dispersion, for the other the processes; the normal sodium cations, found in montmorrilonite, a classic aluminosilicate material, must be replaced by cations which are organophilic enough to permit the introduction of the polymer. In other words clay must be organoclay by modifying. Since the more surface area contacts with the polymer matrix the more enhanced properties obtained for the final material. Ion exchance with clay is usually performed by an ammonium or phosphonium salt which is called as a ‘surfactant’ that contains at least one alkyl chain which is 14 or 16 carbons in length; the other substituents on the ‘onium’ salt may be freely chosen in order to enhance some particular property of the nanocomposites. Also depending on the polymer used if surfactants have similar molecules with the polymer on their structure it is expected to be more compatible with the polymer.

In-situ method is a suitable method to be able to obtain exfoliated structure where the clay layers become completely dispersed in a polymer matrix. Since polystyrene is highly hydrophobic; researchers have been obliged to attempt to generate different methods to make the clay and the polymer more compatible. This new preparation method consist of using surfactants containing functional groups as initiators or double bonds. If the surfactant exists an initiator on its structure polymerization will initiate on the organoclay surface and clay and polymer matrix will be chemically bonded. Similarly, if surfactant contains a double bond, polymerization will propagate onto these structures a chemical bond between polymer and organoclay will exist again. As a result a polystyrene-clay nanocomposite with more compatibility will be obtained.

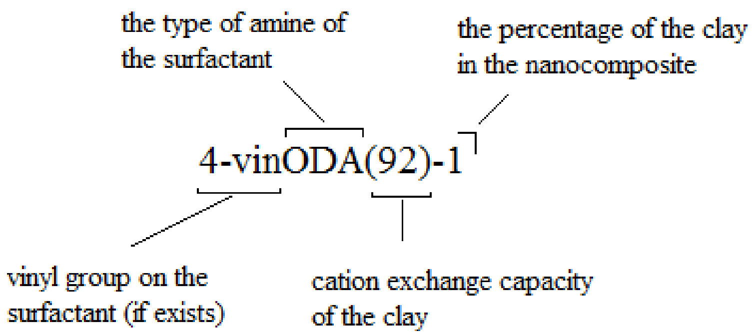
In this study we synthesized polystyrene-clay nanocomposites with in-situ polymerization and the effects of surfactant architecture on the nanocomposite properties is investigated.

Firstly, different surfactants are synthesized depending on the alkyl chain length and having a styrenic structure on its surface and without this structure. Then these surfactants are reacted with the clay for ion exhange reaction. Two different montmorrilonites were used as the layered silicate having cation exchange capacity 92.6 and 145 meq / 100 g.

The organoclays, which are dried and grinded, was added and swelled in toluene, then styrene and initiator were added into the solution and mixed for certain time at room temperature, then mixture is heated and reaction took place for about 5 hours at 80°C.

2,2'-Azodiisobutyronitrile (AIBN) was used as the initiator and 2 clay ratios were used which are 1 and 5 wt% in the nanocomposite.

The notation of the nanocomposite samples is given below, left side defines the clay and the number at the right corner defines the amount of clay in the nanocomposite structure.



Structural analysis of synthesized surfactants, modified clays and nanocomposites were followed by Fourier transform infrared spectrometer (FT-IR).

The interlayer spacing of silicate layers, thermal properties of polystyrene-clay nanocomposite samples were investigated. The interlayer spacing of silicate layers of samples were examined by using the X-ray diffraction spectrometer (XRD) (Table 1 and Table 2).

The thermal properties of nanocomposites are determined by thermogravimetric analyzer (TGA), differential thermal analyzer (DTA) and differential scanning calorimeter (DSC) (Table 1 and Table 2).

Table 1 : Interlayer distances and thermal characterizations of clays and nanocomposites prepared by clay having cation exchange capacity (CEC) of 92.6 meq / 100 g

Sample ID	d_{001}	T_g	$(T_{deg})_{start}$	$(T_{deg})_{finish}$	$(T_{deg})_{mid}$
Na-MMT	11.8	-	-	-	-
DDA(92)	17.5	-	-	-	-
ODA(92)	18.5	-	-	-	-
4-vinDDA(92)	18.7	-	-	-	-
4-vinODA(92)	18.9	-	-	-	-
PS homopolymer	-	85.6	311	378	345
DDA(92)-1	18.0	72.2	309	420	364
DDA(92)-5	19.2	77.0	318	431	371
ODA(92)-1	21.0	66.5	327	429	383
ODA(92)-5	22.4	85.0	350	444	391
4-vinDDA(92)-1	21.2	70.1	328	436	384
4-vinDDA(92)-5	23.0	71.5	341	432	387
4-vinODA(92)-1	23.6	71.0	381	418	407
4-vinODA(92)-5	24.2	86.0	388	440	416

Table 2 : Interlayer distances and thermal characterizations of organoclays and nanocomposites prepared by clay having cation exchange capacity (CEC) of 145 meq / 100 g

Sample ID	d_{001}	T_g	$(T_{deg})_{start}$	$(T_{deg})_{finish}$	$(T_{deg})_{mid}$
Na-MMT	15.9	-	-	-	-
DDA(145)	16.3	-	-	-	-
ODA(145)	16.5	-	-	-	-
4-vinDDA(145)	16.5	-	-	-	-
4-vinODA(145)	16.9	-	-	-	-
PS homopolymer	-	85.6	311	378	345
DDA(145)-1	16.6	68.0	315	382	350
DDA(145)-5	22.8	82.3	317	387	349
ODA(145)-1	20.3	90.0	324	403	352
ODA(145)-5	19.6	99.0	366	408	385
4-vinDDA(145)-1	20.1	93.1	321	392	354
4-vinDDA(145)-5	19.5	87.8	332	395	362
4-vinODA(145)-1	20.1	95.1	357	404	373
4-vinODA(145)-5	19.6	99.1	376	408	387

Glass transition temperature (Tg) of the nanocomposites increased with the organoclay content explained by due to the restricted segmental motions of the polymer chains at the organic–inorganic interface, which is due to the confinement of PS chains between the silicate layers as well as the silicate surface-polymer interactions. Decreases in Tg values may be explained by the high viscosity of organophilic MMT which was dispersed in the styrene monomer affected the diffusion of initiator molecules, and MMT platelets may have blocked chain propagation during polymerization.

The thermal stability increased with the organoclay content and the content of the organoclay, and they may have been influenced by a competition between the incorporation of clay and the decrease in the molecular weight of the polymer matrix.

Interlayer distances of clays and their nanocomposites were increased compared to pristine clay. XRD patterns indicated that the polymer chains were intercalated between the clay platelets. Moreover, distance between clay platelets were increased as the alkyl chain length increased. In addition, it is found that CEC of the clay influences the increment of the interlayer distance of the organoclays and their nanocomposites. XRD results also indicated organoclays prepared with surfactants containing similar units to monomer cause more expanding of the clay platelets with each other.

Among the synthesized organoclays tested in this study, 4-vinODA modified clay containing nanocomposites, an organoclay with a longer alkyl chain length and a benzyl unit similar to the structure of styrene, was most effective in achieving PS intercalation between silicate layers, as confirmed by XRD, DSC, TGA and DTA analyses.

IN-SITU YÖNTEMLE HAZIRLANAN POLİSTİREN-KİL NANOKOMPOZİTLERİ

ÖZET

Polistiren (PS) sahip olduğu düşük maliyet, farklı birçok alanda kullanım imkanı bulması gibi avantajlarından dolayı sanayide en çok kullanılan polimerler arasındadır. Bunun yanında polistiren; kırılganlık, düşük ısıl ve boyutsal kararlılık, yanıcılık gibi zayıflıkları polimerin daha teknik alanlarda kullanımını kısıtlamaktadır. Daha iyi özellikli polistiren elde etmek için polimer üzerine katkı maddesi katmak veya kauçukla modifikasyon, stirenin farklı monomerlerle kopolimerizasyonu, özel katalizörler varlığında taktisite kazandırmak gibi fiziksel veya kimyasal modifikasyonlar uygulanmaktadır.

Polimere tabakalı silikat katılması da polistirenin mekanik, ısıl, boyutsal ve yanmazlık gibi özelliklerinin iyileştirmek için uygulanan diğer bir yöntemdir. Bu, modifiye edilmiş silikatın; polimerizasyon sırasında katılmasıyla (in-situ polimerizasyon), solventle şişirilmiş polimere katılmasıyla (çözeltide dağılma), veya eriyik polimer içersine katılmasıyla (eriyik karıştırma) ile tabakalı silikatın polimer matrisine moleküler düzeyde birleşmesini sağlamakla gerçekleştirilmektedir. Her durumda klasik bir aluminosilikat maddesi olan montmorrilonitin içersinde bulunan normal sodyum katyonları polimerin girişini kolaylaştıracak kadar organofilik olan katyonlarla değiştirilmesi gerekmektedir. Diğer bir deyişle kil,modifikasyonla organokil olmalıdır. Çünkü polimer matris ile kilin temas eden yüzey alanı ne kadar fazla ise elde edilen son ürünün özellikleri o kadar iyi olacaktır. Kil ile iyon değişimi ‘yüzey aktif madde’ denilen 14-16 karbon uzunluğunda en az bir alkil zinciri içeren genellikle amonyum veya fosfonyum tuzlarıyla gerçekleşir. Onyum tuzundaki diğer sübstitüentler nanokompozitin istenen belirli özelliklerini iyileştirmek için serbestçe seçilebilmektedir. Ayrıca yüzey aktif maddeler yapısında polimere benzer moleküller içeriyorsa bu durumda organokilin polimerle daha uyumlu olması beklenmektedir.

In-situ polimerizasyon kil tabakaların polimer matris içersinde birbirinden tamamen ayrışması ile gerçekleşen tam dağılmış tabakalı yapı elde etmek için uygun bir metottur. Polistiren yüksek hidrofobluk özelliği göstermesi araştırmacıları, kil ve polimeri birbirine daha uyumlu hale getirmek için farklı metodlar oluşturmaya zorunlu kılmıştır. Bu yeni hazırlama metodu üzerinde başlatıcı, çifte bağ gibi fonksiyonel gruplar içeren yüzey aktif maddelerin kullanımını kapsamaktadır. Yüzey aktif madde başlatıcı içeriyorsa polimerizasyon organokil yüzeyi üzerinden başlatılacak ve polimer matris ile kil kimyasal olarak birbirine bağlı olacaktır. Benzer şekilde yüzey aktif çifte bağ içerirse bu durumda polimerizasyon kilin yüzeyinde de gerçekleşecek ve polimer ile kil arasında kimyasal bağ mevcut olacaktır. Sonuç olarak birbirine uyumluluğu yüksek polistiren-kil nanokompoziti ele geçecektir.

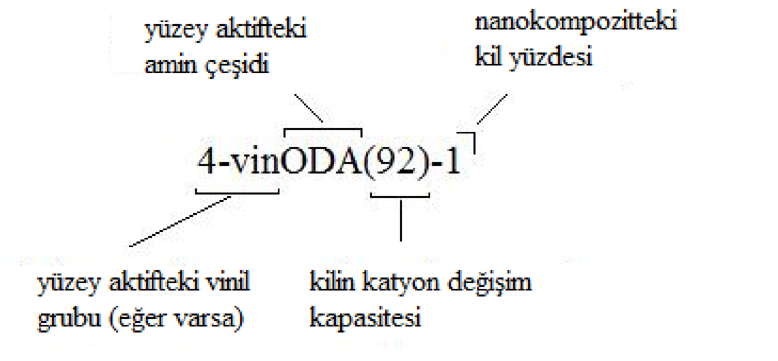
Bu çalışmada in-situ polimerizasyon metodu ile polistiren-kil nanokompozitleri sentezlenmiş ve yüzey aktiflerin yapısının nanokompozit özelliklerine etkisi incelenmiştir.

Öncelikle, alkil zincir uzunluğu, yapısında stiren benzeri yapıya sahip olup olmamasına bağlı olarak farklı yüzey aktif maddeler sentezlenmiştir. Daha sonra bu yüzey aktifler kil ile iyon değiştirerek reaksiyona girmiştir. Çalışmada katyon değişim kapasitesi 92.6 and 145 meq / 100 g olacak şekilde iki farklı montmorrilonit kili kullanılmıştır.

Kurutulup öğütülen organokillerin yapıya eklenmiş ve toluen içinde şişirilmiş, daha sonra da stiren ve başlatıcı eklendikten sonra belirli bir süre oda sıcaklığında karıştırılmış, sonra da ısıtılarak 80^{o}C'de yaklaşık 5 saat boyunca polimerizasyon reaksiyonunun gerçekleşmesi sağlanmıştır.

Başlatıcı olarak 2,2'-azodiisobutironitril (AIBN) kullanılmış ve kilin nanokompozitteki oranı %1 ve %5 olarak alınmıştır.

Nanokompozit örneklerinin tanımlanması sırasıyla aşağıda gösterilmiş olup, sol taraf kili tanımlıyor olup en sağdaki sayı da nanokompozit içersindeki yüzdesine karşılık gelmektedir.



Silikat tabakaları arasındaki tabakalar arası mesafe, polistiren-kil nanokompozit örneklerinin termal özellikleri incelenmiştir.

Sentezlenen yüzey aktifler, modifiye killer ve nanokompozitlerin yapıları FT-IR spektroskopisi ile takip edilmiştir.

Silikat tabakaları arasındaki tabakalar arası mesafe X-ışını dağılımı spektrometresi tarafından ölçülmüştür (Çizelge 1 ve Çizelge 2).

Nanokompozitlerin ısısal özelliklerinin tespiti termogravimetrik analiz, diferansiyel termal analiz ve diferansiyel taramalı kalorimetre cihazları ile gerçekleşmiştir. (Çizelge 1 ve Çizelge 2).

Çizelge 1 : 92.6 mek / 100 g katyon değiştirme kapasiteli (KDK) kil ile hazırlanan kil ve nanokompozitlerin tabakalar arası mesafeleri ve nanokompozitlerin ısısal özellikleri

Örnek kodu	d_{001}	T_g	$(T_{boz})_{baş}$	$(T_{boz})_{bitiş}$	$(T_{boz})_{orta}$
Na-MMT	11.8	-	-	-	-
DDA(92)	17.5	-	-	-	-
ODA(92)	18.5	-	-	-	-
4-vinDDA(92)	18.7	-	-	-	-
4-vinODA(92)	18.9	-	-	-	-
PS (homopolimer)	-	85.6	311	378	345
DDA(92)-1	18.0	72.2	309	420	364
DDA(92)-5	19.2	77.0	318	431	371
ODA(92)-1	21.0	66.5	327	429	383
ODA(92)-5	22.4	85.0	350	444	391
4-vinDDA(92)-1	21.2	70.1	328	436	384
4-vinDDA(92)-5	23.0	71.5	341	432	387
4-vinODA(92)-1	23.6	71.0	381	418	407
4-vinODA(92)-5	24.2	86.0	388	440	416

Çizelge 2 : 145 mek / 100 g katyon değiştirme kapasiteli (KDK) kil ile hazırlanan kil ve nanokompozitlerin tabakalar arası mesafeleri ve nanokompozitlerin ısısal özellikleri

Örnek kodu	d_{001}	T_g	$(T_{boz})_{baş}$	$(T_{boz})_{bitiş}$	$(T_{boz})_{orta}$
Na-MMT	15.9	-	-	-	-
DDA(145)	16.3	-	-	-	-
ODA(145)	16.5	-	-	-	-
4-vinDDA(145)	16.5	-	-	-	-
4-vinODA(145)	16.9	-	-	-	-
PS homopolimer	16.6	85.6	311	378	345
DDA(145)-1	22.8	68.0	315	382	350
DDA(145)-5	20.3	82.3	317	387	349
ODA(145)-1	19.6	90.0	324	403	352
ODA(145)-5	20.1	99.0	366	408	385
4-vinDDA(145)-1	19.5	93.1	321	392	354
4-vinDDA(145)-5	20.1	87.8	332	395	362
4-vinODA(145)-1	19.6	95.1	357	404	373
4-vinODA(145)-5	15.9	99.1	376	408	387

Nanokompozitlerin camsı geçiş sıcaklığının (Tg) organokil içeriği ile artması; polimer zincirlerinin silikat tabakaları arasında hapsedilmesiyle ve silikat-polimer etkileşiminin azalmasıyla meydana gelen organik-inorganik faz arasında polimer zincirlerinin bölgesel hareketliliğinin kısıtlanmış olmasıyla açıklanabilir. Tg değerlerinde görülen düşüşler ise stiren monomeri içinde dağılmış yüksek viskoziteli organofilik montmorillonitin (MMT) başlatıcı moleküllerinin geçişini engellemiş ve MMT tabakalarının polimerleşme sırasında meydana gelen zincir uzamasını engellemiş olabileceği şeklinde açıklanabilmektedir.

Isısal kararlılık organokilin içeriği ve miktarı ile artmış ve kilin yapıya katılımı ile polimer matrisin molekül ağırlığının düşmesi arasındaki rekabetten etkilenmiş olabilmektedir.

Organokil ve nanokompozitlerin tabakalar arası mesafesi saf kile göre artmıştır. XRD sonuçları polimer zincirlerinin kil tabakaları arasında ‘sıralı tabakalı dağılım’ı sağladığını göstermektedir. Ayrıca, alkil zincir uzunluğu arttıkça tabakalar arası mesafenin arttığı da görülmüştür. Buna ilave olarak, kilin katyon değişim kapasitesinin (KDK) tabakalar arası mesafenin artışına da etki ettiği gözlenmiştir. XRD sonuçları ayrıca monomere benzer yapı içeren yüzey aktiflerle hazırlanan organokillerin kil tabakalarının daha fazla açıldığını göstermiştir.

Sentezlenen organokiller arasında, daha uzun alkil zinciri ve stirene benzer yapı içeren 4-vinODA modifiye organokil ile hazırlanan nanokompozitlerin diğerlerine göre PS’in silikat tabakaları arasına girişinde en etkili olduğu XRD, DSC, TGA ve DTA analizleri ile doğrulanmıştır.

Bu çalışma, stiren monomeri ile organofil MMT’in organik grubunun yapısal benzerliğinin nanokompozit hazırlanmasında önemli bir faktör olduğunu göstermiştir.

1. INTRODUCTION

Polystyrene is the fourth biggest polymer produced in the world after polyethylene, polyvinyl chloride and polypropylene. Polystyrene is one of the most versatile plastics. Because of its low cost and acceptable material properties, it is used in packaging, housewares, appliances, and furniture, disposable serviceware and flatware, electrical and electronic parts, construction, transportation, toys and sporting goods.

Although the market finds excellent utilities for polystyrene, polystyrene has deficiencies that limit its applications for specialized uses. Among the important physical deficiencies are that polystyrene is brittle and has poor impact strength. It has a low heat distortion temperature (HDT) of 85°C and is readily attacked by many organic solvents. However because of its low cost, polystyrene is an ideal material for high volume production development. In many cases polystyrene has to be modified chemically or physically. In chemical modifications styrene or polystyrene is reacted with a reagent to introduce chemical functionalities or styrene is copolymerized with other monomers using catalysts or styrene could be polymerized to have different tacticities. In physical type modifications, polystyrenes are processed with additives to achieve specific physical properties such as flexural, tensile, and barrier properties [1].

Synthesizing polystyrene-clay nanocomposite is another way to achieve the desired properties like higher tensile strength, higher dimensional stability, thermal stability, higher HDT, and lower flammabililty compared to pristine PS [2]. This could be achieved by different preparation methods. Clay having hydrophilic character needs to be organically modified to be more compatible with highly hydrophobic PS. Nanocomposites can be prepared by solution dispersion, melt-mixing or by in-situ polymerization. Generally melt-mixing and in-situ polymerization is more applicable for PS-clay systems. Since in solution dispersion and melt mixing long polymer chains are being forced to enter between the clay platelets, in-situ polymerization can be more advantageous since smaller molecules (monomers) intercalate more easily into clay platelets and then polymerization can begin and longer chains would start to force platelets to increase the distance between them. Intercalation and exfoliation are mainly two types of structures obtained in a polymer-clay nanocomposite. Nanocomposites having an exfoliated structure is thought to possess better material properties. Because of this reason studies on polystyrene-clay nanocomposites are mostly focused on obtaining exfoliated nanocomposites. Different kinds of methods have been proposed to achieve this purpose. These methods generally consist of polymerization of styrene in the presence of organoclay which is in-situ polymerization. More succesful results were obtained when the organoclay carries an initiator on its surface or is chemically bonded with a polymerizable group similar to styrene. In the first case polymerization is expected to start on the clay surface where this method is called as 'surface initiated polymerization' and good results were obtained by this method [3]. In the second case polymerization will occur between organoclay and styrene existing in the reaction mixture. Then since organoclay and polystyrene will be chemically bonded, they will be more compatible. There would be more chance to raise the distance between clay platelets, and this will cause to obtain more probably exfoliated structure, which means much more surface area between the polymer matrix and organoclay, finally leads us best material properties obtained in a polymer-clay nanocomposite.

In this study, polystyrene-clay nanocomposites were synthesized by in-situ polymerization. Before the polymerization, clay was organically modified by different surfactants with different chain lengths and/or with and without functional groups. A polymerizable group was added to the surfactant to investigate the effects on the nanocomposite properties. Two different ratios (1 and 5wt%) of organoclay were added to the polymerization medium to investigate the effect of amount of clay in the nanocomposite. The interlayer spacing of silicate layers, structural and thermal properties of nanocomposites were investigated.

2. THEORETICAL PART

2.1 Polymer-Clay Nanocomposites

Nanocomposites are materials that comprise of a dispersion of nanometer-size particles which do not exceed 100 nm in a polymer or copolymer. The most heavily used layered nanoparticles are based on the smectite class of aluminum silicate clays, of which the most common representative is montmorillonite (MMT). In polymer clay nanocomposites (PCN's), a few wt% of each silicate layer of clay mineral is randomly and homogeneously dispersed on a molecular level in the polymer matrix [4].

Polymer/layered silicate (PLS) nanocomposites have received a great deal of attention during the past decade. They often exhibit attractive improvement of material properties when compared with pure polymer or conventional composites (both micro and macro-composites) [5]. These improvements can include, high moduli, increased strength and heat resistance, decreased gas permeability and flammability and increased biodegradability of biodegradable polymers. On the other hand, these materials have also been proved unique model systems to study the structure and dynamics of polymers in confined environments. The main reason for these improved properties is interfacial interaction between the polymer matrix and organically modified layered silicate as opposed to conventional composites. Layered silicates have layer thickness in the order of 1 nm and very high aspect ratios (e.g., 10-1000). A few weight percent of layered silicate that is properly dispersed throughout the matrix thus creates a much higher surface area for polymer-filler interfacial interactions than in conventional composites [6].

Two major findings stimulated the revival of these materials. First, Usuki, Fukushima and their colleagues of Toyota Central Research & Development Co. Inc. successfully prepared, for the first time, exfoliated Nylon 6/LS hybrid via in situ polymerization of ε-caprolactam, in which alkylammonium-modified MMT was thoroughly dispersed in advance. The resulting composite with a loading of only 4.2

wt% clay possessed a doubled modulus, a 50%-enhanced strength, and an increase in heat distortion temperature (HDT) of 80 compared to the neat Nylon 6 [7,8]. Second, Vaia and co-workers found that it is possible to melt-mix polymers with layered silicates without the use of organic solvents [9]. Today, efforts are being conducted globally using almost all types of polymer matrices [6].

PCN's have attracted considerable attention also because of their potential applications in industry. These materials have been widely used in areas of electronics, transportation, and construction products. Recently, studies also increased for the usage of PCN in food packaging industry. PCN's offer attractive combinations of stiffness and toughness, which are difficult to attain from the individual component alone [67].

2.1.1 Properties of Polymer-Clay Nanocomposites

The tensile modulus of a polymeric material expressing the stiffness has shown to be remarkably improved when nanocomposites are formed with layered silicates exhibit a drastic increase in the tensile properties at rather low filler content [10]. There occurs a sharp increase in tensile modulus for a very small clay loading, followed by a much slower increase beyond a clay loading of 4wt%. This is characteristic behavior of polymer/layered silicate nanocomposites with an increase in clay content. The stress is much more efficiently transferred from the polymer matrix to the inorganic filler, resulting in a higher increase in tensile properties [11].

HDT of a polymeric material is an index of heat resistance towards applied load. Most of the studies report HDT as a function of clay content [12].

The thermal stability of polymeric materials is usually studied by thermogravimetric analysis (TGA). The weight loss due to formation of volatile products after degradation at a high temperature is monitored as a function of temperature. Generally the incorporation of silicate in the polymer matrix enhances the thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition [12].

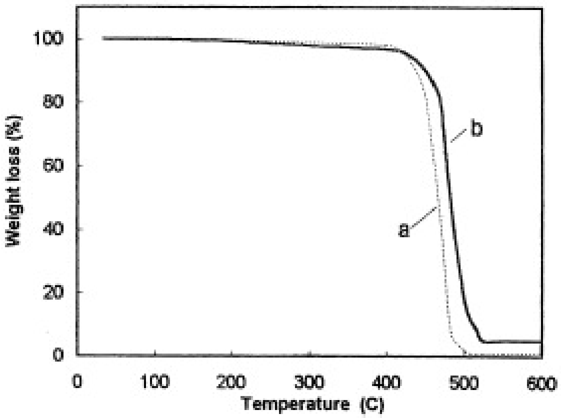


Figure 2.1 : TGA thermograms of weight loss versus temperature (a) pure polymer; and (b) nanocomposite containing 5.6 wt% organoclay [53].

MMT must be nano-dispersed to be able to affect the flammability of the nanocomposites. The layered silicate, however, needs not be completely delaminated for it to affect the flammability of the nanocomposite. In general, the nanocomposites flame retardant mechanism is that a high-performance carbonaceoussilicate char builds up on the surface during burning; this insulates the underlying material and slows the mass loss rate of decomposition products [12].

Nanoclays are believed to increase gas barrier properties by creating a maze or ‘tortuous path’ in Figure 2.2 that retards the progress of the gas molecules through the matrix resin. The direct benefit of the formation of this type of path is clearly observed in polyimide/LS nanocomposites, which show dramatically improved barrier properties with a simultaneous decrease in thermal expansion coefficient [13,14].

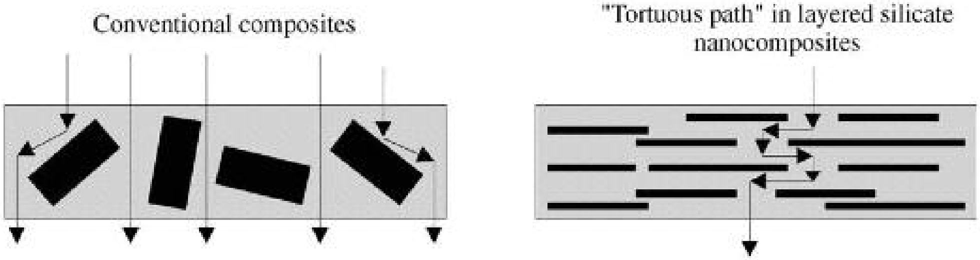


Figure 2.2 : Formation of tortuous path in polymer/clay nanocomposites [6].

Optical transparency studies have also been carried out. For example polyvinyl alcohol (PVA) and PVA/MMT nanocomposites with 4 and 10 wt% MMT. The spectra obtained show that the visible region is not affected at all by the presence of the silicate layers and retains the high transparency of the PVA. For the UV wavelengths, there is strong scattering and/or absorption, resulting in very low transmission of the UV light [15].

2.1.2 Structure of Polymer-Clay Nanocomposites

Depending on the interactions between the clay and the polymer matrix, two main idealized types of polymer–clay morphologies can be obtained, namely, intercalated and exfoliated. In the intercalated nanocomposites, a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers, resulting in a well-ordered multiplayer morphology built up with alternating polymeric and silicate layers. In exfoliated nanocomposites, the silicate layers of MMT are completely separated into individual nanometer thick (about 1 nm) layers and uniformly dispersed in the continuous polymer matrix [16]. There is also a structure which is called flocculated similar with intercalated nanocomposites, however, silicate layers are sometimes flocculated due to hydroxylated edge-edge interaction of the silicate layers, phase separation might be observed in this structure [6], because of this it can not be accepted as a nanocomposite.

Figure 2.3 : Schematic illustrations of two types of polymer-layered silicate morphologies: (left) intercalated and (right) exfoliated [17].

Preliminary studies on nanocomposites have shown that largest improvements in mechanical and physical properties are obtained in exfoliated morphology. Because of this it is important to obtain exfoliated structure when preparing PCN.

2.2 Preparation of Polymer-Clay Nanocomposites

Any physical mixture of a polymer and layered silicate does not form a nanocomposite. This situation is analogous to polymer blends, and in most cases separation into discrete phases normally takes place. In immiscible systems, which typically correspond to the more conventionally filled polymers, the poor physical interaction between the organic and the inorganic components leads to poor mechanical and thermal properties. In contrast, the strong interactions between the polymer and the layered silicate in PLS nanocomposites lead to the organic and inorganic phases being dispersed at the nanometer level. As a result nanocomposites exhibit unique properties not shared by their micro counterparts or conventionally filled polymers. Pristine layered silicates usually contain hydrated Na^+ or K^+ ions. Obviously, in this pristine state layered silicates are only compatible with hydrophilic polymers, such as polyethylene oxide (PEO), polyvinyl alcohol (PVA) etc. To render layered silicates compatible with other polymer matrices, one must convert the normally hydrophilic silicate surface to organophilic, which makes the intercalation of many engineering polymers possible. Generally, this can be done by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkyl ammonium or alkylphosphonium cations. The role of alkylammonium or alkylphosphonium cations in the organosilicates is to lower the surface energy of the inorganic host and to improve the wetting characteristics with the polymer matrix, and results in a larger interlayer spacing. One can evaluate that about 100 alkylammonium salt molecules are localised near the individual silicate layers ($\sim 8 \times 10^{-15}$ m^2) and active surface area (~ 800 m^2/g) [6].

Additionally, the alkylammonium or alkylphosphonium cations could provide functional groups that can react with the polymer matrix or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix [18,19].

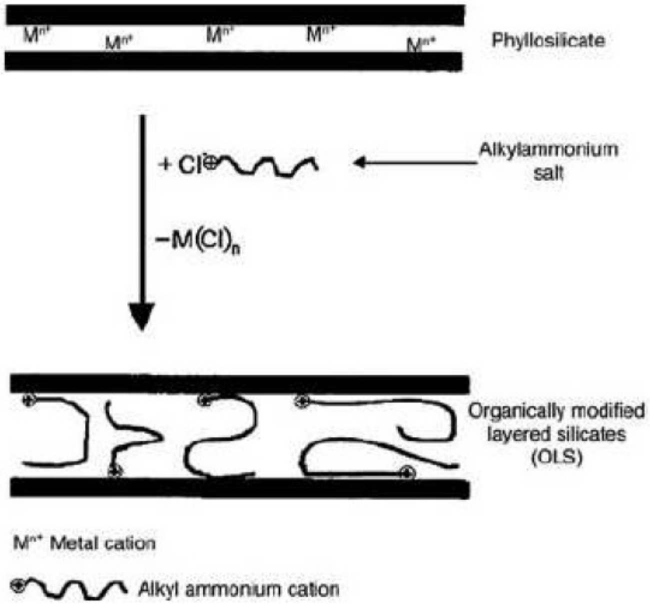


Figure 2.4 : Schematic representation of a cation-exchange reaction between the layered silicate and an alkyl ammonium salt [20].

Intercalation of polymers in layered silicates, has proven to be a successful approach to synthesize polymer/layered silicate nanocomposites. The preparative methods are divided into three main groups according to the starting materials and processing techniques.

2.2.1 Solution Dispersion Method

This is based on a solvent system in which the polymer or pre-polymer is soluble and the silicate layers are swellable. The layered silicate is first swollen in a solvent, such as water, chloroform, or toluene. When the polymer and layered silicate solutions are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in a polymer/layered silicate nanocomposite [6].

2.2.2 Melt-Mixing Method

This method involves annealing-statically or under shear-a mixture of the polymer and organically modified layered silicate above the softening point of the polymer. This method is environmentally benign due to absence of of organic solvents and it allows the use of polymers that were previously not suitable for in-situ polymerization or solution intercalation [6].

2.2.3 In-Situ Polymerization Method

In this method, the organically modified layered silicate is swollen within the liquid monomer or a monomer solution so the polymer formation can occur between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator, or by inorganic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step [6].

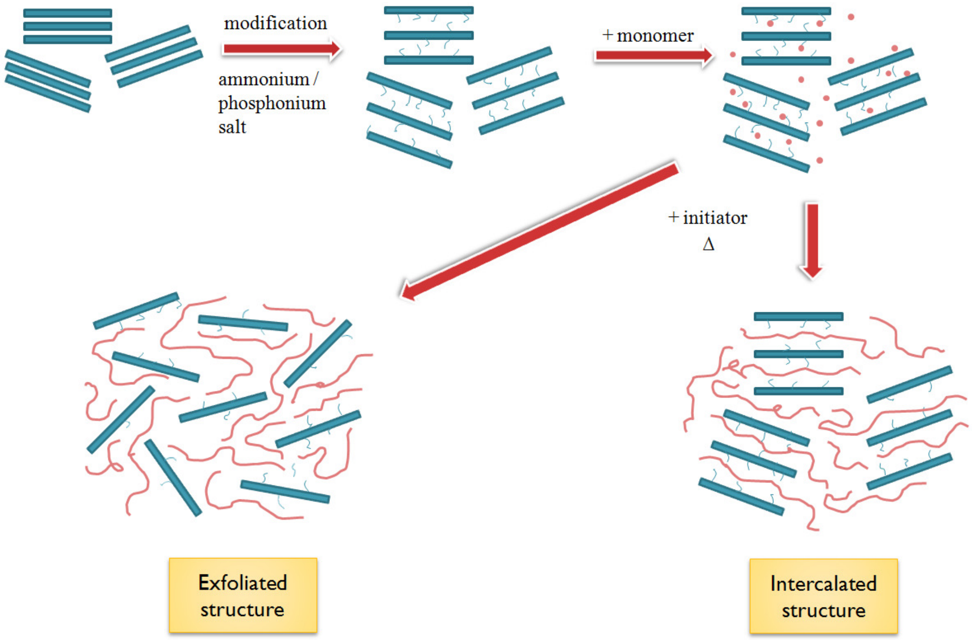


Figure 2.5 : Schematic representation of in-situ polymerization

2.3 Characterization of Polymer-Clay Nanocomposites

Generally, the structure of nanocomposites has typically been established using wide range X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) observation. Due to its easiness and availability, XRD is the most commonly used to probe the nanocomposite structure and occasionally to study the kinetics of the polymer melt intercalation. Other methods to help characterization of polymer-clay nanocomposites may be FT-IR and NMR [12].

By monitoring the position, shape, and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (intercalated or exfoliated) may be identified. For example, in an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers. On the other hand, for intercalated nanocomposites, the finite layer expansion associated with the polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height [21].

The structure of polymer-clay nanocomposites can be interpretated mainly as follows:

- ■ Immiscible (no d-spacing change)
- ■ Decomposed/deintercalated (d-spacing decrease)
- ■ Intercalated (d-spacing increase)
- ■ Exfoliated (d-spacing outside of wide-angle X-ray diffraction, or so expansive and disordered as to give a signal) [22].

The instruments that measure X-ray scattering are divided into more common wide angle and newer small angle X-ray scattering, WAXS ans SAXS, respectively. It is common to consider the scattering angle $2\theta=2^{o}$ as a boundary between these two, but newer WAXS instruments frequently are able to provide reliable scattering profile down to $2\theta=1^{o}$. The interlayer spacing d_{001}, is commonly determined from the XRD spectrum as arbitrary intensity versus 2θ. The spacing is then calculated from the Bragg's law:

$$d_{001} = n\,\lambda / 2\sin\theta \qquad \textbf{(2.1)}$$

where n is an integer, θ is the angle of incidence (or reflection) of the X-ray beam, and λ is the X-ray wavelength – most X-ray machines use Cu-Kα1 radiation with λ=0,1540562 nm.

At limiting low scattering angle $2\theta\cong2^{o}$ the XRD/WAXS scattering intensity and resolution decrease, i.e., the method is not useful for spacing d_{001} > 8,8 nm. Within this range TEM may be used to determine the extent of intercalation/exfoliation [21]. On the other hand, TEM allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and defect structure through direct visualization. However, special care must be exercised to guarantee a representative crosssection of the sample [6]. TEM also offers a direct method for confirming the XRD data and with growing frequency it is being used at low magnification to check on the uniformity (or lack) of clay stack dispersion in polymeric matrix. The low magnifications are also useful to check the purity of clay, e.g., the presence of non-layered particles such as quartz [12]. However, TEM is time-intensive, and only gives qualitative information on the sample as a whole, while low-angle peaks in XRD allow quantification of changes in interlayer spacing.

FT-IR initially has been used in studies of the polymer matrix morphology, e.g., conformation and crystallization behavior of polymers. Studies have shown that in hydrated MMT $\upsilon_{Si\text{-}O}$ exponentially decreases with the clay-to-water ratio, all the way to exfoliation. Oxidation or reduction of the metallic ions within the octahedral clay layers introduces changes to CEC clay hydration and swellability, hence the FT-IR spectrum. However, the Si-O stretching vibration has been found to be very sensitive to long range interactions caused either by imposed stress, or expansion of the interlayer spacing. The advantage of spectroscopic methods, FT-IR and Raman, is that along with XRD they are applicable to the intercalated system, and stretch to exfoliated polymeric nanocomposites that do not scatter X-rays [21].

Nuclear Magnetic Resonance Spectroscopy (NMR) is also used to quantitatively determine the degree of clay dispersion [12]. Solid-state NMR has been used as a tool for gaining greater insight about the morphology, surface chemistry, and to a very limited extent, the dynamics of exfoliated polymer clay nanocomposites [23].

Diverse calorimetric methods have also been used. For example a differential scanning calorimetry (DSC)/ dynamic thermal analysis (DTA) method was used to characterize the layered material, e.g. to study clay hydration. Thermogravimetric analysis (TGA) has been used for examining interlayer packing density.[21]

2.4 Polystyrene

Polystyrene (PS), the parent of the styrene plastics family, is a high molecular weight, linear polymer. Its chemical formula $[\ CH(C_6H_5)CH_2\ ]_n$, where n (which for commercial uses) is between 800 and 1400, tells little of its properties. The main commercial form of PS (atactic PS) is amorphous and hence possesses high transparency. The polymer chain stiffening effect of the pendant phenyl groups raises the glass-transition temperature (Tg) to slightly over 100^oC. Therefore, under ambient conditions, the polymer is a clear glass, whereas above the Tg it becomes a viscous liquid which can be easily fabricated, with only slight degradation, by extrusion or injection-molding techniques. It is this ease with which PS can be converted into useful articles that accounts for the very high volume (>20 billion pounds per year) used in world commerce. Even though crude oil is the source of the polymer, the energy savings and environmental impact accrued during fabrication and use, compared to alternative materials, more than offsets the short life of many PS articles [24].

Ostromislensky of the Naugatuck Chemical Company first introduced polystyrene via a pioneering parent in 1925. At about the same time, work by I.C. Farbenindustrie began that resulted in the commercialization of polystyrene in Europe. The Dow Chemical Company also began development of the polystyrene product and process in 1930.

The commercial production of polystyrene first took place at about the same time in Germany and the US during the early 1930's; it was manufactured primarily for its good electrical properties. The polymer was produced in the UK at about the time of the beginning of the Second World War, when it was used not only as an electrical insulant but also as a glass replacement in optical instruments after lenses and prisms were no longer available from Germany.

Polystyrene is used in applications in the following major markets which is listed in order of consumption: packaging, consumer/institutional goods, electrical/electronic goods, building/construction, furniture, industrial/machinery, and transportation.

Packaging applications using 100% amorphous but named as 'crystal polystyrene' biaxial film include meat and vegetable trays, blister packs, and other packaging where transparency is required. Extruded polystyrene foam sheets are formed into egg carton containers, meat and poultry trays, and fast food containers requiring hot or cold insulation. Solid polystyrene sheets are formed into drinking cups and lids, and disposable packaging of edibles. Injection molded grades of polystyrene are used extensively in the manufacture of cosmetic and personal care containers, jewelry and photo equipment boxes, and photo film packages. Other formed polystyrene items include refrigerator door liners, audio and video cassettes, toys, flower pots, picture frames, kitchen utensils, television and radio cabinets, home smoke detectors, computer housings, and profile moldings in the construction/home-building industry.

Polystyrene has many advantages, which include:

- Lightweight**:** reduces transport fuel consumption and the cost of distributing products.
- Performance: provides insulation and protection from contamination and impact.
- Economy**:** usually less expensive than alternative materials resulting in savings to the consumer.
- Energy Savings**:** polystyrene manufacture requires less energy than alternatives resulting in lower "greenhouse" emissions. As insulation, polystyrene foam enable enormous energy savings in commercial installations such as cool stores.

The annual consumption of polystyrene in US comprises of 8% of the total plastics used in the United States, making it one of the most often used types of polymers [25].

2.4.1 Types of Polystyrene

General Purpose Polystyrene (GPPS) is a high molecular weight ($M_w = 2–3 \times 10^5$), crystal-clear thermoplastic that is hard, rigid, and free of odor and taste. Its ease of heat fabrication, thermal stability, low specific gravity, and low cost results in moldings, extrusions, and films of very low unit cost. In addition, PS materials have excellent thermal and electrical properties, which make them useful as low cost insulating materials. Commercial PS's are normally rather pure polymers. When additional lubricants, eg, mineral oil and butyl stearate, are added to PS, easy-flow materials are produced. Improved flow is usually achieved at the cost of lowering the heat-deformation temperature [24].

In 1954 Styrofoam, the trademarked form of Polystyrene foam insulation, was invented. Expanded polystyrene (EPS) is made from expandable polystyrene, which is a rigid cellular plastic containing an expansion agent. EPS is obtained from oil and the raw material for EPS is produced in the form of small polystyrene beads containing a blowing agent, or pentane, which when exposed to steam, expand to form a light weight "pre-foam" of required density. This pre-foam is then processed by further steam treatment until the beads fuse together, either in a mould to give that material a required shape and size or as large blocks for cutting into sheets and shapes [26].

Rubber is incorporated into PS primarily to impart toughness. The resulting materials are commonly called high impact PS (HIPS) and are available in many different varieties. In standard HIPS resins, the rubber is dispersed in the PS matrix in the form of discrete particles. The mechanism of rubber-particle formation and rubber reinforcement and several general reviews of HIPS and other heterogeneous polymers have been published [24].

Acrylonitrile, butadiene, α-methylstyrene, acrylic acid, and maleic anhydride have been copolymerized with styrene to yield commercially significant copolymers. Acrylonitrile copolymer with styrene (SAN) is the largest volume styrenic copolymer and is used in applications requiring increased strength and chemical resistance over PS. Most of these polymers have been prepared at the crossover or azeotrope composition, which is ca 24 wt% acrylonitrile. Copolymers with over 30 wt% acrylonitrile are available and have good barrier properties. If the acrylonitrile content of the copolymer is increased to >40 wt%, the copolymer becomes ductile. SAN copolymers constitute the rigid matrix phase of the ABS engineering plastics. Unlike PS homopolymers, SAN copolymers turn yellow upon heating [24]. The extent of discoloration is proportional to the percentage of acrylonitrile in the copolymer [27].

Acrylonitrile–Butadiene–Styrene (ABS) polymers have become important commercial products since the mid-1950s. ABS polymers, like HIPS, are two-phase systems in which the elastomer component is dispersed in the rigid SAN copolymer matrix [28]. Generally, they are rigid [modulus at room temperature, and have excellent notched impact strength at room temperature and at lower temperatures, eg, at −40°C This combination of stiffness, impact strength, and solvent resistance makes ABS polymers particularly suitable for demanding applications.

Styrene–butadiene copolymers are mainly prepared to yield rubbers. Many commercially significant latex paints are based on styrene–butadiene (weight ratio usually 60:40 with high conversion) copolymers. Diblock (styrene–butadiene) and triblock (styrene–butadiene–styrene) copolymers are commercially available [24]. Typically, they are blended with PS to achieve a desirable property, eg, improved clarity/flexibility [29]. These block copolymers represent a class of new and interesting polymeric materials. Of particular interest are their morphologies, solution properties, and mechanical behavior.

Maleic anhydride readily copolymerizes with styrene to form an alternating structure. Accordingly, equimolar copolymers are normally produced, corresponding to 48 wt% maleic anhydride. However, by means of CSTR processes, copolymers with random low maleic anhydride contents can be produced [30]. Depending on their molecular weights, these can be used as chemically reactive resins, eg, epoxy systems and coating resins, for PS-foam nucleation, or as high heat-deformation molding materials [31].

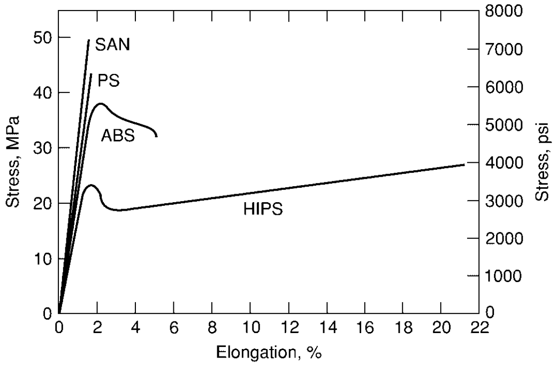


Figure 2.6 : Comparison of tensile properties of styrene and its copolymers [24].

There also exists some specialty polystyrenes prepared depending on the desired material properties like ionomers, tactic, hydrogenated and branched polystyrenes.

Polystyrene ionomers are typically prepared by copolymerizing styrene with an acid functional monomer (eg, acrylic acid) or by sulfonation of PS followed by neutralization of the pendant acid groups with monovalent or divalent alkali metals. The introduction of ionic groups into PS leads to significant modification of both solid state and melt properties. The introduction of ionic interactions in PS leads to increasing Tg, rubbery modulus, and melt viscosity [24]. For the sodium salt of sulfonated PS, it has been shown that the mode of deformation changes from crazing to shear deformation as the ion content increases [32, 33].

Isotactic (iPS) and syndiotactic (sPS) PSs can be obtained by the polymerization of styrene with stereospecific catalysts of the Ziegler– Natta-type. Aluminum-activated $TiCl_3$ yields iPS while soluble Ti complexes [eg, $(\eta_5\text{-}C_5H_5)TiCl_3$] in combination with a partially hydrolyzed alkylaluminum [eg, methylalumoxane] yield sPS. The discovery of the sPS catalyst system was first reported in 1986 [34]. As a result of the regular tactic structure, both iPS (phenyl groups cis) and sPS (phenyl groups alternating trans) are highly crystalline. Samples of iPS quenched from the melt are amorphous, but become crystalline if annealed for some time at a temperature slightly below the crystalline melting point. The rate of crystallization is relatively slow compared to sPS and with other crystallizable polymers, eg, polyethylene or polypropylene. This slow rate of crystallization is what has kept iPS from becoming a commercially important polymer even though it has been known for over 40 years. sPS, on the other hand, crystallizes rapidly from the melt and is currently in the process of being developed for commercial use in Japan by Idemitsu Petrochemical Co. and in the United States and Europe by The Dow Chemical Co. [24]. Crystalline iPS has a melting temperature of around 240°C, while sPS melts at about 270°C [35]. In the crystalline state, both iPS and sPS are opaque and are insoluble in most common organic solvents.

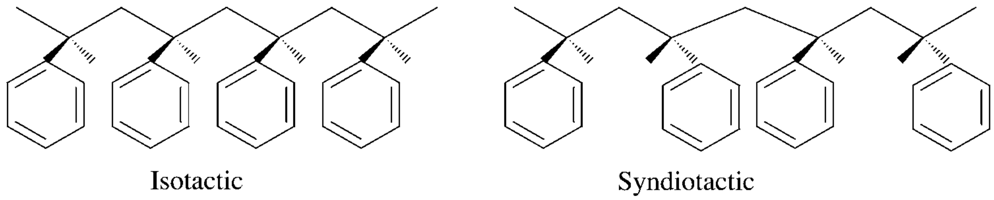


Figure 2.7 : Structure of tactic polystyrenes [24]

Dow researchers have successfully developed a new hydrogenation catalyst that allows complete hydrogenation of the phenyl rings on PS without degrading the molecular weight of the polymer [36]. Complete hydrogenation of the phenyl rings of PS increases the glass-transition temperature (Tg) to 140°C [37]. Because of the hydrophobicity and low birefringence of the saturated polymer, it is well suited for use in optical media applications. Dow is planning to commercialize hydrogenated PS for use as a substrate for DVD discs.

Chain branching in some polymers is known to improve certain properties and is practiced commercially (eg, polyethylene and polycarbonate). In PS, many types of branch structures have been synthesized and the effect of branch structure on properties studied. Some of the branch structures possible in PS are shown in Figure 2.8. Most of the recent studies of branched PS have focused on new synthetic methodologies and on rheological properties [24].

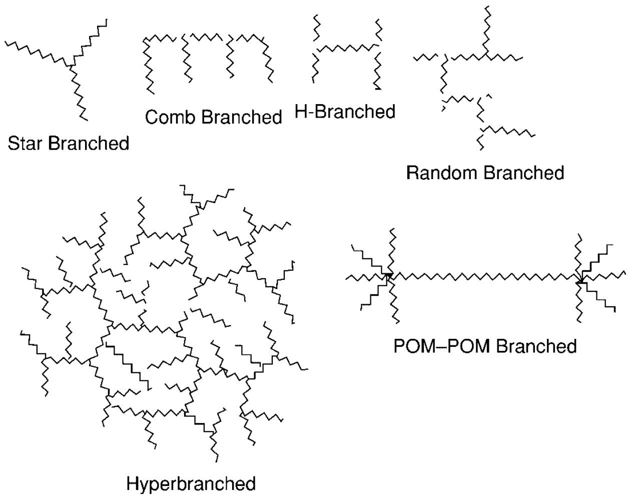


Figure 2.8 : Several possible PS branch architectures [24].

2.4.2 Polymerization of Styrene

Polystyrene is one of the few polymers that can be prepared by radical, ionic and stereospecific polymerization [38-40]. This is because of the unusually resonance stability of the polystyrl radical in the transition state which decreases the activation energy of the propagation reaction and also because of the low polarity of the styrene molecule, which permits reaction with radicals, addition of ions with the opposite charge and also reaction with metal complexes.

Free radical polymerization of styrene has the greatest industrial importance and can be carried out in homogeneous or in heterogeneous systems. Homogeneous system consists of bulk and solution polymerization. Heterogeneous systems can be emulsion and suspension polymerizations. A homogeneous system can be converted to a heterogeneous system during polymerization if the polymer formed is insoluble in the reaction medium.

The kinetics and the mechanism of the cationic polymerization of styrene have not been yet completely elucidated because of the very high reaction rates. Very low temperatures must be employed and there is a difficulty in removing the heat of reaction from the system. The initiators are usually Lewis acids or Friedel-Crafts catalysts [38]. Except the preparation of styrene oligomers and low-molecular-weight polystyrene [41], cationic polymerization has no practical technical importance [38].

In anionic polymerization, the growing polymer chain has the character of a carbanion, it is negatively charged. Typical catalysts of anionic polymerization include the alkali metals and organometals, such as butyllithium. Various mechanisms can pre-dominate, depending on the solvent polarity; the polymerization rate is strongly affected by an increase in the solvent polarity [42]. In nonpolar solvents, the growth sites in the polymer chain consist of associates and polymerization thus proceeds more slowly. Compared to radical polymerization, the molecular weight distribution in the polymer obtained by anionic polymerization is usually narrower [43]. For example, a polydispersity of less than 1.2 was obtained for the lithium-initiated polymerization of styrene [44]. If the polymer chain (macroanion) is not terminated by the addition of a proton-active substance after consumption of monomer in the polymerization system, it remains active (hence the term “living” polymer) and can react with further monomer.

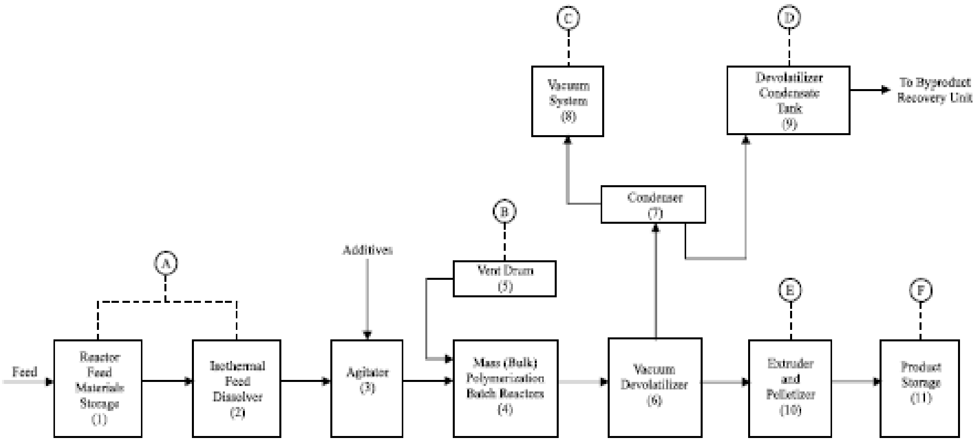


Figure 2.9 : Simplified flow diagram of a batch polystyrene process. [45]

2.5 Polystyrene-Clay Nanocomposites

Polymerization of vinyl monomers intercalating into the montmorillonite (MMT) clay was first reported in the literature as early as 1961 [46]. The most recent methods to prepare polymer-layered-silicate nanocomposites have primarily been developed by several other groups. In general these methods are able to achieve molecular-level incorporation of the layered silicate (e.g. montmorillonite clay or synthetic layered silicate) in the polymer matrix by addition of a modified silicate either to a polymerization reaction (in situ method), to a solvent-swollen polymer (solution blending), or to a polymer melt (melt blending). Recently, methods have been developed to prepare the layered silicate by polymerizing silicate precursors in the presence of a polymer.

2.5.1 Preparative Methods for Polystyrene-Clay Nanocomposites

Several attempts to prepare polystyrene-clay composites have been reported. A common technique involves impregnating clay in styrene monomer followed by polymerization which is the in-situ polymerization [2]. The hydrophilic nature of untreated clay impedes its homogeneous dispersion in polymer matrix. Friedlander and Grink [47] reported a slight expansion of the 001 spacing of clay galleries and concluded that polystyrene was intercalated in clay galleries; but Blumstein questioned intercalation by polystyrene because no increase in the basal spacing could be detected [18]. Later Kato et al. reported the intercalation of styrene into stearyl-trimethyl-ammonium cation exchanged MMT [48]. Kelly et al. reported the modification of MMT by a variety of functional groups in their study of epoxy composites [49]. Giannelis and Vaia et al. developed a new approach to fabricate polymer-clay nanocomposites via polymer melt intercalation. Polystyrene-clay intercalated nanocomposites were prepared using this method [5],[9].

Akelah and Moet have used the in situ intercalative polymerization technique for the preparation of PS/LS nanocomposites. They modified Na^+-MMT and Ca^{+2}-MMT with vinylbenzyltrimethyl ammonium cation by the ion exchange reaction and these modified MMTs were used for the preparation of nanocomposites. They first disperse and swell modified clays in various solvent and co-solvent mixtures such as acetonitrile, acetonitrile/toluene and acetonitrile/THF (tetrahydrofuran) by stirring for 1 hour under N_2 atmosphere. To the stirred solution, styrene and N,N'-azobisisobutyronitrile (AIBN) were added, and polymerization of styrene was carried at 80°C for 5 hours. The resulting composites were isolated by precipitation of the colloidal suspension in methanol, filtered off and dried. In this way, intercalated PS/MMT nanocomposites were produced and the extent of intercalation completely depends upon the nature of the solvent used. Although, the PS is well intercalated, a drawback of this procedure remains that the macromolecule produced is not a pure PS but rather a copolymer between styrene and vinylbenzyltrimethylammonium cations. Polystyrene-clay intercalated nanocomposites with a maximum basal spacing of 2.45 nm were reported. [50].

Zhu and co-workers reported the preparation of three new organically modified clays and their corresponding preparation of PS/clay nanocomposites from these clays by bulk polymerization. Two are functionalized ammonium salts while the third is a phosphonium salt and structures of these salts are shown in Fig 2.10. TGA/FT-IR showed that the phosphonium treatment results in the most thermally stable treatment when compared to the two ammonium salts [51].

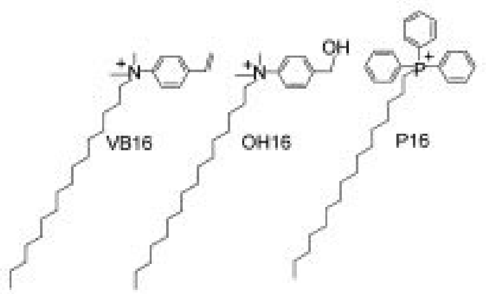


Figure 2.10 : Structures of the salts used to prepare the organically modified clays[51].

Wang used two different organic modifications of the montmorillonite, one contains a styryl monomer on the ammonium ion while the other contains no double bond. A double bond that may be involved in the polymerization reaction is present in the cation of the clay. Polystyrene-clay nanocomposite has been prepared by bulk, solution, suspension, and emulsion polymerization as well as by melt blending. The organic modification as well as the mode of preparation may determine whether the composite is either exfoliated or intercalated. Exfoliation is more likely to occur if the ammonium ion contains a double bond which can participate in the polymerization reaction. However, the mere presence of this double bond is not sufficient to always produce an exfoliated system [52].

Hwang et al. indicated when styrene monomer penetrates the organoclay interlayer and polymerizes, a substantial increase in the interlayer distance occurs because the organoclay structures contain a benzyl group similar to styrene [17].

Fu and Qutubuddin reported the synthesis of exfoliated polystyrene-clay nanocomposite. Vinylbenzyldimethyldodecyl-ammonium chloride (VDAC) a cationic surfactant with a polymerizable group was synthesized for the preparation of exfoliated polystyrene–clay nanocomposites. This surfactant copolymerizes with styrene. VDAC functionalized MMT has strong swelling ability and forms a viscous gel in styrene. The gels exhibit yield stress and shear thinning behavior. Exfoliated polystyrene nanocomposites were successfully synthesized by bulk polymerization PS–VDAC–MMT nanocomposites show a higher thermal degradation temperature than pure polystyrene. The nanocomposites exhibit a higher dynamic modulus with increased loading of VDAC–MMT in polystyrene [53].

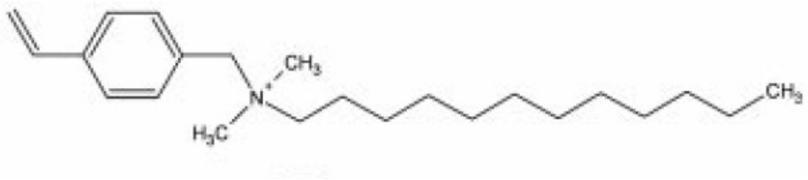


Figure 2.11 : Structure of VDAC used to prepare the organically modified clay.

A mechanism is suggested by Wilkie et al. to prepare exfoliated PNC with PS as the matrix. The COPS is a product of clay intercalation with a copolymer of styrene and vinylbenzyl trimethyl ammonium chloride (VBTACl). The preparation involved two steps: 1) the free radical copolymerization of styrene with vinyl-ammonium compound, followed by 2) Na-MMT intercalation.

However attempts were unsuccessful and two-phase structure was obtained. The reason is explained as the statistics of random copolymerization indicate that a significant proportion of copolymer molecules would have two ammonium groups, which cause bridging the gap between adjacent clay platelets where the bridging creates a clay/oligostyrene network that is immiscible with PS [54].

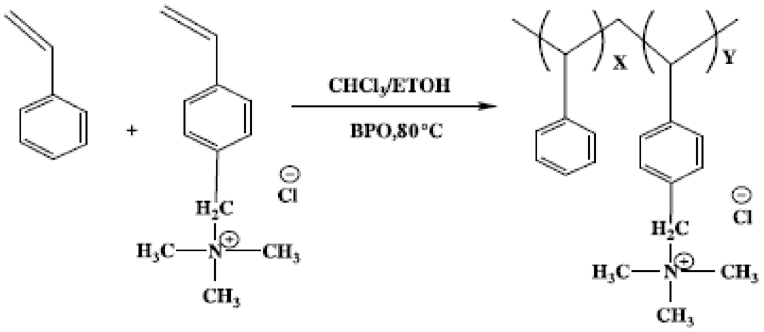


Figure 2.12 : Synthesis of VBTACl COPS salt [54]

Later on in another study, Wilkie et al. suggested using COPS with various copolymers of polystyrene. Two new organically-modified clays were synthesized and used to produce nanocomposites of polystyrene, high impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene terpolymer (ABS). At a minimum, intercalated nanocomposites of all of these polymers have been produced by melt blending and, in some cases, exfoliated nanocomposites have been obtained.

It is expressed as all melt compounding attempts of PS with commercial organoclays with or without compatibilizer failed to result in exfoliation. The only exfoliated PNC were produced using a reactive process, viz. by intercalating clay with vinyl terminated ammonium ions and then initiating polymerization of styrene or by introducing terminal ammonium group to an anionically polymerized PS, and then using it as a macrointercalant [55].

Vinylbenzyldimethylethanolammonium chloride (VBDEAC), a cationic surfactant with a polymerizable group, was synthesized by Tseng et al. for the preparation of exfoliated polystyrene–clay nanocomposites. The PS nanocomposite containing clay–VBDEAC/CPC (cetylpyridinium chloride): 5/5 significantly promotes higher flexural modulus, flexural strength, and impact strength than the pristine PS. This result further confirms that the better dispersibility and increased interfacial adhesion of the clay with PS matrix are responsible for mechanical property improvements [56]. Mechanism is given as Figure 2.13 and Figure 2.14.

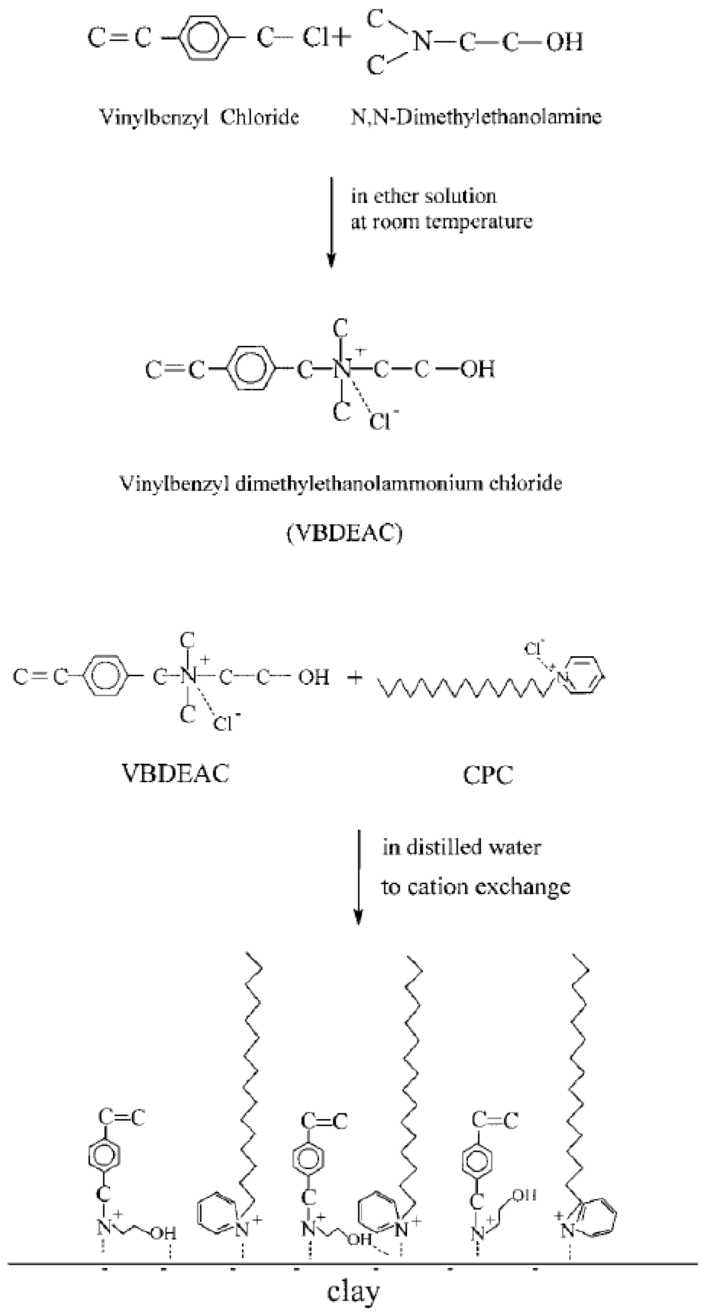


Figure 2.13 : Synthesis of VBDEAC and the structure of organically modified clay with VBDEAC/CPC= 5/5 by cation exchange capacity [56]

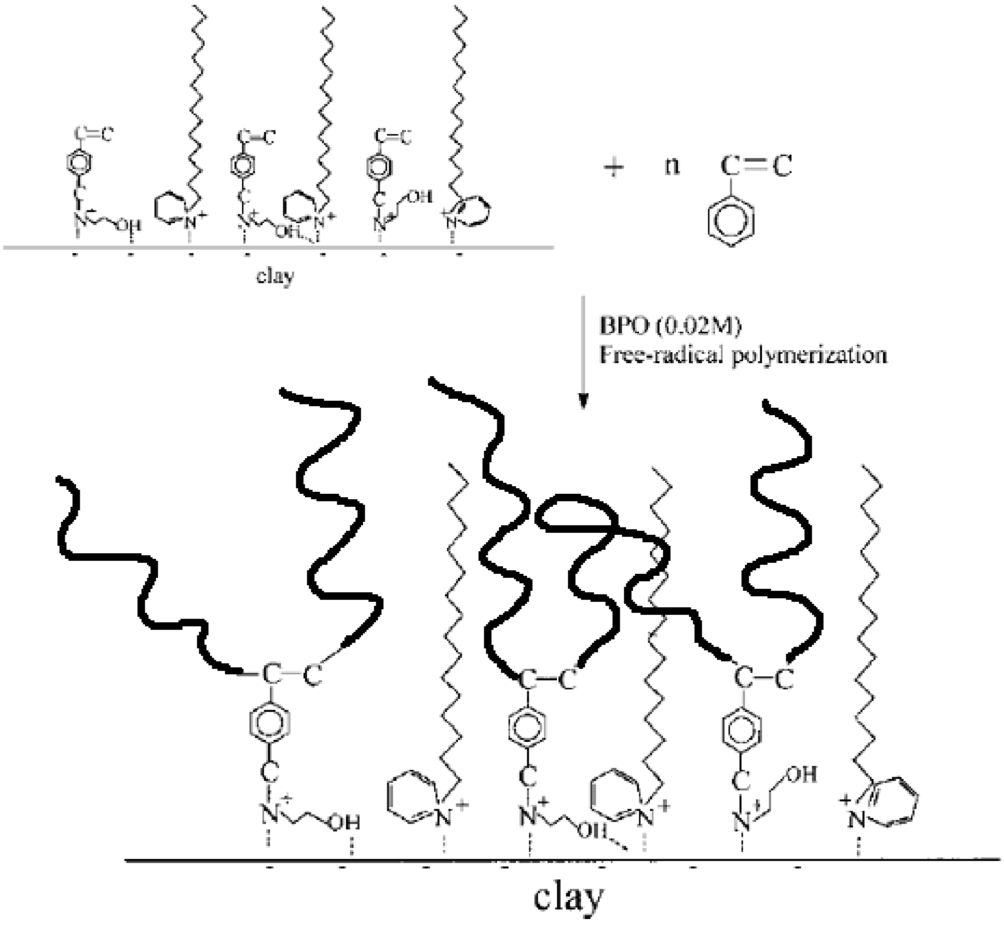


Figure 2.14 : Free radical polymerization of styrene in the presence of clay-[VBDEAC/CPC] intercalate to yield PS/clay nanocomposite [56]

Rather than modifying the clay with organic quaternized ammonium salts, cationically modified polymerization initiators can also be used to prepare organophilic clays. In this method, the in-situ polymerization is initiated by the activation of these initiators which are ionically bound to the clay particle surfaces, that is, through a surface-initiated polymerization (SIP) process. The advantage of SIP is based on the assumption that as the polymer chain grows through surface initiation, the ordered silicate layers can be gradually pushed apart, ultimately exfoliating to discrete laths, resulting in a well-dispersed structure of the final product [2].

An example for this kind of polymerization, Uthirakumar proposed synthesis of PS nanocomposite via in situ intercalative polymerization, using ABTBA-MMT synthesized from 2,2-azobis[2-methyl-N-(2-hydroxyethyl)-propionamide], via esterification with bromoacetyl bromide, and the subsequent quaternization with tributylamine which is a new cationic radical initiator-MMT hybrid clay as shown in Figure 2.15. Good exfoliation and dispersion of the silicate layers were observed in the nanocomposites due to the efficient intra-gallery polymerization [3].

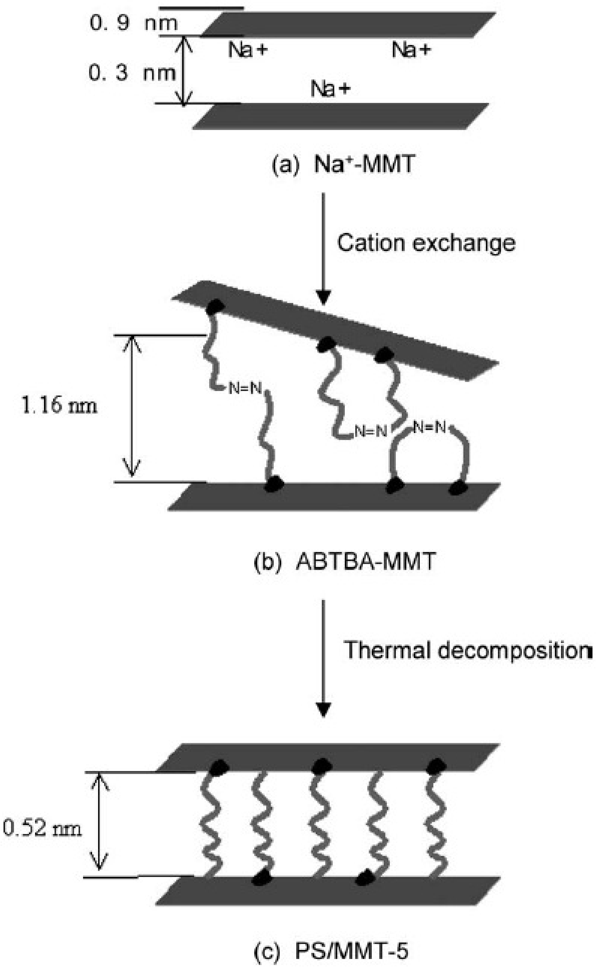


Figure 2.15 : Schematics of the interlayer distances of (a) Na^+MMT (b) ABTBA-MMT and (c) PS/MMT-5 [3]

The compatibility of the initiator and monomer with the clay surface was found to profoundly affect the clay dispersion. By using a surfactant containing a polymerizable group which is a reactive cationic surfactant MHAB (2-methacryloyloxyethylhexadecyldimethylammonium bromide) to modify the clay surface, exfoliated PS/clay nanocomposites were synthesized with a clay concentration of 5 wt % by Zeng et al. As shown in Figure 2.16. It is mentioned as the presence of clay substantially improved the dimension stability [57].

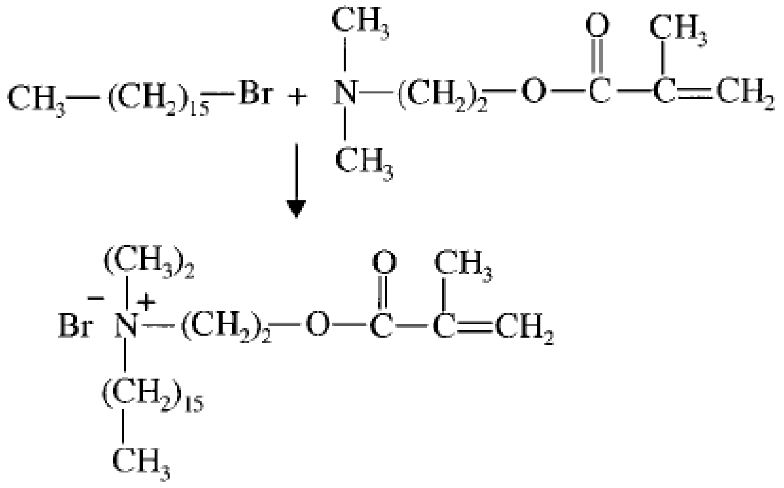


Figure 2.16 : Synthesis of MHAB [57]

Chang and co-workers reported the preparation of two types of nanocomposites formed from CPC and aminopropyl-isobutyl polyhedral oligomeric silsesquioxane (POSS)-treated clays as shown in Figure 2.17 [58].

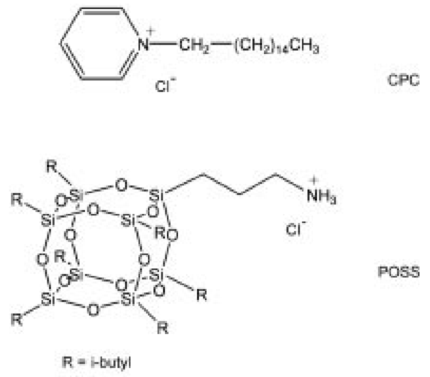


Figure 2.17 : Chemical structures of the surfactants used to prepare the modified clays [58].

The PS/clay nanocomposite formed using the CPC-treated clay exhibited no significant improvement in thermal properties [56],[59-62]. The major advantage of choosing POSS molecules is its thermal stability up to 300°C, higher than the thermal degradation temperatures of most organic molecules. POSS consists of a rigid cubic silica core with 0.53 nm side length, to which organic functional groups can be attached at the vertices for further reactions. POSS derivatives containing amine functional groups can play the role of surfactants for the treatment of clay and the thermal stability of the resulting nanocomposite is enhanced [63].

In addition, Yei and co-workers also reported the preparation of two types of PS/clay nanocomposites formed from clays treated with either CPC or the CPC/α-CD inclusion complex. Structures of these two intercalation agents were shown in Figure 2.18. It is found that CPC, a linear aliphatic surfactant, is able to form a crystalline complex with cyclodextrin (CD). Including CPC within CD channels improves the thermal stability of the virgin CPC. The linear aliphatic chain within the CPC/α-CD cannot bend within the galleries of the clay and the d-spacing of clay intercalated by the CPC/α-CD inclusion complex is significantly higher than that formed using pure CPC. The CPC/α-CD inclusion complex can promote exfoliated structure of clay [64].

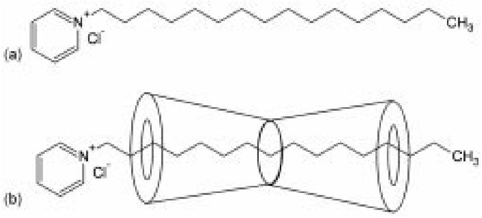


Figure 2.18 : The structures of intercalation agent (a) CPC and (b) CPC/α-CD inclusion complex [64].

Doh and Cho prepared PS/Bz-MMT dimethyl hydrogenated tallow alkyl benzyl ammonium MMT containing benzyl-unit similar to styrene in org-MMT, exhibited higher decomposition temperature even for MMT loading as low as 0.3wt% compared with other PS/org-MMT hybrids. They found that the structural affinity between styrene monomer and the surfactant of modified MMT plays an important role in the final structure and the properties of nanocomposites [65]. This concept was nicely employed by Weimer and co-workers for the preparation of PS/MMT nanocomposites. They modified Na^+MMT by anchoring an ammonium cation bearing a nitroxide moiety known for its ability to mediate the controlled/'living' free radical polymerization of styrene in bulk. The absence of WAXD peaks in the low angle area together with the TEM observations of silicate layers randomly dispersed within the PS matrix attest for the complete exfoliation of the layered silicate [66].

Akelah et al. proposed preparation of a different series of new polystyrene–clay nanocomposites by grafting polymerization of styrene with vinyl-MMT clay. The synthesis was achieved through two steps. The first step is the modification of clay with the vinyl monomers, such as N,N-dimethyl-n-octadecyl-4-vinylbenzyl-ammonium chloride, n-octadecyl-4-vinylbenzyl-ammonium chloride, triphenyl-4-vinylbenzyl-phosphonium chloride, and tri-n-butyl-4-vinylbenzyl-phosphonium chloride. The second step is the polymerization of styrene with different ratios of vinyl-MMT clay as ahown in Figure 2.19. Obtained nanocomposites were fully exfoliated, with high thermal stability and they were exfoliated at up to a 25 wt % of organoclay content [67].

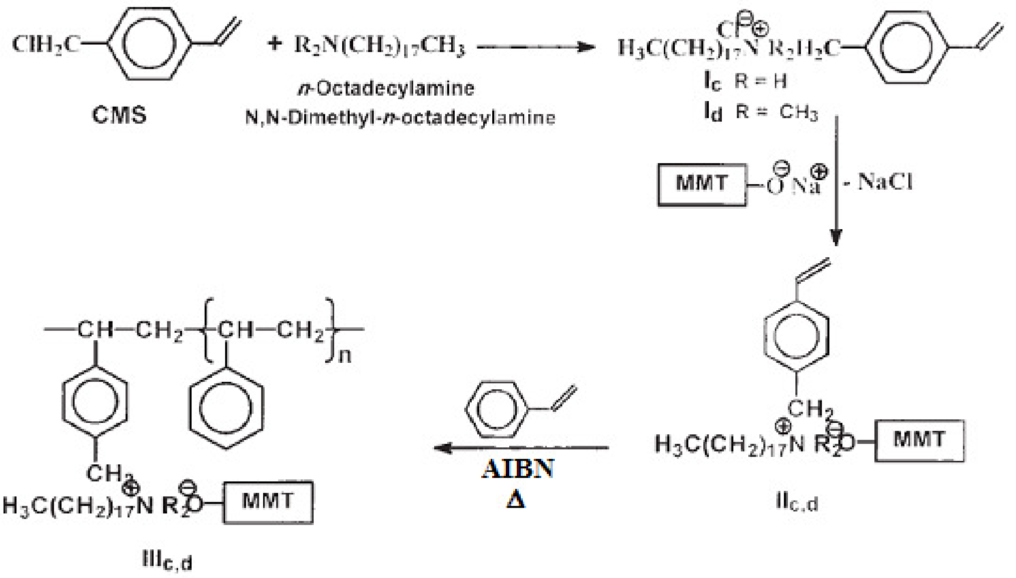


Figure 2.19 : Preparation of n-octadecyl and N,N-dimethyl-n-octadecyl (4-vinylbenzyl) ammonium salt-clay and its polymerization with styrene [67].

2.5.2 Improved Properties of Polystyrene-Clay Nanocomposites

2.5.2.1 Dimensional stability

Dimensional stability is critical in many applications. For example, if the layers of a microelectronic chip have different thermal or environmental dimensional stabilities, then residual stresses can develop and cause premature failure. Poor dimensional stability can also cause warping or other changes in shape that affect the function of a material. Nanocomposites provide methods for improving both thermal and environmental dimensional stability. The possible mechanism by which nanofillers can affect the coefficient of thermal expansion (CTE) of a polymer has also been observed in traditional fillers. The dimension stability of nanocomposites was studied by Zeng and Lee [57]. Figure 2.20 shows the shape changes of injection molded PS and PS/clay nanocomposites under the aforementioned thermal cycle (50^{o}C, 1 h; 75^{o}C, 1 h; 105^{o}C, 1 h; and 135^{o}C, 1 h). The original sample shape is shown in the first row.

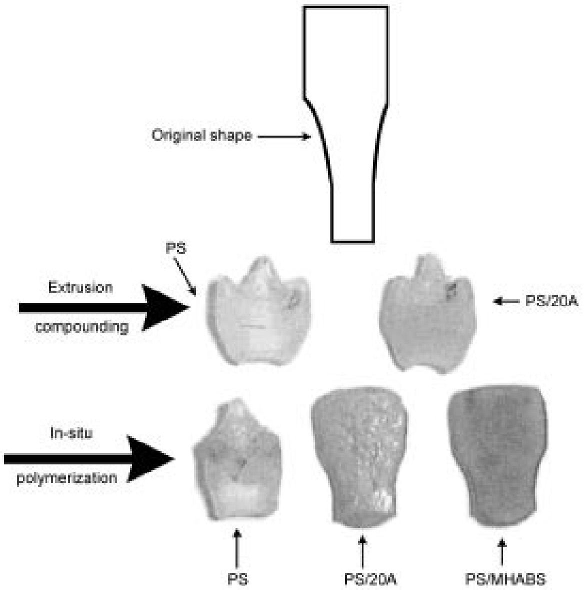


Figure 2.20 : PS and PS/clay nanocomposites after dimension stability test. Clay loading is 5 wt.% for all nanocomposites [57].

Pure PS and the extruded PS/20A (dimethyl dehydrogenated tallow ammonium montmorillonite) nanocomposite are shown in the second row for comparison. The third row shows the in-situ polymerized pure PS, PS/20A, and PS/MHAB (2-methacryloyloxyethylhexadecyldimethylammonium bromide) nanocomposites. All the nanocomposites contain 5 wt.% clay. In the absence of clay, the sample shrank greatly, and the shape became highly irregular. Dimension stability at elevated temperature was improved significantly when 5 wt.% of clay was present in the in-situ polymerized nanocomposites, as shown in the third row. The exfoliate PS/MHAB exhibited the best dimensional stability. After the heating cycle, although the sample shrank to a certain extent, the original shape and surface smoothness remained. It is noteworthy that the PS/20A nanocomposite prepared by extrusion compounding did not show much improvement in dimension stability at elevated temperature, as compared to the in-situ polymerized PS/20A nanocomposite with the same clay content [57].

2.5.2.2. Thermal stability and flammability

Delaminated composites have significantly higher degradation temperatures than intercalated nanocomposites or traditional clay composites [68]. Some speculate that this increase in stability is due to the improved barrier properties of the composites. If oxygen cannot penetrate, then it cannot cause oxidation of the resin [69]. In addition, the inorganic phase can act as a radical sink to prevent polymer chains from decomposing. The improved thermal stability of some composites may be limited by the lower thermal stability of alkylammonium ions. For example, in intercalated clay/polystyrene composites, the intercalating agent decomposes at about 250^{o}C. Bonding the intercalating ion to the polystyrene matrix noticeably improved the thermal stability. Zhu and coworkers investigated thermal property of polymer-clay nanocomposites by TGA and cone calorimetry [51]. The thermal stability of the nanocomposite is enhanced relative to that of virgin polystyrene and this is shown in Figure 2.21. Typically, the onset temperature of the degradation is about 50^{o}C higher for the nanocomposites than for virgin polystyrene. One invariably finds that nanocomposites have a much lower peak heat release rate (PHRR) than the virgin polymer. The peak heat release rate for polystyrene and the three nanocomposites are also shown graphically in Figure 2.22. P16-3 means that the nanocomposite was formed using 3% of P16 clay with polystyrene. The peak heat release rate falls as the amount of clay was increased. The suggested mechanism by which clay nanocomposites function involves the formation of a char that serves as a barrier to both mass and energy transport [70]. It is reasonable that as the fraction of clay increases, the amount of char that can be formed increases and the rate at which heat is released is decreased.

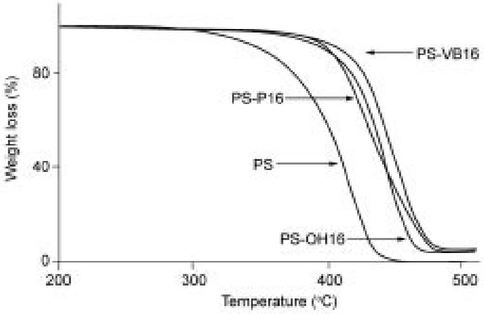


Figure 2.21 : TGA cures for polystyrene, and the nanocomposites[51].

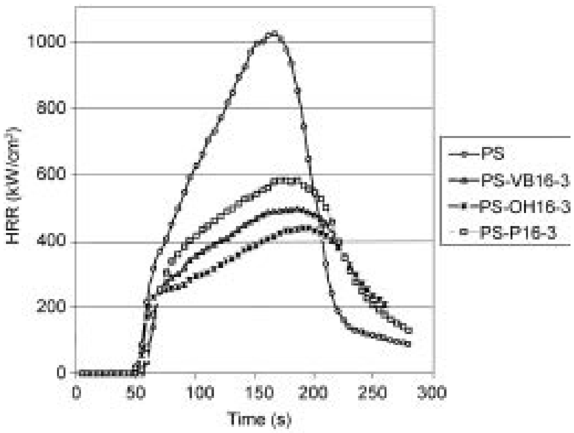


Figure 2.22 : Peak heat release rates for polystyrene and the three nanocomposites[51].

There has been a suggestion that an intercalated material is more effective than is an exfoliated material in fire retardancy [76]. The production of a char barrier must serve to retain some of the polymer and thus both the energy released and the mass loss rate decrease. The amount of smoke evolved, and specific extinction area, also decreases with the formation of the nanocomposite. There is some variability in the smoke production but apparently the formation of the nanocomposite gives a reduction in smoke; however, the presence of additional clay does not decrease smoke [51].

2.5.2.3 Mechanical properties

The cyclic deformation of PS/MMT nanocomposites as a function of temperature was measured by DMA. The temperature dependence of storage modulus and tan δ are shown in Figure 2.23 and Figure 2.24, respectively [2].

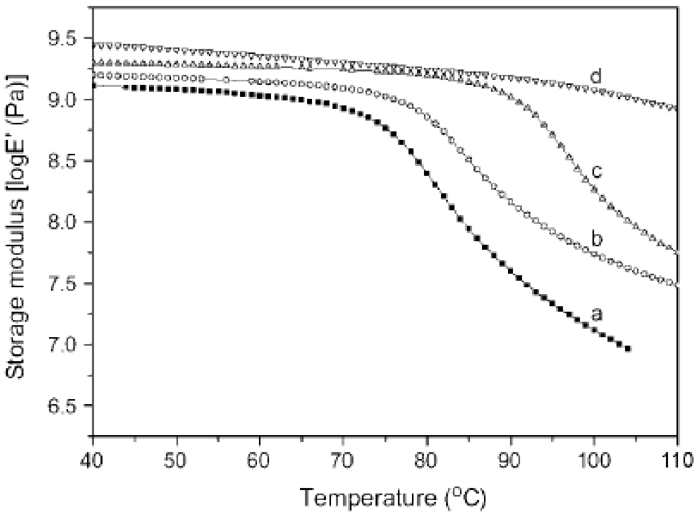


Figure 2.23 : Storage modulus of (a) pure PS, (b) PS/MMT-1, (c) PS/MMT-2 and (d) PS/MMT-3. [2]

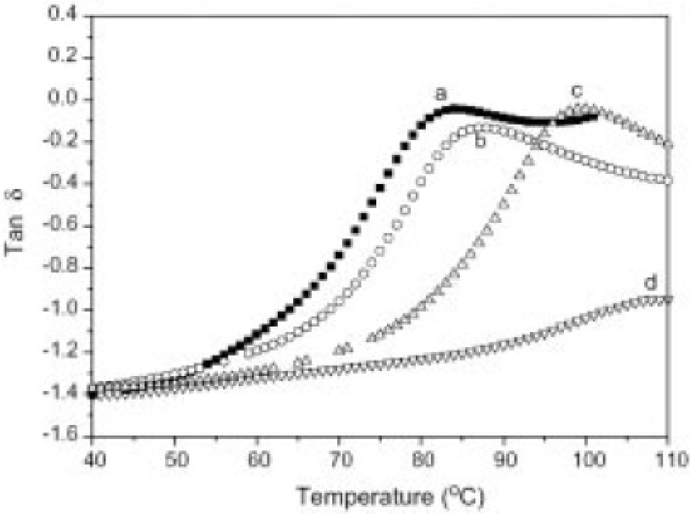


Figure 2.24 : Tanδ values of (a) pure PS, (b) PS/MMT-1, (c) PS/MMT-2 and (d) PS/MMT-3 [2]

The storage modulus of PS/MMT nanocomposites was greater than that of pure PS and monotonically increased with the clay content in both the glassy and rubbery regions. However, the improvements in the rubbery region were much greater than those in the glassy region. This behavior indicates that the restricted segmental motions at the organic-inorganic interface are due to large aspect ratios of the clay platelets, and the polymer chains were also well confined inside the clay galleries at the nanoscale level [72,73]. The storage modulus of PS/MMT-3 was 1.2 times higher than that of pure PS, which is comparable to the earlier reported data (1.4 times improvement) [71]. The Tg's of the nanocomposites were estimated from the peak values of tan δ in Figure 2.24, which were shifted towards higher temperature with increasing clay content. These results indicate that nanoscale clay platelets strongly restrict the polymer segmental motions, resulting in the significant increase in Tg. This improvement in Tg is higher than those of other researchers even though the smaller clay content was used in this experiment [73].

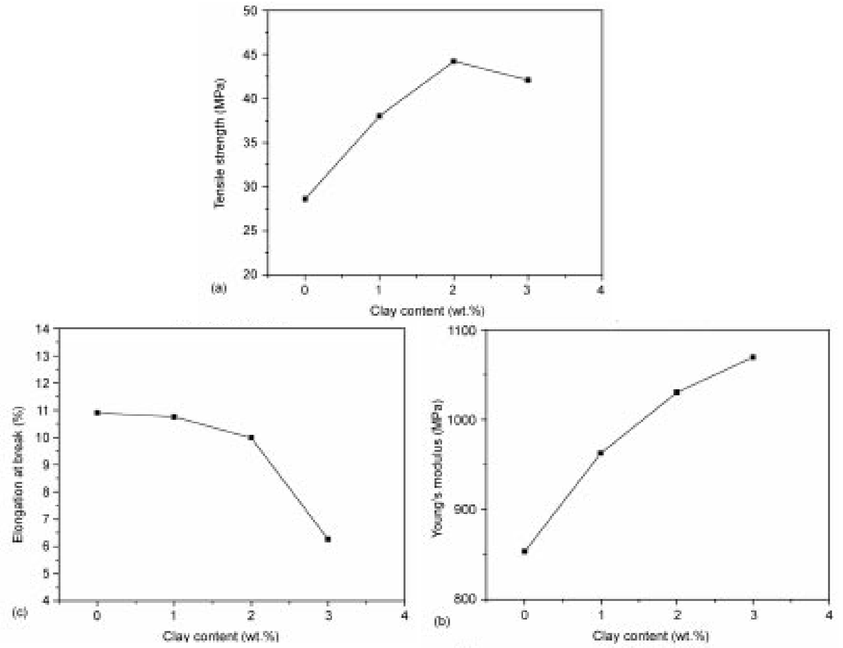


Figure 2.25 : (a) Tensile strengths, (b) Young's modulus and (c) elongations at break of PS/MMT nanocomposites [74].

The effects of clay loadings on tensile properties of the PS/MMT nanocomposites are shown in Figure 2.25. The tensile strength and Young's modulus were significantly enhanced in the presence of the small content of clay, while the elongation at break was reduced with increasing the clay content. The increase in tensile strength was attributed to the stronger interfacial adhesion between PS and the clay platelets. However, the enhancement of modulus was reasonably ascribed to the high resistance exerted by the clay platelets against the plastic deformation and the stretching resistance of the oriented polymer backbones in the galleries. The improvement of tensile strength in PS/MMT-3 compared to pure PS was ~47%, which is greater than the earlier reported value in the literature (~21%) for PS/MMT nanocomposite with 3 wt.% MMT prepared by melt blending [72]. Similarly, the enhancement of Young's modulus in PS/MMT-3 compared to pure PS was ~25%, which is much greater than the reported value (7.4% improvement for PS/MMT nanocomposite with 5 wt.% clay prepared by emulsion polymerization). However, the elongations at break were reduced with increasing the clay content. For example, the reduction of elongation at break in PS/MMT nanocomposite with 4.4 wt.% MMT prepared by melt blending was reported to ~26% [75].

3. EXPERIMENTAL PART

3.1 Chemicals Used

3.1.1 Styrene

Styrene was used as the monomer of the nanocomposites.

3.1.2 2, 2'-Azodiisobutyronitrile (AIBN)

AIBN was used as the initiator, a product of Fluka with a purity of 98% was recrystalized from methanol.

3.1.3 Montmorillonites (MMT)

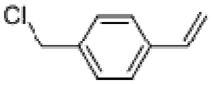
3.1.3.1 MMT-92

CloisiteNa$^+$ was used as the clay with an cation exchange capacity of 92.6 meq/100 g which was a product of Southern Clay Products.

3.1.3.2 MMT-145

Nanocor PGW was used as the clay which is a product of Nanocor with a cation exchange capacity of 145 meq/100 gr.

3.1.4 4-Vinylbenzyl chloride (Chloromethyl Styrene) (VBC)



The product of Fluka A.G. has a chemical formula with a 93.3% purification, was used without any purification. (density: 1.083 g/cm^3, Mw: 152.62 g/mol, $H_2C{=}CHC_6H_4CH_2Cl$).

3.1.5 n-Dodecylamine (DDA)

It was used for synthesizing surfactants for nanoclay which was the product of Merck A.G. having with a purity of >98% (m.p.=25-28 °C Mw: 185 g/mol, $C_{12}H_{27}N$).

3.1.6 n-Octadecylamine

It was used for synthesizing surfactants for nanoclay which was the product of Merck A.G. with a purity of 90% (m.p.=50-55 °C, Mw: 269.51, $C_{18}H_{39}N$).

3.1.7 Hydrochloric Acid, 37% (HCl)

It was used for synthesizing ammonium chloride salt with an amine group. It was a concentrated aqueous solution of HCl with a density of 1.19 g/cm^3.

3.1.8 Toluene

It was used as solvent in polymerization reaction by drying with molecular sieve a product of Merck A.G. was used without further purification.

3.1.9 Dimethyl formamide (DMF)

It was used as solvent in synthesis of vinyl modified ammonium salts, which was a product of Merck A.G. used without further purification.

3.1.10 Methanol

It was used as the solvent, also used for precipitation of polymer nanocomposite used without further purification.

3.1.11 Ethanol

It was used as a solvent without further purification.

3.1.12 Diethyl Ether

It was used for precipitation of vinyl modified salts, was used without further purification.

3.1.13 Silver Nitrate Solution ($AgNO_3$)

0.1 M of $AgNO_3$ solution was used for the detection of chloride ion present in clay suspension.

3.1.14 Distilled Water

It was used to swell and purify the modified clay.

3.2 Equipment Used

3.2.1 Magnetic stirrer

It was used for the preparation of organoclays having a maximum mixing rate of 1250 rpm and a maximum temperature of 300°C.

3.2.2 Magnetic stirrer with heater with temperature sensor

It was used for synthesizing vinyl-ammonium salts and polymer nanocomposites has a maximum mixing rate of 1500 rpm.

3.2.3 X-ray Diffractometer

Measurement were made with Shimadzu XRD 6000 Model and used wavelength was λ=1.5405 Å.

3.2.4 Thermogravimetric Analyzer

Thermogravimetric analysis (TGA) was carried out with Linseis STA PT 1750 thermogravimetric analyzer.

3.2.5 Differential Scanning Calorimeter

DSC analysis isperformed with Shimadzu DSC-50 differential scanning calorimeter.

3.2.6 Fourier Transform Infrared Spectrometer (FT-IR)

FT-IR analysis were carried out with Thermo Nicolet-Nexus 670 infrared spectrometer.

3.3 Experimental Procedure

3.3.1. Synthesis of vinyl-ammonium salts

For synthesis of n-dodecyl(4-vinylbenzyl) ammonium chloride salt; in a round-bottom flask, 6.86 g (37 mmol) of dodecylamine was dissolved in 50 mL of dry DMF, followed by the addition of 0.03 g of hydroquinone; 6.5 g (37 mmol) of vinyl benzyl chloride was added dropwise in a period of 4 h to the stirred solution at 45^{o}C. After cooling, the reaction solution mixture was added dropwise with stirring to an excess of diethyl ether. The white precipitated product was filtered off, washed with diethyl ether, and then dried in vacuum at room temperature.

For synthesis of n-octadecyl(4-vinylbenzyl) ammonium chloride salt; in a round-bottom flask 10.0 g (37 mmol) of octadecylamine was dissolved in 50 mL of dry DMF and same procedure is followed as explained for synthesis of n-dodecyl(4-vinylbenzyl) ammonium chloride salt.

3.3.2 Preparation of the ammonium modified clays

8 organoclays were synthesis which 4 of them containing vinyl groups, and 4 without vinyl groups.

3.3.2.1 Preparation of vinyl-containing ammonium modified clays

Depending on the cation exchange capacity, 2 types of vinyl-containing clays were synthesized which 2 of them having a CEC of 145 meq / 100 g, and the other 2 having a CEC of 92.6 meq / 100 g.

Preparation of vinyl-containing ammonium modified clays with a CEC of 145 meq / 100 g was achieved by synthesizing n-dodecyl(4-vinylbenzyl) and n-octadecyl(4-vinylbenzyl) ammonium modified clays.

For the preparation of n-dodecyl(4-vinylbenzyl) ammonium modified clay with a CEC of 145 meq / 100 g; a suspension of 8.2 g (11.9 meq) of sodium MMT in 300 mL of distilled water was stirred for 24 h in an Erlenmeyer flask to complete swelling. Then, 30 mL of methanol was added dropwise with stirring, and the stirring was continued for 2 h. To the stirred swelled clay suspension, a solution of 4.04 g (11.9 mmol) n-dodecyl(4-vinylbenzyl) ammonium chloride salt dissolved in 100 mL of distilled water/methanol [70 : 30 v/v] was added dropwise. After stirring for overnight, the white precipitate product was filtered, washed with distilled water several times until no chloride ion could be detected by an addition of $AgNO_3$ solution to the filtrate, and then washed twice with 80 : 20 (v/v) ethanol/water. The white powder product was dried in a vacuum oven overnight at room temperature.

For the preparation of n-octadecyl(4-vinylbenzyl) ammonium modified clay with a CEC of 145 meq / 100 g, same amount and procedure was followed as explained in the preparation of n-dodecyl(4-vinylbenzyl) ammonium modified clay with a CEC of 145 meq / 100 g except 5.0 g (11.9 mmol) n-octadecyl(4-vinylbenzyl) ammonium chloride salt was dissolved.

For the preparation of vinyl-containing ammonium modified clays with a CEC of 92.6 meq / 100 g again 2 different organoclays were synthesized which have n-dodecyl(4-vinylbenzyl) and n-octadecyl(4-vinylbenzyl) ammonium modified clays.

For the preparation of n-dodecyl(4-vinylbenzyl) ammonium modified clay with a CEC of 92.6 meq / 100 g, same procedure was followed as explained in n-dodecyl(4-vinylbenzyl) ammonium modified clay having a CEC of 145 meq/100 g, except a suspension of 12.85 g (11.9 meq) of sodium MMT was used.

For the preparation of n-octadecyl(4-vinylbenzyl) ammonium modified clay with a CEC of 92.6 meq / 100 g, same procedure was followed as explained in n-dodecyl(4-vinylbenzyl) ammonium modified clay having a CEC of 145 meq / 100 g, except 12.85 g (11.9 meq) of sodium MMT was used and 5.0 g (11.9 mmol) n-octadecyl(4-vinylbenzyl) ammonium chloride salt was dissolved.

3.3.2.2 Preparation of ammonium modified clays without a vinyl group

Depending on the cation exchange capacity 2 types of clays were synthesized having no vinyl group. 2 of these clays have a CEC of 145 meq / 100 g, and the other 2 have a CEC of 92.6 meq / 100 g.

For the preparation of ammonium modified clays without a vinyl group with a CEC of 145 meq / 100 g 2 different organoclays were synthesized which have n-dodecylamine and n-octadecylamine as alkyl chains.

For the preparation of n-dodecylammonium modified clay with a CEC of 145 meq / 100 g, a suspension of 8.2 g (11.9 meq) of sodium MMT in 300 mL of distilled water was stirred for 24 h in an Erlenmeyer flask to complete swelling. Then, 30 mL of methanol was added dropwise with stirring, and the stirring was continued for 2 h. In a flask containing 2,206 g (11.9 mmol) dodecylamine and 0.986 mL (11.9 mmol) 37% HCl was added dropwise while stirring and then dissolved in 100 mL of distilled water/methanol [70 : 30 v/v] solution. This mixture was added dropwise to the clay suspension while stirring. After stirring overnight, the white precipitate product was filtered, washed with distilled water several times until no chloride ion could be detected by an addition of $AgNO_3$ solution to the filtrate, and then washed twice with 80 : 20 (v/v) ethanol/water. The white powder product was dried in a vacuum oven overnight at room temperature.

For the preparation of n-octadecylammonium modified clay with a CEC of 145 meq / 100 g, same procedure was applied in the preparation of n-dodecylammonium modified clay with a CEC of 145 meq / 100 g with only difference of 3.207 g (11.9 mmol) octadecylamine was used as reactant.

For the preparation of ammonium modified clays without a vinyl group with a CEC of 92.6 meq / 100 g 2 different organoclays were synthesized which have n-dodecylamine and n-octadecylamine as alkyl chains.

For the preparation of n-dodecylammonium modified clay with a CEC of 92.6 meq / 100 g, same procedure was followed as explained in the preparation of n-dodecylammonium modified clay with a CEC of 145 meq / 100 g except 12.85 g (11.9 meq) of sodium MMT was used.

For the preparation of n-octadecylammonium modified clay with a CEC of 92.6 meq / 100 g, same procedure is followed as explained preparation of n-dodecylammonium modified clay with a CEC of 145 meq / 100 g except 12.85 g (11.9 meq) of sodium MMT and 3.207 g (11.9 mmol) octadecylamine was used as reactants.

3.3.3 Preparation of Polystyrene–Organoclay Nanocomposites

In a 250-mL round flask, 0.202 g (for 1% content) / 1.053 g (for 5% content) of organically modified clay was swelled in 5 mL of dry toluene; 20 g of styrene monomer was then added, followed by the addition of 0.1 g of AIBN as a radical initiator, and then stirred at room temperature (2 h) to obtain a swelled suspension. The mixture was heated at 80^{o}C for 5 h. After cooling, the product was precipitated in methanol. The precipitated PS–MMT nanocomposite was filtered, washed with methanol, and finally dried under reduced pressure for 24 h at 60^{o}C.

3.4 Tests and Analyses

3.4.1 Chloride Ion Test

It is important to remove chloride ion formed in the ion exchange reaction before using the modified clay in the polymerization reaction. To do this, after filtration of modified clay suspension, filtrate was taken in a test tube and a few drops of 0.1 M $AgNO_3$ solution was added. Washing with distilled water and filtration were continued until no white precipitate of AgCl occurred.

3.4.2 FT-IR Analysis

Infrared spectra (IR) were carried out on a Thermo Nicolet-Nexus 670 infrared spectrophotometer, using the potassium bromide disc technique within the wavenumber range of 4000–400 cm^{-1}.

3.4.3 XRD Analysis

X-ray diffraction analysis (XRD) is a nondestructive method for the structure analysis of crystals. The sample was irradiated with monochromatic X-ray light and stray radiation recorded. Measurement were made by using Shimadzu XRD 6000 Model and used wave length is λ=1.5405 Å. 2θ values were taken between 2-14^o.

3.4.4 DSC Analysis

Analysis were carried out on Shimadzu DSC-50 with a heating rate of 10 ^oC/min heated from room tempearute to 300 ^oC then cooled with liquid nitrogen, then heated twice with the same values.

3.4.5 TGA Analysis

TGA analysis were established by Linseis STA PT 1750 thermogravimetric analyzer with a heating rate of 10^oC/min in air atmosphere with a gas flow rate of 100 mL/min heated up to 500^oC.

3.4.6 DTA Analysis

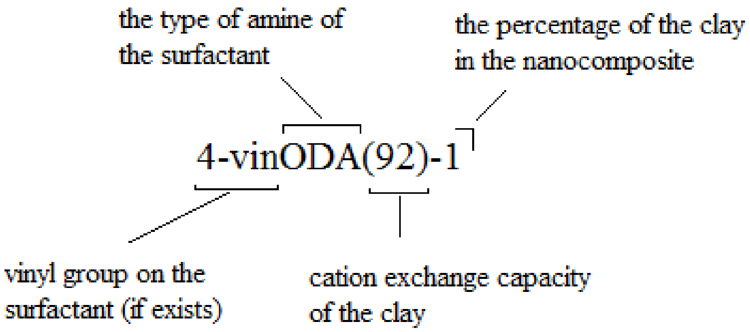
Differential Thermal Analysis were carried out at the same time with TGA analysis. Temperature difference is taken against the temperature value where heating rate is

10°C/min in air atmosphere with a gas flow rate of 100 mL/min and with a maximum temperature of 500°C

4. RESULTS AND DISCUSSION

In this study, polymer-clay nanocomposites (PCN) containing organoclay, polystyrene was synthesized via in-situ polymerization. 8 organoclays were synthesized as explained in 3.3.2. 4 of them have vinyl groups while others have none. To obtain vinyl containing clay 2 different vinyl ammonium salts are synthesized as explained in 3.3.1. Then in-situ polymerization is performed as in 3.3.3. with 2 ratios of 1 and 5% with a total of 16 polystyrene-clay nanocomposite samples and spectroscopic and thermal analysis were carried out on the samples.

The notation of the nanocomposite samples is given below, left side defines the clay and the number at the right corner defines the amount of clay in the nanocomposite structure.



4.1 FT-IR Analysis Results

Structural characterization was followed with FT-IR analysis. In Figure 4.1 FT-IR spectrum of 4-vinyl octadecylammonium salt is given. 1610 cm^{-1} corresponds to C=C stretching region due to the existence of vinyl groups. Also 715 cm^{-1} peak indicate to C-Cl existence of ammonium salt.

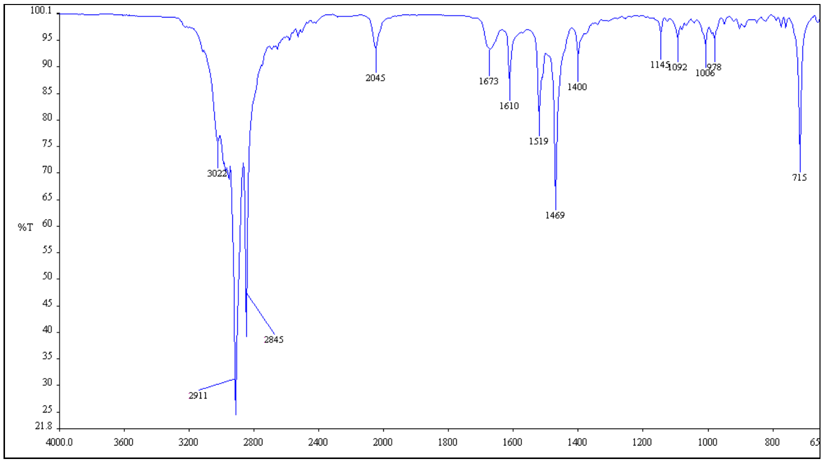


Figure 4.1 : FT-IR spectrum of 4-vinyl octadecylammonium salt.

Na-MMT has characteristic peaks, which can be observed in Figure 4.2. which are mainly absorption band of Si groups at 1038 cm^{-1}, hydroxyl bond which corresponds to 3454 cm^{-1}, and bending peaks of Si-O-Si and Si-O-Al which are 464 and 521 cm^{-1}.

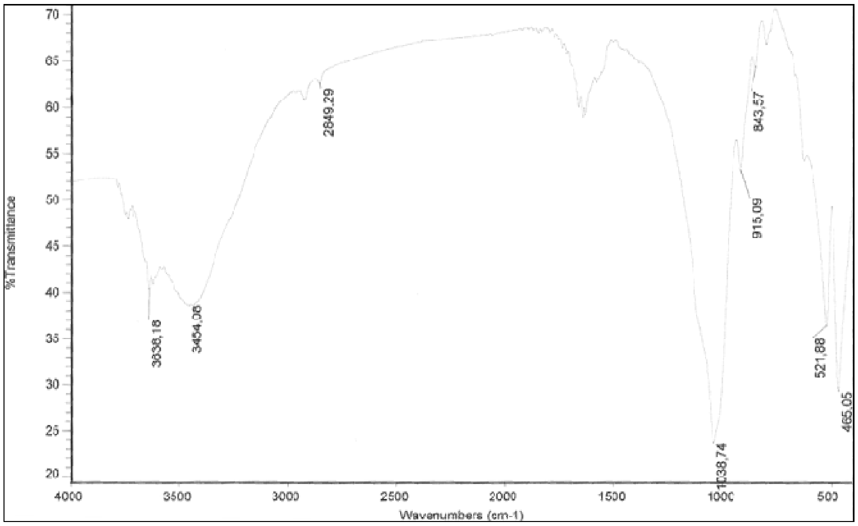


Figure 4.2 : FT-IR spectrum of Na-MMT.

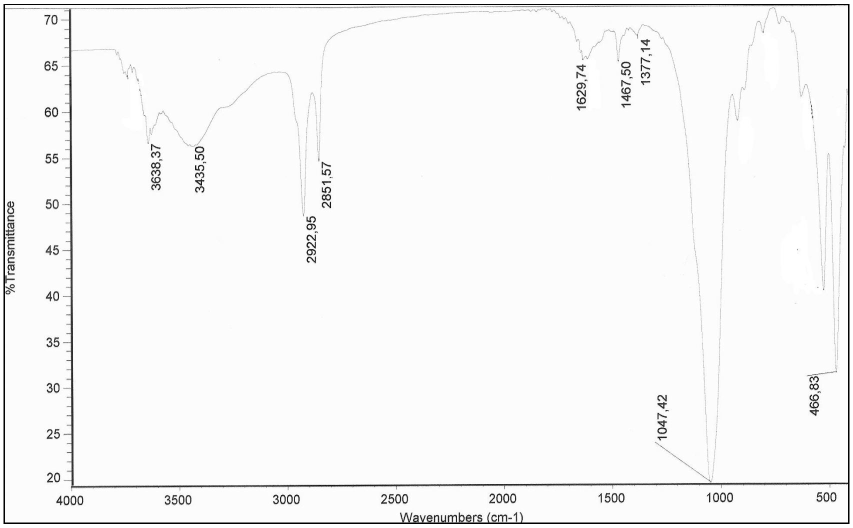


Figure 4.3 : FT-IR spectrum of ODA modified clay.

In case of organoclay preparation new peaks appear on the spectrum, which are 1629 cm^{-1} caused by NH_2 bending, 3435 cm^{-1} NH stretching. Bands at 2922 and 2853cm^{-1}, due to stretching vibrations of –CH_2 groups in octadecylamine seen in Figure 4.3. Decrease in –OH groups due to ion exchange reaction can be observed in 3400 cm^{-1} region in Figure 4.3 and 4.4.

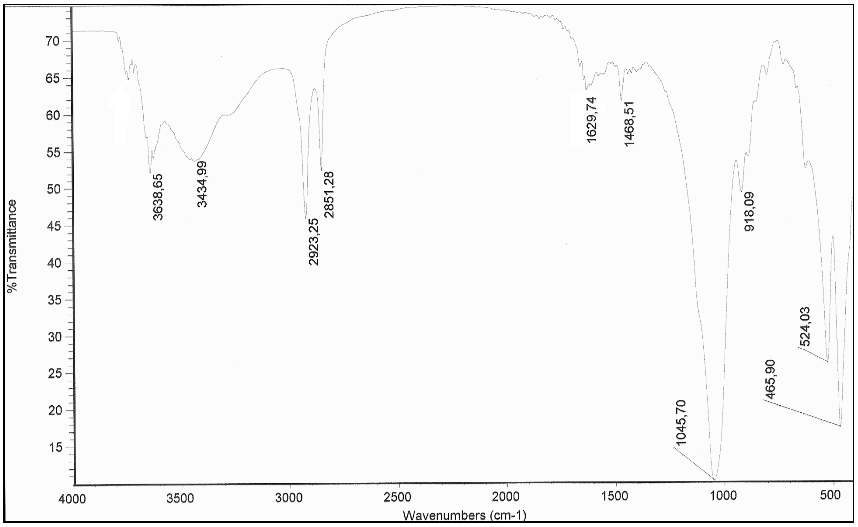


Figure 4.4 : FT-IR spectrum of 4-vinyl ODA modified clay.

In 4-vinyl ODA modified clay an increase in 1618 cm^{-1} corresponds to C=C stretching region. In addition, one can observe the peak disappearance of C-Cl bond because of the ion exchange of 4-vinyl ODA salt with Na-MMT.

The Si–O–Si out of plane stretching peak of Na-MMT at 1038 cm^{-1} shifted to 1045 cm^{-1} in the spectra of all organoclay samples, which was attributed to alteration of the environment of the Si–O–Si groups due to the presence of organic chains because of the intercalation of organic molecules.

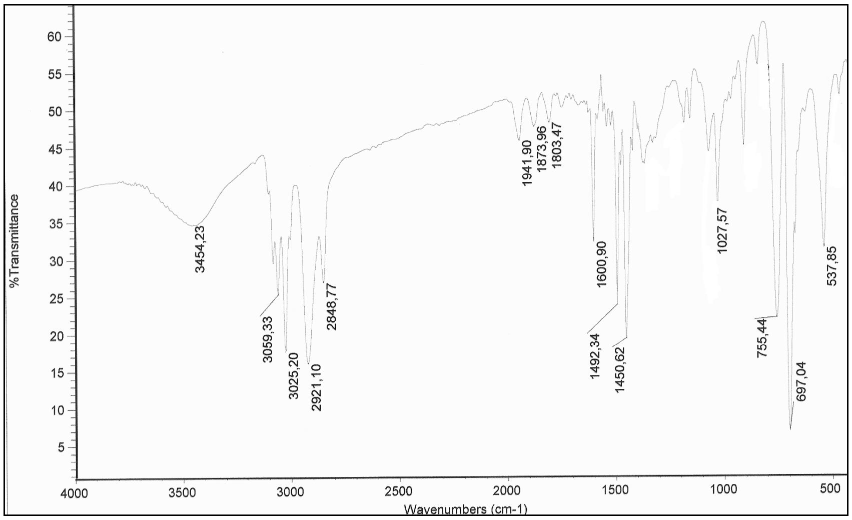


Figure 4.5 : FT-IR spectrum of 4-vinODA(92)-1 nanocomposite.

In Figure 4.5. the FT-IR spectrum of polystyrene nanocomposite is given where –CH aromatic stretching of polystyrene at 3059 cm^{-1} and 3025 cm^{-1}, –CH aliphatic srtretching of polystyrene at 2922 cm^{-1} can be observed. Bands observed at 1941, 1873 and 1803 cm^{-1} is known as the fingerprint region of the polystyrene. In addition the characteristic bands of organoclay is also observed in the spectrum of nanocomposite as expected.

4.2 XRD Analysis Results

The results of the XRD measurements of organoclay and nanocomposite samples with clays having CEC's of 92.6 and 145 meq /100 g are given in Table 4.1. From the diffraction values, the distance between clay layers (d_{001}) of organoclays and nanocomposites were calculated from the Bragg's equation ($n\lambda=2d \sin \theta$).

In comparison with the initial interlayer spacing of pristine MMT, it indicates gallery expansions to higher values. The large expansion of the gallery may indicate that the PS molecules have been successfully intercalated into the organoclay layers.

It should be noted that clay having lower CEC had more increase in interlayer distance due to limiting CEC values of clays used in nanocomposite preparation which are between 50-150 meq/100 g. Since when the cation exchange capacity is higher than 150, the forces between layers prevent separation of clay layers. On the other hand, clay minerals, which cation exchange capacity lower from 50 meq/100 g clay, could not separate clay layers [77].

If one compares the interlayer distance of DDA containing organoclays and ODA containing organoclays, it is seen as the alkyl chain length of the alkylammonium cations in organoclay becomes larger, the basal spacing(d_{001}) of organoclay showed to be increased as expected.

The interlayer distances of PS/4-vinDDA-MMT and PS/4-vinODA-MMT nanocomposites were larger than those obtained for PS/DDA-MMT or PS/ODA-MMT. It implies that the amount of PS polymer intercalated in the interlayers of PS/4-vinDDA-MMT and PS/4-vinODA-MMT are much more than that of other PS/organoclay nanocomposites.

This further increase of basal spacing of for example 4-vinODA(92)-5 from 11.8 Å to 24.2 Å is due to the swelling of the interlayer by the styrene monomer and successive polymerization in 4-vinODA-MMT interlayers. As the structural affinity between styrene monomer and the organic group of organoclay increases, the dispersibility of organoclay in styrene monomer increases. Generally, it is known that the penetration of monomers into the lamellae of organophilic MMT can be facilitated by the attractive forces between the organoclay interlayers and the free monomer molecules.

When styrene monomer penetrates the organoclay interlayer and polymerizes, a substantial increase in the interlayer distance occurs because the organoclay structures contain a benzyl group similar to styrene. As summarized in Table 4.1, the basal spacings of 4-vinDDA and 4-vinODA modified clays and its nanocomposites were larger than those for the others. These results may imply that the insertion of growing polymer chains during polymerization can be facilitated not only by the organophilicity of organic groups but also by the structural affinity between the monomer used and the organic group of the organoclay.

Table 4.1 : XRD results of clays, organoclays and nanocomposites prepared with 92.6 meq/100 g CEC clay and 145 meq/100 g CEC clay.

Sample ID	**2θ**	**d_{001}**	**Sample ID**	**2θ**	**d_{001}**
Na-MMT(92)	7.48	11.8	Na-MMT(145)	5.55	15.9
DDA(92)	5.04	17.5	DDA(145)	5.42	16.3
ODA(92)	4.77	18.5	ODA(145)	5.35	16.5
4-vinDDA(92)	4.72	18.7	4-vinDDA(145)	5.35	16.5
4-vinODA(92)	4.67	18.9	4-vinODA(145)	5.22	16.9
DDA(92)-1	4.90	18.0	DDA(145)-1	5.32	16.6
DDA(92)-5	4.60	19.2	DDA(145)-5	3.87	22.8
ODA(92)-1	4.20	21.0	ODA(145)-1	4.35	20.3
ODA(92)-5	3.94	22.4	ODA(145)-5	4.50	19.6
4-vinDDA(92)-1	4.16	21.2	4-vinDDA(145)-1	4.39	20.1
4-vinDDA(92)-5	3.84	23.0	4-vinDDA(145)-5	4.53	19.5
4-vinODA(92)-1	3.74	23.6	4-vinODA(145)-1	4.39	20.1
4-vinODA(92)-5	3.65	24.2	4-vinODA(145)-5	4.50	19.6

4.3 Thermal Analysis Results

Thermal analysis results are given in Table 4.2 and Table 4.3. Tg's were obtained by DSC and degradation temperatures by TGA. 3 degradation temperatures exist for each nanocomposite which are beginning point of degradation ($(\mathbf{T_{deg}})_{\mathbf{start}}$), finishing point of degradation ($(\mathbf{T_{deg}})_{\mathbf{finish}}$) and midpoint of degradation ($(\mathbf{T_{deg}})_{\mathbf{mid}}$) is also given for comparison. These values were obtained from TGA curves where they are given in Figure 4.6, Figure 4.7 and Figure 4.8.

Table 4.2 : Thermal analysis results of nanocomposites prepared with 92.6 meq/100 g CEC clay

Sample ID	Tg	$(T_{deg})_{start}$	$(T_{deg})_{finish}$	$(T_{deg})_{mid}$
PS homopolymer	85.6	311	378	345
DDA(92)-1	72.2	309	420	364
DDA(92)-5	77.0	318	431	371
ODA(92)-1	66.5	327	429	383
ODA(92)-5	85.0	350	444	391
4-vinDDA(92)-1	70.1	328	436	384
4-vinDDA(92)-5	71.5	341	432	387
4-vinODA(92)-1	71.0	381	418	407
4-vinODA(92)-5	86.0	388	440	416

Table 4.3 : Thermal analysis results of nanocomposites prepared with 145 meq/100 g CEC clay

Sample ID	Tg	$(T_{deg})_{start}$	$(T_{deg})_{finish}$	$(T_{deg})_{mid}$
PS homopolymer	85.6	311	378	345
DDA(145)-1	68.0	315	382	350
DDA(145)-5	82.3	317	387	349
ODA(145)-1	90.0	324	403	352
ODA(145)-5	99.0	366	408	385
4-vinDDA(145)-1	93.1	321	392	354
4-vinDDA(145)-5	87.8	332	395	362
4-vinODA(145)-1	95.1	357	404	373
4-vinODA(145)-5	99.1	376	408	387

It is shown in Table 4.2 and Table 4.3 that Tg increased with the clay content when compared to pristine PS materials. The increased Tg resulted from the restricted segmental motions of the polymer chains at the organic–inorganic interface, due to the confinement of PS chains between the silicate layers as well as the silicate surface-polymer interactions. This increase of Tg can be also ascribed to confinement effects due to intragallery intercalation, strong interfacial interaction, or efficient chemical grafting onto clay surfaces. Some decreases in Tg values were also observed in Table 4.2. These may be affected by two factors: the high viscosity of organophilic MMT dispersed in the styrene monomer affected the diffusion of initiator molecules, and MMT platelets blocked chain propagation during polymerization. This may led to the reduction of Tg and molecular weight of PS. The latter considered organophilic MMT as a plasticizer for PS. Since weak interactions are generally expected for PS/ mineral or PS/alkyl groups and decrease of Tg is more often observed.

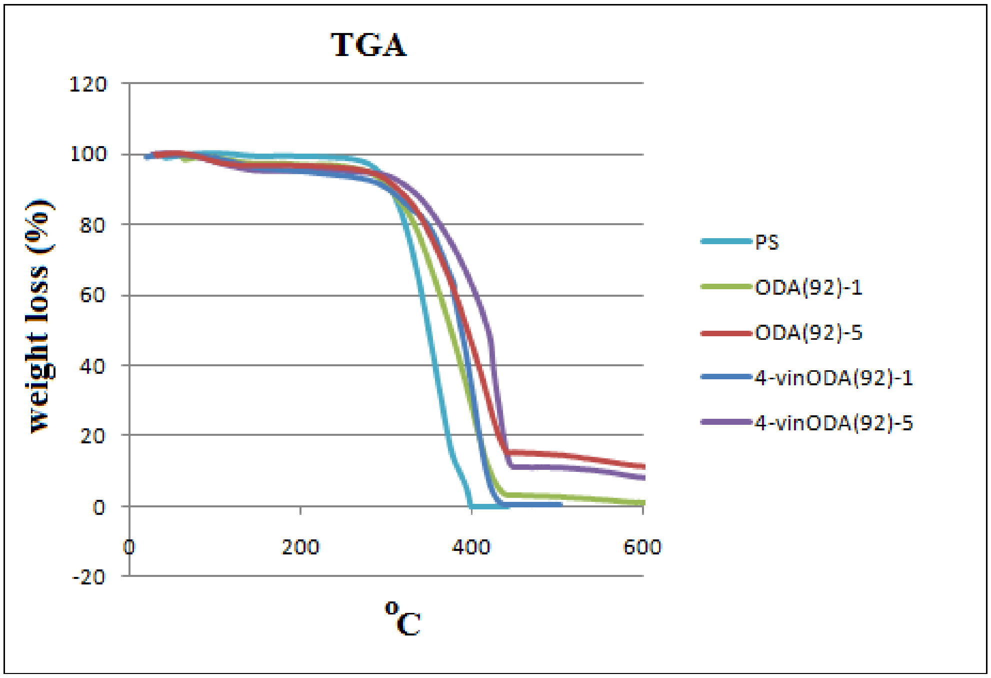


Figure 4.6 : TGA thermograms for homopolymer and CEC= 92.6 meq / 100 g ODA modified organoclay containing nanocomposites.

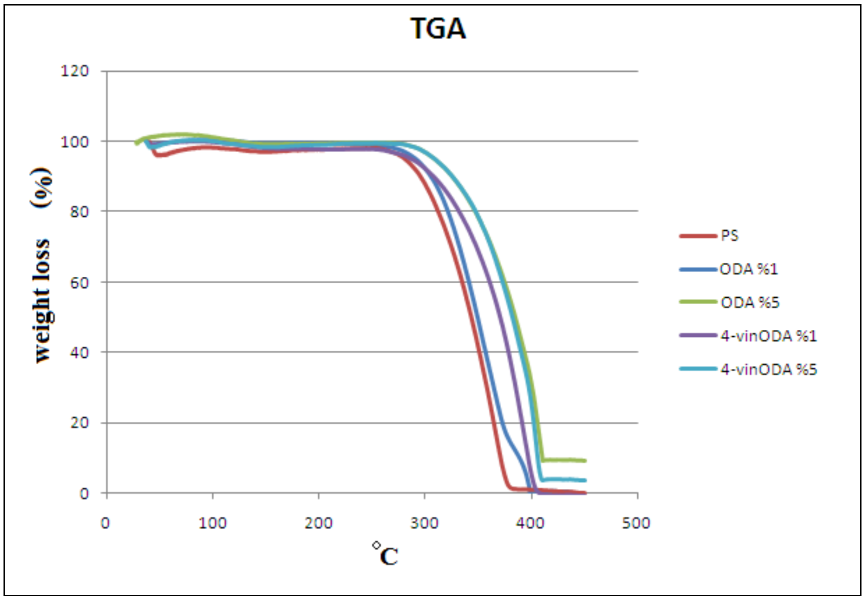


Figure 4.7 : TGA thermograms for homopolymer and CEC= 145 meq / 100 g ODA modified organoclay containing nanocomposites.

As it can be observed in Table 4.2, 4.3 and Figure 4.6, 4.7 and 4.8 the values thermodecomposition temperature of pure polystyrene was the lowest. The thermal decomposition of the pure PS sample occurred in the range 311–378°C, and no residues were left above 400°C. But it can be seen that clay containing nanocomposites were left by some residues of clay contents.

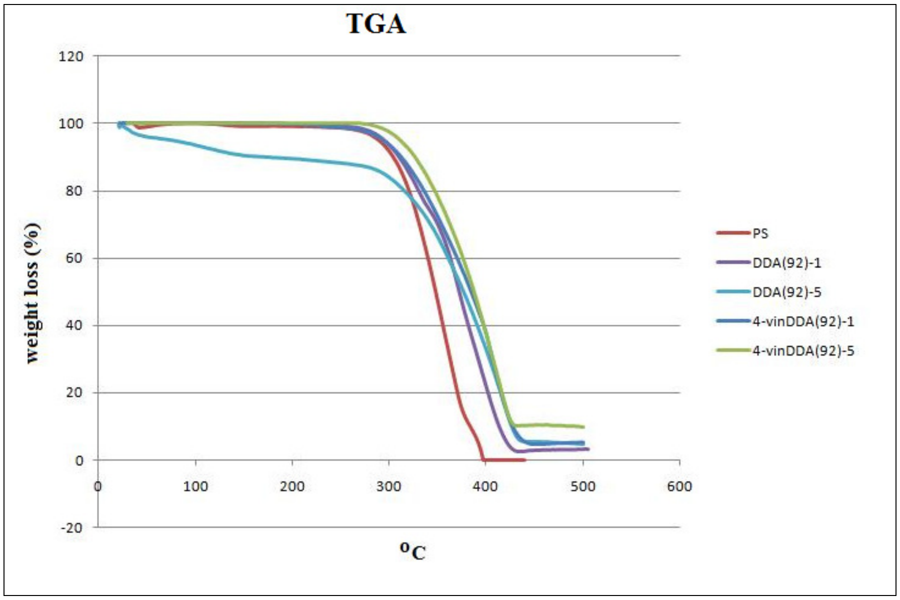


Figure 4.8 : TGA thermograms for homopolymer and CEC= 92.6 meq / 100 g DDA modified organoclay containing nanocomposites.

The decomposition temperatures of the nanocomposites prepared with clays having no vinyl groups increased with the increasing of the amounts of the organoclay content. It is also true for the clays having vinyl groups. It is shown that the thermal stability properties of the nanocomposites with chemical bonds between the organoclay and the polymeric matrix are better than the nanocomposites prepared with organoclays having no vinyl groups and those without chemical bonds.

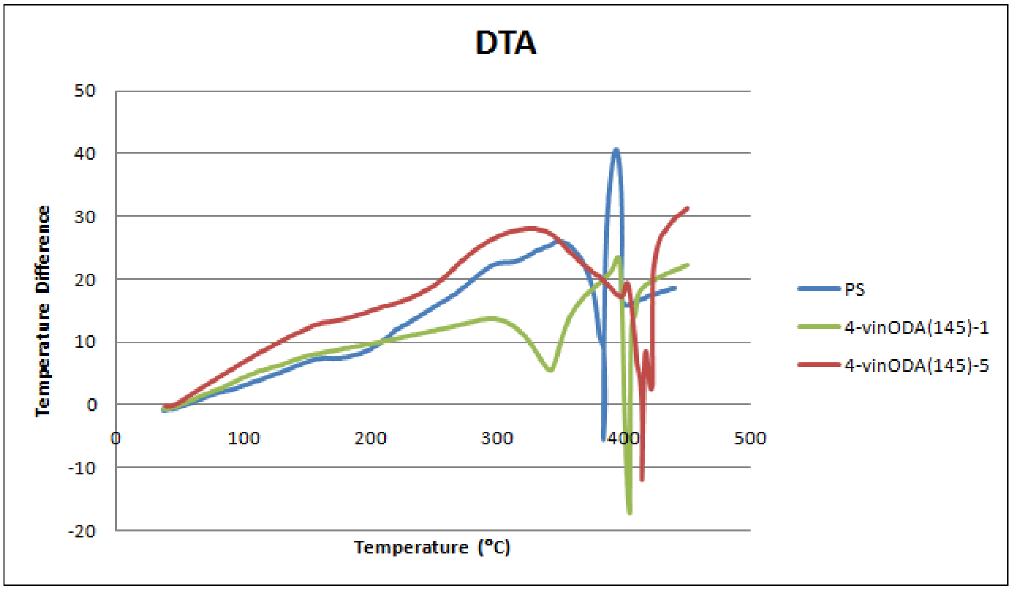


Figure 4.9 : DTA thermograms of nanocomposites prepared with vinyl containing organoclays

In Figure 4.9 DTA thermograms were given where the maximum degradation temperature of pristine PS is the lowest at 380°C. Addition of vinyl containing clay increases the degradation temperature to 400°C. Degradation temperature of the nanocomposite increased slightly with the vinyl containing clay content where 5% content of this clay increased the degradation temperature up to 410°C

5. CONCLUSION

PS-organoclay nanocomposites were synthesized via in situ bulk polymerization, and their structural and thermal properties were investigated. Different kinds of surfactants were synthesized depending on their alkyl chain length and functional groups having similarities with the monomer structure.

The structural changes resulting from synthesis were investigated with FT-IR spectroscopy. XRD analysis was achieved for investigation of the position of the clay platelets. Thermal characterizations of nanocomposites were carried out with DSC, TGA and DTA measurements.

Tg of the nanocomposites increased with the organoclay content explained by due to the restricted segmental motions of the polymer chains at the organic–inorganic interface, which is due to the confinement of PS chains between the silicate layers as well as the silicate surface-polymer interactions. Decreases in Tg values may be explained by the high viscosity of organophilic MMT which was dispersed in the styrene monomer affected the diffusion of initiator molecules, and MMT platelets may have blocked chain propagation during polymerization.

The thermal stability increased with the organoclay content and the content of the organoclay, and they may have been influenced by a competition between the incorporation of clay and the decrease in the molecular weight of the polymer matrix.

Interlayer distances of organoclays and their nanocomposites were increased compared to pristine clay. XRD patterns indicated that the polymer chains were intercalated between the clay platelets. Moreover, distance between clay platelets were increased as the alkyl chain length increased. In addition, it is found that CEC of the clay influences the increment of the interlayer distance of the organoclays and their nanocomposites. XRD results also indicated organoclays prepared with surfactants containing similar units to monomer cause more expanding of the clay platelets with each other.

Among the synthesized organoclays tested in this study, 4-vinODA modified clay containing nanocomposites, an organoclay with a longer alkyl chain length and a benzyl unit similar to the structure of styrene, was most effective in achieving PS intercalation between silicate layers, as confirmed by XRD, DSC, TGA and DTA analyses.

It could be concluded that the interface properties had been improved by the adding of a suitable surfactant to the clay.

This study showed that the structural affinity between the styrene monomer and the organic group of organophilic MMT is an important factor for the preparation of nanocomposites.

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