

**POLY(METHYL METHACRYLATE)/SILICA HYBRIDS:
SYNTHESIS AND CHARACTERIZATION**

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FOREWORD

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ABBREVIATIONS

PLS	: Polymer layered silicate
IPN	: Interpenetrating network
OLS	: Organically modified layered silicate
MMT	: Montmorillonite
XRD	: X-ray diffraction
SEM	: Scanning electron microscope
TEM	: Transmission electron microscope
TGA	: Thermogravimetric analysis
DSC	: Differential Scanning Calorimetry
DMA	: Dynamic mechanical analysis.
DMTA	: Dynamic mechanical thermal analysis.
PMMA	: Polymethylmethacrylate
PGMA	: Polyglycidyl methacrylate
MMA	: Methylmethacrylate
GMA	: Glycidyl methacrylate
T_g	: Glass transition temperature
AMPTS	: 1-Propanamine, 3-(trimethoxysilyl)
TEOS	: Tetraethyl orthosilicate
AIBN	: α,α' -azobisisobutyronitrile
CAN	: Cerium ammonium nitrate
HDA	: Hegzadecyl amine
HTAB	: Hegzadecyl trimethylammonium bromide
THF	: Tetrahydrofuran
NMP	: N-methyl pyrrolidone
HCl	: Hydrochloric acid
SG	: Sol-gel

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LIST OF SYMBOLS

CEC	: Cation exchange capacity
meq	: Miliequivalent gram
T_g	: Glass transition temperature
r	: Reactivity ratio.
T_o	: Oxidation temperature
E	: Young modulus
G	: Shear modulus
B	: Bulk modulus
tan δ	: Mechanical damping
σ	: Uniaxial tensile or compressive stress
τ	: Shear stress
σ_{hyd}	: Hydrostatic tensile or compressive stress
ε	: Normal strain
γ	: Shear strain
ΔV/V_o	: Fractional volume expansion or contraction

POLY(METHYL METHACRYLATE)/SILICA HYBRIDS: SYNTHESIS AND CHARACTERIZATIONS

SUMMARY

Nanocomposites are a new class of composites derived from the ultrafine inorganic particles with dimensions typically in the range of 1 to 1000 nm that are dispersed in the polymer matrix homogeneously. In recent years Polymer/ Layered Silicate (PLS) nanocomposites have attracted great interests in both industry and academia because they exhibit remarkable improvements in material properties when compared with virgin polymer or conventional micro and macro-composites. Nanomaterial additives can provide the following advantages in comparison to their conventional filler counterparts.

- Mechanical properties e.g. strength, modulus and dimensional stability
- Decreased permeability to gases, water and hydrocarbons
- Thermal stability and heat distortion temperature
- Flame retardancy and reduced smoke emissions
- Chemical resistance
- Surface appearance
- Electrical conductivity
- Optical clarity in comparison to conventionally filled polymers

Physical mixture of a polymer and layered silicate may not form a nanocomposite. This situation is analogous to polymer blends, and in most cases separation into discrete phases 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, 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.

There are several different ways of synthesizing of nanocomposite; therefore a means of classification is necessary.

Type I: Organic polymer embedded in an inorganic matrix without covalent bonding between the components.

Type II: Organic polymer embedded in an inorganic matrix with sites of covalent bonding between the components.

Type III: Co-formed interpenetrating networks of inorganic and organic polymers without covalent bonds between phases.

Type IV: Co-formed interpenetrating networks of inorganic and organic polymers with covalent bonds between phases.

Type V: Non-shrinking simultaneous polymerization of inorganic and organic polymers.

The most common and straightforward nanocomposites found in the literature are the Type I composites. The goal in the process is to form a completely interpenetrating network (IPN) of both inorganic and organic phases. Homogeneous nanocomposites with good IPNs are often stronger, more flexible and optically transparent, whereas heterogeneous composites are often mechanically weaker and opaque.

Typically, TEOS is commonly used to form an inorganic network around an organic polymer component.

Also, hybrid materials produced by the sol gel process have a growing scientific and technological interest because of their applications in the fields of optics, electronics, and electrochemistry.

An interesting family of organic/inorganic hybrids (or nanocomposites) is obtained from copolymerization reactions between siloxane and poly (methyl methacrylate) (PMMA) components, which lead to covalently bonded inorganic and organic nanophases. This allows the synthesis of bulk materials with adjustable transparency, refractive index and hardness. Because of such interesting properties, these materials have been used as lenses, coatings on commercial glasses to increase elastic modulus and decrease brittleness.

Glycidyl methacrylate (GMA) is an important vinyl monomer for desirable properties such as high strength. It is relatively less toxic, polar and less expensive than other vinyl monomers. Epoxy group can undergo ring-opening reaction with various nucleophiles. However, its some minor qualities such as thermal stability and poor physical performance need to be improved. Therefore, the presence of glycidyl methacrylate comonomer in the structure of organic/inorganic nanocomposites offer the potential for excellent thermal properties and enhanced physical performance.

In this work we have prepared PLS composites by using organically modified MMT and prepared organic/inorganic hybrids using sol-gel process. Two general methods were applied.

Method A. PMMA / HDA-MMT ve P(MMA-GMA)/ HDA-MMT composites by addition of organically modified silicate to solutions of homopolymer and copolymer, respectively.

Method B. P(MMA-GMA)/SiO₂ hybrid materials, by sol-gel process.

The general application methods of Method A and B are shown in Figure 1.

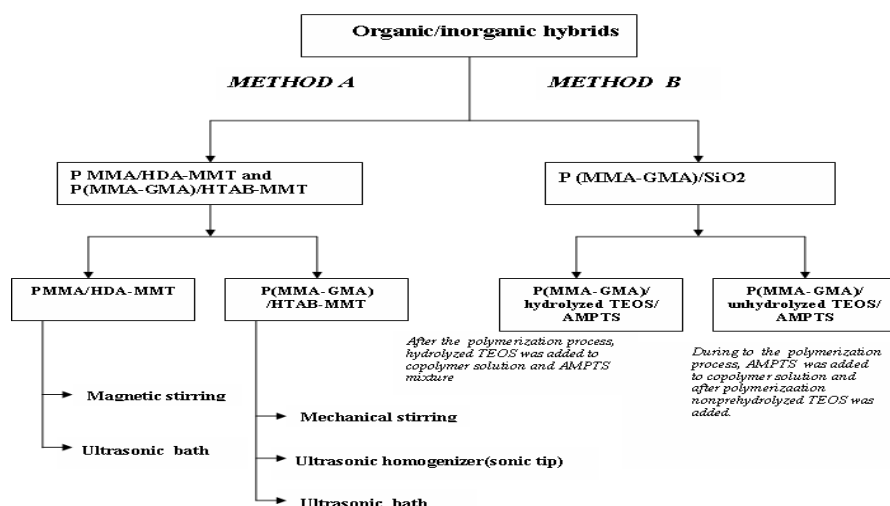


Figure 1: General scheme of preparation of organic/inorganic hybrids

The structures of the materials have been characterized by FT-IR spectra. Thermal properties and mechanical behaviours have been investigated by using, TGA, DSC and DMA, XRD techniques.

The PMMA/composite materials were synthesized through direct mixing of organically modified layered silicate (OLS) into PMMA solution. Organophilic clay was added into the polymer solution and continuously stirred for several hours at room temperature. The solution products were dried under the vacuum. To understand to mechanism and transparency of PMMA/Clay nanocomposites, different mixing methods were applied.

The FT-IR spectra of the composites showed that, PMMA/ HDA-MMT composites could be prepared by ultrasonic agitation technique with higher clay concentration in short time when compare with magnetic stirring technique in the room temperature. Also PMMA/SiO₂ hybrids have been prepared with sol-gel process. For this purpose, prehydrolyzed TEOS solution added to PMMA solutions, stirred and cured at certain temperature. FT-IR spectra of these composites indicated that , PMMA/SiO₂ hybrids obtained with sol-gel process, have similar with polymer layered silicates.

To prepare P(MMA-GMA)/SiO₂ hybrids, first of all, the copolymers of MMA and GMA having different compositions were prepared by free-radical solution polymerization process using ceric ammonium nitrate (CAN) and AIBN as initiators in water and in tetrahydrofurane (THF). Then, using these P(MMA-GMA) copolymers, the polymer/silica hybrid materials have been obtained by sol-gel process in different ways.

After the copolymers were synthesized, copolymer composition of all samples were determined using epoxy group titration method. The FTIR spectra of the copolymers the initiated with both CAN and AIBN showed the intensity of the epoxy band , indicating presence of the epoxy group in the copolymers increased with increase in the glycidyl methacrylate content in the copolymer compositions.

The results of epoxy determination method were used to calculate the reactivity ratios of MMA (2), and GMA (1) using extended Kelen-Tüdös graphical methods for high conversions. The results indicate that GMA is more reactive monomer than MMA

The molecular weights and polydispersity of copolymer samples were determined by using GPC. The molecular weights of the copolymer samples increased with increasing initial concentration.

DSC thermograms of PMMA, PGMA and their copolymers prepared by different feed compositions are tested. With increasing epoxy content in the copolymers, the T_g values shifted to the lower temperature. Glycidyl methacrylate content of copolymers determined by epoxy group titration method were proportional to the decrease in the T_g s of copolymers.

Then, the samples with 2 mol/l initial concentration and containing 10%, 20% GMA in feed were selected to prepare P(MMA-GMA)SiO₂ hybrids materials. The reason for not exceeding > 20% GMA in feed, is that the hybrid samples prepared with higher GMA concentrations were more in the opaque form. These hybrids have been synthesized with sol gel methods with three methods;

Method-I : Copolymer solutions were prepared in THF and AMPTS was added and stirred for a while. Then prehydrolyzed TEOS solution was added to this mixture, stirred.

Method-II : P(MMA-GMA) / SiO₂ hybrids were prepared during the polymerization. During to polymerization process AMPTS was added to copolymer solution and after polymerization nonprehydrolyzed TEOS was added to mixture, stirred.

Method-III : Copolymer solutions were prepared in acetone. HTAB-MMT (10.0 wt % of copolymer concentration) was added into the copolymer solution and different stirring methods were applied.

All the resulting homogeneous mixtures were poured onto Teflon molds and then cured.

FTIR results indicate that covalent bonds are formed between inorganic and organic networks. All these films have the characteristic absorption peaks of Si-O-Si, Si-O-C and C-N-C groups at 1150 cm⁻¹, 1100 cm⁻¹ and 1050 cm⁻¹, respectively, because of the presence of covalent bonds between epoxy groups of copolymer chains, amine group of coupling agent (or HTAB attached to MMT) and inorganic phase (TEOS/H₂O/HCl). The similarities between hybrids obtained by different methods indicate that their structures are much different from those for PMMA, and PMMA/GMA copolymer.

Reaction mechanism of P(MMA/GMA)/AMPTS/TEOS hybrids obtained from Method I and II was given in Figure.2. The thermal and mechanical properties of the materials have been investigated by TGA, DSC, DMA and XRD.

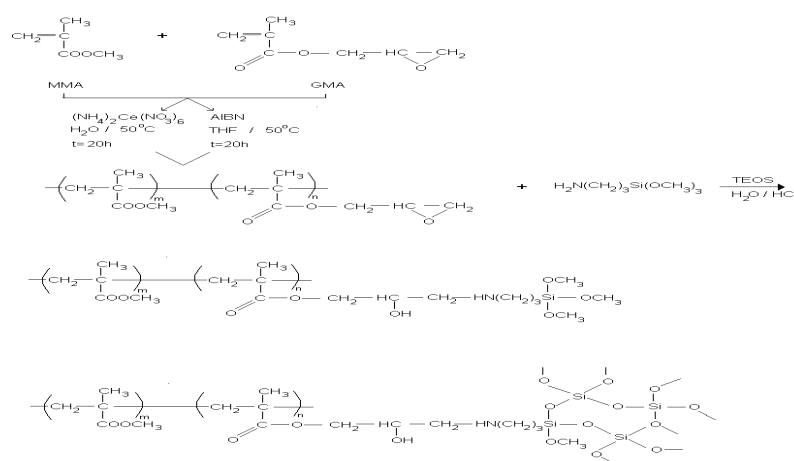


Figure 2: Reaction mechanism of P(MMA/GMA)/AMPTS/TEOS hybrids obtained from Method I and II

TGA results show that thermal degradation temperatures are relatively higher for P(MMA-GMA)/AMPTS/TEOS from Method I. Apparently during the sol-gel process the trimethoxysilyl groups AMPTS/TEOS are transformed into a strong silica network.

At higher temperature the hybrid material shows more stable behavior than the pure polymer. In the presence of silica protect the polymer chains to some extent from the oxidative degradation process. Silica networks in the P(MMA-GMA)/HTAB-MMT hybrids obtained by Method III are unstable which results in beginning of the hybrids degradation already around 250°C . By contrast, for the samples obtained by Method I and II we see higher degradation temperatures. Thus, thermal stability of the P(MMA-GMA)/AMPTS/TEOS hybrids is improved.

DSC was used to study changes in glass transition temperatures T_g . Incorporation of TEOS and HTAB-MMT into the P(MMA-GMA) copolymers produced a slight increase of T_g (3 to 10°C at 10 wt % of inorganic component).

DMA was used to study the mechanical properties of hybrid materials. For the hybrid materials prepared by sol-gel process, Young moduli of P(MMA-GMA)/TEOS and P(MMA-GMA)/AMPTS/TEOS hybrids containing P(MMA-GMA) chains with 10 and 20 mol % of GMA in the feed were higher than those of the copolymers. In the case of the long chains of APTMS connected with the polymer chains by amine bonds, the flexible interfaces form between the organic and inorganic species. These covalent bonds improved the mechanical properties of the hybrid materials.

XRD were also used to characterize the dispersions of the organoclays in PMMA and P(MMA-GMA). As seen from the XRD results, both the structures of organic chains attached to the MMT layers and mixing method which is used to prepare solutions strongly affect interlayer d spacing of polymer / clay composite materials.

All the observed results have shown that there were considerable improvements in both thermal and mechanical properties of the composite and hibrid materials prepared in this thesis.

POLİ(METİL METAKRİLAT)/SİLİKA HİBRİDLER: SENTEZİ VE KARAKTERİZASYONU

ÖZET

Nanokompozitler, polimer matriksinde homojen olarak yayılan ve boyutları tipik olarak 1 ila 1000 nm aralığında olan çok saf inorganik partiküllerden elde edilen yeni bir sınıf kompozittir. Son yıllarda silikat tabakalı polimerler (PLS) nanokompozitler malzeme özelliklerinde saf polimerlere ve geleneksel mikro ve makro kompozitlere nazaran çok daha kayda değer iyileştirmelere neden olmalarından ötürü hem endüstri hem de akademi dünyasının çok ilgisini çekmektedirler. Nano malzeme katkıları diğer geleneksel katkı malzemelerine nazaran aşağıdaki avantajları sağlamaktadır:

- Dayanıklılık, modül, boyutsal stabilite gibi mekanik özellikler.
- Gaz, su ve hidrokarbonlara daha düşük geçirgenlik.
- Termal stabilite ve ısıl deformasyon sıcaklığı.
- Alev geciktiricilik ve daha düşük duman yayını.
- Kimyasal dayanım.
- Yüzeysel görünüm.
- Elektrik geçirgenlik.
- Geleneksel katkılı polimerlere nazaran daha iyi optik berraklık.

Bir polimerin ve tabakalı silikatın fiziksel karışımı bir nanokompozit meydana getirmez. Bu durum polimer karışımlarına benzerdir ve çoğu zaman ayırık fazların oluşmasına neden olur. Karışmaz sistemlerde -ki tipik olarak geleneksel dolgulu polimere karşılık gelirler, organik ve inorganik komponentler arasında olan zayıf fiziksel etkileşim nihayetinde zayıf mekanik ve termal özelliklerin ortaya çıkmasına neden olur. Bunun tam tersi olarak, PLS nanokompozitlerdeki polimer ve tabakalı silikatlarının arasındaki güçlü etkileşim, organik ve inorganik fazların nanometre mertebesinde dağılmasına yol açar. Bunun sonucunda, nanokompozitler diğer mikro karışımlarında veya geleneksel dolgulu polimerlerde olmayan benzersiz özellikler gösterirler.

Nanokompozitleri sentezlemenin bir çok yolu vardır. Bu yüzden belirli bir sınıflandırmaya ihtiyaç vardır:

Tip I: Bileşenler arasında kovalent bağ olmayan bir inorganik matrisin içine gömülmüş organik polimerler.

Tip II: Bileşenler arasında kovalent bağ olan bir inorganik matrisin içine gömülmüş organik polimerler.

Tip III: Fazları arasında kovalent bağ olmayan inorganik ve organik polimerlerin birbirlerinin içine tam olarak nüfuz ederek beraberce oluşturduğu ağlar.

Tip IV: Fazları arasında kovalent bağ olan inorganik ve organik polimerlerin birbirlerinin içine tam olarak nüfuz ederek beraberce oluşturduğu ağlar.

Tip V: İnorganik ve Organik polimerlerin çekmeyen eş zamanlı polimerizasyonu.

Literatürlerde en çok bulunan ve anlaşılması en kolay olan nanokompozitler Tip 1 olanlardır. Prosesteki amaç hem inorganik hemde organik fazların birbirlerine tamamen nüfuz ettikleri iç içe geçmiş bir ağ (IPN) oluşturmaktır. İyi IPN li homojen kompozitler genellikle daha güçlü, daha esnek ve optik olarak daha şeffaftırlar. Öte yandan, heterojen kompozitler genellikle mekanik olarak daha zayıftırlar ve daha az ışık geçirirler.

Tipik olarak, organik bir polimer komponenti etrafında inorganik bir ağ oluşturmak için TEOS yaygın olarak kullanılır

Sol jel proses yöntemi ile üretilen hibrid malzemeler optik, elektronik, ve elektrokimya alanlarında kullanılma imkanları olmalarından ötürü artan bir şekilde bilimsel ve teknolojik ilgiyi üzerlerine çekmektedirler.

Organik/inorganik hibridlerin veya nanokompozitlerin ilgi çekici bir ailesi, inorganik ve organik nanofazların kovalent bağlanmasına yol açan, siloksan ve poli (metil metakrilat) (PMMA) bileşenleri arasındaki kopolimerizasyon reaksiyonlarından elde edilir. Bu ise şeffaflık, refraktif indeks ve sertlikleri ayarlanılabilen birçok malzemenin sentezlenmesine imkan tanır. Bu enteresan özelliklerinden dolayı bu malzemeler lenslerde, ticari camların üzerine yapılan kaplamalarda, elastiklik modülünü arttırmak ve kırılma gücü düşürmek amacıyla kullanılırlar.

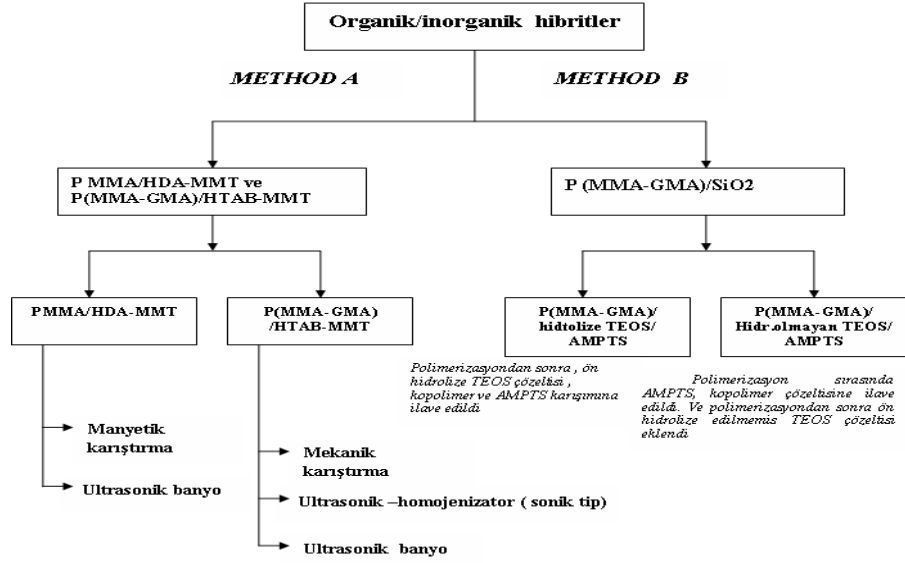
Glisidil metakrilat (GMA), yüksek dayanım gibi istenilen özellikler için önemli bir vinil monomerdur. Diğer vinil monomerlerine göre nisbi olarak daha az toksik, polar ve daha ucuzdur. Epoksi grubu çeşitli nükleofiller ile halka açılması reaksiyonuna girebilir. Bununla beraber, termal stabilizasyon ve zayıf fiziksel performans gibi bazı düşük nitelikleri iyileştirilmelidir. Bu nedenle, glisidil metakrilat yardımcı monomerlerin organik/inorganik nanokompozitlerin yapı içindeki varlığı, mükemmel termal özellikler ve gelişmiş fiziksel performans için büyük potansiyel sunar.

Bu çalışmada, organik olarak modifiye edilmiş MMT kullanarak PLS kompozitler hazırladık ve ayrıca sol jel prosesini kullanarak organik / inorganik hibridler hazırladık. Genel olarak iki yöntem uygulandı.

Metod A. Organik olarak modifiye edilmiş silikatın homopolimer ve kopolimer çözeltilerine ilave edilmesiyle elde edilen PMMA / HDA-MMT ve P(MMA-GMA)/ HTAB-MMT kompozitleri.

Metod B. sol-jel prosesi ile elde edilen P(MMA-GMA)/SiO₂ hibrid malzemeleri.

Metod A ve Metod B nin genel uygulama metodları Şekil 1 de gösterilmiştir.



Şekil 1: Organik/inorganik hibritlerin hazırlanmasının genel şeması

Malzemelerin yapıları FT-IR spektrası tarafından karakterize edildi. Termal ve mekanik davranışlar TGA, DSC , DMA, XRD teknikleri kullanılarak incelendi.

PMMA/ kompozit malzemeleri, organik olarak modifiye edilmiş tabakalı silikat (OLS) nin PMMA matriksi içerisine direk karıştırılması yoluyla sentezlendi. Organofilik kil , PMMA çözeltisi içine katıldı ve oda sıcaklığında çeşitli sürelerde karıştırıldı. Çözelti ürünü vakum altında kurutuldu. PMMA/HD-MMT kompozitinin mekanizması ve şeffaflığı ğını anlayabilmek için çeşitli karıştırma metodları uygulandı.

Kompozitlerin FT-IR spektrası göstermiştir ki, PMMA/HDA-MMT kompozitleri oda sıcaklığında ultrasonik karıştırma ile manyetik karıştırma tekniğine nazaran daha daha yüksek kil konsantrasyonunda ve daha kısa sürede hazırlanabilmektedir. Aynı zamanda, PMMA/ SiO₂ hibritleri sol-jel prosesi ile hazırlandı. Bunun için, önhidrolize edilmiş TEOS çözeltisi , PMMA çözeltisine ilave edilerek karıştırıldı ve belli bir sıcaklıkta çapraz bağlandı (kür edildi) Bu kompozitlerin FT-IR spektrası sol jel prosesi ile elde edilen PMMA/SiO₂ hibridlerinin silikat tabakalı polimerler PMMA/ HDA-MMT ile benzerlik gösterdiğini ortaya çıkardı.

P(MMA-GMA)/SiO₂ hibritleri hazırlamak için öncelikle, çeşitli kompozisyonlarda MMA ve GMA kopolimerleri, su içinde ve tetrahidrofuran içinde (THF) başlatıcı olarak serik amonyum nitrat (CAN) ve AIBN kullanılarak serbest radikal çözelti polimerizasyon prosesi aracılığıyla hazırlanmıştır. Sonra, bu P(MMA-GMA) kopolimerler kullanılarak, çeşitli sol jel yöntemleri ile polimer/silika hibrid malzemeleri elde edilmiştir.

Kopolimerler sentezlendikten sonra, bütün numunelerin kopolimer kompozisyonları epoksi grup titrasyon metodu kullanılarak belilendi. CAN ve AIBN ile başlatılan kopolimerlerin FTIR spektrası epoksi bandının yoğunluğunu gösterdi ki bu da

kopolimer kompozisyonları içindeki glisidil metakrilat muhteviyatındaki artışla kopolimerlerin içindeki epoksi grup varlığının arttığını ifade eder.

Epoksi determinasyon metodunun sonuçları kullanılarak , ileri Kelen-Tüdos yüksek çevirim grafik metodları vasıtasıyla MMA (2) ve GMA (1) nin reaktivite oranları hesaplandı. Sonuçlar, GMA monomerinin, MMA ya göre daha reaktif olduğunu gösterdi.

Kopolimer numunelerin moleküler ağırlıkları GPC kullanılarak tanımlandı. Kopolimer numunelerin moleküler ağırlıkları başlangıç konsantrasyonlarının artmasıyla fazlalaştı.

PMMA, PGMA ‘ ın ve bunların farklı başlangıç kompozisyonları ile hazırlanan kopolimerlerinin camsı geçiş değerleri (Tg) , DSC yöntemiyle belirlendi. Kopolimerlerin epoksi grup titrasyon metodu ile bulunan glisidil metakrilat miktarları kopolimerlerin Tg lerindeki düşüşle doğru orantılıydı. Kopolimerlerin içindeki epoksi oranının artması ile Tg değerleri daha düşük sıcaklık değerlerine kaydı.

Bundan sonra, 2.0 mol/L konsantrasyonlu ve başlangıçta %10, %20 GMA içeren numuneler P(MMA-GMA)SiO₂ hibrid malzemelerin hazırlanması için seçildi. Bunun sebebi, daha yüksek GMA konsantrasyonu ile hazırlanan hibrid numunelerin daha opak bir forma sahip olmalarıdır.

Hibritler sol-jel metodu ile sentezlendiler.

Metod 1: Seçilen kopolimerler , THF de çözüldü ve daha sonra AMPTS eklenerek karıştırıldı. Daha sonra önceden hidrolize edilmiş TEOS çözeltisi bu homojen karışıma ilave edildi.

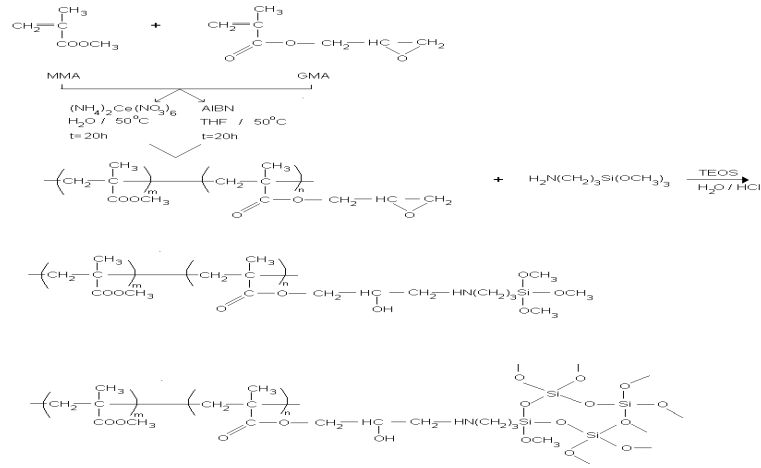
Method-2: P(MMA-GMA) / SiO₂ hibridleri, serbest radikal polimerizasyon sırasında AMPTS nin polimerizasyon karışımına ilave edilmesiyle hazırlandı. Polimerizasyon tamamlandıktan sonra ön hidrolize edilmemiş TEOS karışıma eklendi ve karıştırıldı.

Method-3: Kopolimer çözeltiler aseton içinde hazırlandı. HTAB-MMT (kopolimer konsantrasyonunun ağırlıkça %10 u) kopolimer çözeltisine ilave edildi ve farklı karıştırma metodları uygulandı.

Sonuçta ortaya çıkan bütün homojen karışımlar Teflon kalıplara döküldü ve kür edildi.

FTIR sonuçları inorganik ve organik ağ yapılarının kovalent bağlar oluşturduğunu gösterdi. Bütün bu filmler Si-O-Si, Si-O-C ve C-N-C gruplarının karakteristik bantları olan 1150 cm⁻¹, 1100 cm⁻¹ ve 1050 cm⁻¹ de bant verdiler. Bunun nedeni polimer zincirlerin epoksi gruplarının, bağlayıcı bileşen (veya MMT ye bağlı HDA) nin amin grupları ve inorganik fazlarla (TEOS/H₂O/HCl) kovalent bağlar oluşturmasındandır.

Method I ve II ile hazırlanmış P(MMA/GMA)/AMPTS/TEOS hibridlerinin reaksiyon mekanizması Şekil 2’ de verilmiştir. Elde edilen malzemelerin termal ve mekanik özellikleri TGA, DSC, DMA ve XRD teknikleri kullanılarak irdelendi.



Sekil 2: Yöntem I ve II ile hazırlanmış P(MMA/GMA)/AMPTS/TEOS hibridlerinin reaksiyon mekanizması

TGA sonuçları göstermiştir ki, termal bozulma sıcaklıkları Metod I ile elde edilen P(MMA-GMA)/AMPTS/TEOS 'lerde göreceli olarak daha yüksektir. Bariz bir şekilde, sol jel prosesi süresince trimetoksilil grupları AMPTS/TEOS güçlü silika ağ bağlarına dönüşmüşlerdir. Daha yüksek sıcaklıkta hibrit malzeme saf polimere nazaran daha stabil davranış göstermiştir. Silikanın varlığı polimer zincirlerini bir yere kadar oksidatif bozulma sürecinden korumuştur. Metod III ile elde edilen P(MMA-GMA)/HDA-MMT larının içindeki silika ağ bağları stabil değildir ve hibridlerin bozulmasının daha 250 derecede başlamasına neden olur. Buna tezat olarak, Metod I ve Metod II ile elde edilen numunelerde daha yüksek bozulma sıcaklıkları gördük. Bu yüzden, P(MMA-GMA)/AMPTS/TEOS hibridlerinin termal stabilitesi iyileşmiştir.

Camsı geçiş sıcaklıkları Tg deki değişiklikler irdelemek için DSC kullanıldı. TEOS ve HTAB-MMTnin P(MMA-GMA) kopolimerlerinin içine katılımı az bir miktar Tg artışına yol açtı (ağırlıkça %10 inorganik komponent de 3 ila 10 derece).

Hibrit malzemelerin mekanik özelliklerinin incelenmesi için DMA kullanıldı. Başlangıçta 10 ve 20 % mol GMA içeren P(MMA-GMA)/TEOS ve P(MMA-GMA)/AMPTS/TEOS hibridlerinin Young modülü kopolimerlerden daha yüksek bulunmuştur.

APTMS nin uzun zincirlerinin polimer zincirler ile amin bağlarla bağlanması halinde, organik ve inorganik türler arasında esnek arayüzler oluşur. Bu kovalent bağlar hibrid malzemelerin mekanik özelliklerini iyileştirmiştir.

Orgonakillerin PMMA ve P(MMA-GMA) polimerleri içerisindeki dağılımını karakterize etmek için XRD kullanıldı. Bu sonuçlara göre, hem MMT ye katılan organik zincir yapılarının hemde çözeltileri hazırlamak için kullanılan karıştırma yöntemlerinin polimer/kil kompozitlerindeki tabakalar arası boşlukları ve dağılımları etkilediği görülmüştür.

Bulunan bütün sonuçlar, bu tezde sentezlediğimiz komposit ve hibrit malzemelerin hem thermal hem de mechanical özelliklerinde iyileşmeler olduğunu göstermiştir.

1. INTRODUCTION

1.1 Composites and Hybrid Materials

Nanocomposites are a new class of composites. They are derived from the ultrafine inorganic particles with dimensions typically in the range of 1 to 1000 nm . These particles are dispersed in the polymer matrix homogeneously. Polymer/ Layered Silicate (PLS) nanocomposites show evidence of outstanding improvements in material properties when they compare with the properties of virgin polymer or conventional micro and macro-composites. Therefore, PLS nanocomposites have attracted great interests in both industry and academia.

Nanomaterial additives can make the following advantages in comparison to their conventional filler counterparts [1-5].

- Improved mechanical properties e.g. strength, modulus and dimensional stability
- Decreased permeability to gases, water and hydrocarbons
- Flame retardancy and reduced smoke emissions
- Increased thermal stability and heat distortion temperature, chemical resistance
- Surface appearance, electrical conductivity and optical clarity in comparison to conventionally filled polymers

On the other hand, there have been observed some disadvantages associated with nanoparticle incorporation, concerning toughness and impact performance .

Physical mixture of a polymer and layered silicate may not form a nanocomposite. This situation is equivalent to polymer blends, and in most cases separation into discrete phases occurs. In immiscible systems that correspond to conventionally filled polymers, the poor physical interaction between the organic and the inorganic components leads to

poor mechanical and thermal properties. On the contrary, 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. Thus, nanocomposites exhibit unique properties resulting from the intermolecular interactions. These material properties do not shared by their micro counterparts or conventionally filled polymers [6]

1.1.1. Classification of composites and hybrid materials

There are several different ways to synthesize nanocomposite. Therefore, a means of classification is necessary.

Type I: Organic polymer settled in an inorganic matrix without covalent bonding between the components.

Type II: Organic polymer settled in an inorganic matrix with sites of covalent bonding between the components.

Type III: Co-formed Interpenetrating Network of inorganic component and organic polymer without covalent bonds between phases.

Type IV: Co-formed Interpenetrating network of inorganic component and organic polymer with covalent bonds between phases.

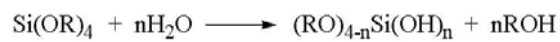
Type V: Simultaneous polymerization of inorganic component and organic polymer.

The most common nanocomposites in the literature are classified as **Type I**. The aim in the process is to form a completely interpenetrating network (IPN) of both inorganic and organic phases. Homogeneous nanocomposites with full-IPNs are often stronger, more flexible and optically transparent, whereas heterogeneous composites are often mechanically weaker and opaque. The select of co-solvents is critical throughout the formation of the inorganic component. As the hydrolysis and/or condensation reaction occurs, changes in the polarity of the solvent mixture can result in undesired phase separation of the inorganic and organic components.

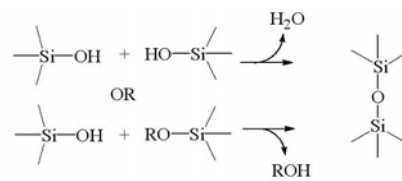
It is better to discuss the sol-gel process before the other types of nanocomposites. Sol-gel chemistry is based on the polymerization of molecular precursors such as

metal alkoxides $M(OR)_n$. Hydrolysis and condensation of these alkoxides lead to the formation of metal oxopolymers. The sol-gel process allows the introduction of organic molecules inside an inorganic network. Then, inorganic and organic components can be mixed at the nanometric scale. They are called as hybrid organic-inorganic nanocomposites. These hybrids are very much versatile in their composition, processing and optical and mechanical properties. Although zirconium, titanium, aluminum and boron oxides have been used as the inorganic component [7], the great majority of nanocomposites include silica from tetraethoxysilane (TEOS). The formation of the inorganic component includes two steps, hydrolysis and condensation as seen in Figure 1.1. The formation of this part of the composite is based on the relative kinetic rates of each step. For example, if the rate of hydrolysis is higher than that of condensation, then simple particles or highly branched silicate matrices are formed. In opposite, if the condensation step is faster than hydrolysis, then string-like filaments are formed. These changes in morphology of the silicate matrix can be affected by the type of sol-gel catalyst. This means that catalysts have dramatic effects on the physical properties of the nanocomposites [8].

Hydrolysis



Condensation



Overall

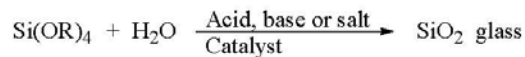


Figure 1.1: Schematic representation for the hydrolysis and condensation steps.

Type II composites use modified organic polymers that have active sites to be able to form covalent bonds directly to the inorganic phase of the nanocomposite. Usually an

organosilane with a reactive pendant group is used to form the covalent bond to the organic polymer component. These pendant groups can be isocyanates, which easily react with polymers containing alcohols or amines [9]. Another option is hydrosilation reactions with polymers containing a terminal alkene [10].

Type V. Novak and Grubbs developed a method for simultaneous polymerization of both inorganic and organic components without shrinkage of the material [11]. The loss of solvents in the sol-gel process creates material shrinkage that leads to cracking. Solvent loss created during the hydrolysis step is eliminated, by replacing the ethoxide found in TEOS with an organic monomer oxide. There are limited number of composites have been formed successfully with this process. This is probably because of the difficulties in definitely matching the rates of polymerization of the organic component with both the rates of hydrolysis and condensation of the inorganic component to prevent phase separations.

1.1.2. Structure of layered silicates

Natural and synthetic silicates such as mica, montmorillonite, saponite and hectorite are used to make nanocomposites that have improved mechanical properties. A few weight percent of layered silicates that are regularly dispersed throughout the polymer matrix create much higher surface area for polymer/inorganic filler interaction as compared to traditional composites. The individual silicate platelets are about 1 nanometer ($1\text{ nm} = 10^{-9}\text{ m}$) thick and 1000 nm across the face, which is 1400 times smaller than the finest talc reinforcements in use today. Pristine layered silicates has been known for more than 60 years [12-17]. Their structural characteristics are identical to the one of talc (2:1 phyllosilicate), and they are formed of hydrated aluminum silicate. Therefore, they are generally classified as clay minerals, which are the most abundant minerals on the surface of the earth. Their crystal structures include two-dimensional layers (thickness = 0.95 nm) formed by fusing two silica tetrahedral sheets with an edge-shared octahedral sheet of either alumina or magnesia [18]. Stacking of these layers result in van der Waals gaps or galleries. The interlayers are occupied by Na^+ and/or Ca^{2+} ions. They balance the charge deficiency that is generated by isomorphous substitution within the layers (e.g., tetrahedral Si^{4+} by Al^{3+} or octahedral Al^{3+} by Mg^{2+}). These cations are not structural and can be easily replaced by other positively charged atoms or molecules, so

they are named as exchangeable cations [19]. In contrast to pristine layered silicates including alkali metal and alkali earth charge balancing cations, organically modified layered silicates (OLS) contain alkyl ammonium or phosphonium cations [20]. In the presence of these organic modifiers in the galleries the originally hydrophilic silicate surface changes to hydrophobic structure. The OLS may be chosen to optimize their compatibility with a given polymer, depending on the packing density, functionality and length of the organic modifiers.

The mostly used layered silicates for the preparation of PLS nanocomposites concern to the same general family of 2:1 layered phyllosilicates. Figure 1.2. shows the structures of layered phyllosilicates.

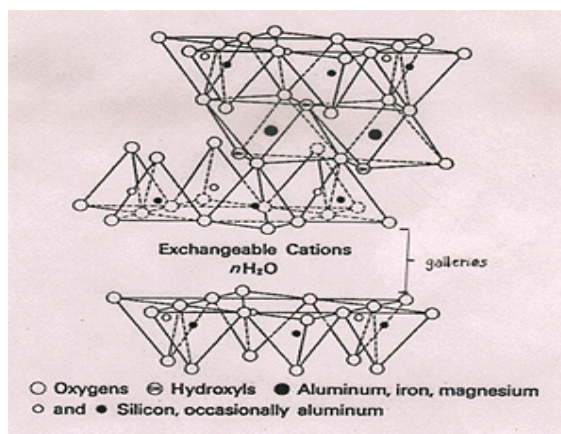


Figure 1.2: TOT structures of layered phyllosilicates (Ref. Polymer Layered-Silicates Nanocomposites Web Page)

Montmorillonite (MMT) is the most common type of natural clay used for nanocomposite formation. The other types of layered silicates can also be used depending on the material properties required from the product. These clays include hectorites (magnesium silicates) containing very small platelets, and synthetic clays (e.g. hydrotalcite), which can be produced in a very pure form. The last one can carry a positive charge on the platelets in contrast to the negative charge found in montmorillonites. MMT has a large layer space and some perfect properties such as good water absorption, swelling, adsorbability, cation exchange and drug-carrying capability. It can be neutralized and bonded either by substitutions within the lattice or by cations in the underlayer region. The degree of substitution depends on the structure of the montmorillonite. In the tetrahedral plane, substitution may progress

up to about 15% but in the octahedral plane, it may extend to completion. Typical cation exchange capacities of MMT clays are between 70 and 110 millequivalents per 100 gram. Hydrophobic nature of the organically modified clay surfaces provides homogeneous dispersion in the organic polymer phase. In addition, when the organic cations are incorporated to modify the clay surface, they will influence the thermal behaviour of the clay materials.

MMT, which is a hydrophilic and swollen natural clay, lacks affinity with the hydrophobic organic polymer. In general, it is treated by long alkylchain ammonium salt to replace Na^+ and Ca^{+2} ions in the galleries.

When MMT / polymer nanocomposite is synthesized, the polymer chains enter the galleries between the layers by diffusion or shear stress effect. It is well known that a number of organic / inorganic nanocomposites can be prepared by intercalation polymerization from organic polymer and MMT [21, 22].

Nanocomposite materials gain significant property improvements with very low amount of nanoparticulate whereas traditional microparticle additives require much higher loading levels to attain similar performance. For example, polyamide / MMT nanocomposites show tensile strength improvements of approximately 40 % and 20 % at temperatures of 23°C and 120°C, respectively, and modulus improvements of 70 % and 220 % at the same temperatures. All of these improvements have been obtained with only 5 % loading of MMT. Similar mechanical improvements have been reported for polymethyl methacrylate / clay hybrids.

1.1.3. Types of PLS Nanocomposites

It is important to improve the interaction between clay and polymer matrix to produce a useful polymer composite. Depending on the strength of interfacial interactions between the polymer matrix and layered silicate (modified or not), three different types of PLS nanocomposites are produced (Figure 1.3):

a. Intercalated nanocomposites: Polymer matrix inserted into the layered silicate structure. They are interlayer by a few molecular layers of polymer and occur in a regular fashion, regardless of the clay to polymer ratio..

b. Flocculated nanocomposites: This is nearly same as intercalated nanocomposites. But in this case silicate layers are flocculated due to hydroxylated edge–edge alternation of the silicate layers.

c. Exfoliated nanocomposites: The individual clay layers are randomly separated in a continuous polymer matrix by an average distances that depend on clay loading. The clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite.

Although most organoclay nanocomposites reported so far are intercalated, exfoliated structures create more acceptable improvement of the polymeric materials. However, further research are necessary to develop better routes to platelet exfoliation and dispersion and to understand the formulation, structure and property relationships.

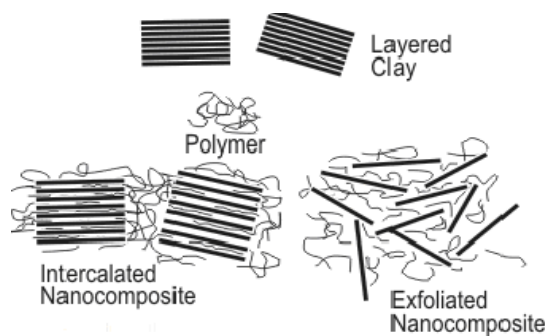


Figure 1.3: Schematic illustration of three different types of PLS nanocomposites (Ref. amazon.com)

1.1.4. Polymer Incorporation into PLS Nanocomposites

Nanostructured materials are intimate combinations of one or more inorganic components with a polymer so that perfect properties of the former can be taken together with the existing qualities of the latter. Many researches concerning the developments of the incorporation techniques of the nanoparticles into the polymeric matrices have been published. Mostly such combinations need blending or mixing of the components, taking the polymer in solution or in melt form. The selection of modified clay is essential to ensure effective penetration of the polymer or its precursor into the interlayer spacing of the clay and result in the desired exfoliated or intercalated product. Polymer can be introduced either as the polymeric species itself

or via the monomer, which is polymerized in situ to give the appropriate polymer/clay nanocomposite. Secondly, polymers can be introduced either by melt blending (for example extrusion) or by solution blending. Melt blending can be less effective than in situ polymerization in producing an exfoliated nanocomposite.

Thermosets and thermoplastics such as nylons, polyolefins, polystyrene, epoxy resins, polyurethanes, polyimides and poly(ethylene terephthalate) have been incorporated into the structures of nanocomposites.

The oldest example of the in situ polymerization method was work by Toyota on synthesis of clay / nylon nanocomposites. In a typical synthesis, ADA-modified clay is dispersed in the monomer caprolactam, which is polymerized to form the Nylon-6 / clay hybrid as an exfoliated composite. Complete exfoliation may be obtained by intercalation of the monomer in the clay. Low concentration of organoclay is incorporated in these nanocomposites, because only a few percent of inorganic nanofiller is sufficient to modify the required properties. Higher contents of clay can increase the viscosity and lead to poor processability. Other nylons and copolyamides (e.g. nylon-6/6,6) have also been incorporated into PLS nanocomposites. Functionality such as hydroxyl groups can be introduced into the onium salt modifiers to improve compatibility with the nylon via hydrogen bonding. This can improve the nanocomposite properties.

1.1.5. Characterization Techniques of Composites and Hybrids

1.1.5.1 Structural Characterizations

Although low cost and a relatively simple processing method, intercalation or exfoliation of clay in a polymer matrix is relatively complicated. Intercalation or exfoliation of clay can be observed by transmission electron micrograph (TEM), scanning electron micrograph (SEM) and X-ray diffraction (XRD) techniques. Generally, the structure of nanocomposites has been tested using wide angle X-ray diffraction (WAXD) analysis and TEM observation. WAXD is mostly used to investigate the nanocomposite structure due to its easiness and availability [1] and to study the kinetics of the polymer melt intercalation [23]. By observing the position,

shape and intensity of the basal reflections distributed from the silicate layers, the nanocomposite structure may be clarified. For example, the extensive layer separation in an exfoliated nanocomposite are related with the delamination of the original silicate layers in the polymer matrix and results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers. For intercalated nanocomposites the limited layer expansion is related with the polymer intercalation and results in the appearance of a new basal reflection that corresponds to the larger gallery height. In other words, the success of intercalation is mainly verified by the increase of the d-basal spacing (interlayer distance) and it is determined by WAXD [24, 25].

WAXD technique is limited to a 2θ angle larger than 2° and does not give the distribution of the clay stacks. Small angle X-ray scattering (SAXS) is suitable for detecting the structure of clay layers at 2θ less than 2° . Detailed information such as the distribution of the clay stacks, mean number of layers per stack, layer distance and disorder of organoclay dispersed in organic media can only be obtained by SAXS patterns together with TEM images. These XRD patterns indicate whether intercalated or exfoliated structure and the effect of mixing technique which is used to prepare polymer / clay composites.

X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV. For diffraction applications, only short wavelength X-rays in the range of a few angstroms to 0.1 angstrom (1 keV - 120 keV) are used. Because the wavelength of X-rays is comparable to the size of atoms, they are useful for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X-rays can penetrate deep into the materials and provide information about the bulk structure.

X-rays are produced generally by either X-ray tubes or synchrotron radiation. In a X-ray tube, which is the primary X-ray source used in laboratory X-ray instruments, X-rays are generated when a focused electron beam accelerated across a high voltage field bombards a stationary or rotating solid target. As electrons collide with atoms in the target and slow down, a continuous spectrum of X-rays are emitted. The high energy electrons eject inner shell electrons in atoms through the ionization process. When a free electron fills the shell, a X-ray photon with energy characteristic of the

target material is emitted. Common targets used in X-ray tubes include Cu and Mo, which emit 8 keV and 14 keV X-rays with corresponding wavelengths of 1.54 Å and 0.8 Å, respectively.

The peaks in a X-ray diffraction pattern are directly related to the atomic distances. An incident X-ray beam interacts with the atoms arranged in a periodic manner as shown in 2 dimensions in the following illustrations (Figure 1.4).

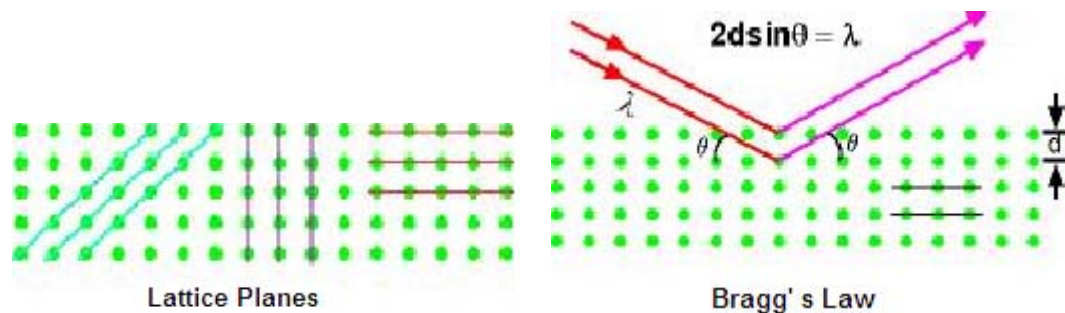


Figure 1.4: X-ray diffraction (Ref. Classic x-ray physics book 1969)

The atoms (represented as green spheres in the Figure above) can be viewed as forming different sets of planes in the crystal (colored lines in graph on left). For a given set of lattice planes with an inter-plane distance of d , the condition for a diffraction (peak) to occur can be simply written as

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

which is known as the Bragg's law. In the equation, λ is the wavelength of the X-ray, θ the scattering angle, and n represents the order of the diffraction peak. The Bragg's Law is one of most important laws used for interpreting X-ray diffraction data. Bragg's Law is applied to scattering centers consisting of any periodic distribution of electron density. In other words, the law holds true if the atoms are replaced by molecules or collections of molecules, such as colloids, polymers, proteins and virus particles.

1.1.5.2 Thermal and mechanical characterizations:

Thermal analysis includes a wide variety of techniques such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), Thermogravimetric

analysis (TGA), dynamic mechanical thermal analysis (DMTA) and dynamic mechanical analysis (DMA).

1.1.5.2.1 Thermogravimetric analysis (TGA)

TGA is an analytical technique which is used to determine thermal stability of material. Its fraction of volatile components is obtained by monitoring the weight change that occurs as a specimen is heated. The measurement is carried out in air or in an inert atmosphere such as Helium or Argon. The weight is recorded as a function of increasing temperature. Sometimes, the measurements are performed in a lean oxygen atmosphere (1 to 5% O₂ in N₂ or He) to slow down oxidation. In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans (differential thermal analysis, or DTA) or the heat flow into the specimen pan compared to that of the reference pan (differential scanning calorimetry, or DSC). The latter can be used to monitor the energy released or absorbed via chemical reactions during the heating process.

In most cases, TGA analysis is performed in an oxidative atmosphere (air or oxygen and inert gas mixtures) with a linear temperature ramp. The maximum temperature is selected so that the specimen weight is stable at the end of the experiment, indicating that all chemical reactions are completed and all of the carbon is burnt. This approach provides two important numerical information: ash content (residual mass, M_{res}) and oxidation temperature (T_o) (Figure 1.5). While the definition of ash content is unambiguous, oxidation temperature can be defined in many ways, including the temperature of the maximum in the weight loss rate (dm/dT_{max}) and the weight loss onset temperature (T_{onset}). The former refers to the temperature of the maximum rate of oxidation, while the latter refers to the temperature when oxidation just begins. The use of the former definition ($T_o = dm/dT_{\text{max}}$) is preferred for two reasons. First, it may be difficult to determine T_{onset} precisely due to the gradual initiation of transition (sometimes up to 100°C, Figure 1.4). Second, weight loss due to carbon oxidation is often superimposed on the weight increase due to catalyst oxidation at low temperatures. In some cases this leads to an upward swing of the TGA curve prior to the bulk of the weight loss, which makes the definition of T_{onset} even more difficult and ambiguous.

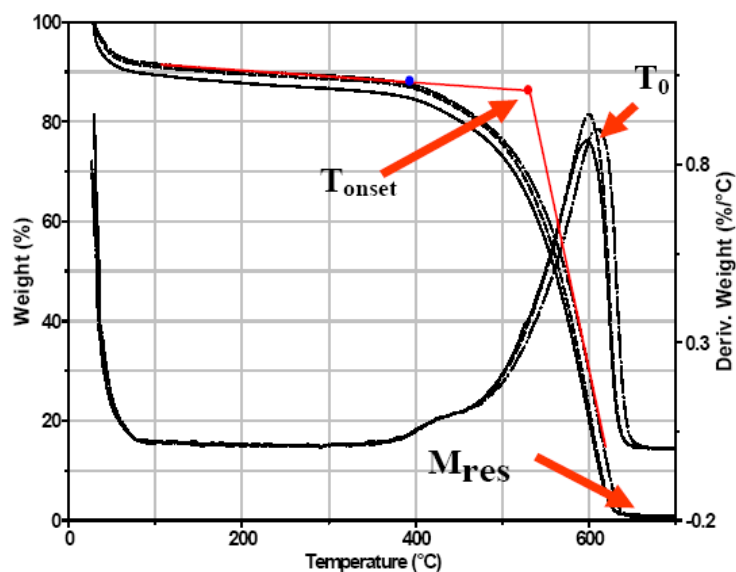


Figure1.5: TGA curves of purified Single-Wall Nanotubes (Ref. TA instruments.)

1.1.5.2.2 Differential scanning calorimetry (DSC)

DSC also is a technique which is part of a group of techniques called Thermal Analysis (TA). Thermal Analysis is based upon the detection of changes in the heat content (enthalpy) or the specific heat of a sample with temperature. As thermal energy is supplied to the sample its enthalpy increases. Its temperature rises by an amount determined, for a given energy input, by the specific heat of the sample. The specific heat of a material changes slowly with temperature in a particular physical state, while it alters discontinuously at a change of state. As well as increasing the sample temperature, the supply of thermal energy may induce physical or chemical processes in the sample, e.g. melting or decomposition. These processes proceed by a change in enthalpy, the latent heat of fusion, heat of reaction etc. Such enthalpy changes may be detected by thermal analysis and related to the processes occurring in the sample.

Both sample and reference are maintained at the temperature predetermined by the program even during a thermal event in the sample. The amount of supplied and/or withdrawn energy from the sample to maintain zero temperature differential between the sample and the reference is the experimental parameter, and it is displayed as the ordinate of the thermal analysis curve. The sample and reference pans are placed in

identical environments. Each of metal pans contains a platinum resistance thermometer (or thermocouple) and a heater. The temperatures of the two thermometers are compared. The electrical power supplied to each heater adjusted so that the temperatures of both the sample and the reference remain equal to the programmed temperature. The specific heat at any temperature determines the amount of thermal energy necessary to change the sample temperature by a given amount. Therefore, the ordinate signal that refers the rate of energy absorption by the sample (e.g. millicalories/sec.) is proportional to the specific heat of the sample. Any transition accompanied by a change in specific heat produces a discontinuity in the power signal. Exothermic or endothermic enthalpy changes give peaks whose areas are proportional to the total enthalpy change (Figure 1.6).

As a summary, in DSC, the measuring principle is to compare the rate of heat flow to the sample and to an inert material which are heated or cooled at the same rate. Changes in the sample that are associated with absorption or evolution of heat cause a change in the differential heat flow which is then recorded as a peak. The area under the peak is directly proportional to the enthalpic change and its direction indicates whether the thermal event is endothermic or exothermic.

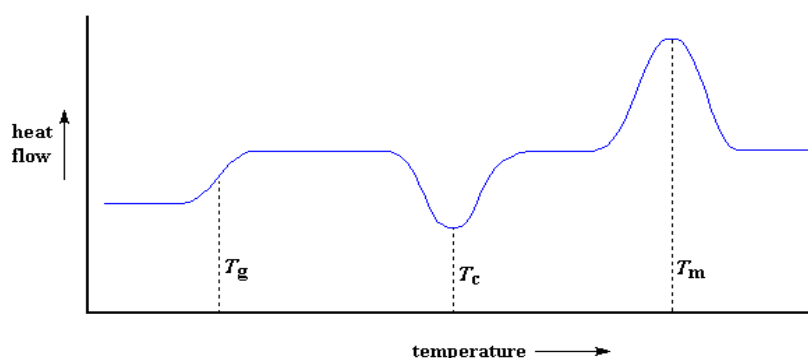


Figure 1.6: Schematic representation of a DSC thermogram (Differential Scanning Calorimetry by Stephen Collins)

It is also possible to determine glass transition temperature of a polymer with DSC. When polymer heat after a certain temperature, the plot will shift upward. This means it is getting more heat flow. This happens because the polymer has just gone

through the phase transition. Polymers have a higher heat capacity above the glass transition temperature than they do below it.

DSC can be used to measure glass transition temperature of a polymer because of the change in heat capacity that occurs at the glass transition. The change does not occur suddenly. It takes place over a temperature range (Figure 1.7).

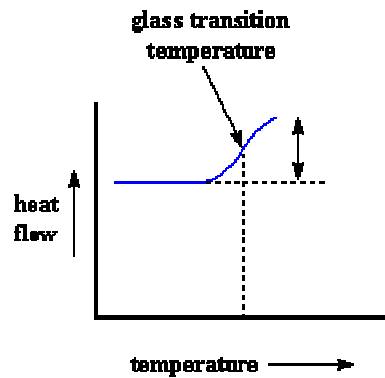


Figure 1.7: Glass transition of a material

1.1.5.2.3 Dynamic mechanical analysis (DMA)

DMA or dynamic mechanical thermal analysis (DMTA) can be used to study and characterize hybrid materials. Some of its applications are

- *Determination of glass transition temperature (T_g) of highly crosslinked or crystalline materials and composites
- *Determination of modulus under a variety temperature and frequency conditions
- *Creep experiments
- *Determination of curing behavior
- *Film/Fiber Stress-Strain measurements

With this technique a sample with well-defined dimensions is exposed to a sinusoidal mechanical deformation at fixed frequency or range of frequencies over a specific temperature range and also isothermally as a function of time and the corresponding forces measured [26]. This can be done in tensile, compression, shear,

flexural and bending modes of operation. In an opposite way, the sample can be subjected to a pre-selected force amplitude and the resulting deformation is measured. The more delayed response is for the more viscous materials while less delayed responses are characteristic of more elastic materials [27].

Strain is a measure of the change in length of a material after a force is applied. Stress is an internal force in a material, being equal and opposite to the applied load. When a sinusoidal stress is applied to a perfectly elastic solid, the deformation occurs exactly in phase with the applied stress. Therefore, the modulus is not time dependent.

A completely viscous material will respond with the deformation lagging 90° behind the applied stress. When the stress is applied to a visco-elastic material, it will behave neither as a perfectly elastic nor as a perfectly viscous body. The resultant strain will lag behind the stress by some angle δ where $\delta < 90^\circ$. The magnitude of the loss angle is dependent upon the amount of internal shift that occur in the same frequency range as the imposed stress. The stress that is in phase with the applied strain is used to determine the elastic or storage modulus (E'). It is an indicator of elastic behavior. It shows the ability of the material to store elastic energy related with recoverable elastic deformation. The stress that is out of phase with the applied strain is used to calculate the viscous or loss modulus (E''). It is an indication of energy absorbed by the resin that is not returned elastically. This energy is used to increase segmental molecular vibration or to translate chain positions.

The loss tangent ($\tan \delta$) or mechanical damping is the phase angle between the dynamic strain and stress in the oscillating experiment. It is given by the ratio of the viscous modulus to the elastic modulus and is dimensionless. This visco-elastic property is a measure of the mechanical energy dissipation or “loss” within the material in the form of heat. A perfectly elastic solid has $\tan \delta = 0$ [26]. The loss tangent reaches a maximum or peak value at the condition of temperature and/or frequency that the internal rate of molecular motion corresponds to the external driving frequency applied to the bulk specimen. The maximum of the loss tangent is frequently associated to T_g . The location of such “loss peaks” provides information about internal molecular mobility. The lower value of loss tangent means the

material will give quicker respond to load. It returns faster to its original shape. However, the higher value of loss tangent corresponds to the higher amount of energy lost as heat (more viscous like) [28].

The magnitude of the applied stress and the final strain are used to calculate the stiffness of the material under stress. The phase lag between the two (or δ) is used to determine $\tan \delta$. The sample can be mounted in the DMA in a number of ways depending on the characteristics of the sample

*where the strain is in phase with the stress (i.e., δ is 0°) the sample is referred as elastic. An example of an elastic material might be a rubber band or a metal spring.

*where the strain is 90° out of phase with the stress (i.e., δ is 90°) the sample is defined as viscous. Viscous materials such as Glycerin exhibit large damping properties.

*Most materials are classified as viscoelastic (i.e., δ is between 0° and 90°). Most polymers exhibit this behaviour and have an elastic and a viscous component.

Most of the polymers exhibit wide range of mechanical strength. A single polymer can exhibit an extremely wide range of mechanical behavior. For example,

- Very hard and rigid solid
- Stiff to Soft rubber
- Viscoelastic liquids.

The Mechanical strength of a polymer is a consequence of

- chemical composition of the polymer
- changes in mechanical properties that occur
- physical molecular structure of the polymer
- dictates how changes in mechanical properties will occur

Figure 1.8 shows a typical DMA curves of poly (methyl methacrylate) (PMMA). As the material goes through its glass transition, the modulus reduces and the material becomes less stiff. The $\tan \delta$ goes through a peak. This means the molecular reorganization of the relaxation induces less elastic behaviour. The data give

information on the position of the glass transition temperature, its frequency dependence, sample stiffness and other viscoelastic properties.

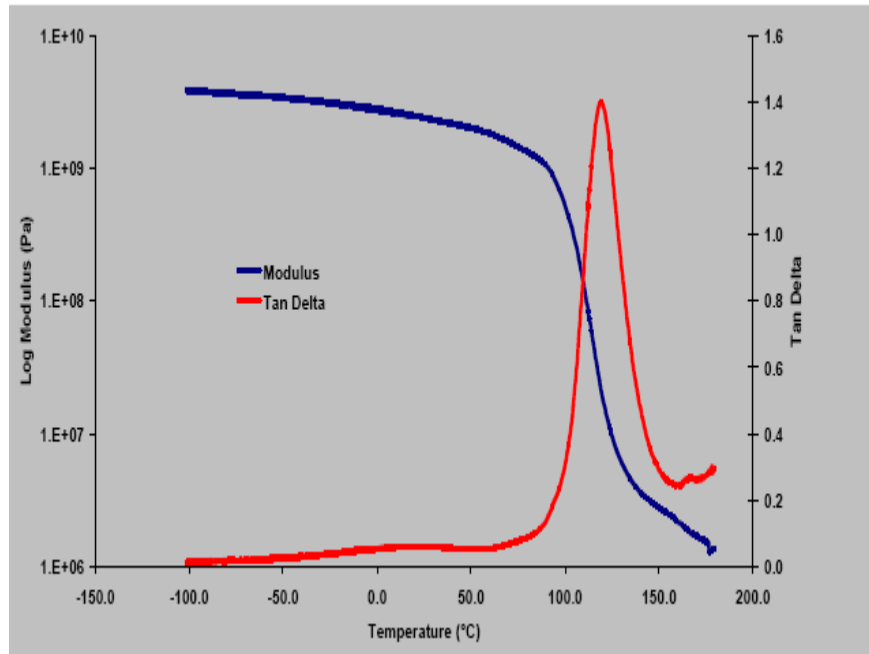


Figure 1.8: Typical DMA curves of PMMA (Ref .TTInf DMA)

Descriptions of all basic parameters, their units and relations for mechanical measurements are given as

* **Stress** = Force /Area [in unit Pa or dyn/cm²]

σ is uniaxial tensile or compressive stress

τ refers shear stress

σ_{hyd} is hydrostatic tensile or compressive stress

* **Strain** = Geometric shape change [no units]

ϵ = tensile strain, γ = shear strain

* **Strain or Shear Rate** = Velocity Gradient or d(strain) / dt (in unit 1/s)

$\dot{\epsilon}$ = tensile strain rate, $\dot{\gamma}$ = shear strain rate

ϵ indicates normal strain while γ refers shear strain

$\Delta V/V_0$ is fractional volume expansion or contraction

All materials change in shape, volume or both under the influence of an applied stress. The modulus measures the resistance to deformation of a material when an external force is applied.

Modulus = Stress / Strain (in unit Pa or dyn/cm²)

Three kind of modulus can be defined (Figure 1.8)

1. Young's Modulus (Modulus of Elasticity), E
2. Shear Modulus (Modulus of Rigidity), G
3. Bulk Modulus, B

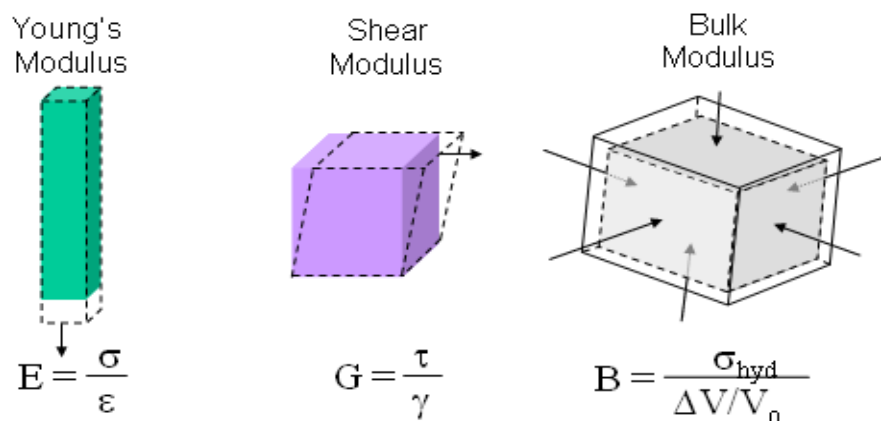


Figure 1.9: Schematic projections of modulus types (dashed lines indicate initial stressed State)

In Figures 1.8 and 1.9

*** The Modulus:** Measure of materials overall resistance to deformation.

***The Storage Modulus:** Measure of elasticity of material. It is equivalent to the ability of a sample to store energy or its elasticity.

$$G' = (\text{stress} / \text{strain}) \cos \delta$$

* **The Viscous (loss) Modulus:** The ability of the material to dissipate energy. Energy lost as heat.

$$G'' = (\text{stress} / \text{strain}) \sin \delta$$

* **Tan Delta** is a measure of material damping such as vibration or sound damping. Damping refers to the loss of mechanical energy as the amplitude of motion gradually decreases, or the ability of a material to dissipate mechanical energy by converting it into heat.

$$\tan \delta = G''/G'$$

Further,

* **Compliance** = Strain / Stress [1/Pa or cm²/dyn]

It is denoted by **J**.

* **Viscosity** = Stress / Strain Rate [Pa.s or Poise]

It is denoted by **η**. Typical stress-strain curve is given Figure 1.10.

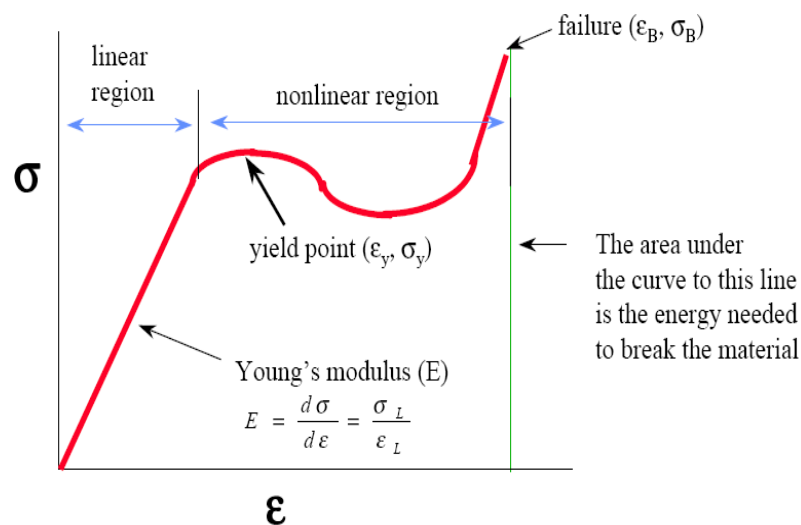


Figure 1.10: Analyzing of a stress-strain curve

1.2 Poly (methyl methacrylate) (PMMA) Hybrids

In recent years, there has been a great attention to polymer / clay nanocomposites because these materials often exhibit greatly improved mechanical, thermal, barrier, optical and fire retardant properties at a very low clay content (in general, less than 5 wt %) [29-32].

Hwu et al. have synthesized the PMMA / clay nanocomposite by direct dissolution method with acetone [33]. A TEM micrograph of PMMA / clay nanocomposite containing 5.0 wt % of organophilic clay is shown in Figure 1.11. The dark lines are the intersection of silicate sheets. The silicate sheets of clay are dispersed in the PMMA matrix homogeneously because of swelling by stearyltrimethyl ammonium chloride (SAC) and further intercalation with PMMA chain. According to DSC results, PMMA exhibits a heat flow change at approximately 82 °C, corresponding to the glass transition temperature (T_g) of PMMA. But, the clay intercalated PMMA shows the higher T_g at about 124°C. The intercalated PMMA chains within the silicate galleries prevents the segmental motions of the polymer chains. Also TGA test show that the PMMA / clay nanocomposite has better thermal stability than that of pure PMMA. The mechanical properties are obtained from DMA and results show that the storage modulus of PMMA / clay is higher than pure PMMA (Ref.33).

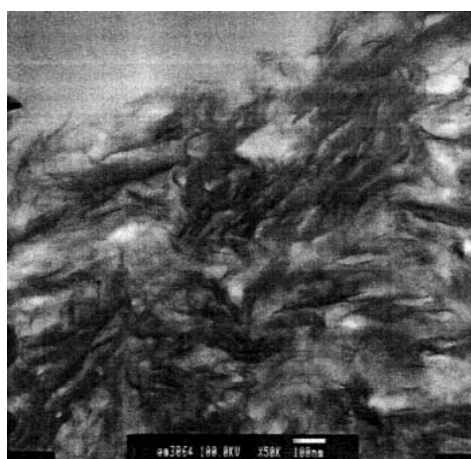


Figure1.11: TEM photograph of PMMA / clay nanocomposite (Ref.33).

In another study, Vasiliu and Wang have produced optically transparent PLS nanocomposites of PMMA and montmorillonite [34]. The nanodispersion of

organically modified montmorillonite (OMM) in PMMA is obtained by mixing in a common solvent with ultrasonic agitation. The composite solution is sprayed into a fine mist to result in a rapid removal of the solvent and to obtain the nanodispersion of the OMM in the polymer matrix. The X-ray scattering patterns and optical transmission spectra of the sprayed polymer composite films are compared with those obtained from the composite films prepared by the conventional solution casting method. Results showed that, PMMA / MMT nanocomposites (20 wt % of the layered silicate) prepared by the spraying process had an optical transmission greater than 80 % in the visible light region.

Hybrid materials produced by sol-gel process have a growing scientific and technological interest because of their applications in the fields of optics, electronics and electrochemistry [35]. An interesting family of hybrid nanocomposites is obtained from copolymerization reactions between siloxane and PMMA precursors, which lead to covalently bonded inorganic and organic nanophases. This permit to the synthesis of bulk materials with adjustable transparency, refractive index and hardness [36-37]. Because of these kind of properties, these materials have been used as lenses, coatings on commercial glasses to increase elastic modulus and decrease brittleness and for micropatterning of thin-channel wave-guides [38].

Regarding the nanocomposites based on PMMA, despite many literatures have been reported on the in situ intercalative polymerization of methyl methacrylate [39– 48], there have been fewer reports on the melt intercalation [49–51] and solution interaction methods [52]. For example, Kumar et al. reported that the melt intercalation method afforded an intercalated nanocomposite which has a higher thermal decomposition temperature (T_d) than pure PMMA [50]. Hwu et al. also reported that the intercalated nanocomposite prepared by the solution method shows a higher glass transition temperature (T_g) and a higher T_d [52]. On the other hand, the nanocomposites of acid anhydride cured epoxy resins can be prepared by essentially in situ intercalative polymerization method [53–60] because the cured polymers are non-fusible and insoluble.

Zhang et al. reported that the nanocomposite prepared from diglycidyl ether of bisphenol A and 4-methyl-1,2-cyclohexanedicarboxylic dianhydride shows a higher

T_g , T_d and storage modulus than the pure cured epoxy resin [53]. New nanocomposites based on the PMMA copolymers with thermosetting epoxy groups are expected to have superior heat resistance and rigidity.

Xie and Yang have studied [43] the influence of methacryloxypropyltrimethoxysilane (MPTMS) as silicone coupling agent on the structure and properties of PMMA / MMT nanocomposite. The silicone coupling agent reacted with the hydrogen group on the clay surface to obtain surface-modified MMT. Then, organophilic clay was obtained via an ion-exchange reaction. The polymer / MMT nanocomposite was prepared by in situ bulk polymerization. The structure and properties of the composites were studied. The results showed that the modification of MMT with silicone coupling agent did not affect the intercalation of the polymer chain, but influenced the dispersion of MMT in the polymer matrix. The smectic structure of the clay layer was maintained in nanocomposites prepared with modified organophilic MMT. XRD analysis showed that the dispersion of clay in nanocomposites with silicone modified organophilic MMT was more ordered than in nanocomposites with unmodified organophilic MMT. DSC and TGA analyses showed great improvements in the thermal properties. The glass transition temperature (T_g) of the nanocomposites was 6-15°C higher and the thermal decomposition temperature (T_d) was 100-120 °C higher than those of pure PMMA.

Huang and Qui [61] prepared PMMA / TiO₂ - SiO₂ hybrid materials from the copolymer of methyl methacrylate and methacryloxypropyltrimethoxysilane (MPTMS) with tetrabutyl titanate and tetraethoxysilane (TEOS). These materials have high transparency and high glass transition temperature. Also Huang and Qui [62] prepared hybrids incorporating the ethylene-propylene-nonconjugated diene terpolymer with tetrabutyl titanate and TEOS. These hybrids are also highly transparent and found to have improved properties over pure terpolymer in the modulus.

The application and industrial processing of these hybrid materials strongly depends on their rheological properties, which are determined by the interactions and motions of the constituent structural units, such as polymeric chains, aggregates, etc. The understanding of the correlations between rheological properties and nanostructural features of gelling systems is one of the great challenges of sol-gel chemistry that would certainly contribute to the molecular design of new materials.

Xie and Zhou [63] have synthesized P(MMA-MAn) with active anhydride groups by radical copolymerization. Using P(MMA-MAn) as a basic polymer, they prepared P(MMA-MAn)/SiO₂ hybrid materials by sol-gel process in different ways. For this purpose, P(MMA-MAn) reacts with aminopropyl trimethoxysilane (APTMS) to form amide bonds and the triethoxysilyl-functionalized polymer is obtained. After the modified polymer was cohydrolyzed with TEOS in solution, they obtained the hybrid materials in which organic species were connected with an inorganic network by chemical bonds. The structures of the materials were characterized by IR spectra. Their thermal and mechanical properties were studied by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and dynamic analysis (DA). The results showed the presence of covalent bonds among polymer chains and silica units and so, transparent materials are obtained. These hybrid materials have improved properties such as heat-resistant, mechanical, optical and other properties over pure P(MMA-MAn) copolymers. The hybrid materials prepared by the co-blending of the inorganic species are opaque. Further, the hybrids with chemical bonds between inorganic and organic species prepared by the sol-gel process have higher mechanical properties than those from the co-blending of inorganic-organic species, because the dispersion and reinforcement of inorganic particles in the latter are different from that in the former.

Sarmiento and Frigerio [64] have also studied the sol-gel process in PMMA. Hybrid of siloxane / PMMA nanocomposites with covalent bonds between the inorganic (siloxane) and organic (PMMA) phases were prepared by the sol-gel process through hydrolysis and polycondensation of 3-(trimethoxysilyl)propyl methacrylate (TMSM) and polymerization of MMA using benzoyl peroxide (BPO) as initiator. The effect of MMA, BPO and water contents on the viscoelastic behaviour of these materials was analysed during gelation by dynamic rheological measurements. The changes in storage (G') and loss moduli (G''), complex viscosity (η^*) and phase angle (δ) were measured as a function of the reaction time that shows the viscous character of the sol in the initial step of gelation and its progressive transformation to an elastic gel. This study was complemented by ²⁹Si and ¹³C solid-state nuclear magnetic resonance measurements of dried gel. The analysis of the experimental results indicates that linear chains are formed in the initial step of the gelation followed by a growth of

branched structures and formation of a three-dimensional network. Near the gel point this hybrid material demonstrates the typical scaling behaviour expected from percolation theory.

Sugimoto and Daimatsu [65] have studied PMMA based hybrids materials prepared from reactive silica nanoparticles. These nanoparticles were obtained by the reaction of 2-(methacryloyloxy)ethyl isocyanate with colloidal silica dispersed in ethyl acetate. They were copolymerized in various ratios with methyl methacrylate. Dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and visible spectrometry were performed to interpret the physical properties of the resulting hybrid materials. The PMMA / silica hybrid copolymers showed high transparency. Their storage elastic modulus and surface hardness increased with increasing silica content. Furthermore, in comparison with PMMA, the hybrid copolymers had better heat resistance and lower volume contraction.

The properties of the organic–inorganic hybrid composites result from the rich interaction between the constituents. They are greatly influenced by the length scale of the component phases (size and shape) and also by their interfacial interaction.

The reaction parameters that influence the sol-gel chemistry are the pH of the solution, the mole ratio of Si to H₂O, catalysts, solvents and reaction temperature. pH plays a key role in determining the nature of the hybrids when all other parameters are kept constant. Landry et al. [37] studied the effects of pH in poly (methylmethacrylate) / silica hybrids. The hybrids formed in both acidic and basic environments show that silica uniformly disperses in the polymer matrix with particles smaller than 100 nm in the presence of an acid catalyst while they form aggregates in basic medium. In general, HCl is used as an acid catalyst during the preparation of polymer-inorganic hybrids. Huang et al. [66] have observed the structure and morphology of the hybrids by using various HCl / TEOS ratios in poly (dimethyl siloxane). Nanolevel dispersion of silica particles within the hybrids in acid environment has also been reported by Zerda et al. [67] and Himmel et al. [68].

Bandyopadhyay has reported [69] a comparative study on structure-property relationship of acrylic rubber (ACM) / silica, epoxidised natural rubber (ENR) / silica and poly (vinyl alcohol) (PVA) / silica hybrid nanocomposites prepared by sol-gel

technique under different pH levels ($\text{pH} = 1.0\text{--}13.0$). The initial concentration of tetraethoxysilane (TEOS) (used as the precursor for silica) was kept at 45 wt %, and tetrahydrofuran (THF) for ACM / silica and ENR / silica while water for PVA / silica were taken as solvents. TEOS to water mole ratio was maintained at 1:2 for the rubber / silica systems to obtain the sol-gel reaction. The structure of the resultant hybrid composites was determined by using electron microscopy, Fourier Transform Infrared Spectroscopy (FTIR) and solubility. Dynamic mechanical and mechanical properties were also investigated. The silica particles were found to exist as nanoparticles (average diameter $< 100\text{ nm}$) at low pH (~ 2.0) beyond which these aggregate, although the amount of silica generation was not strictly influenced by the various pH conditions in all the systems. These nanocomposites were optically clear and showed very good mechanical reinforcement. The nanocomposites exhibited higher storage modulus both at the glassy and the rubbery regions as compared to those microcomposites. The loss tangent peak heights were also minimum and the T_g shifted to higher temperature for those nanocomposites. The maximum improvement of mechanical properties was observed with the PVA / silica nanocomposites due to higher level of interaction between the hydroxyl groups of PVA and the silanol groups of the silica phase.

Wei and Jin have also studied [70] mechanical properties of polyacrylate / silica hybrid sol-gel materials for potential dental applications. Optically transparent and monolithic polyacrylate / silica hybrid materials with composition from organic dominant to silica dominant have been prepared via sol-gel reactions of TEOS with reactive polymeric precursors (MMA-co-MSMA)s having number-average molecular weights of 82,500 and 7100 g/mol. The covalent bonds formed by cross-condensation between TEOS and the trimethoxysilyl groups of the MSMA units in the polymers prevent the organic-inorganic phase separation in the hybrid materials. In contrast to the pure sol-gel silica, the polyacrylate / silica hybrid materials are essentially non-porous even at the polymer content. The compression stress-strain behaviour of the hybrid materials is much different from those of conventional silica-reinforced PMMA composites. The hybrid materials exhibit a perfect strain hardening behaviour in the compression test while the composites show strain softening after yield. The reinforcing effect of silica on both compressive strength

and elastic modulus is greater for the hybrid materials than that for the silica / PMMA composites. The stress-strain behaviour of the hybrid materials can be tuned in between that of tenacious plastic and hard but fragile by varying silica content. These unique properties should make these hybrid materials excellent candidates for applications as dental materials.

Brostow, Datashvili and Hackenberg synthesized Poly(methyl acrylate) (PMA) + SiO₂ composites via a sol-gel reaction [71]. They have synthesized acrylic based copolymers with a content of alkoxysilane groups by copolymerization of methylacrylate (MA) with 3-(trimethoxysilyl) propylmethacrylate (3-MPS) and vinyltrimethoxysilane (VTMS). The products were co-condensed with tetraethylorthosilicate (TEOS). Two different methods have been used to obtain different compositions of PMA with SiO₂. The first one was the formation of covalently connected composites by functionalization of organic polymer backbones with trialkoxysilyl groups. These trialkoxysilyl groups result in hydrolysis and condensation processes providing an inorganic SiO₂ network. The second method is based on grafting polymeric molecules through covalent bonding to the existing hydroxyl groups. This includes silica surface treatment with a silane-coupling agent followed by radical grafting polymerization in aqueous or nonaqueous systems [72]. The PMA + SiO₂ hybrids were characterized by FTIR, Raman spectroscopy, DSC, TGA and environmental scanning electron microscopy (ESEM). Thermal stability of PMA is enhanced by copolymerization with 3-MPS or VTMS and the presence of SiO₂. Significant weight loss occurred only above 400°C. Decomposition temperatures were higher by 20 - 25 K as compared to the initial PMA. Trimethoxysilyl groups in PMA / 3-MPS were transformed into a strong silica network, during the sol-gel process. ESEM shows that only one of them leads to uniform distribution of silica in polymeric matrices.

Carbon nanotubes (CNTs) have generated a great deal of interest since their discovery in 1991 due to their unique physical properties such as large aspect ratio, excellent current-carrying capability and high thermal conductivity [73-75].

They are suitable for a wide range of applications including electrochemical, field-emission and electronic devices [76]. However, the most of the potential applications

are related with their mechanical properties. For example, Young's moduli of nanotubes can reach 1 TPa [77] while their strength has been measured at up to 63 GPa[78]. It has an order of magnitude stronger than high-strength carbon fibers [79]. This has made available the fabrication of materials such as supertough polymer–nanotube composite fibers[80]. Recently, Coleman et al. fabricated the composites based on poly(vinyl alcohol). They demonstrated an increase of $\times 3.7$ in Young's modulus and $\times 3.9$ in strength by adding less than 1 wt% of CNTs [81]. In this case, the increase was intimately related to the nucleation of polymer crystallinity by the nanotubes. The resulting crystalline interfacial region plays a dual role. It acts as a reinforcing agent in its own right because of its natural strength and stiffness. It is thought that crystalline interfacial regions result in better stress transfer to nanotubes compared to amorphous regions [82, 83]. Nevertheless, this method is not suitable for most types of polymer because of their inherently amorphous structure. As such, some method of interfacial engineering is required to maximize stress transfer in amorphous polymer matrices. Many methods have been reported to obtain amorphous polymer–nanotube composites with good dispersion and good stress transfer between polymer and nanotubes. They include extrusion techniques [84] melt processing [85] and the use of surfactants to aid dispersion [86]. Many authors have also studied the use of functionalized CNTs to improve the mechanical properties in polymer / CNT composites [87–91].

Another method involves in situ polymerization in the presence of pristine nanotubes. This can result in covalent attachment of nanotubes to the polymer. As a result, better dispersion and the formation of a strong interface between the nanotubes and the polymer matrix is obtained [92–97]. Using this process with pristine carbon nanotubes, Jia et al. [98] have suggested that the initiator could open the bonds of the CNTs during the polymerization. Therefore, it lead to a strong covalent interaction between the nanotubes and the polymer. However, in situ polymerization in the presence of functionalized nanotubes is even more promising. That is because of there is the superior dispersion of functionalized nanotubes in solvents and the potential for chemical reactions between the initiator and the functional group.

Blond, Barron and Ruether have synthesized PMMA / CNT composites using an in-situ radical polymerization method [99]. Polymer composites have been obtained using PMMA and OH-functionalized Multi Walled Nanotubes (MWNT)s by in situ polymerization. FTIR studies showed that bonding between carbon nanotubes and PMMA may take place at the –OH functionality and also at the outer layer of the CNTs. Mechanical properties have shown an increase in all the parameters investigated for a low content of carbon nanotubes. These improvements are approximately 94 % for Young's modulus, 360 % for ultimate tensile strength, 373 % for breaking strength, 1282 % for toughness, and 526 % for the elongation at break. Tensile measurements were tested to determine the mechanical properties of the PMMA composite films. For low CNT contents, a remarkable increase in stiffness, strength and toughness is clearly visible.

1.3. Poly (glycidyl methacrylate) (PGMA)

Glycidyl methacrylate (GMA) is relatively less toxic, polar and less expensive than other vinyl monomers. Epoxy group can go through ring-opening reaction with different nucleophiles [100-108]. However, it needs to be improved because of some deficiencies such as thermal stability and poor physical performance.

Poly (glycidyl methacrylate) (PGMA) / MMT nanocomposites offer the potential for excellent thermal properties and enhanced physical performance.

Celik and Onal have focused on developing new materials with improved properties. The purpose of their study was to synthesize PGMA / Na⁺- montmorillonite nanocomposites by free-radical polymerization [109]. In addition, the effect of monomer concentration on the physical properties of nanocomposites such as adsorption, moisture regain and water uptake were observed. Besides, the thermal and morphological properties of nanocomposites were characterized by XRD, FTIR, SEM and TGA techniques. XRD results showed that intercalated and partially exfoliated structures have been obtained. In addition, when the polymer content is increased, intercalation structure has increased. Interlayer distance of Na⁺MMT increased with glycidyl methacrylate content up to 68.25 wt % and, no further increase of interlayer distance at higher glycidyl methacrylate content was observed.

Thermogravimetric analysis results showed that these nanocomposites exhibited better thermal stability than pure PGMA. Adsorptive, moisture regain and water uptake properties of composites obviously decreased compared with the pure Na^+MMT . A significant decrease in these parameters with monomer concentration was observed. Moisture regain decreased due to the hydrophobic character of the PGMA and the hydrophilicity of Na^+MMT . The decrease in water uptake can be illuminated by the fact that the percentage of clay in the composites is limited. It reflects that the quantity of the polymer introduced in the layers reaches a limit and is enough to achieve maximum opening of the interlayers of clay [110]. The formation of a crosslinked structure to a certain extent prevents the insert on of water molecules into the structure [111]. Finally, water resistance of these composites can be greatly improved.

PGMA is also used with biodegradable polymers such as poly(3-hydroxybutyrate) (PHB) to increase the thermal properties of these polymers. Biodegradable PHB, which is biosynthesized with a wide variety of bacteria, has big potential in applications such as surgical field, long term carriers for drugs and degradable plastics. On the other hand, thermal stability of PHB is weak and due to this reason, it is not a good material in commercial products.

Lee et al. found that [112-114] poly(3-hydroxyalkanoate)s with epoxide pendants have better thermal stability due to crosslinking reactions of pendant epoxide groups with fragmented carboxyl chain ends. This implies that end group linking reactions with epoxide groups could be used effectively to repolymerize the thermally degraded polymer and subsequently inhibit to rapid decrease in the molecular weight of PHB. They chosen PGMA with epoxide groups. They first synthesized PGMA by radical polymerization and the blended with PHB. The compatibility and thermal reactions of the PHB / PGMA blends were investigated with DSC, TGA and DTA. PHB / PGMA blends were immiscible in the blended state, but for the blends with PGMA contents of 50 wt % or more, the compatibility was radically changed after 1 minute of annealing at 200 °C. During the annealing at this temperature the two polymers, which were phase separated, could react with each other at the interface. This was probably due to crosslinking reactions of the epoxide groups in the PGMA component with the carboxyl chain ends group of PHB during the degradation

process. And so, the thermal behaviors of copolymer blends improved. The reaction mechanism is given in Figure 1.30.

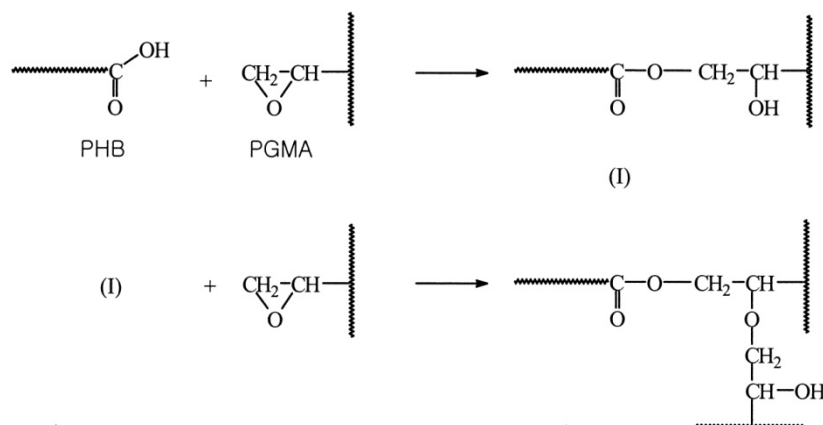


Figure 1.12: Reaction mechanism of PGMA and PHB

In another study, (poly(methylmethacrylate-3-(trimethoxysilyl)propyl methacrylate P(MMA-MSMA) / SiO₂ hybrids were synthesized by in situ polycondensation of alkoxy silane in the presence of trialkoxy silane-functional PMMA by Chang and Wang [115]. To investigate the effect of the interfacial structure between PMMA and silica on the local dynamics of the hybrids, they modified the interfacial structures of the PMMA / SiO₂ hybrid materials. The diethoxysilyl functionalized copolymers of poly(methyl methacrylate-maleic anhydride) P(MMA-MA5), with imide groups and poly(methyl methacrylate-glycidyl methacrylate) P(MMA-GMA5) with amine groups were prepared by in-situ additional copolymerization of 95 mol % of MMA with 5 mol % of MA and GMA, respectively, and then condensation with 3-aminopropyl methyl diethoxysilane (APrMDEOS) coupling agent. P(MMA-MA5) / SiO₂ and P(MMA-GMA5) / SiO₂ hybrids were obtained by co-hydrolysis of P(MMA-MA5) and P(MMA-GMA5) copolymers with TEOS via the sol-gel technique [116].

2-EXPERIMENTAL SECTION

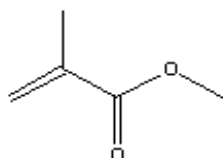
2.1. Materials

2.1.1 Polymethyl methacrylate (PMMA)

Poly(methyl methacrylate)s (PMMA) were purchased from Aldrich Chemical Company Inc. The molecular weights are 35,000 g/mol and 120,000 g/mol.

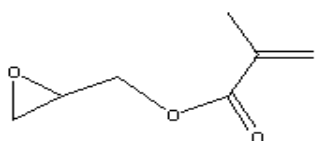
2.1.2. Methyl methacrylate (MMA)

MMA has a closed formula with $C_5H_8O_2$ and molecular weight of 100.12 g/mol. Its density and purity are 0.943 g/cm³ and 99 %, respectively. It was purchased from Fluka.



2.1.3. Glycidyl methacrylate (GMA)

GMA has a closed formula with $C_7H_{10}O_3$ and molecular weight of 142.16 g/mol. Its density and purity are 1.042 g/cm³ and 97 %, respectively. It was purchased from Fluka.

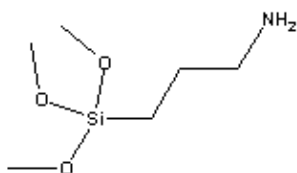


2.1.4. Sodium Montmorillonite (Na^+ - MMT)

It was synthesized from natural bentonite with stepwise purification by Süd-Chemie (Trademark = Nanofil 757). The cation exchange capacity (CEC) 80 meq / 100 g. Powder has particle size $< 10\mu\text{m}$ and $2,6 \text{ g} / \text{cm}^3$ density. The product was used without any further purification.

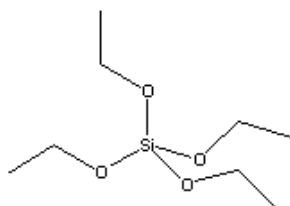
2.1.5. 1-Propanamine-3-(trimethoxysilyl)(AMPTS)

AMPTS is a closed formula with $\text{C}_6\text{H}_{17}\text{NO}_3\text{Si}$ and has molecular weight of 179.29 g/mol. Its density and purity are 1.027 g/cm^3 and 97 %, respectively. It was purchased from Aldrich.



2.1.6. Tetraethyl orthosilicate (TEOS)

TEOS is a closed formula with $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ and has molecular weight of 208.33 g/mol. Its density and purity are 0.943 g/cm^3 and 99 %, respectively. It was purchased from Merck.



2.1.7. α,α' -azobisisobutyronitrile (AIBN)

AIBN is a closed formula with $\text{C}_8\text{H}_{12}\text{N}_4$ and has molecular weight of 164.21 g/mol. It was purchased from Acros (98% purity) and was recrystallized from methanol.

2.1.8. Cerium ammonium nitrate (CAN)

CAN has a formula with $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and molecular weight of 548.23 g/mol. It was purchased from Aldrich (98.5% purity).

2.1.9 Hexadecyl amine (HDA)

HDA has a closed formula with $\text{C}_{16}\text{H}_{35}\text{N}$ and molecular weight of 241.46 g/mol.

It was purchased from Merck.

2.1.10 Organically modified MMT (HTAB-MMT)

Resadiye sodium bentonite which formula $(\text{Na}_{0,56} \text{K}_{0,02} \text{Ca}_{0,03}) [\text{Si}_{7,98} \text{Al}_{0,02}] (\text{Al}_{3,27} \text{Fe}_{0,23} \text{Mg}_{0,44}) \text{O}_{20}(\text{OH})_4$ was used and supplied from Mine Faculty. This bentonite was organically modified with hexadecyl trimethylammonium bromide (HTAB). The cation exchange capacity (CEC) was 76 meq./100g.

2.1.11. Solvents

Tetrahydrofuran (THF) has a closed formula with $\text{C}_4\text{H}_8\text{O}$ and molecular weight of 72.11 g/mol. It was purchased from Merck. N-methyl pyrrolidone (NMP) and Pyridine were purchased from Lancaster (99 %) and Riedel-de Haen (99.5 %), respectively.

2.2. EQUIPMENTS

2.2.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded on Perkin Elmer Spectrum One series spectrometer equipped with an attenuated total reflectance (ATR) objective (diamond and ZnSe). FTIR spectra were collected over the range 4000 to 600 cm^{-1} with the resolution of 4 cm^{-1} . Samples were prepared in the powder form for homopolymers and copolymers, and in the film form for hybrids and composites materials.

2.2.2. Differential Scanning Calorimeter (DSC)

The DSC measurements were performed on a Metler Toledo DSC 821 Model under a nitrogen atmosphere with flow rate 30 ml/min. and heating rate of 10 °C/min. The temperature range extended from 40 to 150 °C. A sealed aluminum type pan was used. Glass transition temperatures, T_g s were evaluated on the basis of thermograms from the second runs.

2.2.3 Gel permeation Chromatography (GPC)

The number average (M_n) - and weight average - molecular weights (M_w) and, dispersities (D) were analyzed using Perkin Elmer Model GPC and carried out with a set up consisting of Agilent pump and refractive index detector and three Agilent Zorbax Columns (1000 S, 300 S and 60 S). THF was used as the eluent at a flow rate of 0.5 ml / min at 30 °C.

2.2.4 Thermogravimetric analysis (TGA)

The TGA measurements were recorded on a TA Instrument TGA Q50 model. All samples were analyzed by TGA in nitrogen atmosphere at the heating rate of 20 °C / min. Several milligrams of each dried sample were placed on a balance located in the furnace, which was heated over the temperature range from 0 to 600 °C. Weight loss (in wt %) and the decomposition temperatures (T_d) were evaluated on the basis of graphics.

2.2.5. Dynamic mechanical analysis (DMA)

The stress-strain measurements at room temperature were performed on a TA Instrument Q1800 dynamic mechanical analyzer in a flexural mode at 1 Hz frequency. Maximum load is 18 N (tensile rate = 1N/min). Geometry of the films is rectangular and their lengths, widths, thickness (in mm) are 30.0 x 6.0 x 1.6

2.2.6. X-Ray diffraction (XRD)

XRD data on clay powder and composite samples were collected on Bruker X-ray diffractometer , a conventional copper target X-ray tube set to 40 kV and 40 mA. The X-ray source was $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). Data were collected from 2 θ of

3.00° to 10.00° (θ being the angle of diffraction) with a step width of 0.02°, step time of 12s and scanning speed of 0.1°/min.

2.2.7. Mechanical mixer

Fisher Scientific Powergen 125 Model mechanical mixer was used to prepare P(MMA-GMA) / HTAB composite materials.

2.2.8. Ultrasonic homogenizer (with sonicator tip)

Bandelin Electronic HD 207 type ultrasonic homogenizer with Titanium probe (MS 72 type) was used to prepare composite materials. Working frequency was 20 kHz.

2.2.9. Ultrasonic bath Elma Transsonic 460 type ultrasonic bath was used to prepare composite materials.

2.3. Experimental procedure:

In this study, different methods were used to prepare organic/inorganic hybrids and composites:

Method A. PMMA / HDA-MMT and P(MMA-GMA)/ HTAB-MMT composites by addition of organically modified layered silicate to solutions of homopolymer and copolymer, respectively.

Method B. P(MMA-GMA)/SiO₂ hybrid materials, by sol-gel process.

2.3.1.1 Method A

The composite materials were synthesized through direct mixing of organically modified layered silicate (OLS) into PMMA solution. To prepare OLS, hexadecyl amine (HDA) was used for the synthesis of organically modified layered silicate. Two mixing methods (magnetic stirring and ultrasonic agitation) were applied to prepare the homogeneous solutions of PMMA and OLS. The effect of process temperature, stirring time and mixing type on the structural, thermal and mechanical properties of the products (i.e., PMMA/HDA-MMT and P(MMA-GMA) / HTAB composites) have been investigated by using FTIR, DSC, TGA and DMA characterization methods.

2.3.1.2 Method B.

The copolymers of MMA with GMA were prepared by free radical solution polymerizations using ceric ammonium nitrate (CAN) and AIBN as initiators in water and in tetrahydrofuran (THF), respectively. Then, polymer/silica hybrid materials prepared by using these P(MMA-GMA) copolymer have been obtained by sol-gel process in different ways. The general application method is shown in Scheme 2.1

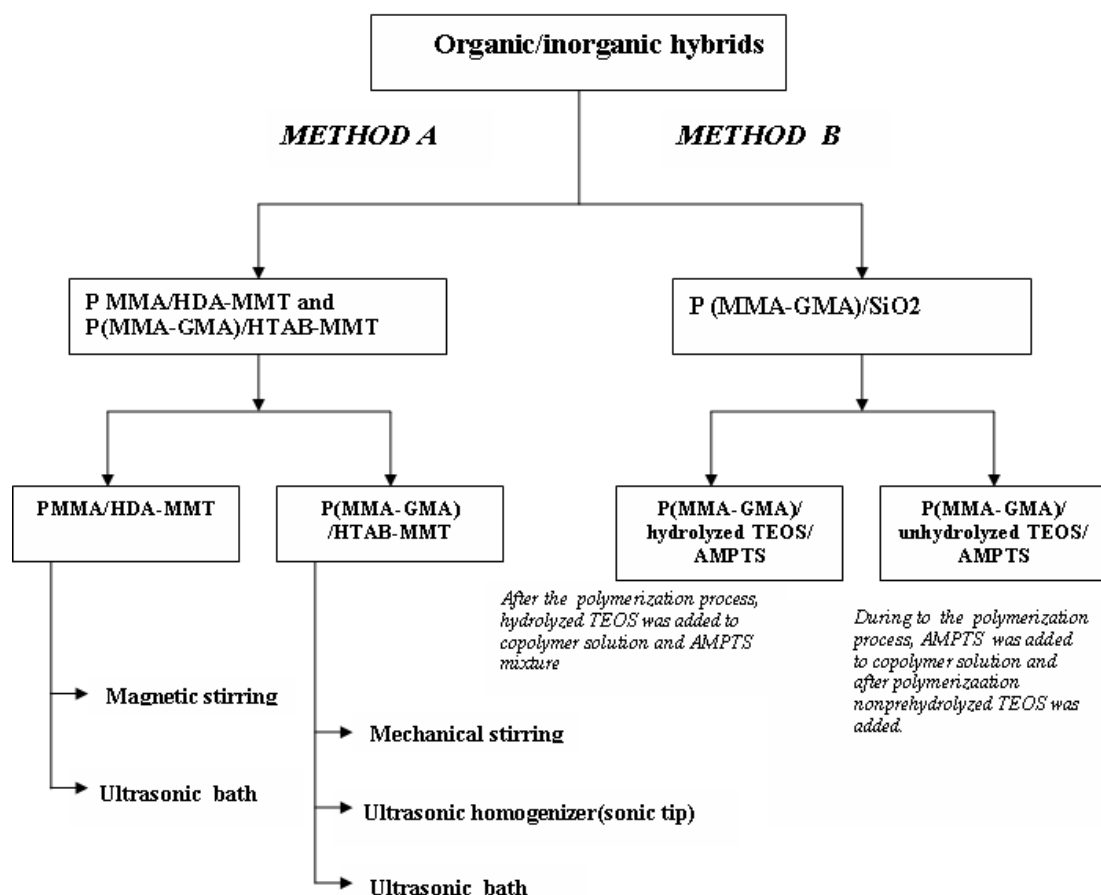


Figure 2.1: General scheme of preparation of organic/inorganic hybrids

The structures of the materials have been characterized by FTIR spectra. Thermal properties and mechanical behaviours have been investigated by using TGA, DSC and DMA techniques.

2.3.2.Preperation of HDA-MMT

Organophilic MMT was prepared by an ion-exchange reaction. Four grams of MMT was suspended in 80 mL of distilled water at room temperature. 2,7 g of HDA was dissolved in 20 mL of hot distilled water and added 1 ml HCl to this solution, then slowly poured into the MMT suspension. The suspension was stirred for 1 h at 80°C. The exchange clay was filtered and washed three times. The product was dried under a vacuum at room temperature for 24 h and crushed into a powder form. The organophilic MMT was designed as HDA-MMT.

2.3.3. Preparation of PMMA/HDA-MMT hybrids (Method A)

1 gr PMMA was dissolved in 25 ml of acetone and stirred vigorously at 40°C for 1 hour. The organophilic clay (in 5.0 wt % based on polymer concentration) was added into the polymer solution. The mixtures were continuously stirred for 5, 10, 20, 40 and 60 hours at room temperature (RT) (Sample a). Then, the composite solutions mixed magnetically were pured into petri dishes. They were dried first at room temperature for 24 hours, then under the vacuum at 70°C for 8 hours. The FTIR spectra are given in Figure B-1. To understand the effect of the mixing type on the homogeneity (i.e., transparency) of PMMA/clay composite films, the same method was applied with ultrasonic agitation (UA) for 1, 2, 3 and 5 hours (Sample b). FTIR spectra are given in Figure B-2. Further, four different HDA-MMT concentration (3.0, 5.0, 7.0 and 10.0 wt / wt %) were chosen to mix the PMMA and HDA-MMT solutions with ultrasonic agitation technique for 3 hours (Sample c). Experimental conditions are given in Table 3.1 and FTIR spectra are given in Figure B-3.

2.3.4 Synthesis of P(MMA-GMA) copolymers

Copolymers of MMA with GMA, having different compositions were synthesized by free radical solution polymerization in water with cerium ammonium nitrate (CAN) (5.0×10^{-3} mol / L) as initiator at 50°C under nitrogen atmosphere, while keeping total monomer concentration constant (0.4 M). Further, copolymers of MMA with GMA, having different compositions were synthesized by free radical solution polymerization in THF with AIBN (5.0×10^{-3} mol / L) at 50°C under nitrogen atmosphere, while keeping total monomer concentration constant (0.4 and 2.0 M). The polymerization mixtures were introduced into a flat bottomed reaction flask equipped with a rubber cap and a syringe. Nitrogen was bubbled through the polymerization solution for 5 min to remove oxygen dissolved in the reaction mixture. The precipitated copolymers during the copolymerization reactions of MMA/GMA initiated with CAN in water (because of heterogeneous polymerization) were filtered and washed with water. Hexane was used to purify the copolymers of MMA/GMA initiated with AIBN in THF. The copolymers were filtered and then, washed with hexane. All products were dried under vacuum at 50°C. The feed

compositions of MMA (2) and GMA (1), experimental conditions and gravimetric results (yield %) are given in Table 3.3.

2.3.4.1. Synthesis and characterization of P(MMA-GMA)s

FTIR spectra of the samples A,B,C,D,I,J,K,L,M,N and O are given in Figures B-5a, -5b and -5c.

The molecular weights and molecular weight distributions of copolymer samples were determined by using GPC. The results are given in Table 3.7.

The glass transition temperatures of homopolymer and copolymers were detected by DSC. Thermograms obtained from DSC measurements are given Figure B-6a, -6b and -6c. The glass transition temperature (T_g) values are given in Table 3.8.

Epoxy group determination

After the synthesis of the copolymers, copolymer compositions of all samples were determined using epoxy group titration method. For this purpose, first of all, the copolymer sample (0.5-1.0 g) was dissolved in pyridine-HCl mixture. Then, the solution was refluxed for 20 minutes while heating. After it was cooled, the copolymer solution was titrated with 0.1 M NaOH solution. Epoxy values of the samples were calculated from equation (1):

Epoxy value = epoksi equavelent / 100 g of polymer

$$= \frac{(B-A)M}{E} \quad (1)$$

E

B = Sample titration value (ml)

A = Blank sample titration value (ml)

M = Molar concentration of titrant

E = Weight of sample (g)

The results obtained are given in Table 2.1 and compared with feed compositions, which are given Table 3.4

Table 2.1:Copolymer compositions obtained from epoxy titration test method

Sample	Epoxy equivalent (ml)	mmol GMA/g polymer	mmol MMA/g polymer	Total mmol of copolymer	GMA(1) (mol %)	MMA(2) (mol %)
A	1,15	22.750	67.578	90.328	25.19	74.81
B	1,20	23.033	67.176	90.209	25.53	74.47
C	1,35	26.062	62.875	88.937	29.30	70.70
D	1,40	27.370	61.017	88.387	30.97	69.03
E	1,45	28.320	59.668	87.989	32.19	67.81
F	1,05	20.548	70.704	91.252	22.52	77.48
G	1,20	23.871	65.986	89.857	26.57	73.43
H	1,40	27.850	60.337	88.186	31.58	68.42
I	1,80	34.123	51.429	85.552	39.89	60.11
J	2,00	37.736	46.299	84.035	44.90	55.10
K	0,70	12.908	81.559	94.462	13.66	86.84
L	1,10	20.295	71.063	91.358	22.23	77.77
M	2,45	26.445	33.932	80.378	42.21	57.79
N	1,90	35.849	48.978	84.827	42.29	57.71
O	3,05	56.066	20.272	76.338	73.45	26.55

2.3.5 PMMA/TEOS Hybrids

Polymer solutions were prepared at 15 wt % of polymer concentrations in THF. TEOS content of the mixtures was chosen as 45.0 % of PMMA concentration

Hydrolysis of these solutions was affected by addition of four molar equivalents of acidic water (0.10 M HCl) based on the mole of TEOS. Hybrids with PMMA were prepared by stirring the PMMA and TEOS solutions with the calculated amount of 0.10 M HCl for about 20 h. The sol-gel (SG) solutions were poured into petri dishes. The solutions of these organic/inorganic hybrids were dried at room temperature for 1 day and then cured at 50°C for 12h. The FTIR spectra of these hybrids were compared with PMMA/HDA-MMT composites (Figure B-4 and Table 3.2).

2.3.6 P(MMA-GMA) / silica hybrids

2.3.6.1. Method I

Copolymer solutions were prepared at 10 wt % concentrations in THF. TEOS content of the mixtures was chosen as 40.0 % of P(MMA-GMA) concentration. Hydrolysis of these solutions was affected by addition of four molar equivalents of acidic water (0.15 M HCl) based on the mole of TEOS. To prepare the hybrids with nonprehydrolyzed TEOS solutions, P(MMA-GMA) solutions were mixed with the calculated amount of TEOS and HCl for about 16 h. This method of preparation will be referred to herein as nonprehydrolyzed (*nph*)TEOS.

All hybrids used for thermal and mechanical measurements were prepared with prehydrolyzed (*ph*) TEOS by first reacting 43 ml of TEOS, 20 ml of THF, and 14 ml of 0.15 M HCl in closed vessel for 24 h at room temperature. The stock TEOS (*ph*) solution was added to the copolymer solution in the appropriate amount to give the desired wt % of Si. Then, the solution was mixed for 30 min. and cast. In the case of prehydrolyzed TEOS, the copolymer/ TEOS solutions were allowed to stir only 30 min prior to casting due to rapid gelation. Their sol-gel (SG) solutions were cast into teflon molds (area = 36 cm² and depth = 3.5 mm). These organic/inorganic hybrids were dried at room temperature for 1 day and then cured at 50°C for 4h, at 70°C for 16 h and finally, cured at 150°C for 4 h in vacuum oven. These hybrids were named as **P(MMA-GMA)-*ph*T**].

The copolymer /AMPTS / prehydrolysed TEOS hybrids were prepared with the same method. First, copolymer solutions were prepared at 10 wt % concentration in THF.

Then, AMPTS (it was taken as 1.3 times of GMA in the copolymer composition) was added into the copolymer solution and stirred continuously for 30 min. at 50°C. The appropriate amount of prehydrolyzed TEOS solution was added to this mixture and allowed the stir 30 min prior to casting. The curing method was the same with [P(MMA-GMA)-*ph*T] hybrid. This hybrid was named as **P(MMA-GMA)-A&*ph*T**. The general scheme was given in Figure 2.2

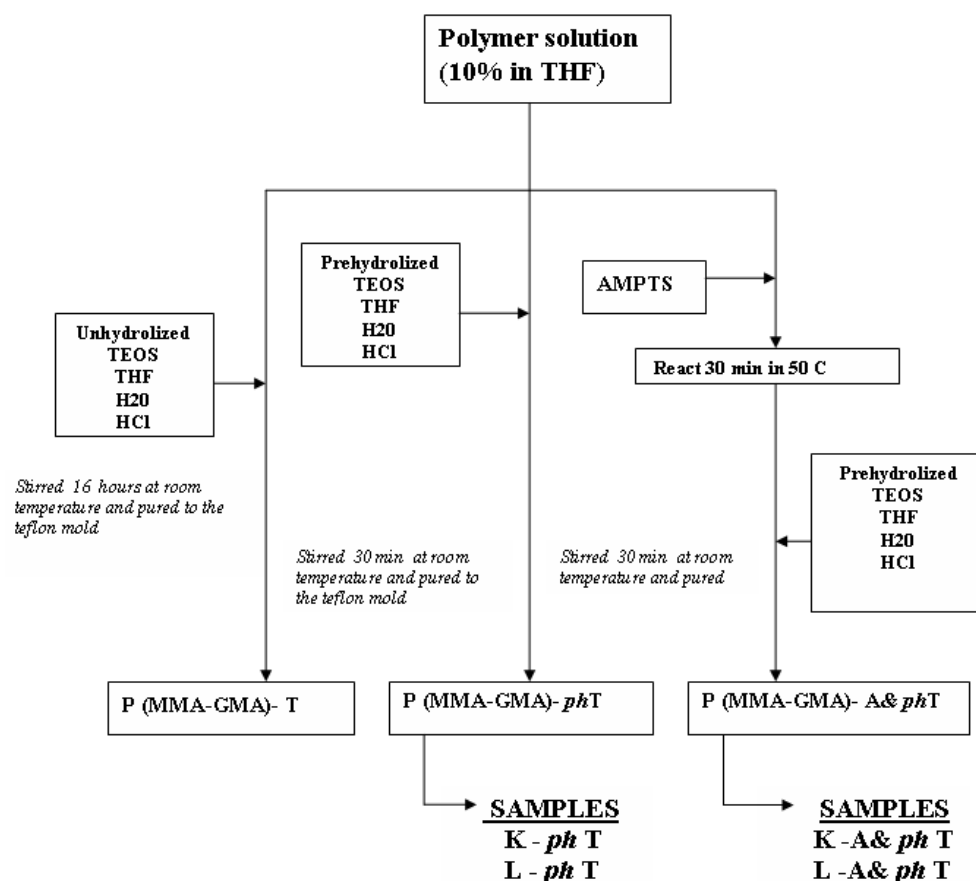


Figure 2.2: General scheme of organic/inorganic hybrids prepared by Method I (from Method B)

2.3.6.2. Method II

P(MMA-GMA) / SiO₂ hybrids were prepared by in situ sequential synthesis, as shown in Scheme 2.3. The mol ratios of MMA and GMA in the feed were chosen as 90:10 and 80:20 because opacity of the films increase with increasing GMA content of the copolymers. They were dissolved in THF , then AMPTS (1.3 times of GMA content in the feed) was added into this solution. AIBN (5.0×10^{-3} mol / L) was

used as initiator . Total monomer concentration was taken as 2.0 M. The solutions were introduced into flat bottomed reaction flasks equipped with rubber cap and a syringe. Nitrogen was bubbled through the polymerization solution for 5 min to remove oxygen dissolved in the reaction mixture. The solution was stirred at 50°C for 20 hours. Then, a desired amounts of water, TEOS / HCl ratio and THF were added and the mixture was vigorously stirred for 10 min. at room temperature. TEOS content of the mixtures was chosen as 40.0 % of P(MMA-GMA) concentration. The resulting homogeneous mixtures were pured onto Teflon molds, dried at room temperature for 1 day and cured at 50°C for 4h, at 70°C for 16 h and then, cured at 150°C for 4 h in vacuum oven. Hybrid samples of K-PL and L-PL (90:10, 80:20, in mol ratio, respectively) were obtained. Experimental conditions are given in Table 2.2 and general scheme is given in Scheme 2.3

Table 2.2: Experimental conditions of Method II

Sample	Monomer 1 (in mole%)	Monomer 2 (in mole%)	AMPTS	TEOS
K-PL	10	90	1.3 times of GMA content	40% of P(MMA-GMA) concentration
L-PL	20	80	1.3 times of GMA content	40% of P(MMA-GMA) concentration

*Monomer 1 = GMA; Monomer 2 = MMA; total monomer concentration = 2M;
Initiator = AIBN; Initiator concentration = 5.0×10^{-3} mol/L; $T = 50^{\circ}\text{C}$; $t = 20$ hours
Solvent: THF*

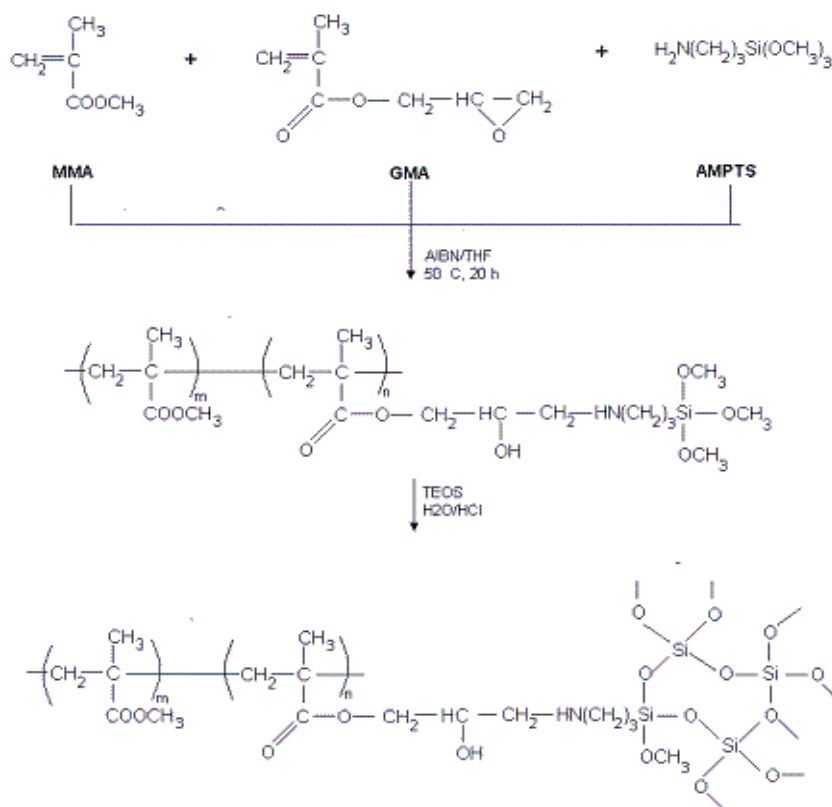


Figure 2.3: Reaction mechanism of P(MMA-GMA)/AMPTS/TEOS hybrids prepared with Method II

2.3.6.3. Method III

Copolymer solutions were prepared at 10 wt % concentrations in acetone. HTAB-MMT (10.0 wt % of copolymer concentration) was added into the copolymer solution and continuously stirred for ;

a- 20 minutes with mechanical stirrer at room temperature.

b- 1 hour with ultrasonic homogenizer(sonicator tip) at room temperature

c- 3 hour with ultrasonic agitation at room temperature.

All the resulting homogeneous mixtures were poured onto Teflon molds and then cured with the procedures used for Method I and Method II . The films of P(MMA-GMA)/HTAB-MMT hybrids were identified as L-C1, LC2 and LC3. Their experimental conditions are given in Table 2.3

Table 2.3: Experimental conditions of Method III

Sample	Solution	Method
L-ph T	5 g of copolymer L solution (10 wt % in acetone) + 0.38 g of prehydrolyzed TEOS solution	Magnetic stirring/16 hrs (RT)
L-C1	5 g of copolymer L solution (10 wt % in acetone) + 10 wt % of HTAB-MMT	Mechanical stirring /20 min (RT)
L-C2	5 g of copolymer L solution (10 wt % in acetone) + 10 wt % of HTAB-MMT	Stirring with ultrasonic homogenizer (high power sonic tip) / 30 min. (RT)
L-C3	5 g of copolymer L solution (10 wt % in acetone) + 10 wt % of HTAB-MMT	Ultrasonic agitation in an ultrasonic bath /3 hrs (50 °C)

3. RESULTS AND DISCUSSION

PMMA/HDA-MMT composites and PMMA/TEOS hybrids have been synthesized as mentioned in part 2.3.3. The experimental conditions and FTIR spectra are given in Table 3.1 and Figures B-1, -2 and -3.

Table 3.1: Preparation methods for PMMA/HDA-MMT composites

Sample	Solution	Method
a	1 g of PMMA /25 ml Acetone + 5.0 wt % of HDA-MMT	Magnetic stirring / 5,10,20,40 and 60 hrs (RT)
b	1 g of PMMA/25 ml Acetone + 5.0 wt % of HDA-MMT	Ultrasonic agitation / 1, 2, 3 and 5 hrs (50 °C)
c	1 g of PMMA /25 ml Acetone + 3.0, 5.0, 7.0 and 10.0 wt % of HDA-MMT	Ultrasonic agitation / 3 hrs (50 °C)

The best ones among these composites were selected and compared with PMMA/TEOS hybrids (Table 3.2).

Table 3.2: Preparation methods for composite materials

Sample	Solution	Method
I	1 g of PMMA/25 cc Acetone + 5.0 wt % of HDA-MMT	Magnetic stirring/40 hrs (RT)
II	1 g of PMMA/25 cc Acetone + 10.0 wt % of HDA-MMT	Ultrasonic agitation/3 hrs (50 °C)
III	1 g of PMMA/5 cc THF + 45 % of TEOS	Magnetic stirring/20 hrs (40 °C)

FTIR spectra of PMMA/clay composites and PMMA/TEOS hybrids are shown in Figure B-4. The absorption bands of the PMMA/SiO₂ hybrids obtained with sol-

gel process showed similarities with the ones for PMMA/clay composites. The formation of Si-O bonds resulting from TEOS and HDA were confirmed by the observation of new bands at 1080, 800 and 456 cm⁻¹. Further, the wide overlapping band centered at 1100 cm⁻¹ indicates the superposing effect of Si-O (1068 cm⁻¹) from inorganic silica particles and C-O-C (1100-1300 cm⁻¹) from organic PMMA matrix. The FTIR spectrum of HDA-MMT (as a control experiment) also exhibited a very strong peak at 1068 cm⁻¹. Both the experimental conditions which are summarized in Tables 3.1 and 3.2 and the FTIR spectra which are given in Figure B-4 of the samples was used to chose the optimum conditions for Method B (I, II , III)

Preparation conditions of MMA/GMA copolymers with different compositions are given in Table 3.3.

Table 3.3: Polymerization conditions

Sample	Monomer 1 (in mole%)	Monomer 2 (in mole%)	Initiator	Monomer concentration in mol (g/L)	Yield (%)
A	10	90	CAN	0,4	89,3
B	20	80	CAN	0,4	49,8
C	30	70	CAN	0,4	36,4
D	40	60	CAN	0,4	62,2
E	50	50	CAN	0,4	59,8
F	10	90	AIBN	0,4	42,4
G	20	80	AIBN	0,4	40,1
H	30	70	AIBN	0,4	35,2
I	40	60	AIBN	0,4	44,5
J	50	50	AIBN	0,4	53,6
K	10	90	AIBN	2,0	46,4
L	20	80	AIBN	2,0	48,0
M	30	70	AIBN	2,0	49,7
N	40	60	AIBN	2,0	60,6
O	50	50	AIBN	2,0	56,4

Monomer 1 = GMA; Monomer 2 = MMA; Initiator concentration = 5.0×10^{-3} mol/L ; T = 50°C; t = 20 hours; Solvent = Water for sample A, B, C, D, E and THF for sample F, G, H, I, J,K,L,M,N,O

Epoxy group determination results (Table 2.1) and DSC thermograms of the samples also support the FTIR results. The copolymer compositions obtained from epoxy group titrations were compared with feed compositions. The results are given in Table 3.4

Table 3.4: Comparison of feed compositions with copolymers compositions

Sample	FEED COMPOSITION		COPOLYMER COMPOSITION	
	GMA (1)	MMA(2)	GMA(1)	MMA(2)
	(in mole%)	(in mole%)	(in mole%)	(in mole%)
A	13,48	86,52	25,19	74,81
B	25,87	74,13	25,53	74,47
C	37,38	62,62	29,30	70,70
D	48,06	51,94	30,97	69,03
E	58,00	42,00	32,19	67,81
F	13,36	86,64	22,52	77,48
G	25,71	74,29	26,57	73,43
H	37,15	62,85	31,58	68,42
I	47,79	52,21	39,89	60,11
J	57,70	42,30	44,90	55,10
K	13,57	86,02	13,66	86,34
L	26,10	73,52	22,21	77,79
M	37,69	61,94	57,78	42,22
N	48,41	51,19	42,26	57,74
O	58,49	41,17	73,44	26,56

The results of epoxy determination method were used to calculate the reactivity ratios of MMA (2) and GMA (1) using extended Kelen-Tüdös graphical methods for high conversions.

Finemann-Ross (FR) method is the earliest way for determining reactivity ratios [117]. G and H have linear relationship with each other according to the following equations ;

$$G = r_{\text{GMA}} H - r_{\text{MMA}} \quad (2)$$

The inverted FR equation (IFR) gives r_{GMA} as the intercept and r_{MMA} as the slope:

$$G / H = r_{\text{GMA}} - r_{\text{MMA}} (1 / H) \quad (3)$$

Kelen and Tüdös (KT) apply these two parameters, G and H in the linearized copolymerization equation, along with new parameters such as α , η and ζ [118]:

$$\eta = [r_{\text{GMA}} + r_{\text{MMA}}/\alpha] \zeta - r_{\text{MMA}}/\alpha \quad (4)$$

The intercepts at $\zeta = 0$ and $\zeta = 1$ of the η versus ζ plots yield $-r_{\text{MMA}}/\alpha$ and r_{GMA} , respectively.

The effect of conversion is considered in the extended Kelen-Tüdös equation (EKT)

$$\eta = r_{\text{GMA}} \zeta - r_{\text{MMA}}/\alpha (1 - \zeta) \quad (5)$$

The effect of conversion is given by partial molar conversion

$$\xi_{\text{MMA}} = w (\mu + X) / (\mu + Y) \quad (6)$$

where w is the weight conversion of polymerization and μ is the ratio of molecular weight of MMA (2) to that of GMA (1). The partial molar conversion of GMA is

$$\xi_{\text{GMA}} = \xi_{\text{MMA}} Y / X \quad (7)$$

$$\text{Then; } z = \log (1 - \xi_{\text{GMA}}) / \log (1 - \xi_{\text{MMA}}) \quad (8)$$

$$H = Y/Z^2 \quad (9)$$

$$G = (Y-1)/Z \quad (10)$$

$$\eta = G/(\alpha + H) \quad (11)$$

$$\xi = H/(\alpha + H) \quad (12)$$

EKT parameters were calculated from the above equations using experimental data in Tables 3.5 and 3.6.

Table 3.5: GMA/MMA compositions in the feeds (f) and copolymers(F)

Sample	f _{GMA}	f _{MMA}	^a Epoksi equivalent (ml)	F _{GMA}	F _{MMA}	X (GMA/MMA)	Y (GMA/MMA)
F	10	90	1,05	22.52	77.48	0.1111	0.2906
G	20	80	1,20	26.57	73.44	0.2500	0.3617
H	30	70	1,40	31.58	68.42	0.4286	0.4616
I	40	60	1,80	39.88	60.12	0.6667	0.6633
J	50	50	2,00	44.90	55.10	10.000	0.8149

^a the results were obtained by Epoxy test

Table 3.6: EKT parameters

Sample	w	ξ_{MMA}	ξ_{GMA}	Z	H	G	η	ζ
F	0.4243	0.3477	0.9095	56.245	0.0092	-0.1262	-0.9905	0.0722
G	0.4010	0.3590	0.5194	16.479	0.1332	-0.3873	-15.406	0.5299
H	0.3515	0.3416	0.3678	10.970	0.3832	-0.4906	-0.9785	0.7643
I	0.4448	0.4459	0.4437	0.9930	0.6724	-0.3390	-0.4287	0.8505
J	0.5358	0.6011	0.4898	0.7321	15.196	-0.2528	-0.1543	0.9278

The EKT plot for high conversion data of this system are given in Figure 3.1. Reactivity ratios were calculated from this plot.

The reactivity ratios of MMA and GMA ($r_2 = 0.41$ and $r_1 = 6.94$) were calculated from the equations summarized above. The data given in Tables 3.5 and 3.6. The equation obtained from Figure 3.1 indicates that GMA is more reactive monomer than MMA.

η

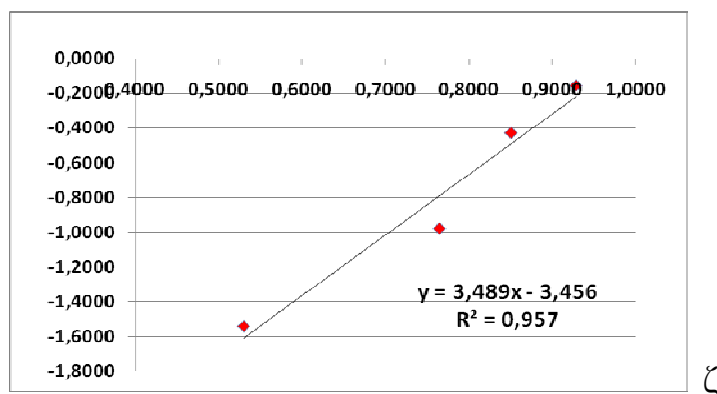


Figure 3.1: EKT method for determining monomer reactivity ratios in the copolymerization of GMA and MMA by using epoxy titration data

The molecular weights and dispersities of copolymer samples were determined by using GPC. The results are given in Table 3.

Table 3.7: GPC results of copolymers initiated with AIBN

Sample no	Mn (x 10 ⁴ g/mol)	Mw (x 10 ⁴ g/mol)	D (Mw/Mn)
F	1,64	2,94	1,79
G	1,44	2,82	1,95
H	1,84	3,29	1,78
I	1,71	2,95	1,73
J	1,57	2,82	1,79
K	10,8	21,9	2,02
L	12,3	26,5	2,16
M	11,6	33,1	2,85
N	11,7	42,2	3,61
O	14,1	43,4	3,08

As seen from these results, both the number average- and weight average-molecular weights, and the heterogeneity index of the copolymers increased with increasing initial monomer concentration.

DSC thermograms of PMMA, PGMA and their copolymers prepared with different feed compositions are shown Figures B-6a, -6b and -6c. The homopolymers of MMA and GMA exhibit endotherms at around 120 °C and 72 °C, corresponding to T_{gs} of PMMA and PGMA, respectively. With increasing epoxy content in the copolymers, the T_g values shift to the lower temperatures. Glycidyl methacrylate content of copolymers determined by epoxy group titration method were proportional to the decrease in the T_{gs} of copolymers (Table 3.8).

Table 3.8: Glass transition temperatures (T_g) of homopolymers and compolymers

Sample	T_g °C	GMA (1) (in mol%)
PMMA^a (Ce)	121	-
A	113	25,19
B	98	25,53
C	92	29,3
D	94	30,97
E	88	32,19
PGMA^a (Ce)	72	100,00
PMMA^b (AIBN)	118	-
F	107	22,52
G	104	26,57
H	100	31,58
I	92	39,89
J	84	44,90
K	105	13,66
L	89	22,21
M	73	57,78
N	71	42,26
O	68	73,44
PGMA^b (AIBN)	72	100,00

a = initiated with CAN, b = initiated with AIBN

In this study, the epoxy groups of GMA attached to the side chains of MMA/GMA copolymers were reacted with APTMS to form the triethoxysilyl functionalized polymer chains. After the modification of copolymers, they were mixed with prehydrolyzed TEOS in solution. Thus, the hybrid materials in which organic species were connected with an inorganic network by chemical bonds (because of the secondary amine formation between epoxy group and AMPTS). The processes which are given in Method I and II were shown in Figure 3.1. From the results, it was observed that the covalent bonds between polymer chains and the inorganic network prevented the phase separations, so transparent materials were obtained.

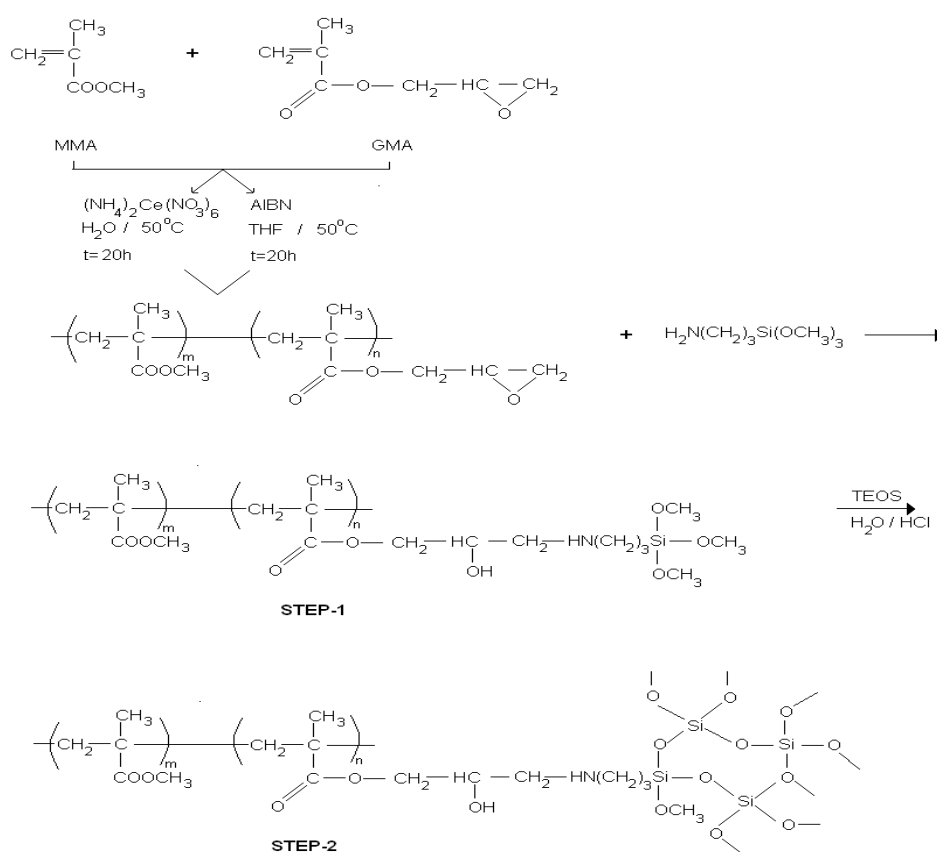


Figure 3.2 Reaction mechanism of P(MMA-GMA)/AMPTS/TEOS hybrids

When the copolymer solutions are mixed with the amines, the following reaction is possible:



Because of the low activation energy, this reaction between epoxy group of glycidyl methacrylate and amine group of AMPTS tends to proceed rapidly.

The samples prepared with CAN could not dissolve when AMPTS was added. It was assumed that the reason of these undissolved materials was grafting and crosslinking reactions during the polymerization. (Figure B-7). Therefore, hybrid materials were prepared by using the copolymers initiated with AIBN. At first, we have used the copolymers prepared by the lower total monomer concentration, i.e., 0.4 mol/L. But then, the copolymers with high molecular weight (obtained with 2.0 mol/L total concentration of monomers) and containing 10 and 20 mol % of GMA in feed were chosen because the hybrid materials prepared with higher GMA concentration and lower molecular weight had brittle and opaque form.

The samples marked with K and L were chosen to prepare P(MMA-GMA) / SiO₂ hybrids with prehydrolyzed TEOS as well as to prepare polymer / layered silicate composites, (P(MMA-GMA)/HTAA-MMT) with organically modified HTAB-MMT.

FTIR analysis is known as a suitable method to determine the presence of specific interactions between various groups in polymer compositions. It is sensitive to both inter- and intra-molecular interactions.

The sol-gel reactions are catalyzed by acid or base molecules (in our case, HCl). Before hydrolyze-condensation processes, it should be mentioned that the amine reagent (AMPTS) reacts with copolymer chains and open the ring of epoxy group. Then, the reaction of Si-OH groups of prehydrolyzed silica with CH₂- group of the organic molecule result in hybrid network. The FTIR spectra of hybrids (Samples K and L) after curing in teflon moulds (Figures B-9 and -10) indicated the decreasing of the peak of epoxy group, and so the epoxy ring opening. The absorption band of epoxy group at 916 cm⁻¹ was decreased but was not disappeared. Stretching vibrations of secondary amines appeared at 1050 cm⁻¹ and 810 cm⁻¹, respectively

FTIR results indicated the formation of covalent bonds between inorganic and organic networks. The formation of newly formed groups was observed in the 650 –

1150 cm^{-1} region. These signals were characteristic for the -Si-O-C and Si-O-Si groups.

The solvent effect on the hybrid materials have also studied. From the comparison of the FTIR spectra (Figure 11) and external view of the films prepared with THF and NMP, it can be said that they show the same structural properties, but more transparent materials are obtained with THF. This can be attributed to the solvent nature. In the case of NMP, solvent-solvent interaction would be predominant compared with the solvent-polymer interaction; hence, in NMP, the complex formation might be effective. The intermolecular interactions between the solvent molecules is higher in NMP compared to the hydrolysis and condensation reaction of TEOS. The formation of interpenetrating polymer network (IPN) structure with growing silica network was not possible due to increasing the particle size of the organic domain. In the case of acetone and THF, the structure of the polymer-solvent interaction is network, which favors the formation of IPN with growing silica network. This results in the homogeneous mixing of organic gel and silica gel, and hence, transparent hybrid materials were obtained in acetone and THF.

On the other hand, structural properties of P(MMA-GMA)/SiO_2 hybrids prepared with Method I and Method II are compared. FTIR spectra (Figure B 12) showed the same characteristic bands.

Figures B9 - B13 show FTIR spectra of PMMA, P(MMA-GMA) , and three hybrids (P(MMA-GMA) / TEOS , $\text{P(MMA-GMA) / AMPTS / TEOS}$ and $\text{P(MMA-GMA) / HTAB-MMT}$ (prepared with Method I, II, III) each with 10 wt % of silica content). The characteristic peak of the secondary amine groups are formed by the interaction of AMPTS and HTAB-MMT with the epoxy group of glycidyl methacrylate at mild temperatures via condensation. All these films have the characteristic absorption peaks of Si-O-Si , Si-O-C and C-N-C groups at 1150 cm^{-1} , 1100 cm^{-1} and 1050 cm^{-1} , respectively, because of the presence of covalent bonds between epoxy groups of copolymer chains, amine group of coupling agent (or HTAB attached to MMT) and inorganic phase ($\text{TEOS/H}_2\text{O/HCl}$). The similarities between hybrids obtained by different methods indicated that their structures were much different from those for PMMA and P(MMA-GMA) copolymers.

In addition, the intensity of the Si–O–Si band implied that the three-dimensional Si–O–Si hybrid network was formed by the cross-linking reaction of the hydrolyzed TEOS.

The thermal properties of the P(MMA-GMA) copolymers, P(MMA-GMA)/TEOS, P(MMA-GMA)/AMPTS/TEOS and P(MMA-GMA)/HTAB-MMT hybrid materials have been investigated by TGA and DSC.

TGA diagrams of the samples are shown in Figures 14 and 15. The thermograms show a single stage weight loss in all the copolymer samples. We see thermal stability up to 350°C. Decomposition temperatures T_d and weight loss ΔY (wt %) evaluated from TGA curves are listed in Table 3.9.

Also, TGA results show that above 400 °C the weight loss increases noticeably and thermal degradation is completed around 500 – 550 °C. We find clearly that the thermal stability of the copolymers is enhanced by the presence of AMPTS as compared to the pure P(MMA-GMA).

Table 3.9: Thermal properties of the P(MMA-GMA)/SiO₂ hybrids

Sample	T_d /°C	ΔY / (wt %)
K	335	96.7
K-ph T	350	82.5
K-A& ph T	380	74.1
K-PL	365	80.7
L	340	97.4
L-ph T	360	82.7
L-A& ph T	385	72.4
L-C1	350	86.2
L-C2	345	89.1
L-C3	370	88.3

Three methods have been used to obtain the hybrids (see the Experimental section). TGA curves of PMMA, P(MMA-GMA), P(MMA-GMA)/AMPTS/TEOS,

P(MMA-GMA)/HTAB-MMT homopolymer, copolymers, and copolymer-silica hybrid and composite systems are shown in Figures B 14-15. Here, thermal degradation occurred at temperatures higher than those for P(MMA-GMA) copolymers.

We find that thermal degradation temperatures are relatively higher for P(MMA-GMA)/AMPTS/TEOS from Method I. Apparently, during the sol-gel process the trimethoxysilyl groups of AMPTS and TEOS molecules are transformed into a strong silica network.

At higher temperature the hybrid material shows more stable behavior than the pure polymer. It seems the presence of silica protect the polymer chains to some extent from the oxidative degradation process.

Silica networks in the P(MMA-GMA)/HTAB-MMT hybrids obtained by Method III were unstable which resulted in beginning of the hybrids degradation already around 250⁰C. By contrast, for the samples obtained by Method I and II we observed higher degradation temperatures. Thus, thermal stability of the P(MMA-GMA)/AMPTS/TEOS hybrids was improved. The crosslinks and covalent bonds between the polymer, amine and silica decrease the degree of thermal degradation of Sample K-A_{ph}T and Sample L-A_{ph}T. The weight retained after decomposition temperature was found to be almost proportional to the amount of silica in the matrix. This confirms that alkoxysilanes were completely hydrolyzed and condensed to silica network and there was no loss during the sol-gel process. The residues of P(MMA-GMA)/AMPTS/TEOS hybrids are equal to the theoretical contents of SiO₂, but those of the Samples L-C1, L-C2, LC-3 is larger. It means that in the case of the former one, the connection of the organic molecules with the inorganic network by chemical bonds can improve the heat-resistant stability.

DMA and DSC were used to study differences in mechanical and thermal properties caused by inclusion of TEOS, AMPTS and HTAB-MMT, and by application of various stirring and preparation methods.

DSC was used to study the changes in glass transition temperatures T_g due to the presence of GMA (comonomer), MMT(clay) and TEOS. The PMMA exhibits a T_g at 118°C while T_g s of copolymers (105°C and 89°C for copolymer K and L) are quite low. T_g s of copolymers containing a slight amount of GMA (10 and 20 mol % in the feed, respectively) decreased. Incorporation of TEOS and HTAB-MMT into the P(MMA-GMA) copolymers produced a slight increase of T_g (3° to 10°C at 10 wt % of inorganic component). This is because, during the process of hydrolysis, the molecules of TEOS diffused into the free volumes of the polymers and then hydrolyzed to form microparticles, which decreases the free volumes of the system and makes the T_g increase, whereas the SiO₂ particles filled in among the molecules make the T_g decrease. However, the former effect is larger than the latter, making the T_g s of the hybrids increase. T_g values of hybrids are given in Table 3.10. Figures B18 - B21 show DSC plots of the final hybrids and composites. They are prepared by using AMPTS/TEOS and HTAB-MMT for 10 wt %, which are representative of all P(MMA/GMA)/SiO₂ hybrids and P(MMA-GMA)/HTAB-MMT composites .

Table 3.10: Glass transition temperatures (T_g) of homopolymers, copolymers and their hybrids

Sample	$T_g/^\circ\text{C}$
PMMA	118
K	105
K-A& <i>ph</i> T	111
K-PL	107
L	89
L-A& <i>ph</i> T	92
L-C1	104
L-C2	103
L-C3	102

DMA was used to study the mechanical properties of hybrid materials. Figures B22 - B25 show stress-strain curves for P(MMA-GMA)/SiO₂ hybrids and P(MMA-GMA)/HTAB-MMT composites at room temperature. Neat PMMA has a modulus of

1.39 GPa as measured for the control. It can be clearly seen from these Figures that Young Modulus, which is defined as the slope of linear elastic deformation of the stress-strain curve increase with the quality of MMT dispersion, addition of AMPTS and HTAB to form covalent bonding to SiO₂ groups and organic modification of MMT layers and, processing methods to synthesize the composites and hybrids greatly affect the properties of the end product. Young Modulus of these hybrid materials calculated from stress-strain curves are given in Table 3.11.

Table 3.11: Young moduli of homopolymers, copolymers and their hybrids.

Sample	Young Modulus (GPa)
PMMA	1,39
K	1,45
K-<i>ph</i> T	2,03
K-A& <i>ph</i> T	2,78
K-PL	2,17
L	1,62
L-<i>ph</i> T	2,5
L-A& <i>ph</i> T	2,21
L-C1	2,01
L-C2	2,27
L-C3	1,61

For the hybrid materials prepared by sol-gel process (Figures B-22 and B-23), Young moduli of P(MMA-GMA)/TEOS and P(MMA-GMA)/AMPTS/TEOS hybrids containing P(MMA-GMA) chains with 10 and 20 mol % of GMA in the feed were higher (2,03 GPa and 2.78 GPa for hybrids based on Sample K and 2.21 GPa and 2.49 GPa for hybrids based on Sample L) than those of the copolymers (1.45 and 1.62 GPa for pure copolymers designated as K and L). These improvements are approximately 92% and 37%, respectively . In addition, Young modulus of the hybrid synthesized by in-situ polymerization (Method II) has nearly same value

(2.17 GPa) with the ones prehydrolyzed TEOS solution (Method I) (Figure B-24). The reason of this is, during the process of hydrolysis, the molecules of TEOS diffused into the free volumes among the polymer molecules and then hydrolyzed to form SiO₂ microparticles. In the case of the long chains of APTMS connected with the polymer chains by amine bonds, the flexible interfaces form between the organic and inorganic species. These covalent bonds improved the mechanical properties of the hybrid materials.

For P(MMA-GMA)/HTAB-MMT composite materials, three mixing methods, i.e., mechanical stirring, ultrasonic homogenizer (high-power sonic tip) and sonic bath were applied to preparing the homogeneous copolymer/clay dispersions. The highest Young modulus (2.27 GPa) was observed for the one prepared by sonic tip whereas the lowest value of the Young moduli was obtained for sonic bath (1.61 GPa) (Figure B-25). The improvement is approximately 37 %. For the latter one, the composite solution is under ultrasonic agitation. When high intensity energy of this process is introduced into the solution, the covalent bonds between repeat units may be broken, so Young modulus of the material is dropped. In the first case, it is assumed that exfoliated / intercalated dispersion having high modulus of an organically modified montmorillonite (HTAB-MMT) in P(MMA-GMA) solution may be achieved by mixing in acetone with sonication using high-power sonic tip (70 W, 20kHz).

XRD analysis was used to follow the clay's d spacing in the composite materials by applying mechanical stirring and sonication during dispersion. Organoclays prepared via cationic exchange with cationic surfactants, HDA and HTAB are marked as HDA-MMT and HTAB-MMT, respectively.

XRD is a common technique used for examining surfactant intercalation and expansion of clay interlayer spacing after cation exchange. As the MMT interlayer spacing expands or contracts, the reflection of XRD will shift proportionally. The d spacing of clay particles are calculated according to Bragg's law ($d = \lambda / 2 \sin \theta$). The interlayer spacing of Na⁺MMT is around 7.5° ($d = 1.18$ nm) as determined by XRD. The interlayer of the unmodified MMT contains sodium cations surrounded by one water layer in the equilibrium state.

Figure B-26 shows X-ray diffraction patterns of cation exchanged MMTs, HDA-MMT and HTAB-MMT. The organic cations (HDA and HTAB) moved into the interlayer space, by replacing the inorganic cations (in this case Na^+). Both HDA

MMT and HTAB-MMT showed broad peaks and the peak positions shifted to lower angles. The broad peaks on the XRD patterns of HDA-MMT and HTAB-MMT were centered nearly $2\theta = 3.0^\circ$ and 5.0° , respectively ($d = 2.94$ and 1.77 nm). The different shifts were observed by depending on alkyl chain length and structure of the surfactants.

XRD were also used to characterize the dispersions of the organoclays in PMMA and P(MMA-GMA). For PMMA / HDA-MMT and P(MMA-GMA) / HTAB-MMT composite materials, three mixing methods, i.e., mechanical stirring, high-power sonic tip and sonic bath were applied to prepare the homogeneous copolymer / clay dispersions. Figures B-27 shows XRD patterns of these composite materials containing 10.0 wt % of organoclays. The main peak for the P(MMA-GMA) / HTAB-MMT composites shifted to 2.8° ($d = 3.15$ nm), while the XRD patterns of PMMA / HDA-MMT ones had a broad peak centered at $2\theta = 4.1^\circ$. As to these results, both the structures of organic chains attached to the MMT layers and mixing method which is used to prepare solutions strongly affect interlayer d spacing of polymer / clay composite materials.

Organoclay was dispersed into PMMA and P(MMA-GMA) solutions by mechanic stirring (without sonication), ultrasonic agitation or sonication using high-power sonic tip (20kHz). The sharp peak located at $2\theta = 2.8^\circ$ by incorporation of HTAB-MMT into copolmer indicated the possibility of having intercalated silicate nanolayers of organo-MMT clay dispersed in the copolymer matrix. The changing intensity of this XRD diffraction peak by depending on the mixing methods can be shown as an indicator for intercalation degree. Further, the high intensities of the two sharp peaks at 6.0° and 7.0° correspond to the interlayer structure and indicate a small amount of the clay that exists in particles and well ordered stacking of platelets. This means that even after sonicating or mechanical stirring, clay particles are still present together with intercalated and flocculated platelets.

The sharp peak located at 2.8° has lower intensity for mechanical stirring. Further, in the case of PMMA/HDA-MMT materials, the main peak that corresponds to HDA-MMT shifted to lower interlayer d spacing. These results can be discussed as

intercalated-flocculated structure destroyed by ultrasonic agitation or sonication using high-power sonic tip

4. CONCLUSION

-In this work we have prepared PLS composites by using organically modified MMT and organic/inorganic hybrids using sol-gel process.

-To prepare P(MMA-GMA)/SiO₂ hybrids, first of all, the copolymers of MMA and GMA (with different compositions) were prepared by free radical solution polymerization process using ceric ammonium nitrate (CAN) and AIBN as initiators in water and in tetrahydrofuran (THF), respectively.

-The copolymer composition of all samples were determined using epoxy group titration method. The FTIR spectra of the copolymers initiated with both CAN and AIBN showed that the epoxy band indicates the presence of the epoxy group in the copolymers and, its intensity increased with increase in the glycidyl methacrylate content in the copolymer compositions.

-The results of epoxy titration method were used to calculate the reactivity ratios of MMA (2), and GMA (1) using extended Kelen-Tüdös graphical methods for high conversions. The results indicate that GMA is more reactive monomer than MMA.

-The molecular weights and dispersities of copolymer samples were determined by using GPC. The molecular weights of the copolymer samples increased with increasing initial monomer concentration.

-DSC thermograms of PMMA, PGMA and their copolymers prepared by different feed compositions are showed that with increasing epoxy content in the copolymers, the T_g values shifted to the lower temperature.

-Then, the samples with 2M initial concentration and containing 10 and 20 mol % of GMA in feed were selected to prepare organic / inorganic hybrid materials. The reason for not exceeding > 20 mol % of GMA in feed was that the hybrid samples prepared with higher GMA concentrations were more in the opaque form. These hybrids have been synthesized with sol-gel process using different methods.

- These hybrids have been characterized with FTIR, DSC, TGA and DMA methods. FTIR results indicate that covalent bonds are formed between inorganic and organic networks.

-TGA results show that thermal degradation temperatures are relatively higher for P(MMA-GMA)/AMPTS/TEOS from Method I and II. The hybrid material shows more stable behavior at higher temperature than the pure polymer. Apparently, during the sol-gel process the trimethoxysilyl groups of AMPTS and TEOS are transformed into a strong silica network. The presence of the covalent bonded-silica in the hybrids protect the polymer chains to some extent from the oxidative degradation process. Silica networks in the P(MMA-GMA)/HTAB-MMT hybrids obtained by Method III are unstable which results in beginning of the hybrids degradation already around 250⁰C. By contrast, for the samples obtained by Method I and II we observed higher degradation temperatures. Thus, thermal stability of the P(MMA-GMA)/AMPTS/TEOS hybrids were improved.

-DMA results show that, Young moduli of P(MMA-GMA)/TEOS and P(MMA-GMA)/AMPTS/TEOS hybrids containing P(MMA-GMA) chains with 10 and 20 mol % of GMA in the feed were higher than those of the copolymers. In the case of the long chains of APTMS connected with the polymer chains by amine bonds, the flexible interfaces form between the organic and inorganic species. These covalent bonds improved the mechanical properties of the hybrid materials.

-When the P(MMA-GMA) / HTAB-MMT hybrids obtained by Method III with different stirring techniques, we have seen that, stirring method was very important for the mechanical and thermal properties of composite materials. The highest Young modulus was observed for the one prepared by ultrasonic homogenizer (sonic tip) whereas the lowest value of the Young moduli was obtained for sonic bath. For the latter one, the composite solution is under ultrasonic agitation.

-The Young moduli result of P(MMA-GMA)/ HTAB-MMT composite obtained by Method III with ultrasonic homogenizer was nearly the same with P(MMA-GMA)/AMPTS/TEOS hybrids obtained with Method I and II.

- As seen from the XRD results, both the structures of organic chains attached to the MMT layers and mixing method which is used to prepare solutions strongly affect interlayer d spacing of polymer / clay composite materials.

All the observed results have shown that there were considerable improvements in both thermal and mechanical properties of the composite and hybrid materials we have synthesized.

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APPENDIX

APPENDIX A

Table-A.1: Polymerization conditions

Sample	Monomer 1 (in mole%)	Monomer 2 (in mole%)	Initiator	Monomer concentration in mol (g/L)	Yield (%)
A	10	90	CAN	0,4	89,3
B	20	80	CAN	0,4	49,8
C	30	70	CAN	0,4	36,4
D	40	60	CAN	0,4	62,2
E	50	50	CAN	0,4	59,8
F	10	90	AIBN	0,4	42,4
G	20	80	AIBN	0,4	40,1
H	30	70	AIBN	0,4	35,2
I	40	60	AIBN	0,4	44,5
J	50	50	AIBN	0,4	53,6
K	10	90	AIBN	2,0	46,4
L	20	80	AIBN	2,0	48,0
M	30	70	AIBN	2,0	49,7
N	40	60	AIBN	2,0	60,6
O	50	50	AIBN	2,0	56,4

Monomer 1 = GMA; Monomer 2 = MMA; Initiator concentration = 5.0×10^{-3} mol/L ; T = 50°C; t = 20 hours; Solvent = Water for sample A, B, C, D, E and THF for sample F, G, H, I, J,K,L,M,N,O

APPENDIX B.

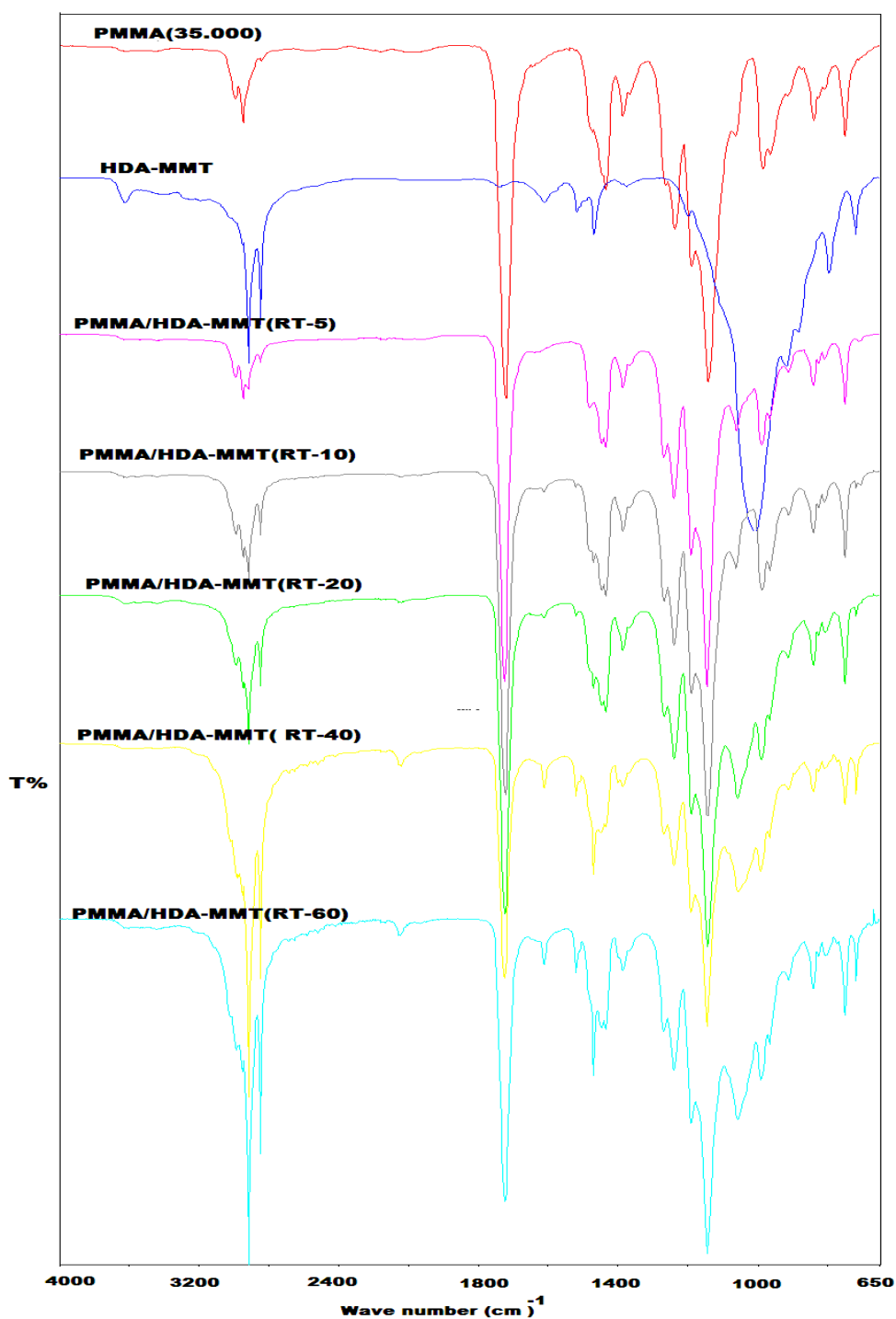


Figure B-1: FT-IR spectra of PMMA/HDA-MMT nanocomposites were prepared by applying magnetic stirring with durations of 5,10,20,40,60 hours at room temperature (RT5, RT10, RT20, RT40, RT60) .

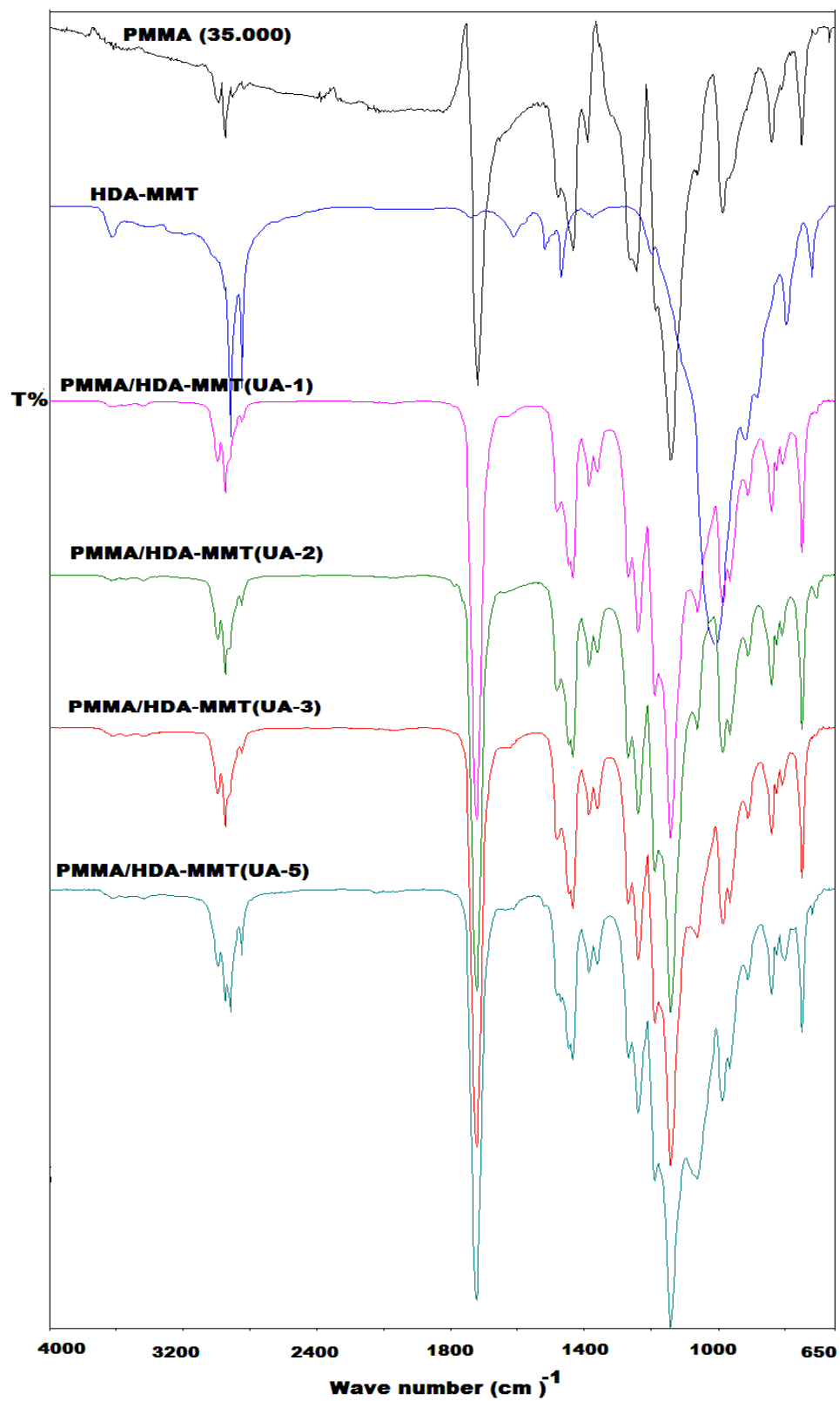


Figure B-2: FT-IR spectra of PMMA/HDA-MMT nanocomposites were obtained using ultrasonic agitation method(UA) with different hours. (UA1, UA2, UA3, UA5).

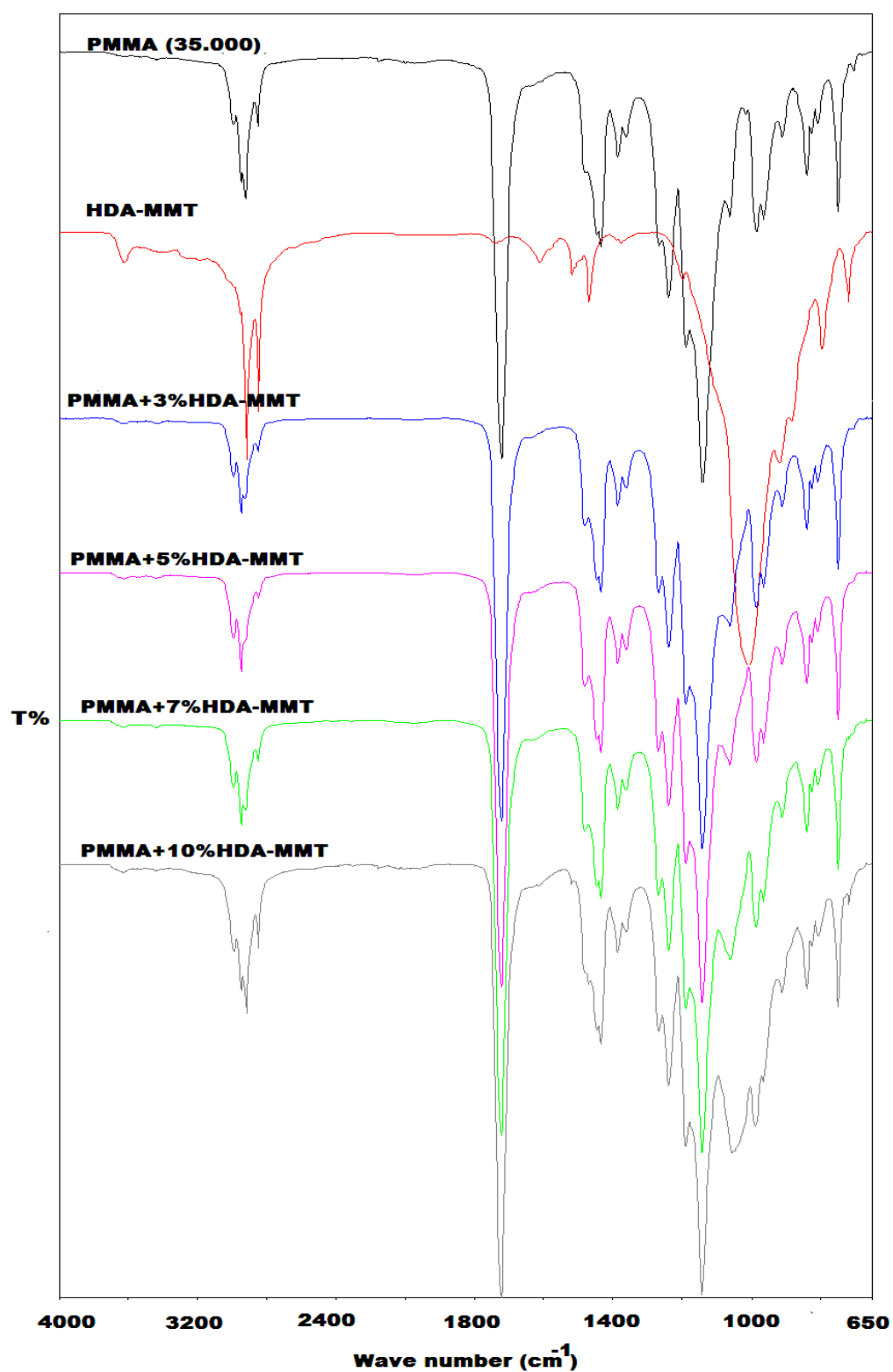


Figure B-3: FT-IR spectra of PMMA/HDA-MMT nanocomposites were obtained using ultrasonic agitation(UA) method with different HDA-MMT concentrations (3.0, 5.0, 7.0, 10.0%).

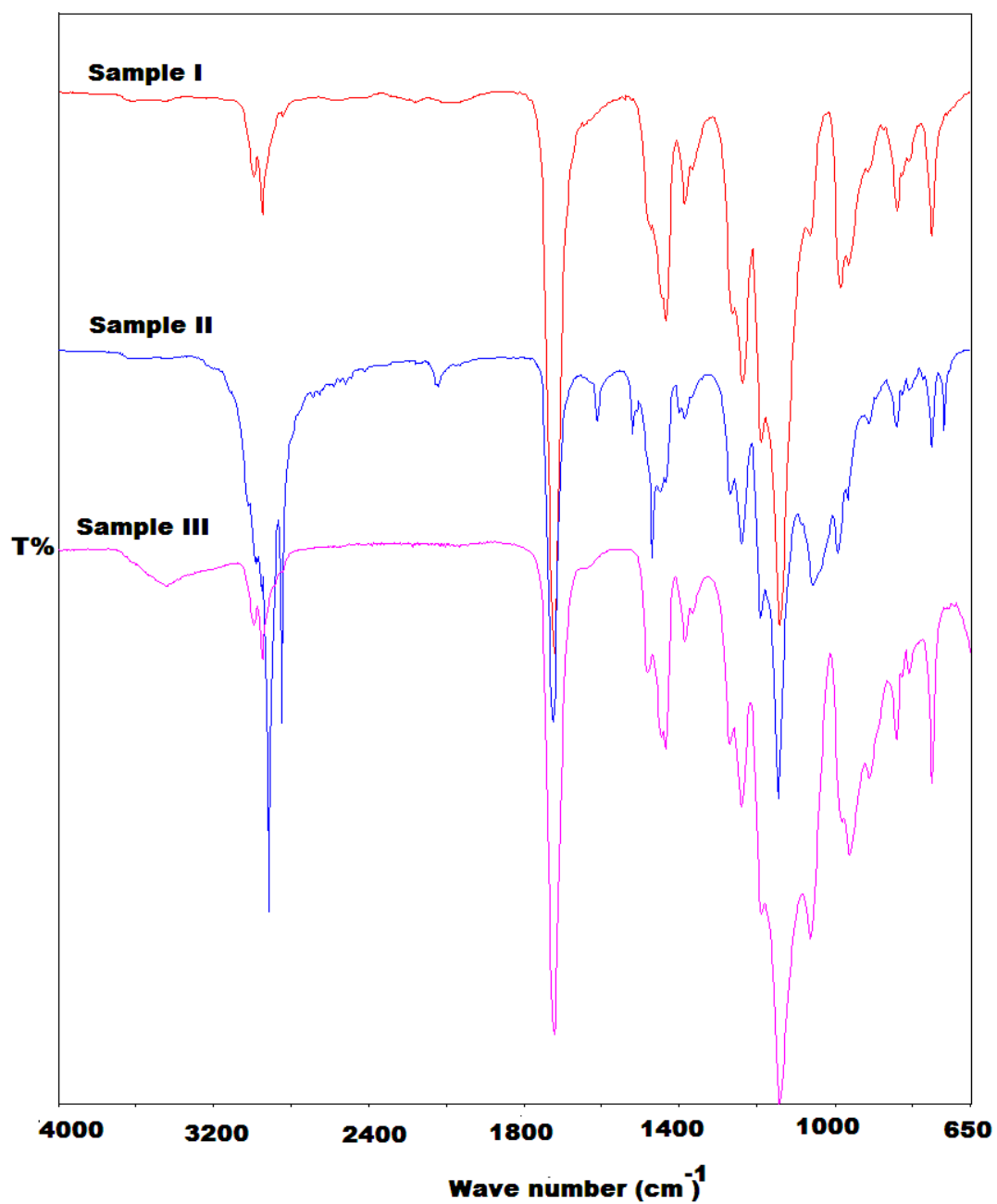


Figure B-4 : FT-IR spectra of PMMA/HDA-MMT nanocomposites were obtained using ultrasonic agitation(UA 40) method (sample I), and 10% HDA-MMT concentration(sample II) and 45% TEOS solution (sample III)

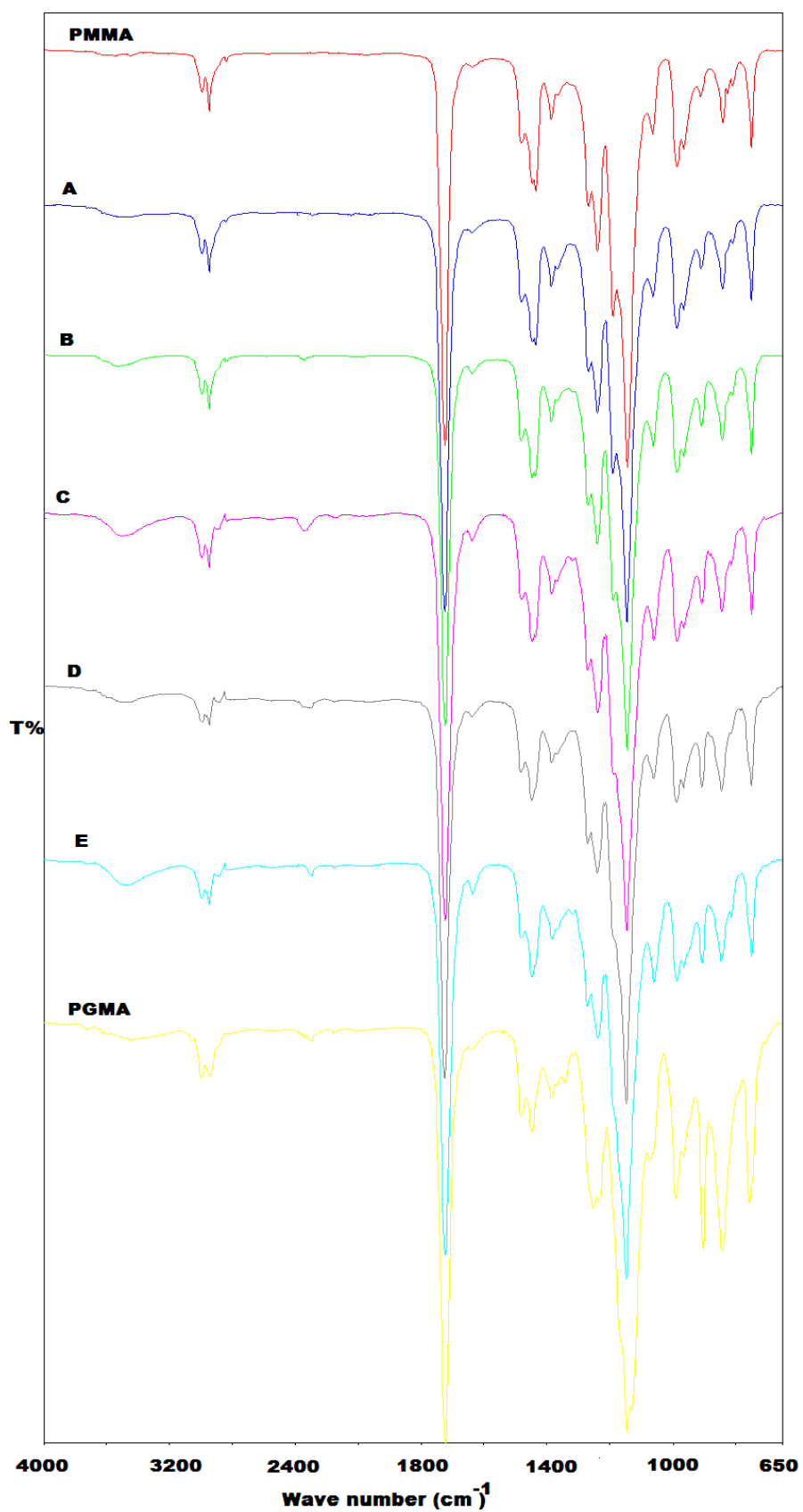


Figure –B-5 a: FT-IR results of PMMA-PGMA copolymers (with CAN)

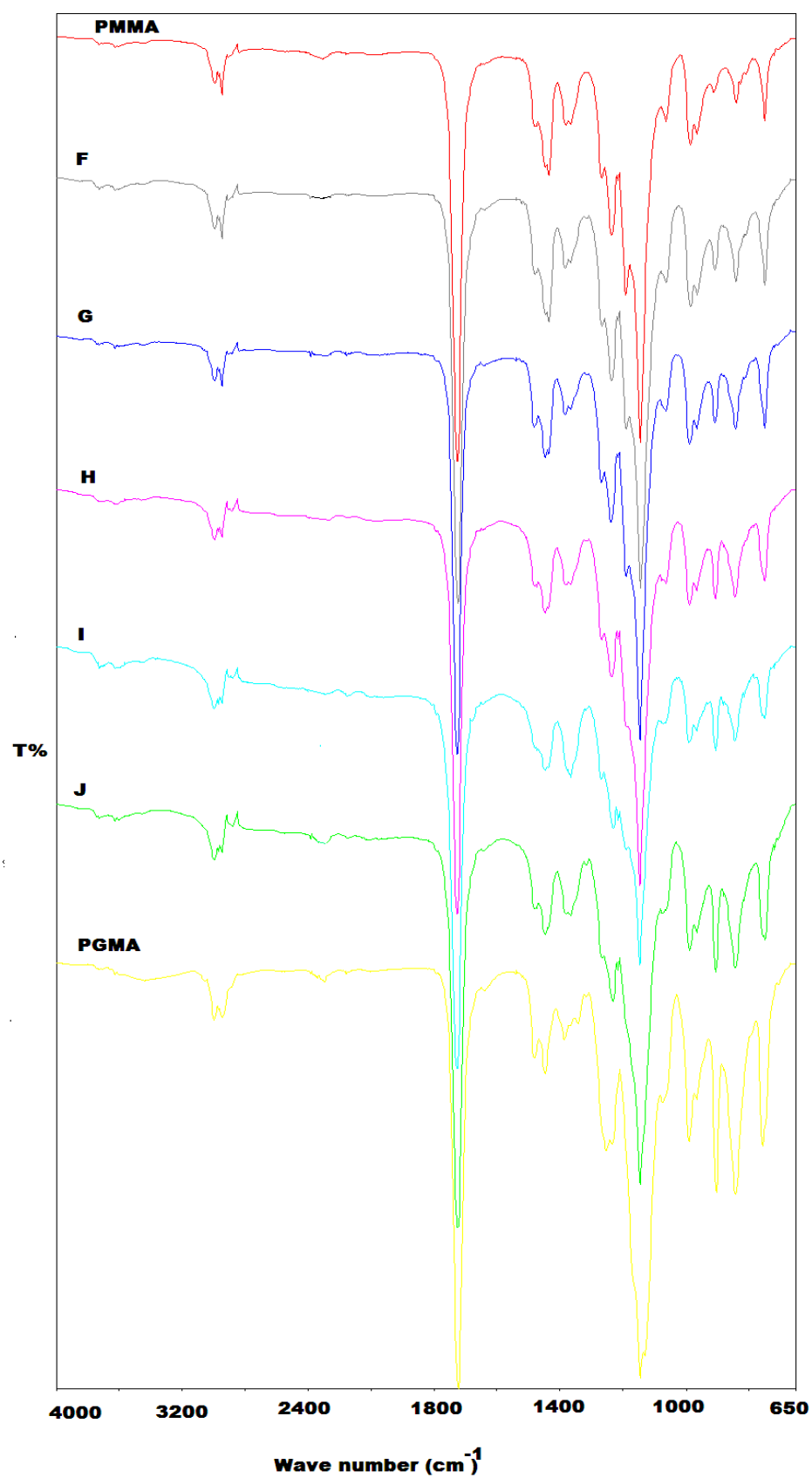


Figure-B-5 b: FT-IR results of PMMA-PGMA copolymers (with AIBN)

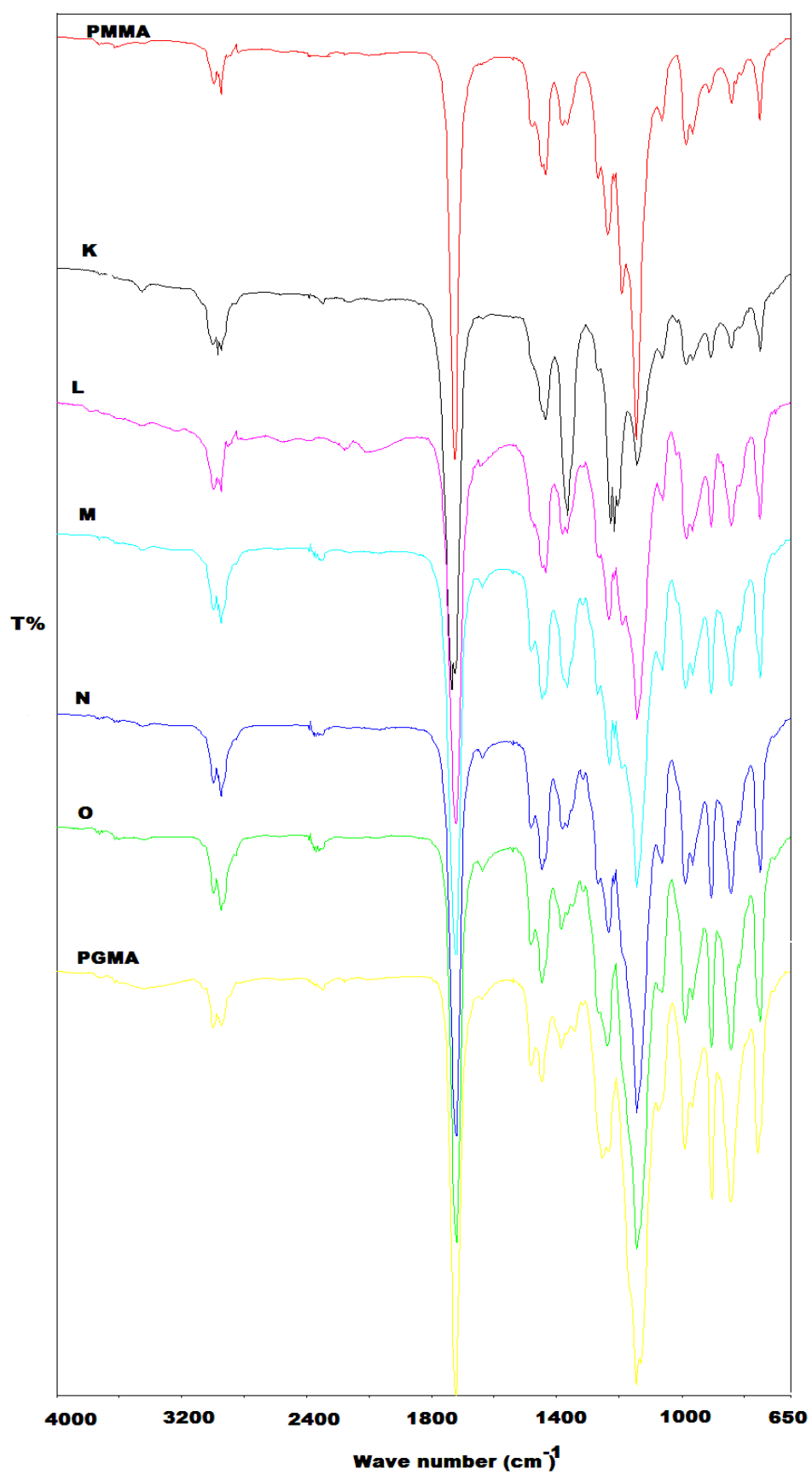


Figure-B-5 c : FT-IR results of PMMA-PGMA copolymers (with AIBN)

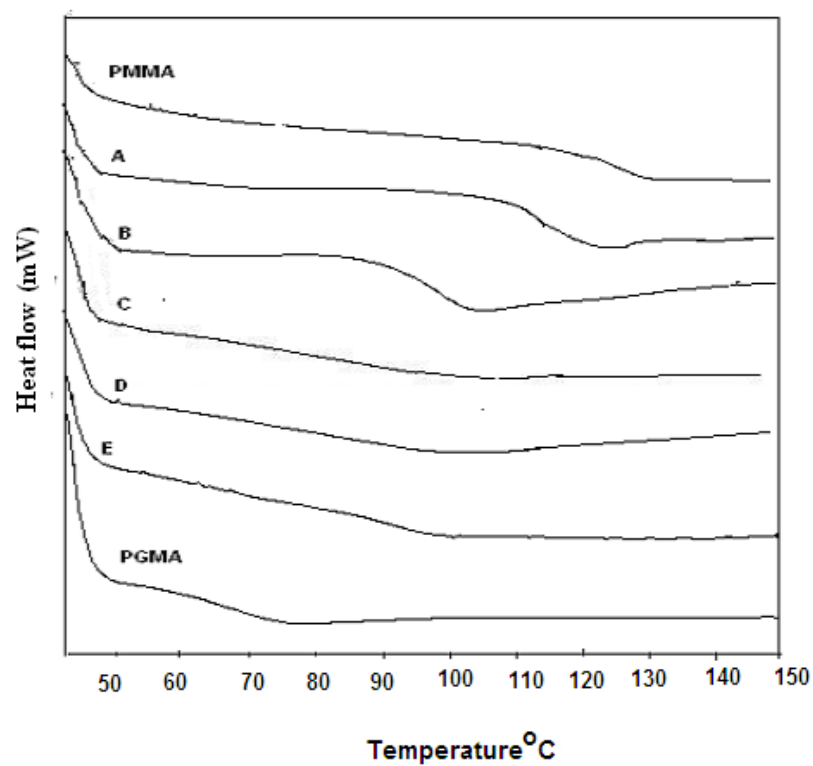


Figure-B-6 a: DSC thermograms of the P(MMA-GMA) blends (with CAN) second heating.

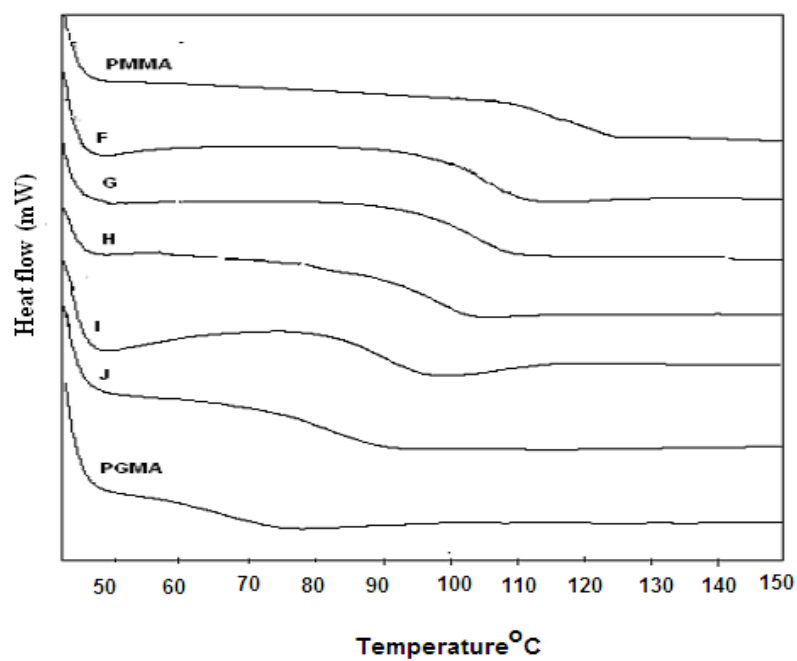


Figure-B-6 b: DSC thermograms of the P(MMA-GMA) copolymers (initiated with AIBN) second run.

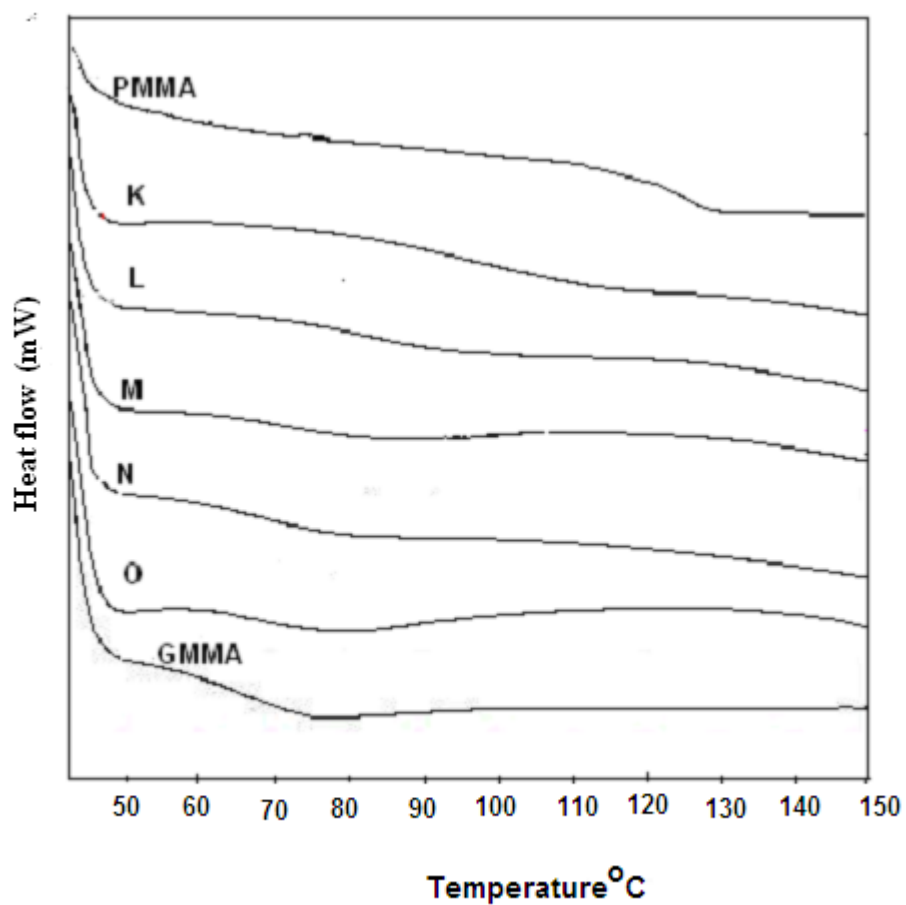


Figure-B-6 c: DSC thermograms of the P(MMA-GMA) copolymers (initiated AIBN), second run.

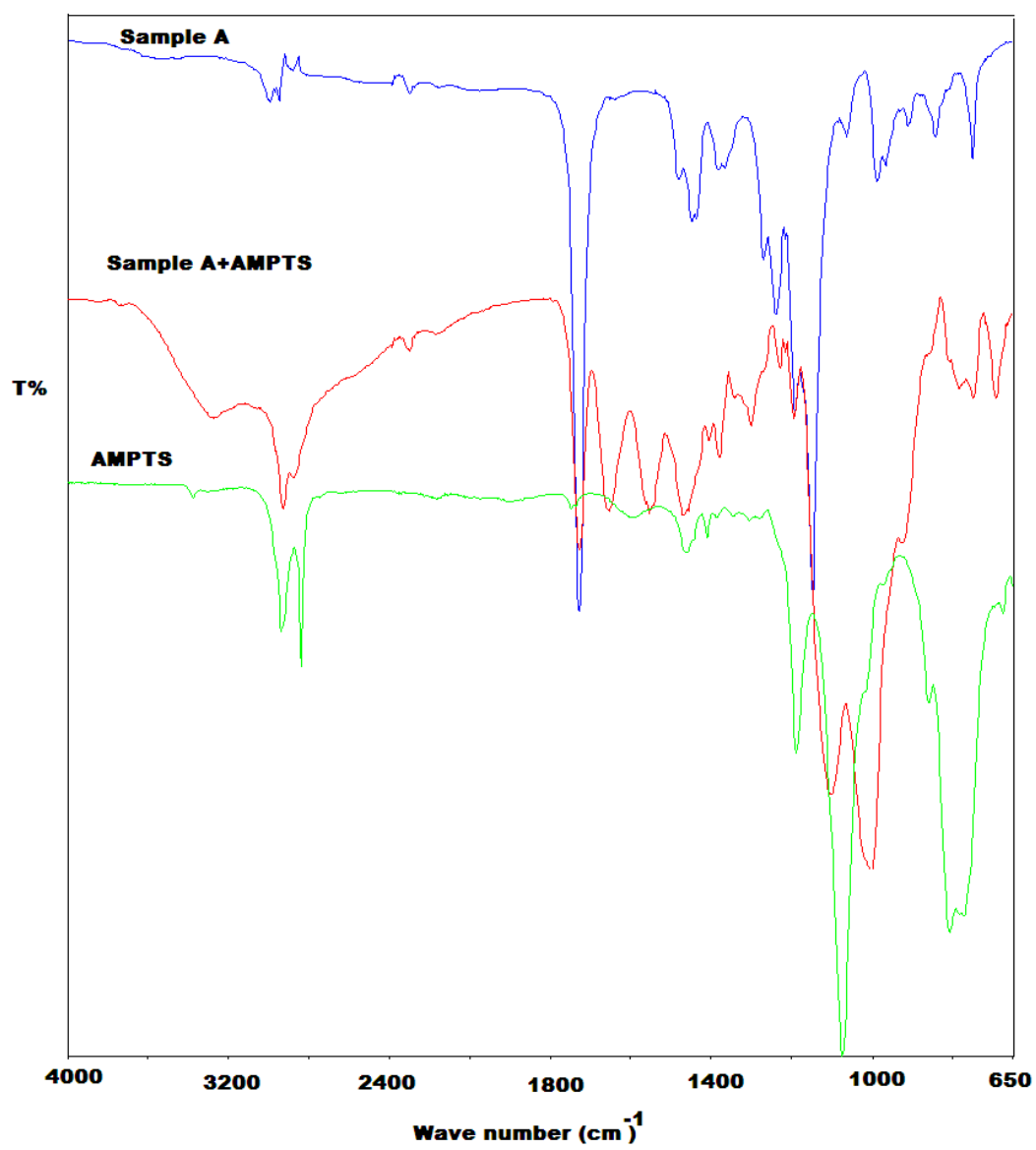


Figure B-7: FT-IR spectra of P(MMA/GMA)/Silica hybrids

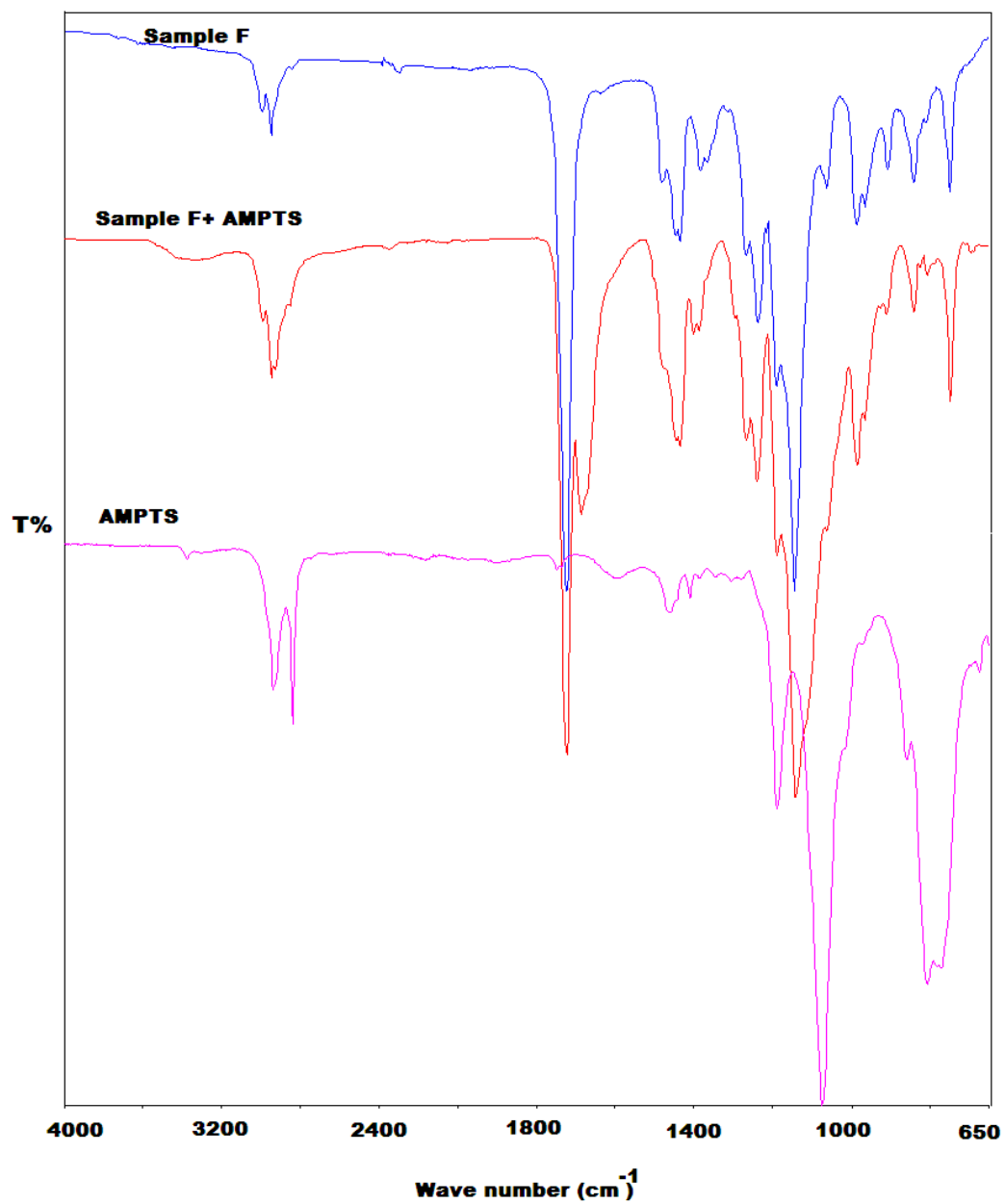


Figure B-8: FT-IR spectra of P(MMA/GMA)/Silica hybrids

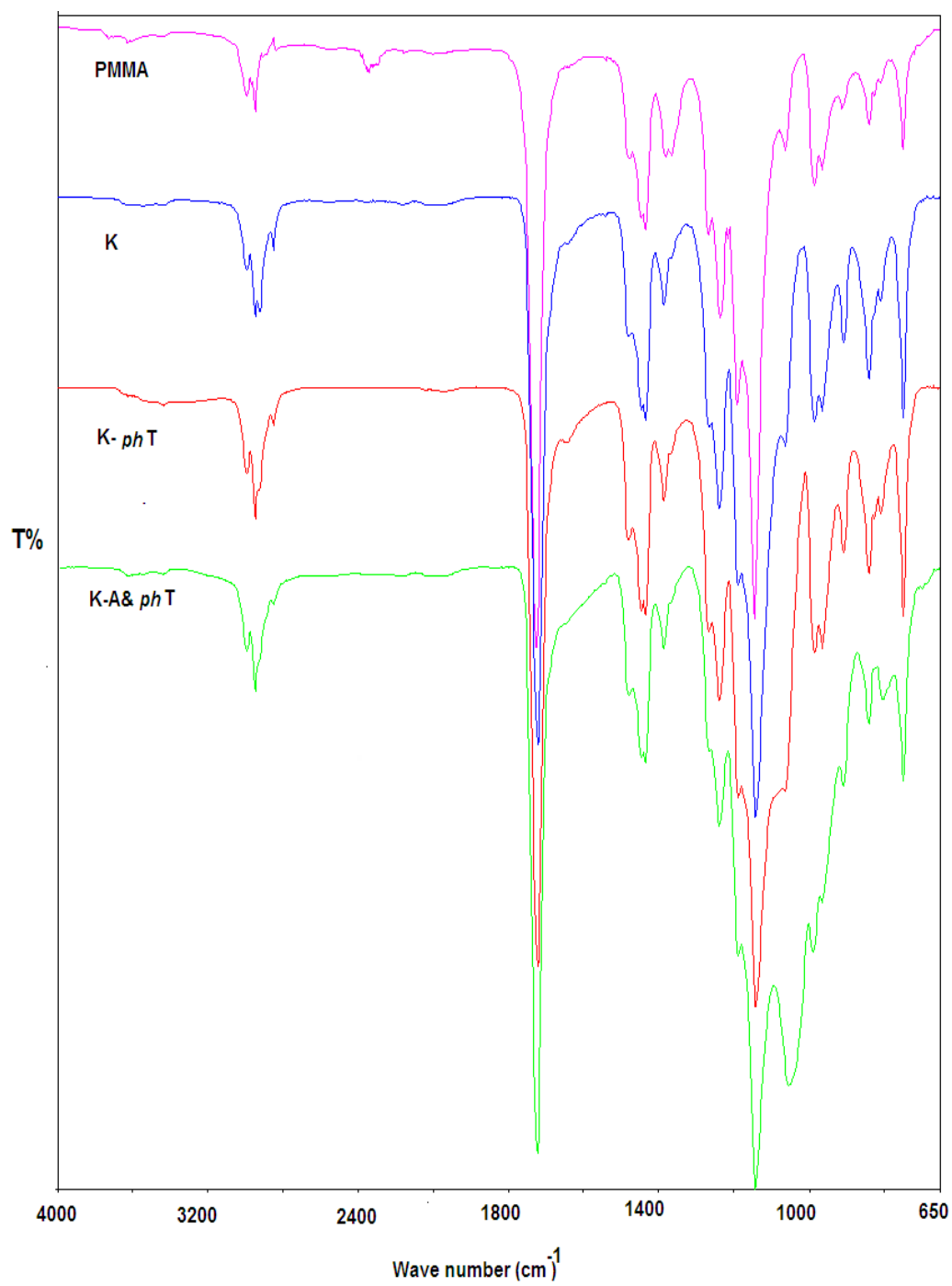


Figure B-9: FT-IR spectra of copolymer K /Silica hybrids (Method I)

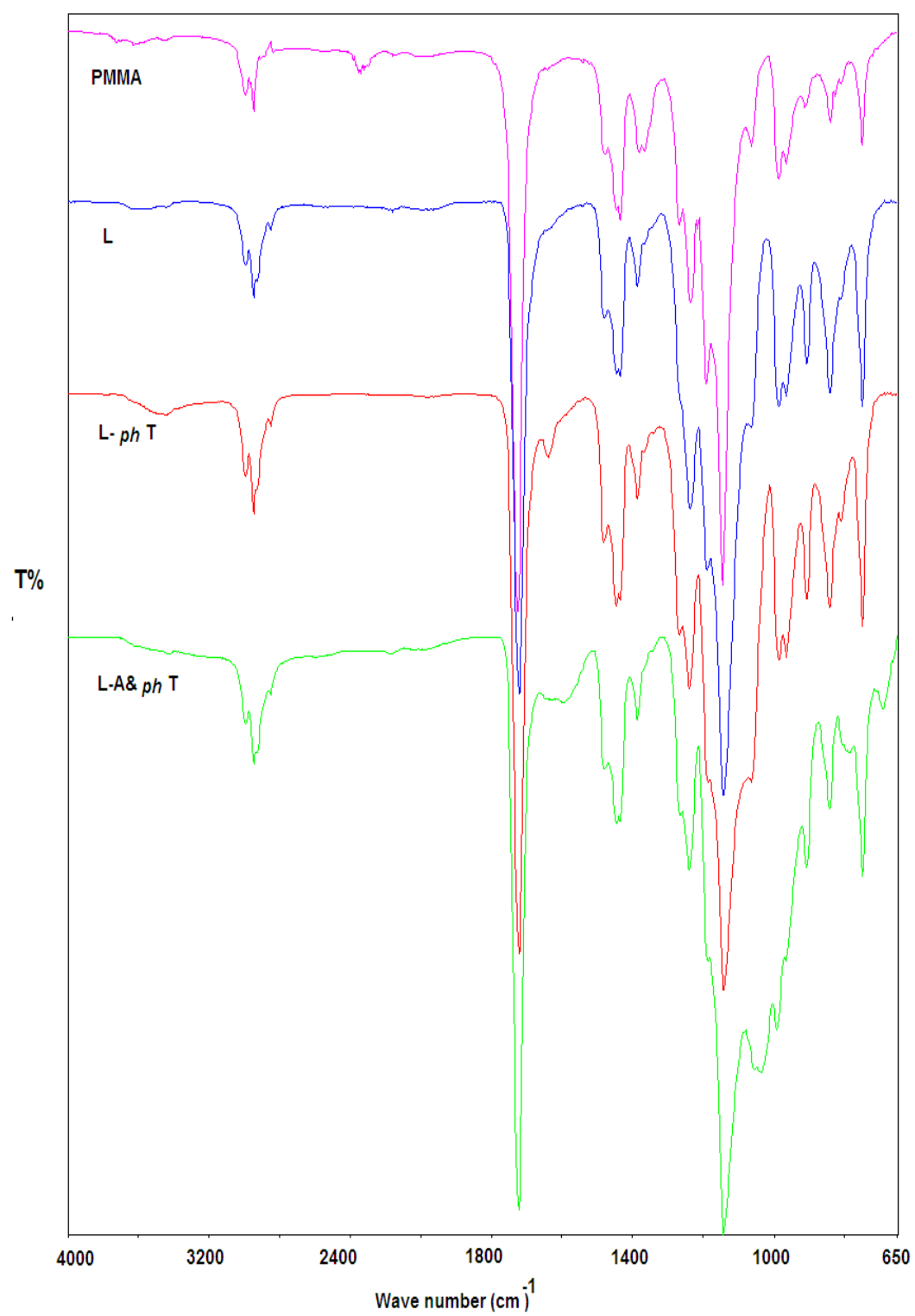


Figure B-10 : FT-IR spectra of copolymer L /Silica hybrids (Method I)

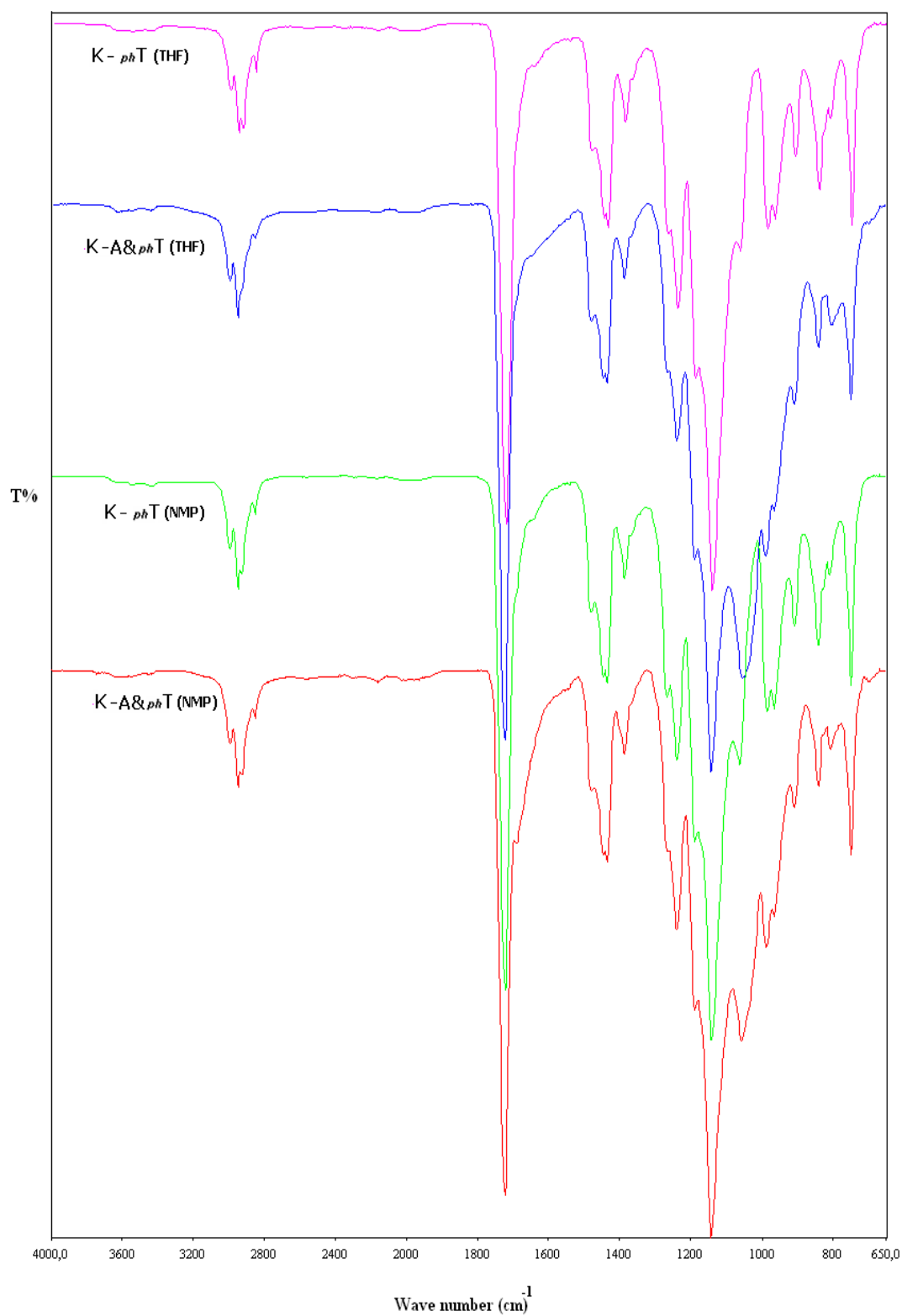


Figure B-11: FT-IR spectra of copolymer L /Silica hybrids prepared with different solvent (Method I)

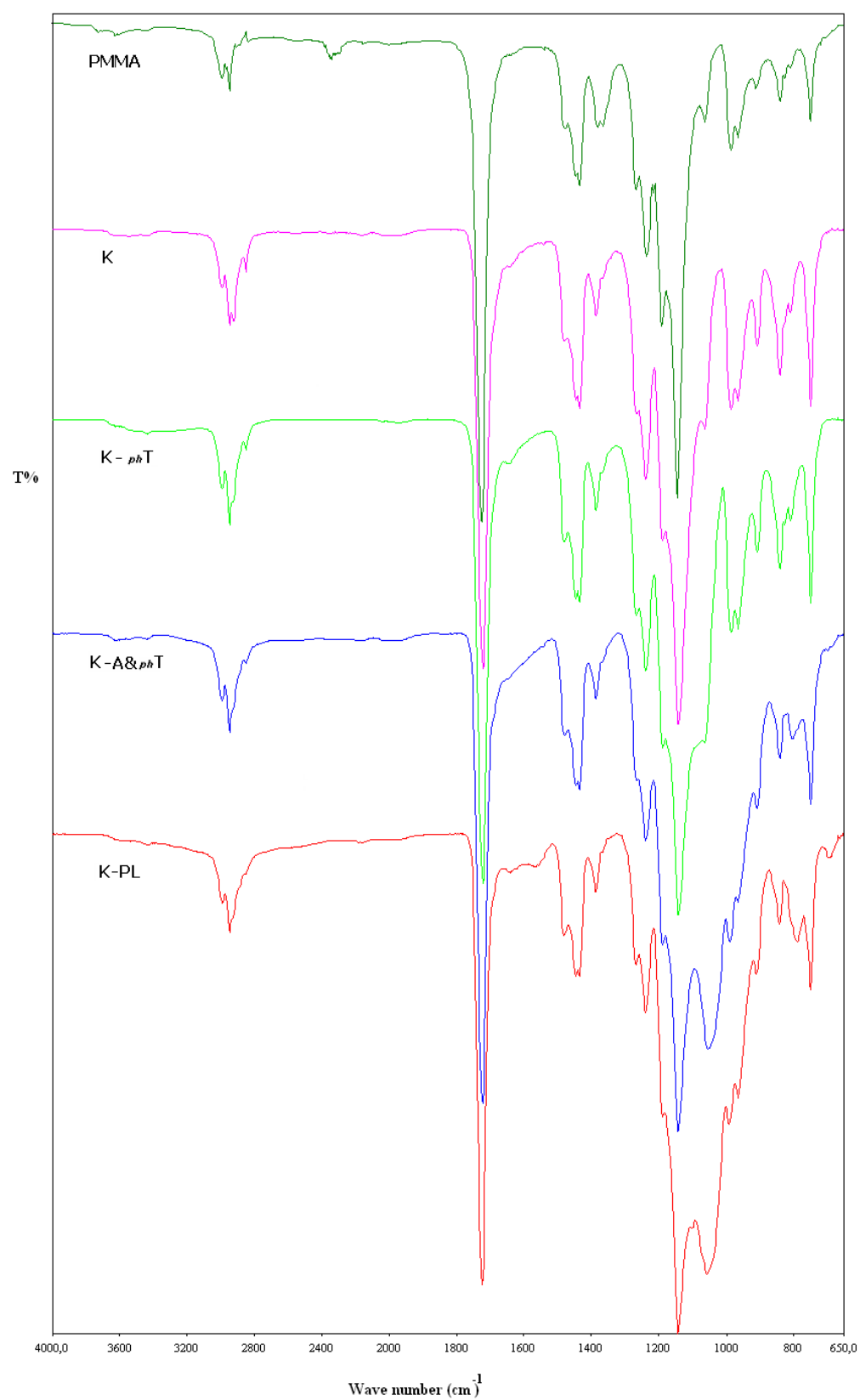


Figure B-12: FT-IR spectra of copolymer K /Silica hybrids prepared with Method I and II

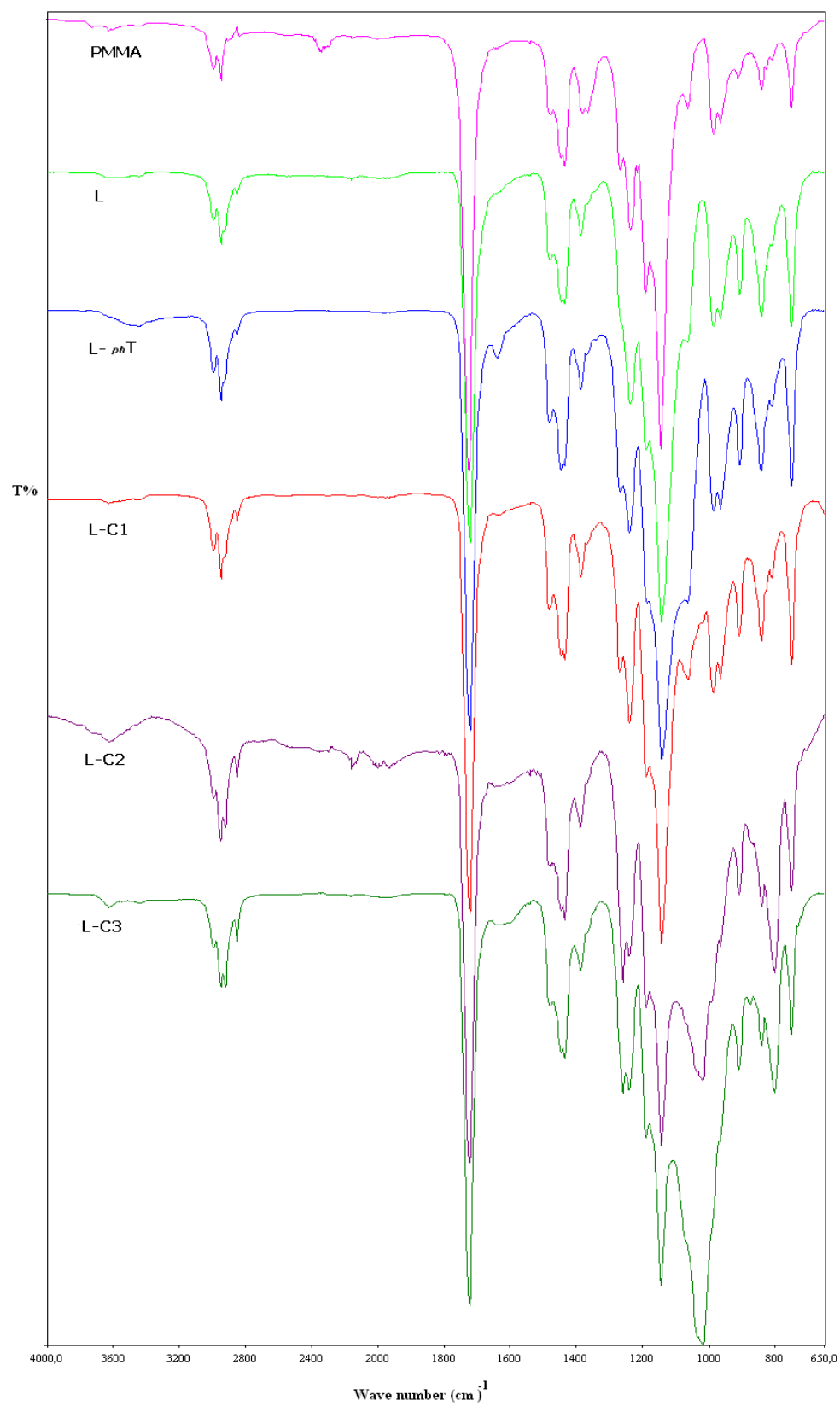


Figure B-13: FT-IR spectra of copolymer L /Silica hybrids prepared with Method I and III

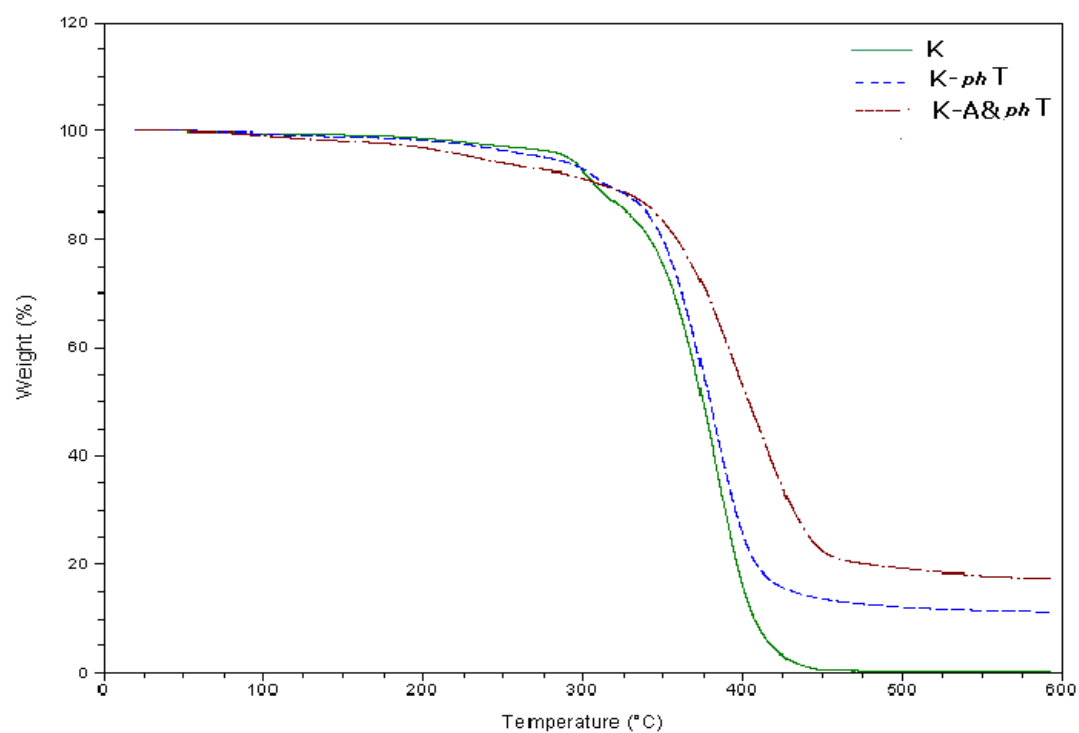


Figure B-14: TGA curves for the sample K and its SiO₂ hybrids (Method I)

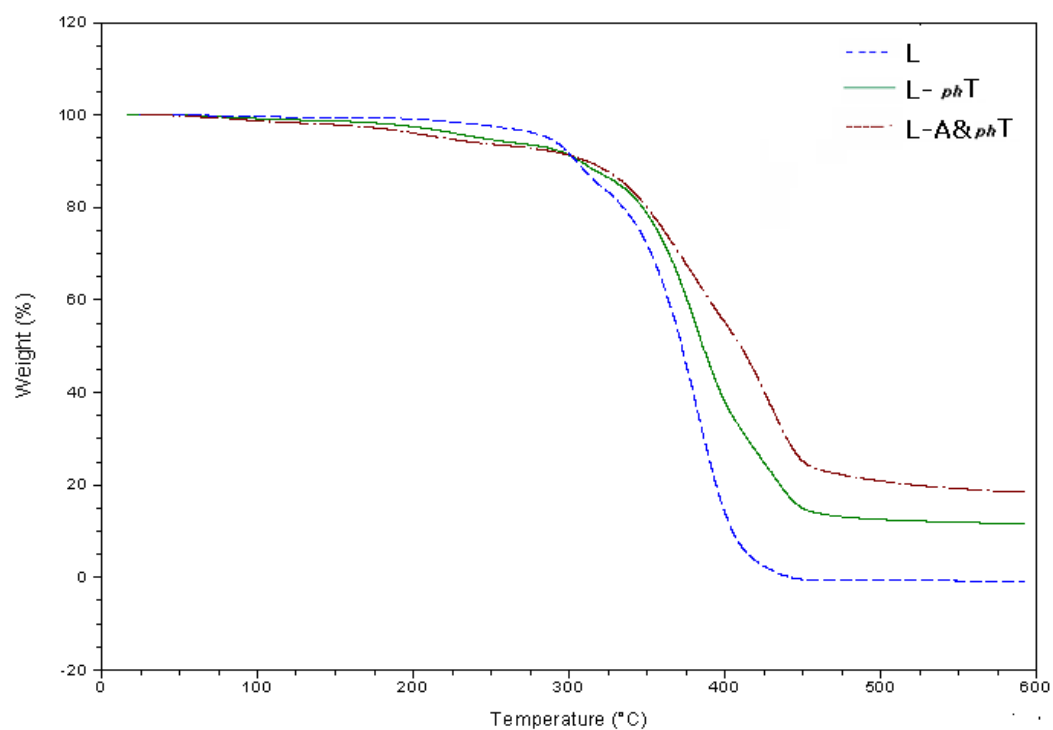


Figure B-15: TGA curves for the sample L and its SiO₂ hybrids (Method I)

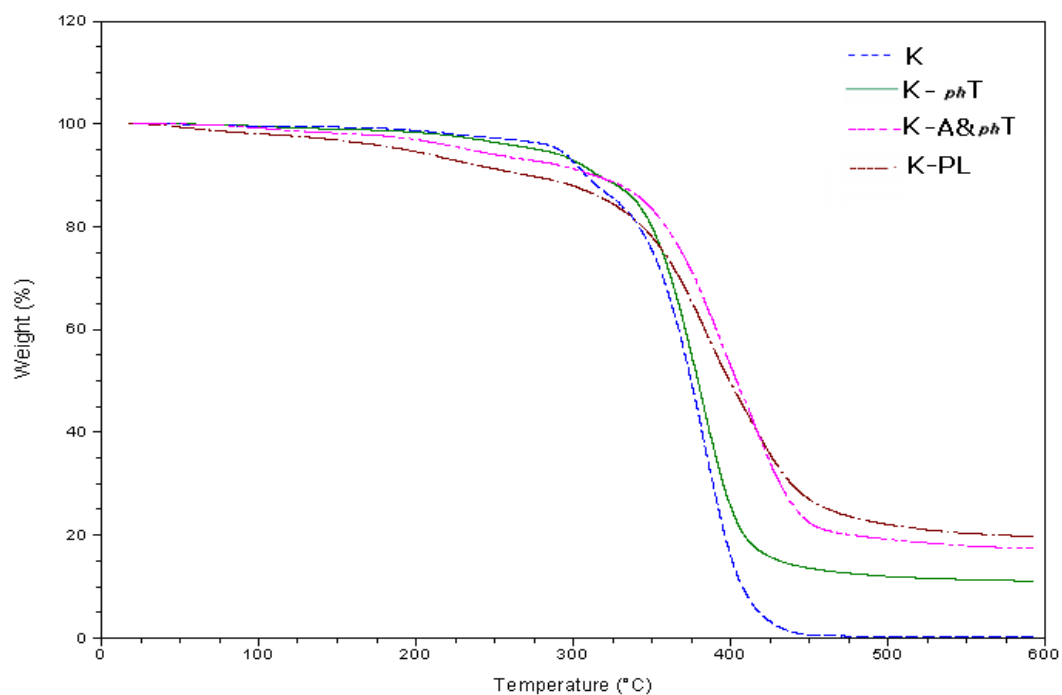


Figure B-16: TGA curves for the sample K and its SiO₂ hybrids (Method I and II)

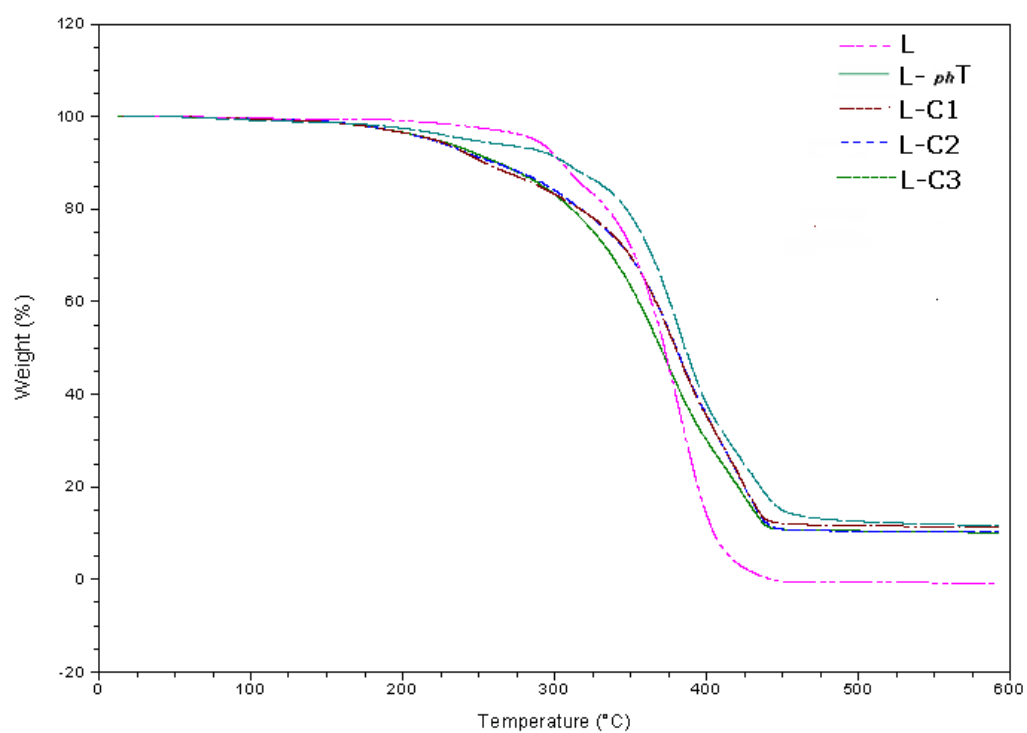


Figure B-17: TGA curves for the sample L and its HAD/MMT composites (Method I and III)

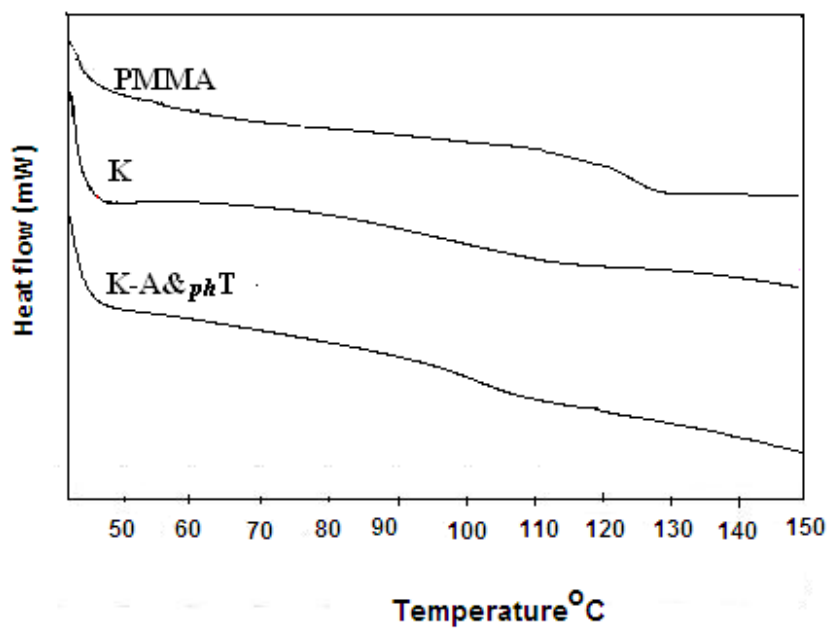


Figure B-18 : DSC curves of sample K and its SiO₂ hybrids (Method I)

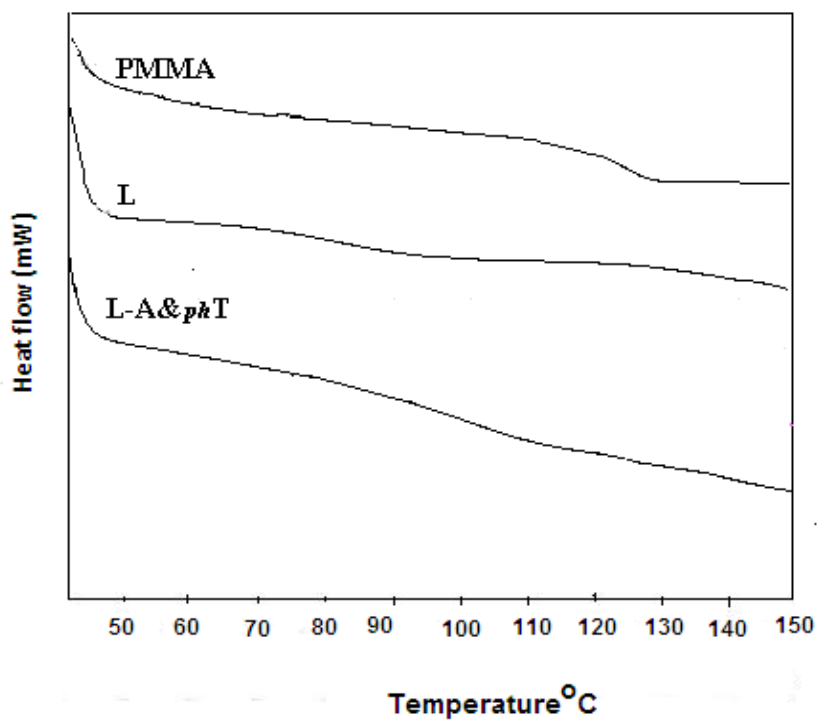


Figure B-19 : DSC curves of sample L and its SiO₂ hybrids (Method I)

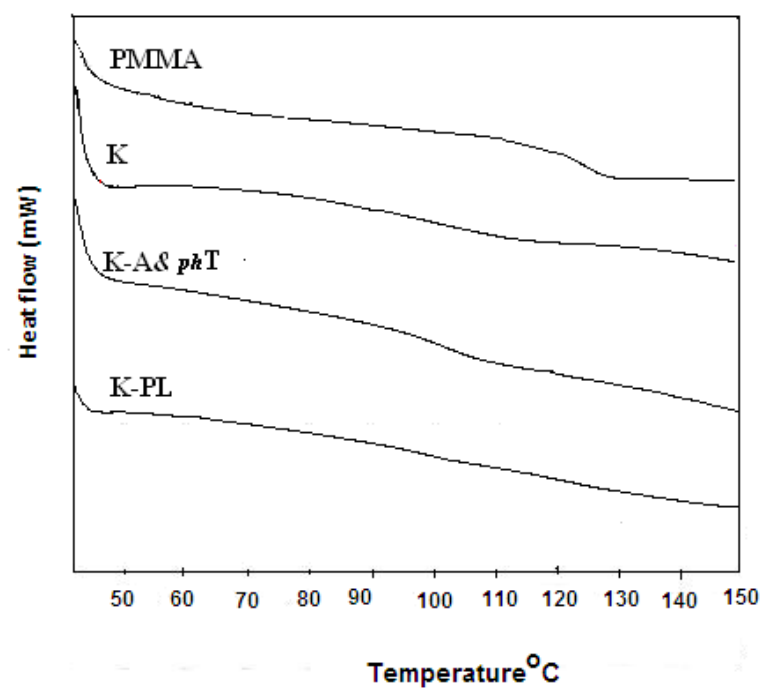


Figure B-20: DSC curves of sample K and its SiO₂ hybrids (Method I and II)

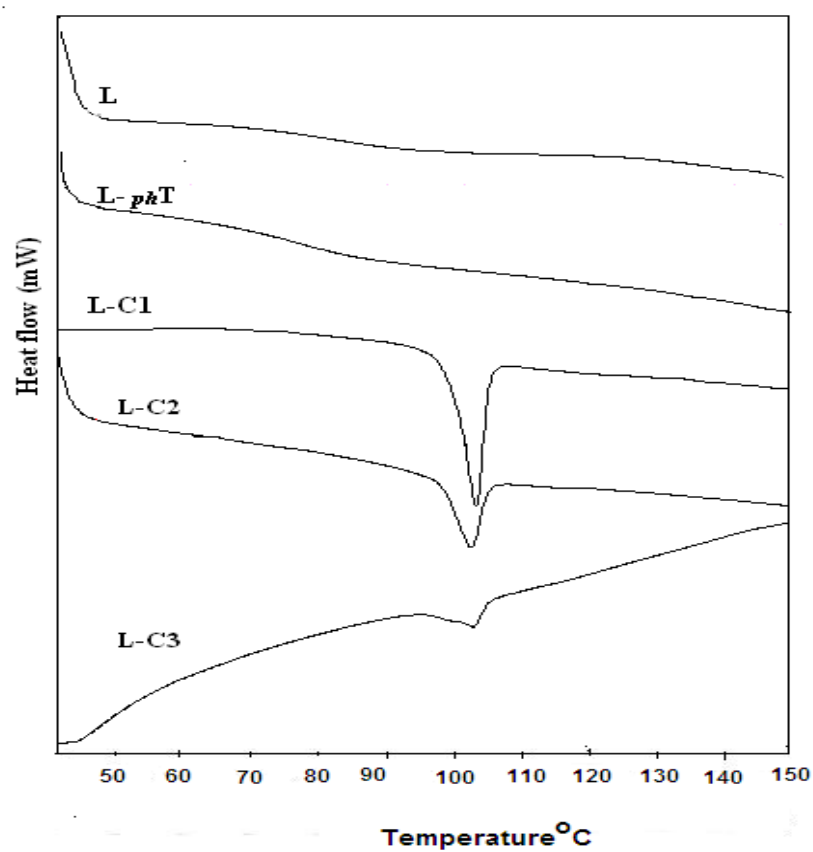


Figure B-21: DSC curves of sample L and its hybrids (Method I and III)

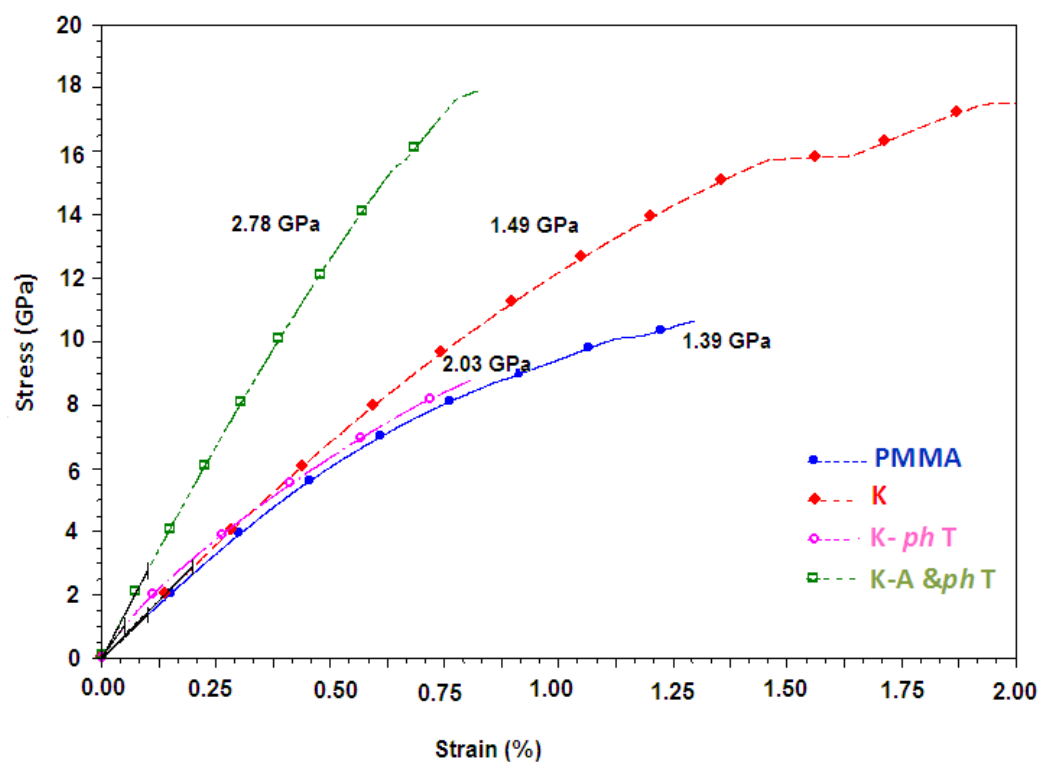


Figure B-22: DMA curves of copolymer K and its hybrids

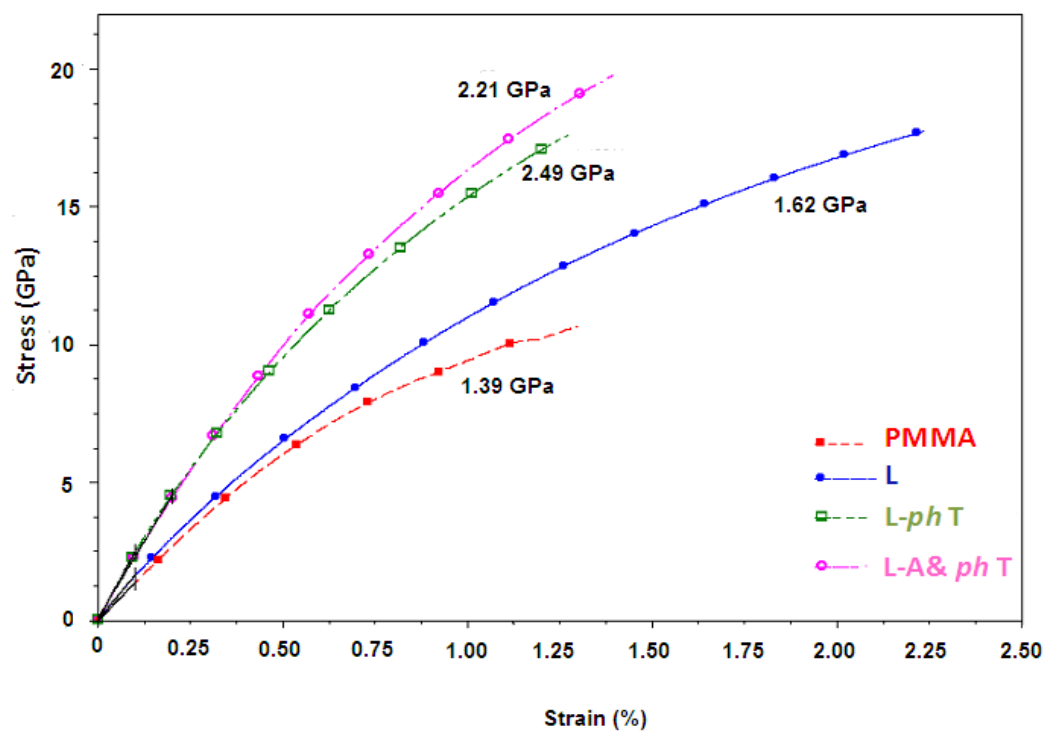


Figure B-23: DMA curves of copolymer L and its hybrids

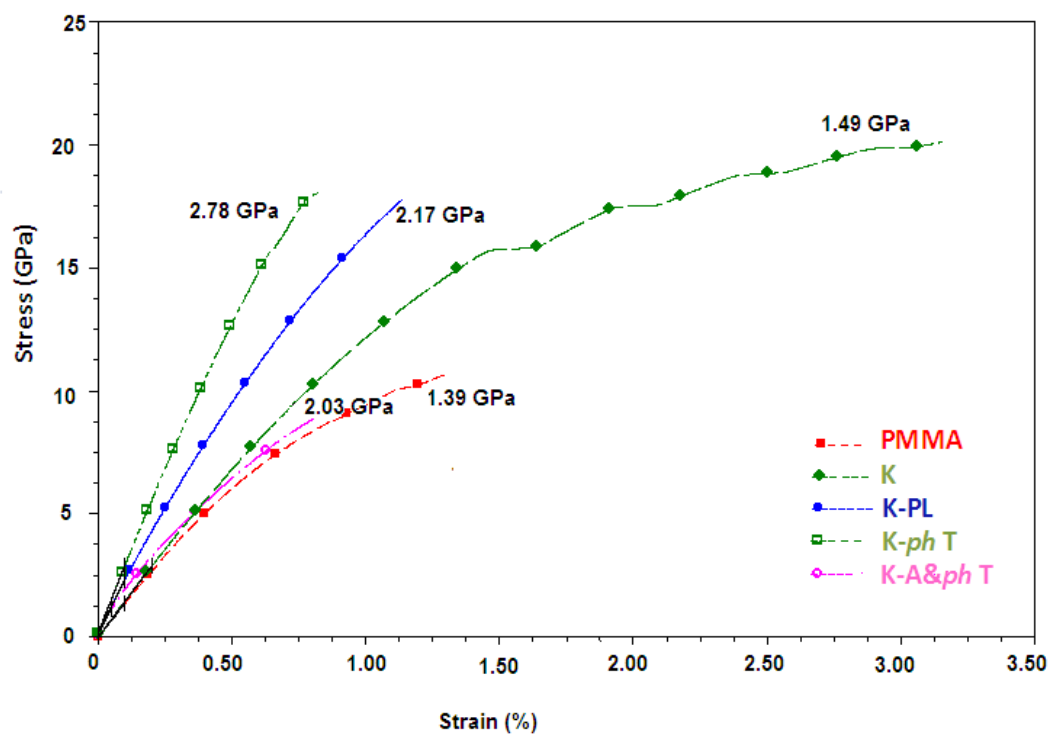


Figure B-24: DMA curves of copolymer K and its hybrids

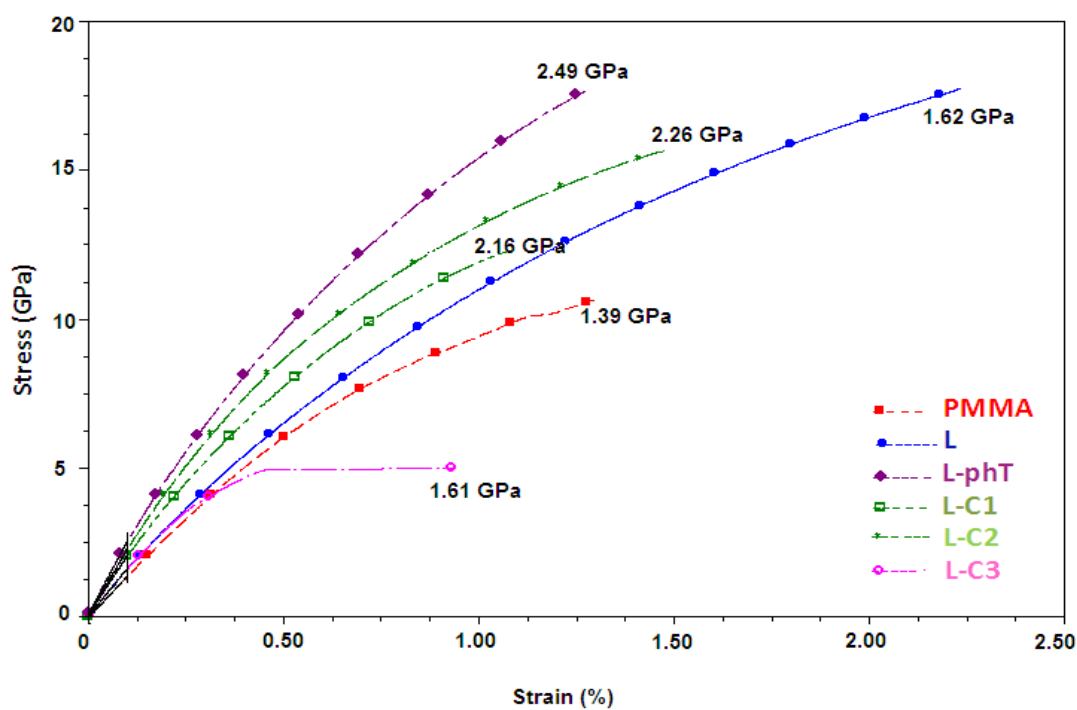


Figure B-25: DMA curves of copolymer L and its hybrids

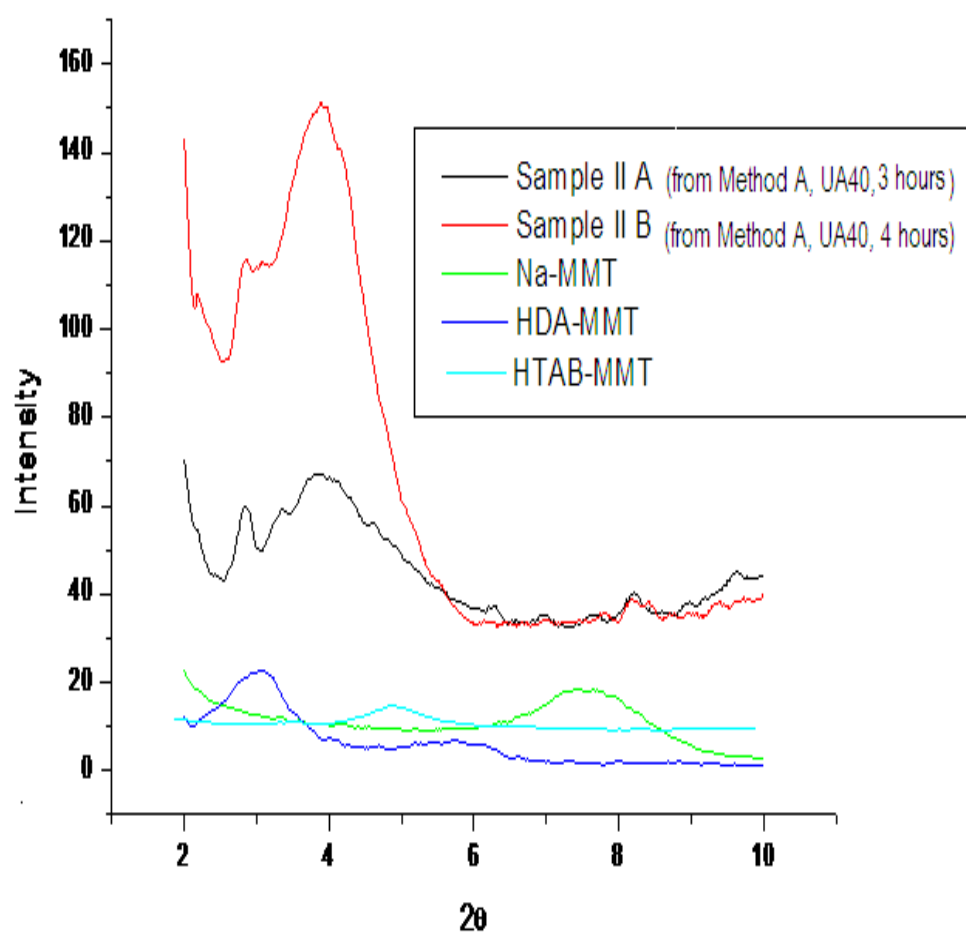


Figure B-26: XRD patterns of Na-MMT, HDA-MMT, HTAB-MMT and Sample II (from Method A)

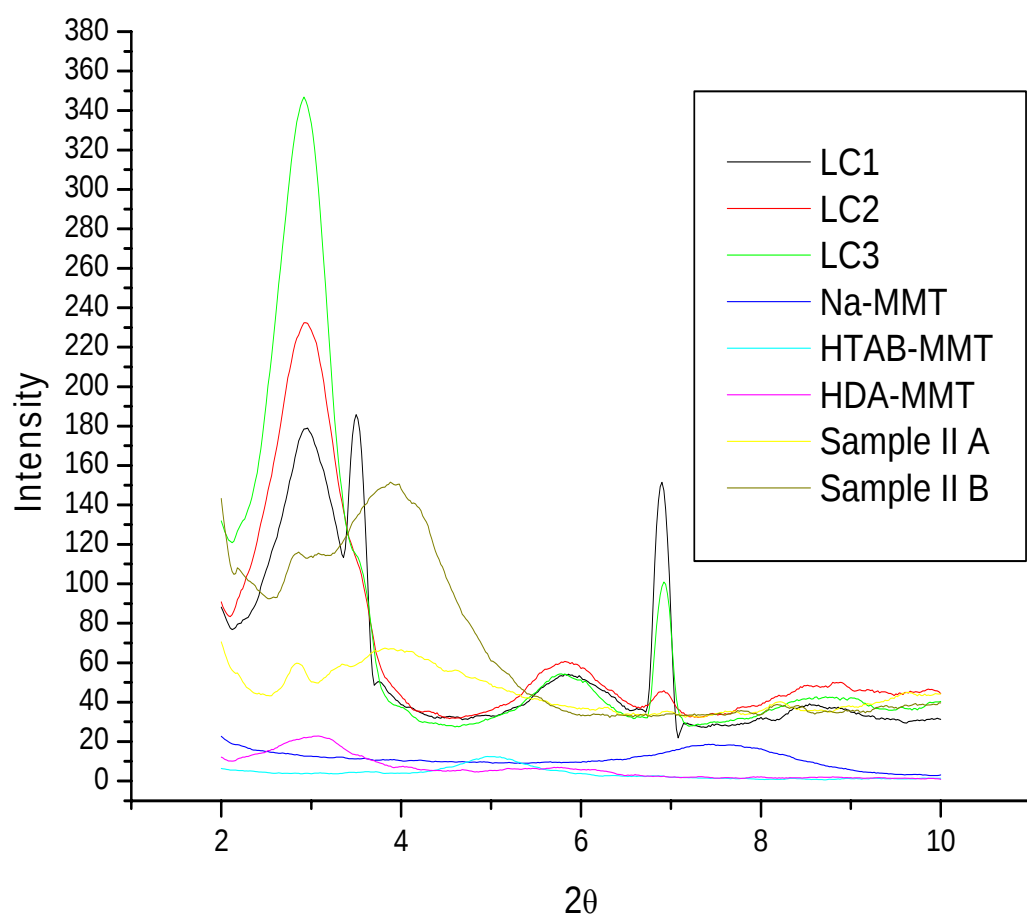


Figure B-27: XRD patterns of Na-MMT, HDA-MMT, HTAB-MMT and Sample II (from Method A and Sample LC1, LC2, LC3 (from Method III))



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Structural definitions for soluble portions of polyacrylamides
synthesized with Ce(IV)-chelating agent redox systems.
Polymer International, Vol.40, Issue 3, 179-185