İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PREPARATION AND CHARACTERIZATION OF POLY(METHYL METHACRYLATE) NANOCOMPOSITES

MSc. Thesis by

Engin AÇIKALIN, B.Sc.

Department : Organic Chemistry

Programme: Chemistry

JUNE 2006

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Supervisor (Chairman): Prof. Dr. Oya ATICI

Members of the Examining Committee Doç. Dr. Nilgün KIZILCAN (İ.T.Ü)

Prof.Dr. Seniha GÜNER (İ.T.Ü)

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FOREWORD

There are many people whom I would like to acknowledge in making the research presented in this thesis possible. I would especially like to acknowledge the guidance and encouragement of my research advisor Prof.Dr. Oya ATICI and her family.

A very special thanks is made to assistants H. Cüneyt Ünlü and Ebru Günister for the support that they have provided throughout this work.

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May, 2006 Engin AÇIKALIN

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ABBREVATIONS

FTIR	**:** Fourrier Transform Infra Red
NMR	**:** Nuclear Magnetic Resonance
DSC	**:** Diferrential Scanning Calorimetry
XRD	**:** X-Ray Diffraction
SEM	**:** Scanning Electron Microscopy
TEM	**:** Transmission Electron Microscopy
DP	**:** Number-average degree of polymerization
PLS	**:** Polymer-Layered Silicate
MMA	**:** Methyl Metacrylate
PMMA	**:** Poly(methyl metacrylate)
APS	**:** Ammonium Persulfate
EDDA	**:** Ethylene Diamine Diasetic Acid
MC	**:** Methyl Cellulose
PEG	**:** Poly(ethylene glycol)
DTABr	**:** Dodecyl Trimethyl Ammonium Bromide
PCN	**:** Polymer Clay Nanocomposites
MMT	**:** Montmorrilonite
OMMT	**:** Organic Modified Montmorrilonite
Tg	**:** Glass Transition Temperature
Tm	**:** Melting temperature
Td	**:** Thermal Decomposition Temperature

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PREPARATION AND CHARACTERIZATION OF POLY(METHYL METHACRYLATE) NANOCOMPOSITES

SUMMARY

Poly (methyl metacrylate) is a member of acrylate esters family and can be polymerized by addition polymerization mechanism either ionic or radical depending on the type of initiator used. Industrially, poly (methyl metacrylate) produced by free radical polymerization using one of the techniques such as bulk, solution, suspension and emulsion polymerization.

The presence of surfactant is a disadvantage for certain applications of emulsion polymers such as those involving instrument calibration and pore size determination. Emulsifier free emulsion polymerization is a useful approach to solving this problem. In recent years, many works have been done related to this topic.

Polymer/clay composites are prepared by two methods as in situ polymerization and solution dispersion. The clay initially modified with cationic surface active material to have silicate layers of clay intercalated. In in situ method, polymerization is carried out in the interlayer of clay. Diferrently, the polymer, which prepared before, dispersed into intercalated silicate layers.

In this work, the aim is that first to prepare methyl metacrylate homopolymer and its copolymers with methyl cellulose and poly(ethylene glycol) by emulsifier free emulsion polymerization using ammonium persulfate initiator which has surface active property when dissociates into radical species and has frequent use in industrial applications. Secondly, to prepare composites of homo and copolymers by in situ and solution dispersion methods. Finally, to characterize prepared polymers and composites.

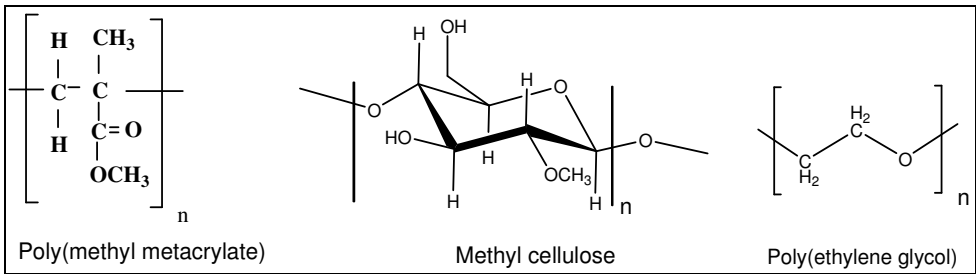


Figure 1. The monomers which were used our work.

In all experiments of methyl metacrylate homo and copolymer preparation, deionized water used emulsifying media, ammonium persulfate used as initiator, and all experiments performed at 80^{o}C temperature under magnetic stirring at 1100rpm for 6h. At the end of reaction, the polymer tried to precipite by adding excess ethanol(Table i).

Table 1. The polymerization results and conditions of 15 gr(1,06 M) MMA monomers which are polymerized with 5 gr(2,3mmol/l) APS initiator in 120 ml of water at 800 C individually.

Code	MC 400 gr	PEG 1500 gr	Cu(II)/ EDDA comple x	Thickener PMMA gr	Reaction time hr	Stopper hydroquinone 20 ppm	Yield %
PMMA1	-	-	-	-	6	-	61
PMMA1-1*	-	-	-	-	6	+	80
PMMA2**	-	-	+	+	3	-	99
PMMA3***	-	-	-	+	6	-	83
PMC	1	-	-	-	6	-	57
PPEG	-	1	-	-	6	-	87

*20 ppm of hydroquinone is added at the end of the reaction.
**Copper sulfate 0.0225gr (1mmol/lt), EDDA 0,061gr (1,5mmol/lt) are added to obtain a complex before reaction and 0,75 gr PMMA thickener is added at the end of the reaction before precipitation
*** 1,5 gr PMMA thickener is added before the reaction starts.

In the prearation of MMA homopolymers some investigations have done to destabilize the emulsion and precipitate to polymer. The mechanisms used to precipitate the polymer was that saturation with excess NaCl, termination with hydroquinone, using Cu(II)/EDDA complex with poly(methyl metacrylate) thickener. However, the polymer emulsion obtained could precipitate by only centrifuge. Solid polymer particles which precipitated, filtered, washed and dried in the oven. The method of PMMA1 used to prepare composites by in situ method because of being free of additives, and PMMA1-1 used to prepare composites by solution dispersion method due to its high molecular weight and low polydispersity index.

As FTIR spectra shows that PMMA polymers have characteristing absorption bands of 1732 cm^{-1} (C=O) symmetric stretching, 2997,2952 and 2850 cm^{-1} C-H stretching, at 1272, 1243 ve 1194 cm^{-1} C-C-O ve C-O-C stretching.

As FTIR spectra shows that PMMA polymers have characteristing absorption bands of 1732 cm^{-1} (C=O) symmetric stretching, 2997,2952 and 2850 cm^{-1} C-H stretching, at 1272, 1243 ve 1194 cm^{-1} C-C-O ve C-O-C stretching. It could caused that effect of Cu(II) on PMMA2 polymer which has not sharp peaks. In FTIR spectra, changes

on the peaks at 1000-1300 cm^{-1} region and in ^{1}HNMR spectra, the sharp peak at 0,8 δppm implies that syndiotactic rich structure has gained.

The same reaction conditions used in the preparation of methyl cellulose and poly(ethylene glycol) copolymers of methyl metacrylate. After emulsification of MC400(or PEG1500) in water, polymerized with methyl metacrylate(PMC and PPEG).

FTIR spectra of both PMC and PPEG copolymers is similar with poly(methyl metacrylate) except the change of peaks ±1 cm^{-1} that associated with OH stretching, C-C-O, C-O-C stretching bands. It could easily be seen that especially for methyl metacryate methyl cellulose copolymer, OH stretching band changed from 3441 to 3444 cm^{1} and broadened. This result showed that poly(methyl metacrylate) and methyl cellulose have similar functional groups, and thought that this is caused by low amounts usage of either methyl cellulose and poly(ethylene glycol) against methyl metacrylate.

Methyl cellulose copolymer of methyl metacrylate (Code PMC) has characteristic peaks of methyl groups on glucose at 3-4,5 δppm. The sharp and single peak at 3,6 δppm assigned to methylene groups on the chain of poly(ethylene glycol) in methyl metacrylate poly(ethylene glycol) copolymer (Code PPEG). Those peaks are similar to characteristic methylene groups on MC and PEG. Therefore, methyl metacrylate copolymers (PMC and PPEG) could not be identified clearly by ^{1}HNMR analysis. Clear increase can be seen on –OCH integral of methyl cellulose in PMMA-co-MC at 3,6 δppm. It was thought that especially sharp difference on methylene integral at 1,6 δppm proves that poly(ethylene glycol) and particularly methyl cellulose effective on tacticity.

Organophilic clay used in the preparation of methyl metacrylate composites which was modified with cation exchange reaction of dodecyl trimethyl amonnium bromide. The initial dispersion of organoclay in water is very important to prepare composites by both in situ and solution dispersion methods. In addition, 80^0C was selected as an optimum working temperature for both methods.

In order to prepare methyl metacrylate homo and copolymer composites, certain amounts of organoclay dispersed overnight in water, then methyl metacrylate monomer added, dispersed during 36 hours and finally polymerized for 6h. The composite obtained precipitated using ethanol, washed, filtered and dried.

In order to prepare the composites of methyl metacrylate copolymers with methyl cellulose and poly(ethylene glycol) which prepared by in situ method, dispersion of

organoclay in water followed by addition of methyl cellulose (or poly(ethylene glycol)) into flask and emulsification. Then methyl metacrylate monomer added and the same steps applied. As a result the yield increased as the clay content increased with respect to monomer.

Besides, some difficulties were experienced that probably caused by the strong polarity of methyl metacrylate.

Table 2. Results and conditions of in situ polymerized polymer/clay composites of which 7,5 gr MMA emulsified in 60 ml water and polymerized using 2,5 gr (1,06 mmol/lt) APS initiator during 6h at 80 °C.

Code	OMMT(%)*	MC400 gr	PEG gr	yield(%)
$N_{insitu}P1$	1	-	-	53
$N_{insitu}P3$	3	-	-	66
$N_{insitu}P5$	5	-	-	76
$N_{insitu}PMC1$	1	0,5	-	49
$N_{insitu}PMC3$	3	0,5	-	82
$N_{insitu}PMC5$	5	0,5	-	85
$N_{insitu}PPEG1$	1	-	0,5	**98**
$N_{insitu}PPEG3$	3	-	0,5	25**
$N_{insitu}PPEG5$	5	-	0,5	-**

*weight percent with respect to monomer
**experienced with technical problems.

FTIR-spectra of polymethylmetacrylate adsorbed on OMMT via in situ polymerization was similar to that obtained for poly(methyl metacrylate). But PMMA adsorbed on OMMT, the O-H stretching peak centered on 3441 cm^{-1} was broadened and gave maxima at 3445 cm^{-1}. In addition, methylene C-H asymmetric/ symmetric stretching peak at 2850 cm^{-1} changed to 2844 cm^{-1}, $-CH_3$ symmetric bending peak at 1386 cm^{-1} changed to 1388 cm^{-1} and another C-C-O, C-O-C stretching bands changed -1 cm^{-1}. The peaks at 600-400 cm^{-1} which are associated with Si-O bending changed as clay content increased. Similar effects on the spectra of methyl metacrylate copolymers composites. Those of 512-517 cm^{-1} and 462-472 cm^{-1} Si-O bending peaks obtained as the loading of MMT increased. Differently, as clay content increase C=O stretching band at 1731 cm^{-1} changes and turnes to two different signals at 1738 and 1731 cm^{-1}. As clay content increase, peaks of PPEG composites broadened and a different peak obtained at 2926 cm^{-1} associated with –CH stretching. When ^{1}HNMR spectra investigated, as the clay content increases change of the peak at 1,6 δppm shows that tacticity changes in methyl metacrylate homo and copolymer composites

In order to prepare methyl metacrylate homo and copolymer composites by solution dispersion method, w/w %1, 3, 5 organoclay with respect to polymer used dispersed

in water initially. Then methyl metacrylate homo / copolymers (PMMA1/ PMC or PPEG) added and dispersed at room temperature for 24h and at 80^0C for 24h in two stages. At the end of the experiment, the composites, which obtained with %100 yield, filtered, washed with water and dried in the oven.

The FTIR spectra shows that as the amount of organoclay increased, characteristic Si-O bending absorption peaks obtained between 467-472 and 512-517 cm^{-1} from FTIR spectra of MMA homopolymer composites that prepared by solution dispersion method similar to those prepared by in situ method. In addition, the peak at 482 cm^{-1} broadened and shortened. While the amount of OMMT increases Si-O bending peaks at 471 ve 516 cm^{-1} can be identified clearly similar to those of MMA homopolymer composites and from the ^{1}HNMR spectra shows that as the organoclay amount increased sharp changes of the peaks at 0,8δppm, 1δppm 1,6δppm related to varied tacticity.

The XRD spectra of the composites investigated which have been obtained by both methods. Basal spacing of Edirne-Lalapaşa montmorrilonite clay, which has an interlayer spacing of 12,98 A^o, increased to 19,82 A^o after purification and modification with DTABr. It can easily be seen from XRD data shifts that there is no diffraction peak at the region of organoclay (2θ=4,42) 2θ degree which are supposed to belong both composites with different clay loading. These results indicated that methyl metacrlate polymer settled interlayer region of OMMT galleries and exfoliated structure gained for composites for both made by in situ and solution dispersion methods. Besides, the peaks that supposed to be seen for composites were probably below 2θ degree. Therefore, the composites prepared by both methods called as nanocomposite.

In rheological measurements of nanocomposites prepared by both methods, rheological paramaters changes with the effect of increased clay content and interaction between clay and polymer. As clay content increased appearent viscosity values increased.

As a result of morphological analysis which made by SEM, polymer particles in composites prepared by in situ methods more likely to enter silicate layers rather than composites prepared by solution dispersion method. Besides, SEM pictures supports the XRD results and shows that the composites prepared are nanocomposites.

DSC analysis of PMMA-co-MC composites which prepared both in situ and solution dispersion methods shows that the T_g can vary from 40^{o}C to 140 ^{o}C based on the

function of isotactic and syndiotactic portion contained within the polymer. It can easily be seen that nanocomposites prepared by both methods have an elevated transition temperature(T_g) and 4-15 ^oC increase compared with that of pure polymer. However, some T_g 's decreases as rhe clay content increases. This may be associated with the dispersion of the clay layers The more disordered dispersion of clay layer causes the higher T_g increase. On the other hand decomposition rate of composites decreased as the clay content increased. However thermal properties of the composites prepared by in situ method are much better than the composites prepared by solution dispersion method.

POLİ(METİL METAKRİLAT) NANOKOMPOZİTLERİNİN ELDESİ VE KARAKTERİZASYONU

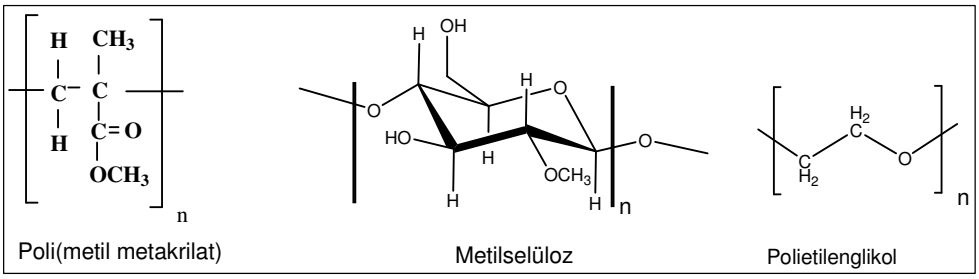
ÖZET

Poli(metil metakrilat), akrilat esterleri ailesinin bir üyesi olup ilave polimerizasyonu ile kullanılan başlatıcının tipine göre iyonik ya da radikal polimerizasyon ile elde edilir. Endüstriyel olarak poli(metil metakrilat), kütle, çözelti, süspansiyon ve emülsiyon polimerizasyonu tekniklerini kullanarak serbest radikal polimerizasyon sistemi kullanılarak elde edilir.

Polimerizasyon reaksiyonlarında emülsiye edici yüzey aktif maddeler kullanımı, emülsiyon polimerlerinde cihaz kalibrasyonu ve gözenek boyutu belirleme gibi bazı uygulmalarda dezavantajlara neden olur. Emülsiye edicisiz emülsiyon polimerizasyonu böyle durumlarda bu dezavantajı ortadan kaldırmaktadır. Son yıllarda emülsiye edicisiz emülsiyon polimerizasyonu üzerine çalışmalar yapılmaktadır.

Polimer/kil nanokompozitleri in-situ polimerizasyon ve çözelti dispersiyonu olmak üzere iki yöntemle yapılırlar. Kullanılacak olan kil öncelikle katyonik yüzey aktif madde ile modifiye edilerek silikat tabakalarının arasının açılması sağlanır. In situ metodu ile kompozit eldesinde arası açılan kil tabakaları içerisinde polimerizasyon yapılır. Çözelti dispersiyonu yönteminde ise arası açılan silikat tabakaları içerisine daha önceden sentezlenmiş olan polimerin yerleşmesi sağlanır.

Çalışmamızda öncelikle metil metakrilat homopolimeri ile metil metakrilatın metil selüloz ve poli(etilen glikol) ile ayrı ayrı kopolimerlerinin radikallere ayrıştığında yüzey aktif özellik gösteren ve endüstriyel uygulamalarda sıklıkla kullanılan amonyum persülfat başlatıcısı kullanarak emülsiye edicisiz emülsiyon polimerizasyonu ile elde edilmesi, elde edilen homo ve kopolimerlerin in situ ve çözelti dispersiyonu yöntemi ile kompozitlerinin yapılması, son olarak da elde edilen polimer ve kompozitlerin karakterizasyonu amaçlanmıştır.



Şekil 1. Çalışmada kullanılan monomerler.

Metil metakrilatın homo ve kopolimerlerinin eldesinde deneylerin hepsinde emülsiye edici ortam olarak deionize su, başlatıcı olarak amonyum persulfat kullanılmış, deneylerin hepsi 80°C sıcaklıkta, 1100 rpm manyetik karıştırma altında ve 6 saat sürede gerçekleştirilmiş, reaksiyon sonunda aşırı etilalkol ilavesi ile çöktürülmeye çalışılmıştır(Tablo i).

Tablo 1. 120 ml suda emülsiye edilmiş her biri 15 gr(1.06 mol/l) MMA monomerlerinin 5 gr (2.3 mmol/lt) APS başlatıcı ile ve 80 °C reaksiyon sıcaklığında polimerizasyonun koşulları ve neticeleri

Deney kodu	MC 400 gr	PEG 1500 gr	Cu(II)/ EDDA kompleksi	Kalınlaştırıcı PMMA gr	reaksiyon süresi saat	sonlandırıcı hidrokinon 20 ppm	verim %
PMMA1	-	-	-	-	6	-	61
PMMA1-1*	-	-	-	-	6	+	80
PMMA2**	-	-	+	+	3	-	99
PMMA3***	-	-	-	+	6	-	83
PMC	1	-	-	-	6	-	57
PPEG	-	1	-	-	6	-	87

* Reaksiyon tamamlandıktan sonra 20 ppm hidrokinon ilave edilmiştir.
** Bakır sülfat 0.0225gr (1mmol/lt), EDDA 0,061gr (1,5mmol/lt) ilave edilmiştir. Ayrıca reaksiyon sonunda 0,75 gr PMMA kalınlaştırıcı ilave edilmiştir.
*** Reaksiyon sırasında 1,5 gr PMMA kalınlaştırıcı ilave edilmiştir.

Metil metakrilat homopolimerlerinin eldesinde reaksiyon sonucu elde edilen emülsiyon halindeki polimerin emülsiyonunu bozarak polimerin katı halde çöktürülmesi için çalışmalar yapılmıştır. Çökmenin incelenmesi sırasında kullanılan mekanizmalar aşırı NaCl ile doyurma, hidrokinon ile sonlandırma, Cu(II)/EDDA kompleksi ve kalınlaştırıcı olarak poli(metil metakrilat) ilavesidir. Ancak tüm deneylerde ancak santrifüjle çöktürülebilen polimer emülsiyonu elde edilmiştir. Çöktürülen katı haldeki polimer süzülmüş ve etüvde kurutulmuştur. Çöktürmenin katkısız olması nedeniyle PMMA1, in situ metodu ile kompozit eldesinde, molekül ağırlığı yüksek polidispersite indeksi düşük olan PMMA1-1 blend kompozit yapımında kullanılmıştır. FTIR spektrumunda absorpsiyon bantlarının yorumlanması sonucunda PMMA polimerinin 1732 cm^{-1}'de (C=O) simetrik gerilme, 2997, 2952 ve

2850 cm^{-1} C-H gerilmeleri, 1272, 1243 ve 1194 cm^{-1}'' ler de C-C-O ve C-O-C gerilmeleri gibi karakteristik absorpsiyon bantlarına sahip olduğu görülmektedir. FTIR spektrasındaki 1000-1300 cm^{-1} bölgeleri arasındaki piklerdeki değişmelerle birlikte ^{1}HNMR spektrumunda görülen 0,8 δppm deki pikin baskın olması elde edilen poli(metil metakrilat) homopolimerlerinin sindiotaktik ağırlıklı yapıda olduğunu göstermektedir.

Metil metakrilatın metil selüloz ve poli(etilen glikol) ile ayrı ayrı kopolimerlerinin yapımında aynı reaksiyon şartları izlenmiş, MC400 (veya PEG1500) su içinde emülsiye edildikten sonra metil metakrilat monomeri ile polimerize edilmiştir(PMC ve PPEG).

Hem PMC, hem de PPEG kopolimerinin FTIR spektrumu poli(metil metakrilat)' ın FT-IR spektrasına benzemektedir. Sadece OH stretching, C-C-O, C-O-C stretching bantlarının pikleri ±1 cm^{-1} kaymıştır. Metil metakrilatın özellikle metil selüloz kopolimeri için OH stretching bandı 3441' den 3444 cm ^{1}'e, kaydığı ve yayvanlaştığı açıkça görülmüştür. Bu sonuç ile, poli(metil metakrilat) ile metil selüloz ve poli(etilen glikol)' ün benzeri fonksiyonel gruplara sahip olduğu, ayrıca başlangıçta metil selüloz ve polietilen glikol oranının metil metakrilat monomerine göre oldukça düşük oranda olmasından kaynaklandığı düşünülmüştür.

Metil metakrilatın metil selüloz kopolimerinde ^{1}HNMR spektrumları incelendiğinde ise piklerin, 3-4,5 δppm arası olan selüloz birimlerinin glikoz üzerindeki metil gruplarının karakteristik piklerine benzeşmektedir. Benzer şekilde poli(etilen glikol)' de zincir üzerindeki metilen gruplarına ait 3,6 δppm' deki pikler, metil metakrilat polimerinin karakteristik pikine benzemektedir. Bu pikler MC ve PEG üzerindeki metilen gruplarının karakteristik piklerine benzeştiğinden NMR analizi ile PMMA kopolimerlerinde (PMC ve PPEG) kesin olarak ayırt edilemediği düşünülmüştür. Bununla birlikte ^{1}HNMR spektrumlarında metil metakrilatın metil selüloz kopolimerinde metil selülozun 3,6 δppm'deki –OCH integralinde belirgin bir artış görülmüştür. Ayrıca 1,6 δppm' de çıkan metyhlene intagralinde gözle bile görülen önemli farklılaşma poli(etilen glikol) ve özellikle metil selülozun tacticity üzerinde etkili olduğu düşündürmüştür.

Metil metakrilat homo ve kopolimerlerinin kompozitlerinin eldesinde, dodesil trimetil amonyum bromür katyonik yüzey aktif maddesi ile iyon değiştirme reaksiyonu ile modifiye edilerek organofilik hale getirilmiş kil (organokil) kullanılmıştır. Organokilin su içerisinde iyi bir şekilde dispersiyonu, in situ veya çözelti dispersiyonu yöntemlerinin her ikisi için de çok önemlidir. Bununla berarber her iki yöntemde de organokil ve metil metakrilat için optimum çalışma sıcaklığı olan 80^0C seçilmiştir.

Metil metakrilat homopolimerinin kompozitlerinin in situ yöntemi ile eldesinde belirli miktarlarda organokilin su içinde gece boyunca dispers edildikten sonra metil metakrilat monomeri ilave edilmiş ve 36 saat boyunca dispers edilmiştir. Daha sonra homopolimer sentezindeki gibi aynı şartlarda 6 saat reaksiyona tabi tutulmuştur. Elde edilen kompozit etil alkol ilavesi ile çöktürülmüş, yıkanmış ve kurutulmuştur.

Metil metakrilatın metil selüloz ve poli(etilen glikol) ile kopolimerlerinin in situ metodu ile yapılan kompozitlerinde organokilin su içerisinde disperiyonundan sonra metil selüloz (veya poli(etilen glikol)) ilave edilmiş ardından metil metakrilat monomeri ilave edilerek aynı basamaklar uygulanmıştır. Deney sonucunda organokil yüzdesi arttıkça elde edilen kompozitin veriminin arttığı görülmüştür.

Bununla beraber organokilin monomer ile dispersiyonunda bazı güçlükler yaşanmış, bunun metil metakrilat monomerinin aşırı polar yapısından kaynaklandığı düşünülmüştür.

Tablo 2. 60 ml suda emülsiye edilmiş 7,5 gr MMA monomerlerin 2,5 gr (1,06 mmol/lt) APS başlatıcı ile ve 80 ^{o}C reaksiyon sıcaklığında 6 saat sürede in-situ metodu ile elde edilen polimer-kil kompozitlerinin koşulları ve neticeleri.

Deney kodu	OMMT(%)*	MC400 gr	PEG gr	verim(%)
N_{insitu}P1	1	-	-	53
N_{insitu}P3	3	-	-	66
N_{insitu}P5	5	-	-	76
N_{insitu}PMC1	1	0,5	-	49
N_{insitu}PMC3	3	0,5	-	82
N_{insitu}PMC5	5	0,5	-	85
N_{insitu}PPEG1	1	-	0,5	**98**
N_{insitu}PPEG3	3	-	0,5	25**
N_{insitu}PPEG5	5	-	0,5	-**

*monomere göre ağırlıkça.
**teknik sorunlar yaşanmıştır.

FTIR spektrumu incelemesi sonucunda in situ metodu ile elde edilen homopolimer kompozitlerin spektrumlarının poli(metil metakrilat) ile oldukça benzer olduğu görülmüştür. Ancak O-H gerilmelerinin 3441 cm^{-1}' den 3445 cm^{-1}' e kaydığı ve genişlediği, 2850 cm^{-1} de çıkan metilen C-H gerilmelerinin piki 2844 cm^{-1} e, 1386 cm^{-1} de çıkan $–CH_3$ eğilme piki 1388 cm^{-1} e ve diğer C-C-O, C-O-C gerilme bantları -1 cm^{-1} kaydığı görülmüştür. 600-400 cm^{-1} arasında Si-O bending pikleri organokil yüzdesinin artması ile değişiklik göstermiştir. Kopolimer kompozitlerin spektrumlarında da benzer etkiler görülmüştür. 512-517 cm^{-1} ve 462-472 cm^{-1}'deki Si-O bükülme pikleri organokil yüzdesi artırıldıkça belirginleşmektedir. Farklı olarak metil selüloz ile yapılan kopolimerin kompozitinde kil yüzdesi arttıkça 1731 cm^{-1} de çıkan C=O gerilme piki 1738 ve 1731 cm^{-1} olmak üzere iki ayrı sinyal oluşturmuştur.

Poli(etilen glikol) ile yapılan kopolimerin kompozitinde ise kil miktarı arttıkça hem pikler yayvanlaşmış hemde 2926 cm^{-1} de farklı –CH gerilme piki oluşmuştur.

^{1}HNMR spektrumları incelendiğinde metil metakrilat homo ve kopolimer kompozitlerinde organokil yüzdesi arttıkça 1,6 δppm' deki piklerin değişimi metil metakrilat homo ve kopolimerlerin kompozitlerinde taktisitenin de değiştiğini göstermektedir.

Metil metakrilat homo ve kopolimerlerinin çözelti dispersiyonu yöntemi ile eldesinde polimere göre ağırlıkça %1, 3, 5 olacak şekilde organokilin su içindeki dispersiyonundan sonra ayrı ayrı önceden sentezlenen metil metakrilat homo / kopolimerleri (PMMA1/ PMC veya PPEG) ilave edilerek 24 saat sıcak, 24 saat 80^{0}C' de olmak üzere iki kısımda dispers edilmiştir. Deney sonunda %100 verimle elde edilen karışım kompozitler direkt olarak süzülmüş, su ile yıkanmış ve etüvde kurutulmuştur.

FTIR spektrumları incelemesinden, in situ metodu ile elde edilen kompozitlere benzer olarak organokil miktarı arttıkça 467-472 cm^{-1} ve 512-517 cm^{-1} arasında karakteristik Si-O bükülme pikleri oluşmuştur. Bununla birlikte 482 cm^{-1} deki pik giderek yayvanlaşmıştır. Metil metakrilat kopolimerleri kompozitlerinde organokil yüzdesi arttıkça 471 ve 516 cm^{-1} de bulunan Si-O bending piklerinin belirginleştiği gözlenmektedir. ^{1}HNMR spektrumları incelendiğinde ise 0,8 δppm,1,6 δppm,1 δppm ve 1,6 δppm deki piklerin organokil yüzdesi arttıkça farkılaştığı stereoisomerismdeki değişimi göstermektedir.

Organokilin XRD spektrumu incelendiğinde tabaka aralığı 12,98 A° olan Edirne-Lalapaşa montmorillonit kili, saflaştırıldıktan ve DTABr ile modifiye edildikten (OMMT) sonra yaklaşık 7 A° daha açılarak tabaka aralığı 19,82 A° olduğu görülmüştür. Metil metakrilat homo ve kopolimerlerinin in situ ve çözelti dispersiyonu metodları ile yapılan kompozitlerinin XRD verileri incelenmiştir. In situ ve solution dispersiyon yöntemlerinin her ikisi ile yapılan kompozitlerde MMA homo ve kopolimer kompozitlerinin piklerinin bulunduğu bölgede OMMT pikine(2θ=4,42) rastlanmadığından dolayı metil metakrilat homo ve kopolimerinin OMMT tabakaları arasına girerek, tabakaları tamamen dağıtmış olduğu sonucuna varılmıştır. Bununla beraber kompozitlerde görünmesi beklenen piklerin 2θ değerinin altında kalması nedeniyle her iki metodla da elde edilen kompozit, nanokompozit olarak değerlendirilmiştir.

Elde edilen nanokompozitler reolojik olarak incelendiğinde kil miktarı arttıkça organokil ile polimerin etkileşimi sonucu reolojik parametrelerin değiştiği

gözlenmiştir. Akma gerilme değerindeki değişiklik Bingham Plastik yapısına doğru geçişi gösterir. Ayrıca organokil miktarı arttıkça görünür viskozitede de artma gözlenmiştir.

Morfolojik incelemeler sonucunda taramalı elektron mikroskobu (SEM) görüntülerinden in situ metodu ile elde edilen kompozitte polimer taneciklerinin kil tabakaları arasına çözelti dispersiyonu ile elde edilen kompozitlere göre daha fazla girdiği gözlenmiştir. Ayrıca SEM görüntüleri XRD sonuçlarını destekleyerek elde edilen kompozlerin nanokompozit olduğunu göstermektedir.

Metil metakrilatın metil selüloz kopolimerinin in situ ve çözelti dispersiyonu metodu ile yapılan kompozitlerinin DSC verileri incelendiğinde değerlerin, 40 ile 140 ^{o}C arasında isotaktik ve sindiotaktik yapıya göre dağıldığı görülmüştür. T_g değerlerinin genelinde polimerlerle karşılaştırıldığında kil yüzdesi arttıkça 4-15 ^{o}C arası yükselme olduğu görülmüştür. Bununla beraber bazı T_m değerlerinde düşme görülmüş, bu sonuç kil tabakalarının dispersiyonunun iyi olmadığını düşündürmüştür. Bununla beraber TGA verileri incelendiğinde ise kil yüzdesi arttıkça malzemenin bozunma oranının azaldığı gözlenmiştir. Polimer ile kil tabakalarının etkileşimi ile gerçekleşen bu özellik in situ metodu ile elde edilen kompozitlerde daha belirgindir.

1.INTRODUCTION

Poly(methyl metacrylate) belogs to the family of polyacylic and metacrylic esters and posess many desirable properties such as optical clarity, good weatherability, good strength and excellent dimensional stability[1]. Poly(methyl methacrylate) is made commercially by bulk casting, suspension, bulk, and emulsion polymerization techniques[2]. Each of these methods utilizes free radical chemistry. Polymers made from poly(methyl methacrylate) and copolymers that are largely poly(methyl methacrylate) are used primarily in plastics applications and emulsion polymers of poly(methyl metacrylate) are used as specialty polymers, such as processing aids and impact modifiers for thermoplastics, adhesives, caulks, and coatings or binders in floor polishes, paints, and paper applications.

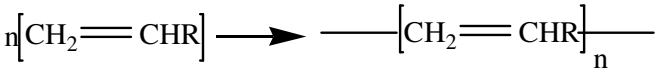
Within the fascinating world of nanomaterials in general, polymer/clay nanocomposites (PCN) more than carry their weight in terms of intrigue and applicability. Consider all the factors that must be involved in the dramatic modification and improvement of a polymer's behavior in terms of thermal, mechanical, rheological properties, upon the addition of just a few weight percent (wt%) of a nano-size inorganic sheet compound[3] .Polymer/Clay nanocomposites are prepared via *in situ* polymerization and solution dispersion (melt or in solution blending) methods. Organoclay which is used to prepare PCN's obtained from cation exchange reaction between clay and intercalating agent.

The aim in this work is to investigate preparation of methylmetacrylate homo and copolymers by free radical emulsifier free emulsion polymerization and preparation of their composites by in situ and solution dispersion methods and finally to characterize and compare polymers and composites in terms of their rheologic, electrokinetic, morphologic and thermal properties.

2. THEORY

2.1. The Free Radical Addition Polymerization

Vinyl monomers, such as vinyl acetate and acrylate esters, polymerize only by addition processes[4]. In addition polymerizations, after chain initiation has begun there follows the successive addition of a large number of monomer molecules to the growing polymer chain. Eventually, this growth ends by a termination mechanism. The process of the addition polymerization is shown generally as:



(2.1)

Addition polymerizations are further characterized by the type of initiator used. They can be induced by free radical, ionic, or high-energy mechanisms. These mechanisms, however, are quite similar, including initiation, propagation, and termination steps. A free radical is an extremely short-lived, highly energetic molecular fragment containing a single, unpaired electron. It reacts readily with the unsaturated vinyl double bond of a monomer molecule to begin a polymer chain growth. Radicals generally arise either by absorption of sufficient vibration energy by initiator precursors or by chemical reaction of a precursor with reducing agents involving a one electron transfer. When the radical reacts with a monomer molecule a larger free radical is formed which, in turn, reacts with another monomer molecule, thus propagating the polymeric chain. While individual monomer addition reactions are almost instantaneous, the polymerization may take several hours to complete in the reaction mixture depending on the method and the temperature of polymerization. Growing polymer chains are finally terminated (free electrons coupled) in a variety of ways including disproportionation, biradical coupling, and one or more chain transfer mechanisms.

2.1.1. Initiation

The initiator (I) dissociates homolytically to yield a pair of free radicals (R·), followed by addition of a free radical to the first monomer (M) molecule having a vinyl double bond to produce chain-initiating species (M·).

$$I \xrightarrow{k_d} 2R\cdot \qquad (2.2)$$

$$R\cdot \xrightarrow{k_i} RM\cdot \qquad (2.3)$$

Where kd is the rate constant for the initiator dissociation and ki is the rate constant for the initiation step. Free radicals can be generated by two processes: thermal cleavage through absorption of sufficient vibrational bond energy and chemical reaction involving electron transfer mechanisms. Although all chemical bonds will cleave if sufficient energy is absorbed, relatively few types of chemical bonds have the required bond dissociation energies to be useful as free radical precursors. If bond dissociation energies are too high, rates of free radical generation at reasonable temperatures are much too slow to be practical. If too low, rates of free radical generation are so rapid that storage and handling of the precursors presents problems. Two important chemical bonds meet the requirements of safety, practicality, and versatility: the peroxide (O–O) and azo (N=N) bonds. Typical homolytic cleavage of each of these bonds into free radicals is shown below:

Peroxide

$$RO-OR' \rightarrow RO\cdot + R'O\cdot$$

Azo

$$RN=NR' \rightarrow R\cdot + R'\cdot + N_2 \qquad (2.4)$$

The rate of thermal dissociation of an initiator, R , is given by,

$$R_d = 2fk_d[I] \qquad (2.5)$$

where [I] is the concentration of the initiator and f is the initiator efficiency. The initiator efficiency is defined as the fraction of the radicals produced in the dissociation reaction which initiates polymer chains. The value of f is usually less than unity due to wastage reactions. The use of the factor of 2 in the decomposition reaction follows the generally accepted convention for reactions producing radicals in pairs. The second step where the primary radical adds to monomer is much faster than the first step. Therefore, the dissociation of the initiator is the rate-determining step in the initiation sequence.

2.1.1.1. Initiators in Emulsion Polymerization

The function of the initiator is to generate free radicals, thereby initiating the polymerization reaction. Emulsion polymerizations have been restricted almost entirely to catalysis by free-radical initiation. Use of water-soluble, free-radical

precursors predominates over oil-soluble types in aqueous emulsion polymerization practice. The initiators fall into two broad classifications: (1) the dissociative initiators which arise through thermal bond scission (dissociation) of the free-radical precursor without interacting with any other molecule, and (2) the redox initiators which comprise at least two types of molecules and are generated by electron transfer mechanisms involving free-radical precursors and reducing agents (reduction-oxidation or redox).

Persulfates are the most commonly used thermal dissociation type free radical initiators for the preparation of polymer emulsions are of the water-soluble, free-radical-producing persulfates (peroxodisulfates), usually in the form of potassium, sodium, and ammonium persulfate. They are used in the temperature range of 50-90℃. Persulfate initiator is insoluble in VAc and in most water-immiscible monomers. Persulfate ion decomposes in the aqueous phase thermally to give sulfate ionradicals, which initiate polymerization either in that phase or in the monomer swollen polymer phase after diffusing across the interface.

$$S_2O_8^{-2} \rightarrow 2 \cdot OSO_3^{-1} \qquad (2.6)$$

The decomposition of persulfates is accelerated at acid pH; however, the acidcatalyzed decomposition does not yield free radicals. When anionic emulsifiers are used, the emulsifier anions are adsorbed onto the monomer-swollen polymer particles and monomer-containing micelles, and also onto the monomer droplets. Then they form a repulsion barrier to the diffusion of sulfate ion radicals through that interface. Thus, the initiation of polymerization in the water phase is the more likely reaction, with the oligomeric sulfate ion radical adding monomer units until it was adsorbed at the interface between the monomer-swollen polymer and water phases, with the radical end oriented toward the monomer-swollen polymer phase. The sulfate ion-radical may react with water to form bisulfate ions and hydroxide radicals as follows:

$$\cdot OSO_3^{-1} + H_2O \rightarrow HSO_4^{-1} + HO\cdot \qquad (2.7)$$

Therefore, the initiation of polymerization may occur by reaction of a vinyl monomer molecule either with a sulfate ion-radical or with a hydroxyl radical. The propagating polymer chain has a hydrophilic moiety at the end in either case since the initiating radical is hydrophilic.

Hydrogen peroxide and other peroxides are soluble in both the aqueous and monomer- swollen polymer phases and thus distribute themselves between the two phases. In principle, hydroperoxides could decompose in either phase to form a hydroxyl radical and another oxygenated radical according to the particular hydroperoxide used. The distribution of any hydroperoxide between the two phases may be changed by dissolving suitable ingredients in both phases.

$$HO - OH \rightarrow HO + OH \quad (2.8)$$

$$RO - OR' \rightarrow RO\cdot + R'O\cdot \quad (2.9)$$

:Initiators of the redox type generate free radicals through an oxidation-reduction reaction at relatively low temperatures. The components of a redox initiation system are unreactive at normal ambient temperatures, provided that they are kept separate from each other. Redox initiators can be used at near-ambient temperatures, and at subambient temperatures such as 5℃.

For many reasons free radical generation by thermal scission may be undesirable in emulsion polymerization. Most obvious, of course, is the need to conduct polymerizations at temperatures well below those at which the precursor decomposes rapidly enough for utility. The use of redox initiators has many advantages. Lower temperature polymerizations are possible, resulting in higher molecular weight polymers. Lower temperature polymerizations favor more linear polymers due to suppression of high temperature-accelerated chain transfer (as chain transfer to solvent, monomer, and polymer) and termination reactions, resulting in low levels of polymer branching. In addition, better control of polymerization rates and more efficient catalyst activity result when redox systems are used.

2.1.2. Propagation

Propagation is a process of the growth of M· by the successive addition of a large number of monomer molecules (n) as shown below.

$$RM + nM \xrightarrow{k_p} P_{n+1} \quad (2.10)$$

where kp is the rate constant for propagation. In this step, a large number of monomer molecules is converted to polymer for each initial radical species produced in the first step. Monomer is consumed by the initiation reaction as well as by the propagation reactions. The rate of monomer consumption, which is synonymous with rate of polymerization is given by,

$$\frac{d[M]}{dt} = R_i + R_p \tag{2.11}$$

where Rp is the rate of propagation. However, the number of monomer molecules reacting in the initiation step is far less than the number in the propagation step for a process producing high polymer. The rate of initiation can be neglected and a very close approximation of the polymerization rate can be given simply by the rate of propagation:

$$\frac{d[M]}{dt} = R_p \tag{2.12}$$

As a consequence, the rate of polymerization is the sum of all the individual propagation steps and, since the rate constants for all the propagation steps are the same as kp, then the polymerization rate is given as:

$$R_p = k_p[M^{\cdot}]\,[M] \tag{2.13}$$

where [M] is the monomer concentration and [M·] is the total concentration of every size of chain radicals. However, radical concentrations are difficult to measure since they are very low and they should be eliminated.

2.1.3. Termination

The propagating polymer chain stops growing and terminates at some point. There are two mechanisms of termination:

When radical coupling occurs two polymeric radicals terminate each other by the occurrence of the annihilation of the radical centers.

$$P_n^{\cdot} + P_m^{\cdot} \xrightarrow{k_{bc}} P_{n+m} \tag{2.14}$$

In disproportionation, one polymeric radical abstracts a hydrogen atom from another, leaving it with a terminal vinyl double bond. Disproportionation occurs more rarely than biradical coupling. It results in the formation of two polymer molecules, one saturated and one unsaturated. Termination can also occur by a combination of bimolecular coupling and disproportionation. Bimolecular coupling termination always results in longer chains and thus higher molecular weight polymer than disproportionation. The propagation reaction would proceed indefinitely until all the monomer in a reaction system was exhausted if it were not for the strong tendency toward termination.

$$P_n^{\cdot} + P_m^{\cdot} \xrightarrow{k_{bc}} P_n + P_m \tag{2.15}$$

2.1.4. Degree of Polymerization

The number-average degree of polymerization, DP, is the average number of monomer units per polymer molecule and is equal to the rate of chain growth divided by half the rate of chain termination. DP is inversely dependent on the square root of the initiator concentration. Increasing the initiator concentration leads to smaller sized polymer molecules. Assuming all the termination reactions were bimolecular coupling only made the above derivation.

The number-average molecular weight of a polymer is given by

$$M = DP.M_w \tag{2.16}$$

where M_w is the molecular weight of the monomer. When termination by disproportionation occurs, the molecular weight of the polymer decreases. Nevertheless, most polymer radicals appear to terminate predominantly or entirely by bimolecular coupling.

2.1.5. Chain Transfer

The polymer weight is observed to be lower than predicted on the basis of termination by bimolecular coupling or disproportionation in many polymerizations. This effect is due to other mechanisms of premature termination that involve chain transfer in which growing polymeric radicals abstract hydrogen atoms from polymer, monomer, solvent, additives, impurities, or initiator. The resulting new radical formed can initiate new polymer chain growth at the same rate as the primary radicals, at a

slower rate, or not at all. If the effect of chain transfer is merely to reduce chain length (lower polymer molecular weight) with little or no effect on the rate of polymerization, the chemical agent is called a “modifier.” When polymerization rate is slowed considerably, the chemical agent is called a “retarder.” In both cases, nondegradative chain transfer is said to prevail. However, when the resulting free radical will not initiate polymerization, the agent is called an “inhibitor,” and the chain transfer is referred to as degradative.

2.2. Polymerization Techniques

In Table 2.1 types of polymerization systems explained in terms of monomer-polymer phase relationship and monomer location[5].

Bulk polymerization is the simplest of the techniques requiring only monomer and monomer-soluble initiator, and perhaps a chain transfer agent for molecular weight control. Characterized on the positive side by high polymer yield per volume of reaction, easy polymer recovery. Difficulty of removing unreacted monomer and heat control are negative features.

Table 2.1: Types of polymerization systems.

Monomer-polymer phase relationship	Monomer Location	
	Continuous	Dispersed
Homogeneous (same phase)	Bulk, solid state solution	Suspension
Heterogeneous (different phases)	Bulk with polymer precipitating	Emulsion; suspension with polymer precipitating

In solution polymerization, monomer and initiator must be soluble in the liquid and the solvent must have the desired chain transfer characteristics, boiling point (above the temperature necessary to carry out the polymerization and low enough to allow for ready removal if the polymer is recovered by solvent evaporation). The presence of the solvent assists in heat removal and control (as it also does for suspension and emulsion polymerization systems). Polymer yield per reaction volume is lower than for bulk reactions. Also, solvent recovery and removal (from the polymer) is necessary. Many free radical and ionic polymerizations are carried out utilizing solution polymerization including water-soluble polymers prepared in aqueous solution.

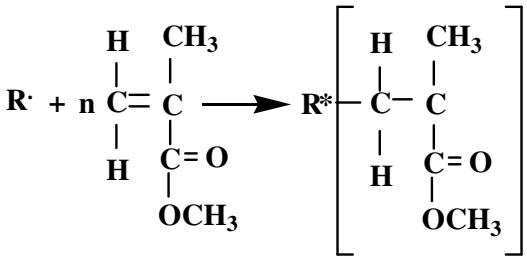
A water-insoluble monomer and initiator are used in suspension polymerization. Again, a chain transfer agent may be used to control chain size. Stirring is usual. Droplets of monomer containing initiator and chain transfer agent are formed. A protective colloidal agent, often poly(vinyl alcohol), is added to prevent coalescence of the droplets. Near the end, the particles become hard and are recovered by filtration. Because the liquid is water-based, solvent recovery and treatment problems are minimal. The products may contain a number of impurities including any of the agents added to assist in the polymerization process.

In emulsion polymerization, the system usually contains a water-soluble initiator (in contrast to the requirement that the initiator must not be water-soluble in suspension polymerizations), chain transfer agent, and a surfactant. The hydrophobic monomer forms large droplets that are stabilized by the surfactant. At a certain surfactant concentration, the surfactant molecules form micelles that contain 50–100 surfactant molecules. During the polymerization, the monomer, which has a small but real water solubility, migrates from the monomer droplets through the water and into these micelles. Polymerization begins when the water-soluble initiator enters into the monomer-containing micelle. Because the concentration of micelles (about 10^{21}/Liter) is high compared with the concentration of monomer droplets (about 10^{14}/Liter) the initiator is more likely to enter a micelle than a monomer droplet. As polymerization continues, monomer is transferred to the growing micelles. At about 50–80% conversion the monomer droplets disappear and the micelles become large polymer-containing droplets. This suspension is called a latex. The latex is stable and can be used as it is or the polymer recovered by coagulation. In inverse emulsion polymerization, the monomer, which is hydrophilic, is dispersed in an organic liquid. Here the monomer is usually contained in an aqueous solution.

2.3. Methyl Metacrylate Polymers

2.3.1. Preparation

The polymerization of methyl methacrylate readily accomplished by bulk, solution, suspension and emulsion techniques[6]. Of these methods, bulk and suspension polymerization are mainly used for the production of the homopolymer.



(2.17)

Poly(methyl methacrylate) is made commercially by four different polymerization methods: bulk casting, suspension polymerization, bulk polymerization, and emulsion polymerization[2]. Each of these methods utilizes free radical chemistry. Other forms of polymerization (for example, anionic, group transfer, and other types of “living” polymerizations) are known but are not commercially important today. Commercially available methyl methacrylate (MMA) polymers have molecular weights ranging from about 70,000 to about 200,000 for those polymers produced for molding or extrusion applications. Cast sheets and polymers made by emulsion polymerization can have molecular weights greater than 1,000,000. MMA polymerization is accompanied by the liberation of the heat of polymerization, (13.8 kcal/mol) which must be controlled to allow for safe operation and to prevent unwanted side-reactions. Volumetric shrinkage during polymerization is about 21%. MMA polymerization follows classical free-radical polymerization chemistry and consists of four basic steps as initiation, propagation, chain transfer and termination (See also section 2.1)

Bulk casting polymerization is the oldest of the four commercial polymerization methods and is still used today, primarily for manufacture of sheet, rods, and blocks. The sheet-casting process employs a mold of glass plates, matched to yield a sheet of uniform thickness. The glass plates, separated by a vinyl spacer, are clamped together. A partially polymerized syrup containing initiator(s) is injected between the plates while air is excluded. The clamped assemblies are then heated, first at a temperature of 60–80 °C (usually in a water bath) to begin the polymerization and then at a temperature greater than the T_g of the polymer (ca. 115 °C) to complete the polymerization process. Conversions of about 99% are attainable. When bulk casting is used to make pellets for injection molding applications, chain transfer agents are used to control molecular weight.

Suspension and bulk polymerized MMA are generally used for injection molding and extrusion applications. In either case other monomers, for example, methyl acrylate or ethyl acrylate, are usually copolymerized with MMA to modify the properties of the

resulting copolymer. Inclusion of an acrylate in the poly(methyl methacrylate) chain imparts additional flexibility to the chain, reducing both the melt viscosity and the T_g of the resulting copolymer. Commercial poly(methyl methacrylate) polymers contain as much as 15 wt % methyl acrylate or ethyl acrylate comonomer. In addition to lowering the melt viscosity and T_g, the co-acrylates also impart increased thermal stability to the polymer backbone as a result of the ability of acrylates to slow down radical induced depolymerization. Other non-reactive components, such as lubricants (for example, stearic acid), colorants and various UV absorbers are frequently added to enhance the performance of the resulting products.

In the suspension polymerization process, beads of monomer are formed in de-ionized water by continuous agitation. The size of the bead is determined by the rate of agitation, the presence of dispersants, and other components. Peroxy or azo initiators are used. Polymerization temperatures are usually kept below 100 °C. During polymerization the polymer is formed and remains dissolved in the monomer droplets. The partially converted droplets become sticky between about 20% and about 80% conversion requiring the presence of dispersing agents to stabilize the suspension and prevent agglomeration of the beads. The reactions are driven to high conversion. The resulting beads of polymer can be used as it is, but are often extruded to yield pellets. This extrusion step adds substantial cost to the process.

Continuous bulk polymerization can be carried out using methyl methacrylate as both reactant and solvent or, alternatively, using an “inert” solvent such as toluene. When monomer is used as the reaction medium the residence time and initiator concentration are usually adjusted to permit adiabatic polymerization, with the heat of polymerization being equally balanced by the cooling effect of the feed mix. Conversion, based on monomer, is typically in the 50–80% range. Unreacted monomer is separated from the polymer product and reused as part of the monomer feed to the reactor. Unreacted monomer and other volatiles can be separated from the polymer in a number of ways, including falling strand devolatilization and extruder devolatilization. When an inert solvent is used as reaction medium, the additional option of removing the heat of reaction by reflux cooling of the solvent exists.

Poly(methyl methacrylate) can be prepared by emulsion polymerization. Typically the monomer is polymerized as sub-micron size (from 50 to 1000 nm) particles in aqueous medium. Polymerization temperature is typically below 100 °C. Noteworthy features of this preparation method include ease of heat removal, low polymerization medium viscosity, ability to achieve high molecular weight, and high monomer

conversion. Because of these features, this polymerization method has become an important commercial manufacturing method for methacrylate polymers and copolymers.

In a typical polymethacrylate or polyacrylate emulsion, the polymer is 30 to 60% of the total emulsion weight, with water being the other major component. An anionic, cationic, or non-ionic surfactant is used to stabilize the colloidal particles. The surfactant level in an emulsion ranges from about one-half to a few percent of the total monomer plus polymer weight depending on the nature of the surfactant. Exemplary anionic surfactants include long chain alkyl sulfate, sulfonate, and carboxylate. Quaternary ammonium salts with a long chain alkyl group are a common cationic surfactant, and a molecule with a poly(ethylene oxide) chain is a typical non-ionic surfactant. Polymerization is preferably initiated by water soluble initiators, including the common thermal initiators such as persulfates, peroxides, and azo compounds. Water-soluble redox initiators are also popular owing to their low initiation temperatures, such as persulfate with sulfites or related compounds, and hydroperoxide with iron salts. Other ingredients that are often used in emulsion polymerization are chain transfer agents to modify the polymer molecular weight, buffers to modulate the pH of the aqueous phase, and various kinds of electrolytes to further control colloidal stability.

Emulsion polymerization can be run batch-wise or continuously, however, continuous emulsion polymerization is kinetically complex, involving numerous steady state conditions. The following describes typical procedures to carry out a batch emulsion polymerization of methacrylate or acrylate to form homopolymer or copolymer. To a reaction vessel, water and surfactant are charged and heated to a desired temperature with agitation. Some or all of the surfactant can be added to the monomers when the monomers need to be emulsified before polymerization begins. All the monomers are added at one time, in either neat or emulsified form, to the reactor. In a semi-batch emulsion polymerization, monomer or monomer emulsion is added gradually into the reactor at a carefully regulated rate. Sometimes a seed latex polymer is added before monomer addition to control the latex particle size and particle size distribution. Aqueous solutions of initiators are then added. Owing to the fast kinetics of polymerization for methacrylates and acrylates, temperature control of the exothermic reaction is very important. As a safe practice, the total heat evolution and maximum temperature increase is usually calculated before the polymerization. The polymerization usually can reach 95% or higher conversion of the total monomer charged. Chasing of the residual monomers, or their removal

from the emulsion, can be accomplished by adding more initiator, or by physical means such as steam stripping. Chasing can reduce the final volatile component level down to few hundred ppm or lower. In the case of the polymers needing to be isolated from water, spray drying or coagulation techniques are used to produce dry polymers.

The presence of surfactant is a disadvantage for certain applications of emulsion polymers such as those involving instrument calibration and pore size determination[7]. The presence of adsorbed surfactant gives rise to somewhat variable properties since the amount of adsorbed surfactant can vary with the polymerization and application conditions. Removal of the surfactant, on the other hand, can lead to coagulation or flocculation of the destabilized latex. The technique requires the use of an initiator yielding initiating species that impart surface-active properties to the polymer particles. Persulfate is a useful initiator for this purpose. Lattices prepared by the surfactant-free technique are stabilized by chemically bound sulfate groups of the SO_4^- initiating species derived from persulfate ion. Since the surface-active groups are chemically bound, the lattices can be purified (freed of unreacted monomer, initiator, etc.) without loss of stability. Their stability is retained over a wider range of use conditions than the corresponding latices produced using surfactants a characteristic surfactant free emulsion polymerization. The particle number is generally lower by up to about two orders of magnitude compared to the typical emulsion polymerization, typically 10^{12} versus 10^{14} particles per milliliter. This is simply a consequence of the lower total particle surface area that can be stabilized by the sulfate groups alone relative to that when added surfactant is present.

2.3.2. Properties

Poly(methyl methacrylate) is a hard, rigid transparent substance[6]. Straight poly(methyl methacrylate) is somewhat tougher than polystyrene but is less tough than the ABS polymers. An outstanding property of poly(methyl methacrylate) is its clarity. The material absorbs very little visible light but there is about 4% reflection at each polymer-air interference for normal incident light. Thus the transmission of normal incident light through a sheet of the polymer is about 92%. Poly(methyl methacrylate) is a polar material and has a rather high dielectric conslant and power factor; it is a good electrical insulator at low frequencies but is less satisfactory at high frequencies.

Poly(methyl methacrylate) prepured by free radical polymerization is amorphous and

is therefore soluble in solvents of similar solubility parameter. Effective solvents include aromatic hydrocarbons such as benzene and toluene; chlorinated hydrocarbons such as chloroform and ethylene dichloride; and esters such as ethyl acetate and amyl acetate. Some organic materials, although not solvents for the polymer, cause crazing and cracking, e.g. aliphatic alcohols and amines. Poly(methyl methacrylate) has very good resistance to attack by water, alkalis, aqueous inorganic salts and most dilute acids. Some dilute acids such as hydrocyanic and hydrofluoric acids, however, do attack the polymer, as do concentrated oxidizing acids. Poly(methyl methacrylate) has much better resistance to hydrolysis than poly(methyl acrylate), probably by virtue of the shielding presented by the α-melhyl group. Poly(methyl methacrylate) may be converted to poly(sodium methacrylate) only by rather drastic treatment with, for example, molten sodium hydroxide.

A further outstanding property of poly(methyl melhacrylate) is its good outdoor weathering, in which respect the material is markedly superior to most other thermoplastics. After several years under tropical conditions the colour change is extremely small. When poly(methyl methacrylate) is heated above the glass transition temperature (105℃) it becomes rubbery and sheet material is easily manipulated at 150- 160℃. Above about 200℃ decomposition becomes appreciable and at 350--450℃ a nearly quantitative yield of monomer is readily obtained. Thus the recovery of monomer from scrap polymer is a feasible proposition.

2.3.3. Applications

Polymers made from poly(methyl methacrylate) and copolymers that are largely poly(methyl methacrylate) are used primarily in plastics applications[2]. These poly(methyl methacrylate) products have a unique combination of properties including crystal clarity, resistance to light and weathering, breakage resistance, and mechanical strength, making them unique among plastics. The hardness of poly(methyl methacrylate) allows it to be substituted for glass, metals, and wood in many applications.

All poly(methyl methacrylate)s sold for plastics applications share a number of similar properties, and are differentiated largely by two specific properties: melt viscosity and service temperature. Service temperature can be measured by T_g, VICAT softening point, and DTUFL(Deflection temperature under load) as well as a large number of specific use tests. Since the use of acrylate comonomers invariably

reduces the service temperature, the highest commercial service temperature is exhibited by poly(methyl methacrylate) homopolymer, although specialty copolymers containing other functional groups (such as glutarimide or α-methyl styrene) have recently appeared on the market with notably higher service temperature. Inclusion of acrylate comonomer in the chain yields both a lower service temperature and lower melt viscosity, both properties being useful in applications requiring filling of intricate molds but not needing the maximum service temperature.

Today the principal injection molding uses for poly(methyl methacrylate) are in automotive taillight lenses, numerous medical applications, and glazing (both in cell cast and extrusion melt-calendered sheet). The high optical clarity and low birefrigence of poly(methyl methacrylate) make it attractive for use in laser-disk applications, although it has not been widely used for compact disks owing to its relatively high co-efficient of expansion when exposed to water vapor, a critical property for one-sided disks. Methyl methacrylate polymers are also used extensively for extrusion applications such as sheet, film, profiles, and rods.

Emulsion polymers of methacrylates and acrylates are usually used as specialty polymers, such as processing aids and impact modifiers for thermoplastics, adhesives, caulks, and coatings or binders in floor polishes, paints, and paper applications.

2.4. Polymer/Clay Nanocomposites

Nanocomposites are 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[9]. Recently, these kinds of materials are attracting the attention of government, academic, and industrial researchers because of their outstanding properties. These polymer layered silicate (PLS) nanocomposites can attain a certain degree of stiffness, strength, and barrier properties with far less ceramic content than comparable glass- or general inorganic-reinforced polymers.

Furthermore, PLS nanocomposites exhibit a significant increase in thermal stability as well as self-extinguishing characteristics. Although other solids can be used, the most common reinforcements currently used to make nanocomposites are natural silicates, such as mica, montmorillonite, saponite, and hectorite. What makes nanocomposites unique is the size and shape of the silicate particles dispersed through the polymer matrix. These particles are infinitesimally small, typically

individual silicate platelets are only about 1 nanometer thick and 1000 nm across the face, which is 1400 times smaller than the finest talc reinforcements in use today.

Idealized formulas for montmorillonite, the aluminum-based version, and hectorite, the magnesium-based version, are

$$Ex_{0.66}[Si_8Al_{3.34}Mg_{0.66}O_{20}(OH)_4] \cdot H_2O \text{ and } Ex_{0.66}[Si_8Mg_{5.34}Li_{0.66}O_{20}(OH,F)_4] \cdot H_2O \quad (2.18)$$

respectively[3]. Notice the isomorphous substitution of these clays, primarily within the octahedral layer, which gives rise to a net negative charge on the basal oxygen surfaces. This is compensated for by the presence of hydrated exchangeable cations in the interlayer or gallery regions, which in nature are usually alkali or alkaline earth cations. These cations are easily exchanged by larger species such as long-chain alkylammonium ions. The distance from one basal surface to the next in registry is called the basal spacing and is measured as the lowestangle peak in x-ray powder diffraction spectra. Natural clays have basal spacings in the range of 1.2 to 2.0 nm, depending on the type of cation and the amount of water present. This ability to swell is one of the most important characteristics of a smectite clay. They can, in fact, swell so greatly in some situations, such as in the presence of large concentrations of macromolecules, that the sheets can lose interaction with each other, the registry is lost, no basal spacing is observed, and the system is said to be exfoliated. Other clays have been exploited in PCN research as well, including saponite, beidellite, and a synthetic swelling fluorine–mica. All are smectites, with differences primarily in elemental composition, cation exchange capacity, abundance, aspect ratio, and particle size. The interactions of smectite clays with polymeric molecules both in nature and for industrial applications have been exploited for quite some time, although the development of polymeric nanocomposites has occurred fairly recently. The fundamental inorganic unit is comprised of two tetrahedral silicate layers that sandwich a central metal octahedral layer which can be seen from an SEM of the flexible “cornflakes” plate morphology to stacked individual plates to atomic assignments(see Figure 2.1). The height of a 2:1 clay layer is about 1 nm. The height of the gallery region is variable depending on the type of cation and the amount of water present, and is generally 1 nm or less for natural clays.

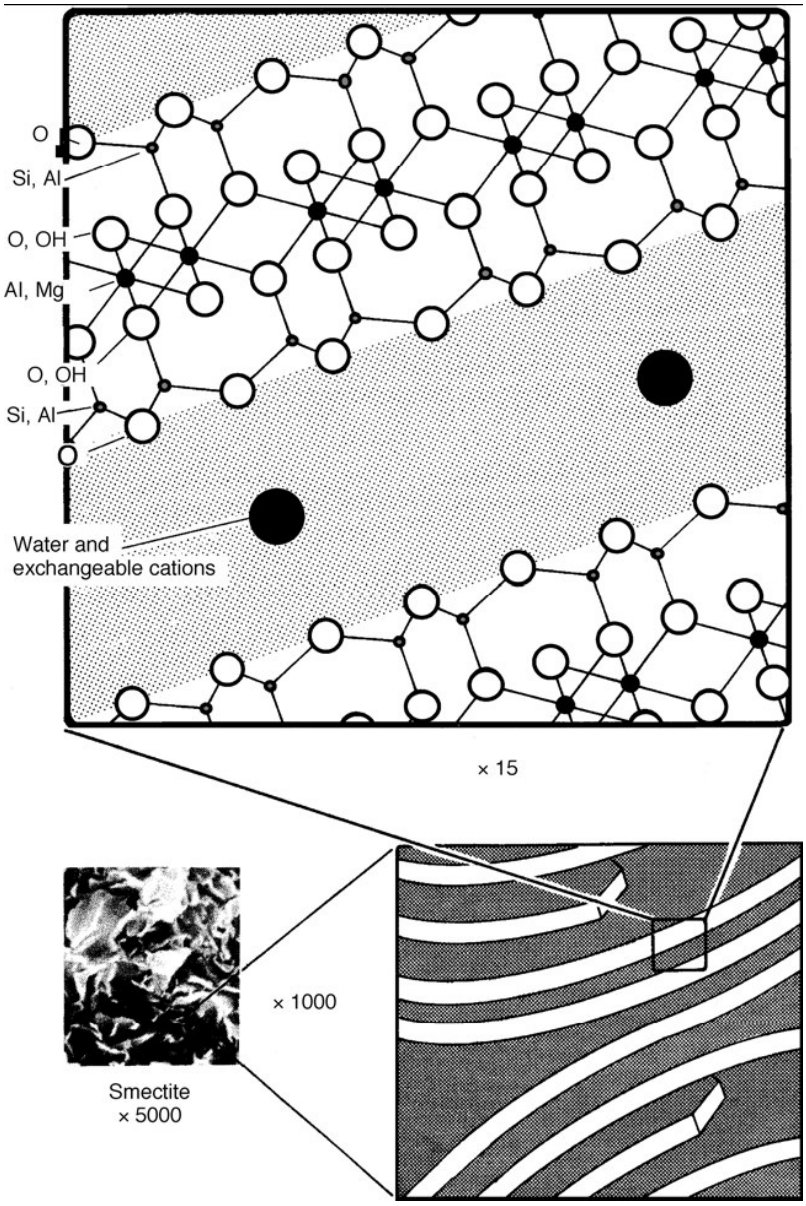


Figure 2.1: Schematic representation of a montmorillonite smectite clay structure and SEM image.

2.4.1. Polymer/Clay Nanocomposite Preparation and Characterization

There are two end members that delineate the realm of PCN architectures possible in polymer/clay nanocomposites. At one end of the spectrum are well-ordered, stacked multilayers that result from intercalated polymer chains within host silicate clay layers. At the other end of the spectrum are exfoliated materials, wherein the host clay layers have lost their entire registry and are well dispersed within a continuous polymer matrix. These two cases are shown schematically in Figures 2.3 (a) and (b). Exfoliated (also called delaminated) polymer/clay nanocomposites display acceptable stiffness, strength, and barrier properties with far lower ceramic

content than is achieved for more conventional particulate-filled (e.g., glass fibers) polymer composites. Generally, the larger the degree of exfoliation in polymer–clay nanocomposites, the greater the enhancement of these properties. Figure 2.2(c) provides an idealized view of a mixed intercalated–exfoliated structure. All three of these morphologies have been observed, and representative transmission electron microscopy (TEM) images of each are provided in Figure 2.2 (d) intercalated polystyrene–fluorohectorite showing 2.9-nm registry (e) exfoliated nylon–montmorillonite and (f) a mixed intercalated–exfoliated epoxy– montmorillonite (10% clay).

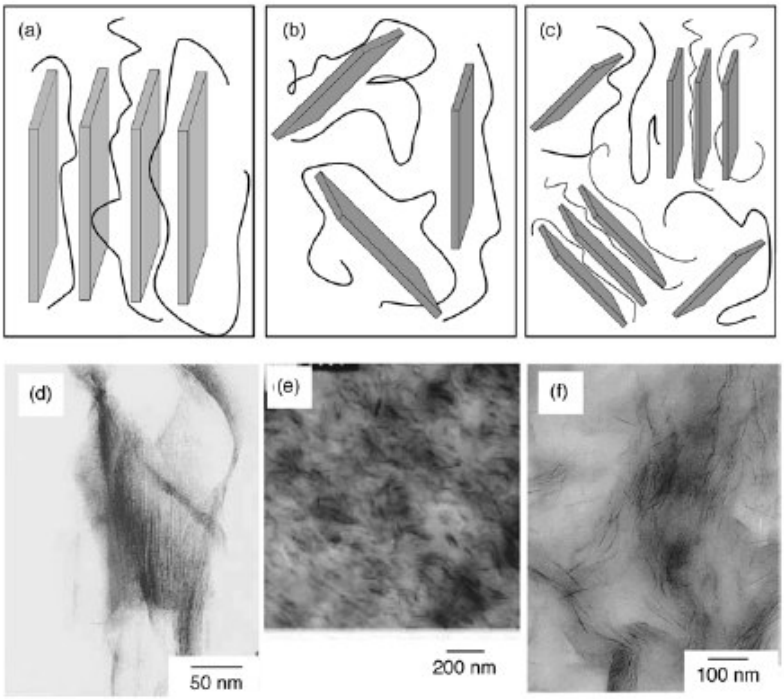


Figure 2.2. Schematic representation of the various PCN architectures.

Microscopy is a useful tool to provide real-space information on the spatial distribution of phases and defect structures[9]. However, it is not always feasible to use microscopy as a rapid characterization tool or for in situ, real time studies. In contrast, diffraction and scattering rapidly provide globally averaged information, potentially over six or more orders of magnitude, and with the potential for in situ, real time studies. Traditionally, powder diffraction is used to characterize the structure of PCNs. Most commonly used is the Bragg-Bentano reflection geometry(powder diffraction) in which the normal of the sample surface bisects the angle (2θ) between the incident and reflected beam.

Powder diffraction is used to monitor the position, full width at half maximum and intensity of the basal reflection corresponding to the repeat distance parpendicular to the layers[10]. Figure 2.3 shows an example of WAXD patterns of PMMA/MMT composites containing different organo-MMT contents together with the pure organoclay(OMMT).

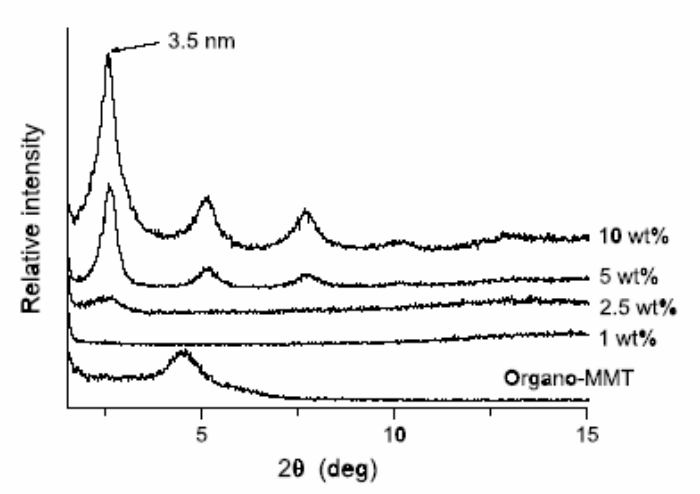


Figure 2.3. XRD patterns of organoclay (organo/MMT) and PMMA/MMT composites.

Often, there are occasions where retention of the layered nature of a polymer/clay nanocomposite is the desired outcome. Such regular nanoassemblies have the following unique characteristics and applications[3]:

- There are a wide variety of both host materials (clay and nonclay) and polymers.
- Anisotropic arrangements of polymers in two-dimensional microenvironments occur.
- The variable gallery spacing is adaptable to polymer size.
- Microenvironments can induce spatial chemistry and host surface chemistry effects.

Two primary methods are utilized to prepare intercalated polymer/clay materials. These are shown schematically in Figure 2.4 as direct intercalation (melt and in-solution blending) and as in situ polymerization of preintercalated monomers.

The former route is limited because the types of polymers that can be intercalated directly are limited. The latter route, while more universal, results in a loss of control over the molecular weight of the final polymer. Another way to intercalate polymers directly is through a melt method, where the polymers are heated with a preexfoliated (in most cases) clay. In this way, a conventional polymer extrusion process can often be utilized. The formation of PCNs via melt intercalation depends

on the thermodynamic interaction between polymer chains and host layers, and also on the diffusion of polymer chains from bulk to interlayers. For more hydrophobicpolymers, however, the clays must be rendered more organophilic to enhance their compatibility. The most common method for this purpose is to preexchange the clay with alkylammonium ions, often of substantial chain length. There are, in fact, various commercial sources of such modified clays due to the demand of applications such as this. Examples of well-intercalated PCNs derived from organophilic clays and melt processing include nylon (although here it is concentration dependent; at < 10% clay the system exfoliates), polymethyl methacrylate (PMMA), polypropylene, polyvinyl chloride (PVC) etc.

Probably the most successful route to creating PCNs in general has been the in situ process, wherein monomers are polymerized in the presence of clay mineral layers. In terms of well-ordered polymer–clay intercalates, reports using in situ polymerization have included polyacrylamide, nylon, polyaniline, polycaprolactone, polyimide, PMMA, polystyrene, polyurethane, polyethynylpyridine, and epoxy resins.

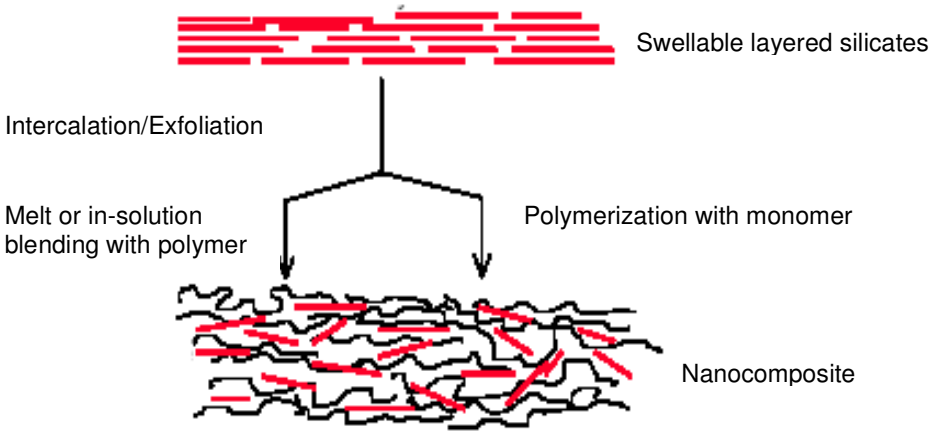


Figure 2.4. Methods for creating intercalated polymer/clay nanocomposites.

Before delving into the details of PCN exfoliated systems, a brief discussion is warranted as to why the nano in the term nanocomposite is critical for this application. The dispersion of mineral reinforcing components to a polymeric matrix has been utilized for many decades. Inactive fillers or extenders act to simply reduce costs, and their chemistry is less important than factors such as particle size, shape, morphology, distribution, and, of course, cost. Active fillers are reinforcing materials and require at least some compatibility between polymer and inorganic, and they must often undergo a surface modification process to insure this. In contrast to conventionally scaled composites on the micrometer level, nanocomposites exhibit

changes in composition and structure over the nanometer length scale. Individual clay layers fall into this realm because they have a thickness on the order of 1 nm. Clays such as kaolinite, mica, and talc have been important plate-shaped conventional fillers in the past. However, preparation of a true nanocomposite requires complete dispersion, or exfoliation, of the elementary clay layers within the polymer matrix, without any aggregation into larger units such as tactoids or intercalation products. This is a serious challenge that has been addressed well since the first pioneering research was published in 1987 from Toyota workers There are very few successful reports of making fully exfoliated PCNs from dissolved polymer solutions. This is because even when dispersions of fully exfoliated clays are exposed to macromolecular solutions, the strong interactions between macromolecules and silicate layers often just reaggregate the layers. As in the case for intercalated materials, the clays need to be premodified by reaction with alkylammonium ions in order to make them more compatible with the hydrophobic polymers.

As might be expected, PCNs that are perhaps considered to be partially successful preparations in that exfoliation occurs only to some degree. These mixed systems in many cases contain units of just a few intercalated clay layers, rather than an entire extended registry, that are themselves randomly oriented within the polymeric matrix. In most of these cases, conditions can be varied to foster full exfoliation. Examples of mixed intercalated–exfoliated (I-E) systems made using various methods (solution, melt, or in situ) include the polymers polyacrylamide, PACN, polyaniline, polyetherimide, polyimide, PMMA etc.

2.4.2. Polymer/Clay Nanocomposite Properties and Applications

Polymer composites are widely used in applications such as transportation, construction, electronics and consumer products[11]. The properties of particle-reinforced polymer composites are strongly influenced by the dimensions and microstructure of the dispersed phase. Recently, there has been a growing interest in the development of polymer-clay nanocomposites. Nanocomposites constitute a new class of material that involves nano-scale dispersion in a matrix. Nanocomposites have at least one ultrafine phase dimension, typically in the range of 1–100 nm, and exhibit improved properties when compared to micro- and macro-composites. Strong interfacial interactions between the dispersed clay layers and the polymer matrix lead to enhanced mechanical, thermal and barrier properties of

the virgin polymer. Since clay is hydrophilic, it is necessary to make it organophilic via cation exchange, typically with alkylammonium cations.

Once true clay nanolayer exfoliation is achieved, improvements in a polymer's performance can be manifested in increased tensile properties, enhanced barrier properties, decreased solvent uptake, increased thermal stability, and increased flame retardance[3]. Complete dispersion optimizes the number of reinforcing elements (individual plates) for carrying an applied load and for deflecting cracks. Although conventional polymer–clay composites that contain aggregated clay tactoids, or many associated sheets in registry, show improved rigidity characteristics, they also often display diminished strength, toughness, and elongation properties. On the other hand, truly exfoliated PCN systems, like those for nylon-6 and epoxy, for example, show improvements in nearly all aspects of their mechanical performance. The high-aspect-ratio nanoplates (up to 0.5 microns in length and width, but only 1 nm in thickness) also make possible certain applications that cannot be considered for the larger-scaled composites. Orientation of plates along a plane normally occurs due to processing conditions (melt extrusion, for example).

2.4.2.1. Thermal Properties

Works on polymer/clay nanocomposites show that enhancement on thermal properties can be obtained by increasing the weight percentage of the clay loading[12]. Thermal decomposition temperature (T_d) of PCN materials and the weight percentage of the clay loading can be obtained from TGA measurements (Table 2.2). T_d of the PCN materials prepared by either in situ polymerization or in solution blending methods increases higher temperature range than that of neat PMMA polymer, on the other hand this confirms the enhancement of the intercalated and exfoliated composites. However, exfoliated composites exhibit higher thermal stability enhancement than intercalated composites. T_g of the composites increases with an increasing concentration of clay platelets in the polymer framework (Table 2.2). This is attributed to the confinement of the intercalated polymer chains within the clay galleries, which prevents the segmental motions of the polymer chains. The composites prepared by in situ polymerization exhibits higher T_g's than their counterparts. This phonemenon can be explained as the composite showing an exfoliated or intercalated structure with larger basal spacing that resulted from in situ polymerization significantly enhanced the interfacial interactions (in comparion with the intercalated composite) between the organic polymer framework and the

inorganic clay platelets, and this leads to an increasingly restricting strength of the clay nanolayers on the PMMA molecules.

Table 2.2. Relationship of the composition of PMMA–Clay nanocomposite materials prepared by both in situ emulsion polymerization and solution dispersion with the thermal stability, and gas barrier properties[1].

	Feed composition (wt %)		Thermal Properties (^oC)		Barrier properties	
compound	PMMA	MMT	Tg	Td	O_2	$H_2O(g/m^2h)$
Polymer A	100	0	98,7	281,6	0,811	177
In situ polymerization	99	1	103,2	287,3	0,631	136
	97	3	111,3	292,2	0,532	117
	95	5	120,7	296,5	0,442	104
Polymer B	100	0	97,7	277,3	0,951	236
Solution dispersion	99	1	101,7	280,6	0,933	206
	97	3	103,2	282,7	0,777	204
	95	5	113,6	285,1	0,726	191

2.4.2.2. Mechanical Properties

One of the most striking examples of increasing the mechanical properties of a polymer upon incorporation of exfoliated clay nanolayers is the first reported PCN system, that of nylon-6 montmorillonite[3]. At loadings of just 4.7% clay, the modulus doubles, its strength increases by over 50%, and the heat distortion temperature increases by 87℃ when compared to the purenylon also shows the advantages of clay nanolayer exfoliation over a more conventional composite made using a clay (talc) filler that neither intercalates nor exfoliates. Montmorillonite and talc share similar rigidity characteristics, but the former has a larger aspect ratio. Compared with the popular, conventional glass fibers, the aspect ratios are similar, but montmorillonite is much more rigid. Different types of functionality on the organocations that are used to premodify the clay are found to have profound effects on degrees of exfoliation. The best balance between increased stiffness and toughness at 5 to 10 wt% clay loadings was observed for fluoromicas preintercalated with specific ammonium cations. In addition, while larger anisotropic intercalated particles led to increased toughness, exfoliated nanoplates best led to increased stiffness properties. Overall, clay nanolayers are more effective in mechanical improvement when the polymer is in its rubbery state than when it is in the glassy state.

Dynamic mechanical analysis (DMA) is often employed in PCN characterization to determine temperature dependence of the storage modulus. Workers have

tentatively attributed this to better stiffness characteristics of the clay layers rather than to exfoliation.

Table 2.3. Mechanical properties of different nanocomposites and PMMA[12].

MMT content(wt %)	0	0,2	0,4	0,6	0,8	1,0
Tensile strength(MPa)	68	77	81	88	85	80
Tensile modulus(MPa)	730	810	913	1013	1051	1103
Tensile elongation(%)	9,31	9,50	8,87	8,69	8,10	7,30

The mechanical properties of the materials from solution polymerization show a significant increase over PMMA[13]. In general, the mechanical performance of polymer composites is associated with the interface strength between the inorganic phase and the organic phase. In most cases, the inorganic additives show much better mechanical properties than the organic polymer. If the interface between the inorganic phase and the polymer matrix is strong enough, the external force will transfer from the polymer matrix to the inorganic phase through the interface, and therefore reinforce the mechanical properties of the whole material. In contrast, if the interface is not strong enough, the interface will break down first and the inorganic domains become the weak points in composites, and further deteriorate the mechanical properties. Chemical bonding is a very strong connection compared with physical entanglement, so the interface between silica and the PMMA matrix is strong enough for transportation of external stress to silica particles, which will lead to a significant increase in mechanical properties.

2.4.2.3. Gas Barrier Properties

There is an enormous and varied use of plastics in the food packaging industry, where they have replaced much traditional glass, metal, and paper packaging[3]. There are limitations, however. For example, certain foods, such as tomato-based products and wine, are sensitive to oxygen and cannot be stored in plastic containers due to oxygen permeability.

The membranes of PCN materials and PMMA used for the molecular barrier measurements as shown on Table 2.2[1]. As clay content increases, permittivity of both O_2 and water vapor decreases comparatively. This enhanced gas/vapor barrier could be associated with having a better dispersion of clay platelets in the PMMA matrix which lead to a longer tortuosity of the diffussion pathway of oxygen and water as shown in Figure 2.5.

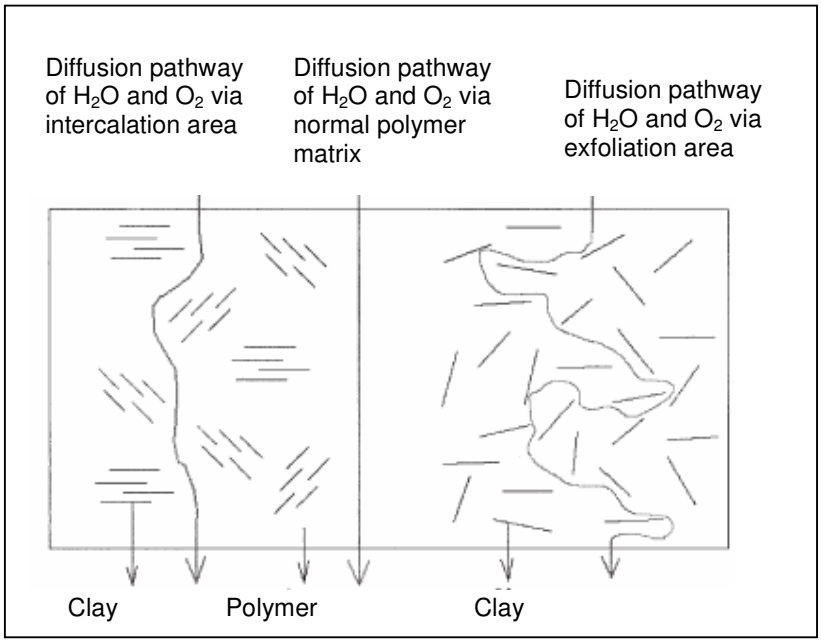


Figure 2.5. Permeability of gases in terms of structure on neat PMMA polymer and PMMA/Clay nanocomposites.

2.4.2.4. Rheological Properties

Knowledge of the rheological properties of PCNs is fundamental to understanding their processability and structure–property relationships[3]. A recent review focuses on the linear and nonlinear viscoelastic rheological properties of PCNs in the melt state. Three detailed examples are used to highlight the assumption that the melt rheological properties are dependent upon a combination of the overall, long-range (mesoscopic) structure and the strength of the nanoscale interaction between polymer and clay. The specific examples used are an exfoliated end-tethered poly (ε-caprolactone), an exfoliated nylon-6, and intercalated polystyrene–polyisoprene diblock copolymer PCNs. A pseudo-solid-like behavior that is observed at long times in the linear viscoelastic response is attributed to the percolation of locally correlated layers that are treated as randomly oriented grains. Nonlinear viscoelastic behavior is strongly dependent on the physical connectivity or interaction between the polymer and the clay layer. Strong end-tethering interactions result in strain hardening, while weaker interactions lead to shear thinning.

Rheological measurement shows that, an increase in shear viscosity and storage moduli of the nanocomposites with increasing both PMMA and silicate content from the rheological measurements[14]. Based on the dynamic oscillatory shear experiments, it is clear that the addition of PMMA to PVDF(Polyvinylidene fluoride) in the presence of the organophilic layered silicate has a profound influence on the

long-time relaxation of the nanocomposites (at low frequencies). With increasing PMMA content at a given silicate loading (5 wt%), the liquid-like relaxation observed for the conventional filled composites (microcomposites) gradually changes to a solid-like behavior for nanocomposites.

2.4.2.5. Flame Retardance and Ablative Performance

Most of the flame retardant approaches for polymers come at the expense of physical properties[3]. Exploration of various PCNs for flame retardance have proven fruitful, however, especially since this approach can simultaneously improve the mechanical strength and other properties of the polymer. Reviews of PCNs with respect to flammability characteristics and thermal stability have begun to appear, along with studies specific to polystyrene, polypropylene, nylon-6, epoxy, and polycarbonate PCNs. The cone calorimeter is an effective bench-scale method for studying flammability properties. One parameter that this method yields, peak HRR, has been determined as the most relevant in evaluating fire safety. By studying PCN combustion residues using TEM and XRD. It has been deduced that during combustion, the PCN architecture collapses and the resulting multilayered carbonaceous-silicate structure appears to enhance the performance of the char through structural reinforcement. The general approach is to incorporate a portion of premade PCN to a conventional flame retardant formulation. Improvements occur due to a reduction in the amount of conventional flame retardant used, which often degrades properties, and from the normal reinforcement effects of the nanodispersed silicate layers. Related to this matter, materials with high ablation properties are critical for insulation against the severe effects of very high temperatures and incident heating rates. High-performance applications include aerodynamic surface protection and insulation for space and launch systems, propulsion structures, payloads, and ground equipment. During the firing of a solid rocket motor, for example, insulation is subjected to temperatures in excess of 2000℃; pressures of 1000 psi or greater; compressive, tensile, and shear stresses; and oxidizing atmospheres.

The thermal and flammability properties of PMMA nanocomposites containing OMMT and/or metal oxide nanoparticles are investigated by TGA and cone calorimeter experiments and compared to those of unfilled PMMA and PMMA-oxide microcomposites[15]. As a result, an improvement of thermal stability and flammability properties was observed, which increases with the amount of nanoparticles oxide. A synergistic effect on thermal stability and fire performance

was achieved by the combination of oxide nanoparticles and organoclays resulting mainly in enhanced ignition times, reduced total heat and smoke release and significant increase in total burning period.

3.EXPERIMENTAL

3.1. Materials

Table 3.1. Materials used in the experiments.

Methyl metacrylate (MMA)	:(Commercial) Kept in a fridge at -10 ^{o}C before use.
Ammonium persulfate (APS)	:(Commercial) Kept in a dry place for stability.
Methyl cellulose (MC400)	:(Henkel) Kept in a dry place.
Cu(II)/EDDA kompleksi	:Aqueous solution of 0.0225gr Cuprium sulfate (Merck) as 1mmol/lt and 0,061gr (1,5mmol/lt) ethylene diamine diaceticacid (Merck) added into flask.
Poly(ethylene glycol) (PEG1500)	:(Henkel) Kept in a dry place.
Organophylic Clay (OMMT)	:Na- Montmorrilonite (CEC value: 135 meq) from Edirne Lalapaşa region purified, dried and modified with w/w %2 DTABr [$C_{12}H_{25}(CH_3)_3N^+Br^-$][16].
Ethanol	:(Commercial) used for precipitation of polymers and composites.
Hydroquinone	:(Merck)
Deionized water	:water, which is the main component of polymerization , used after deionized.

3.2. Characterization and Measurements

Table 3.2. Devices used in the experiments.

FT-IR Spectroscopy	:(Perkin Elmer spectrum one) KBr was used as a background material and disks of %1 w/w samples/ KBr mixtures were prepared to obtain the FT-IR spectra.
^{1}H NMR	:(250MHz Bruker AC-300)
DSC	:(Perkin Emler DSC6) Scan rate of 10^{o}C/min
TGA	:(TGA Q50 V 6.3 Built 189) Heating rate of 20^{o}C/min
Rheology	:(Brookfield DV-III+ low shear rheometer)
XRD	:(Philips PW 1140 model X-Ray diffractometer) Measurements were performed on using Ni-filtered Cu-Kα radiation.
SEM	: (Hitachi S-570 20kV) Samples coated with Au.

3.3. Preparation of Methyl Metacrylate Polymers

3.3.1. Homopolymer Preparation

MMA polymers were prepared in a 500ml volume three necked flask under 1100 rpm magnetic stirring and nitrogen atmosphere. 120ml distilled water in flask were started to heat into an oil bath. When it came to 50°C, 15 gr(1,06 mol/l) MMA monomer added and stirred 15 minutes to obtain emulsion. When temperature came to 80°C 5 grams of (2,3 mmol/lt) %1 APS solution added into flask and reaction started. At the end of 6 hours reaction time polymer emulsion kept 24h at room temperature and then tried to precipitate with excess ethanol (Code PMMA1). Polymer particles dried in a vacuum oven.

At the end of experiment reaction stopped by adding hydroquinone (Code PMMA1-1).

Differently, Cu(II)/ EDDA complex added into reaction flask followed by MMA monomer(Code PMMA2) and PMMA added into reaction flask ,which was prapared from first experiment, at the rate of 1,5grams / 15grams of MMA[17].

3.3.2. Copolymer Preparation (PMC and PPEG)

1 gr MC400 (or 1 gr PEG1500) emulsified at the rate of MMA/MC400 15/1 w/w (or MMA/PEG1500 15/1 w/w) in 120 ml of water in a three necked flask under magnetic stirring at 800 rpm. After that 15 grams of MMA monomer (1,06 mol/l) was added into flask and PMMA1 preparation steps in the section 3.3.1 were followed (Code: PMC and PPEG)

3.4. Preparation of Polymer/Clay Composites by *in-situ* reaction ($N_{insitu}P$)

3.4.1. Preparation of PMMA/OMMT Composites

OMMT was dispersed overnight at the rate of %1,3 or 5 w/w OMMT/MMA in 60ml of water under magnetig stirring at 1100rpm in a 250ml volume three necked flask. Then, 7,5 grams of MMA monomer added and dispersed during 36h at 1100rpm. Reaction flask was heated to 80°C and 2,5 grams of (2,3 mmol/lt) %1 APS solution added into flask and reaction continued 6h. At the end of reaction, composit solution was precipitated by adding excess ethanol and dried in a vacuum oven(Code $N_{insitu}P1$, $N_{insitu}P3$ and $N_{insitu}P5$).

3.4.2. Preparation of PMMA-co-MC/OMMT Composites (N_{insitu}PMC)

Certain amounts of OMMT was dispersed overnight in 30ml of water in a 250 ml volume three necked flask as explained section 3.4.1. Then, MC400 added into the flask at the rate of MMA/MC w/w 7,5 / 0,5 and steps followed as section 3.4.1. (Code N_{insitu}PMC1, N_{insitu}PMC3 and N_{insitu}PMC 5).

3.4.3. Preparation of PMMA-co-PEG/O-MMT Composites (N_{insitu}PPEG)

Certain amounts of OMMT was dispersed overnight in 30ml of water in a 250 ml volume three necked flask as explained Section 3.4.1. Then, PEG1500 added into the flask at the rate of MMA/MC w/w 7,5 / 0,5 and steps followed as section 3.4.1. (Code N_{insitu}PPEG1, N_{insitu}PPEG3 , N_{insitu}PPEG5).

3.5. Preparation of Polymer/Clay Composites by solution dispersion (N_{blend}P)

The polymers P(code PMMA1-1),PMC and PPEG of which their preparation explained in section 3.3 used to prepare blend composites with OMMT. OMMT was dispersed overnight at 1100rpm in 30ml of water in 250ml volume three necked flask at the rate of w/w %1,3 or 5 of polymers. Then 3,75 grams of P(or PMC or PPEG) was added and dispersed in two stages as 24h at room temperaturee and then 24h at 80^{o}C. Finally, samples were filtered and dried in a vacuum oven. (Code: N_{blend}P1, N_{blend}P3, N_{blend}P5, N_{blend}PMC1, N_{blend}PMC3, N_{blend}PMC5, N_{blend}PPEG1, N_{blend}PPEG3, N_{blend}PPEG5)

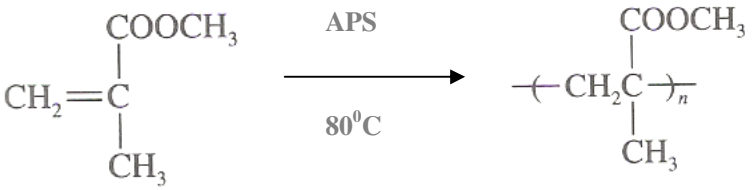
4.RESULTS AND DISCUSSION

The results obtained from this work will be investigated in four sections:

- Preparation of methylmetacrylate homopolymer, methylcellulose methylmetacrylate copolymer and polyethylene glycol copolymer by emulsifier free emulsion polymerization and their characterizations.
- Preparation of poly(methyl metacrylate), poly(methyl metacrylate)-co-methylcellulose and poly(methyl metacrylate)-co-poly(ethylene glycol) composites by in situ polymerization and characterizations of composites obtained.
- Preparation of poly(methyl metacrylate), poly(methyl metacrylate)-co-methylcellulose and poly(methyl metacrylate)-co-poly(ethylene glycol) composites by solution dispersion and characterizations of composites obtained.
- Comparison of polymers and composites obtained in terms of therir rheologic, electrokinetic, morphologic and thermal properties.

4.1. Preparation and Characterization of Methyl Metacrylate Homo and Copolymers

4.1.1. Preparation and Characterization of Methyl Metacrylate Homopolymers



(4.1)

Polymerization was catalyzed by ammonium persulfate and performed in aqueous media at 80^0C. Persulfate initiators are convenient powerful oxidizers, have good storage stability and frequently used in industrial polymerization processes

Water not only provides the dispersing medium for the final emulsion particles, but serves as a solvent and diffusing medium for small quantities of monomers, as solvent for initiator (and activator, if used)[4]. In addition, it is a dispersing medium

for monomer droplets, the reservoirs for feeding the growing polymer chains either in “micelles” or in monomer-polymer particles. Most importantly, it functions as an excellent heat transfer medium, allowing large amounts of the exothermic heat of polymerization to be quickly dissipated.

The conditions and results of polymerization experiments can be seen in Table 4.1. All experiments carried out in a three necked flask under 1100 rpm magnetic stirring at 80^{o}C. 120ml of deionized water used as emulsifying media, MMA used as monomer, 5 gr %1,5 APS solution used as initiator in all reactions. MMA monomer was emulsified in water for 15 minutes before the reaction start. Then APS solution added and reaction started. After the reaction emulsion polymer kept 24h in room temperature and tried to precipitate it with excess ethanol. However, the polymer obtained could precipitate by only centrifuge. Therefore, the polymer solution saturated with NaCl and then precipitated rapidly (Code PMMA1).

Table 4.1. The polymerization results and conditions of 15 gr(1,06 M) MMA monomers which are polymerized with 5 gr(2,3mmol/l) APS initiator in 120 ml of water at 800 C individually .

Code	MC 400 gr	PEG 1500 gr	Cu(II)/ EDDA cmplx	Thickener PMMA gr	Reaction time hr	Stopper hydroquinone 20 ppm	Yield %
PMMA1	-	-	-	-	6	-	61
PMMA1-1[1]	-	-	-	-	6	+	80
PMMA2[2]	-	-	+	+	3	-	99
PMMA3[3]	-	-	-	+	6	-	83
PMC	1	-	-	-	6	-	57
PPEG	-	1	-	-	6	-	87

Retarders decrease the rate of polymerization from that which would be obtained with highly purified monomers[18]. Inhibitors prevent the polymerization from occurring for some period of time. Both retarders and inhibitors react with initiator fragments or growing chains to terminate radicals that would otherwise lead to polymer formation. Retarders are just less efficient and do not terminate all of the radicals. Reactions can also be both inhibited and retarded. Inhibitors and retarders are characterized by having the ability to form a stabilized free radical, generally by delocalization of the unpaired electron throughout a conjugated system. An effective inhibitor can be of the addition type, such as oxygene or quinine, where the radical

[1] 20 ppm of hydroquinone is added at the end of the reaction.
[2] Copper sulfate 0.0225gr (1mmol/lt), EDDA 0,061gr (1,5mmol/lt) are added to obtain a complex before reaction and 0,75 gr PMMA thickener is added at the end of the reaction before precipitation.
[3] 1,5 gr PMMA thickener is added before the reaction starts.

adds to the component or of the chain transfer type, such as the quinone where the active radical is terminated by transfer of a hydrogen atom with the generation of a less reactive, stabilized radical. This less reactive radical does not participate in the polymerization process and the overall rate of polymerization is reduced.
Therefore, it was tought that the process would be stopped and reaction rate decreased to give high yield, finally the polymer could precipitate easily by addition of hydroquinone at the end of the reaction if free MMA monomer still exist in reaction media. However, the polymer emulsion at the end only could precipitate with centrifuge after addition of ethanol at the end (code PMMA1.1).

The effect of Cu(II)-EDTA system has been known in emulsifier free emulsion polymerization[17]. The aim is to investigate whether Cu(II)-EDDA complex make the precipitation easier or not. At the end of reaction, the emulsion was kept 24h in a room temperature and then excess ethanol added. But the emulsion was stil stable and no precipitation occured. After that PMMA thickener was added. However, the polymer could not be precipitated easily and agan centrifuge method used (Code PMMA2). The yield is high as seen in Table 4.1.

Finally, it was investigated that whether using the polymer prepared before as thickener during the reaction has positive effect on precipitation or not. Reaction time determined as 6h. Similarly, after the reaction ethanol added and polymer obtained could only precipitate by centrifuge method(Code:PMMA3)

The polymer yield of %61(Code PMMA1) which can be seen in Table 4.1 increased with addition of hydroquinone(Code PMMA1-1). Addition of Cu(II)-EDTA has a good effect to occur complex and increase the yield at the end(Code PMMA2). The yield of the polymer rather increased in which thickener added during reaction(Code PMMA3). Hovewer, the emulsion could not be destabilized easily at the end of the all reactions. Those yields obtained with additional processes.

FTIR spectrums of homopolymers can be seen in Figure 4.1 and explained Table 4.2. Samples prepared with %1 w/w KBr mixtures. As spectra shows that PMMA polymers have characteristing absorption bands of 1732 cm^{-1} (C=O) symmetric stretching, 2997,2952 and 2850 cm^{-1} C-H stretching, at 1272, 1243 ve 1194 cm^{-1} C-C-O ve C-O-C stretching. It could caused that effect of Cu(II) on PMMA2 polymer which has not sharp peaks.

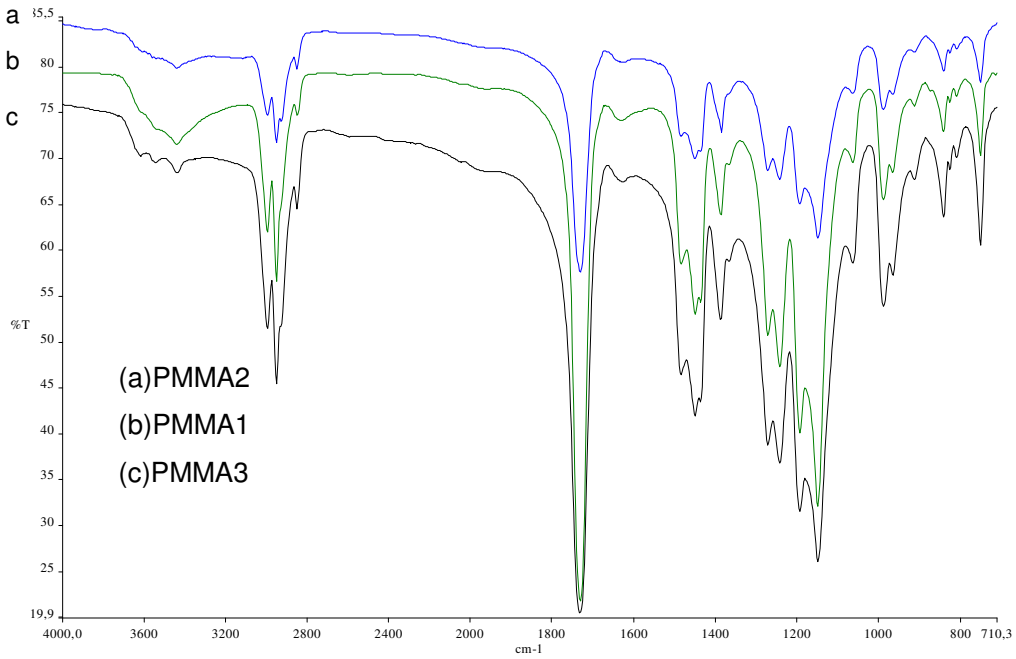


Figure 4.1. FTIR spectra of MMA homopolymers.

Table 4.2. Characteristic FTIR absorption bands of PMMA[19].

wavenumber (cm^{-1})	assignment
2997	α-CH3 asymetric stretching, OCH3 asymetric stretching
2952	α-CH3 symetric stretching, OCH3 symmetric stretching, CH_2 stretching
2850	Methylene C_H asym./sym. Stretch
1732	C=O symetric stretching
1485	α -CH3 asymetric bending
1450	CH_2 scissor bending,OCH3 asymetric bending
1436	OCH3 symmetric stretching
1387	α -CH3 symetric bending
1272	out-of-phase asymetric C-C-0 stretching, coupled with CH_2
1243	in-phase asymetric C-C-O stretching, coupled with CH_2
1194	possibly C-0-C stretching
1150	combination of delocalized modes of various ester vibrations and CH_2 rocking modes
1064-751	Skeletal C-C vibrations

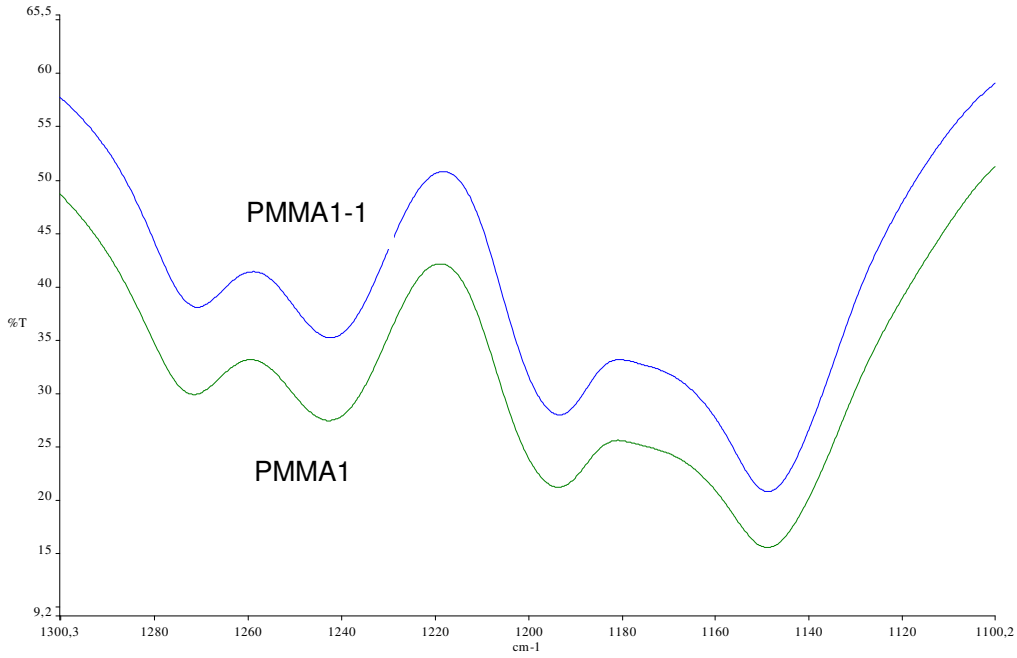


Figure 4.2. FTIR spectra of syndiotactic MMA polymers.

It is well documented that bonds in the region of 1100-1300 cm^{-1} are sensitive to conformational changes. The bands have been assigned to the C-C-O stretching mode coupled to the C-O stretching mode[19].

Changes on the peaks between 1240- 1260 cm^{-1} and between 1260-1280 cm^{-1} proved that syndiotactic rich polymethylmetacrylate prepared.

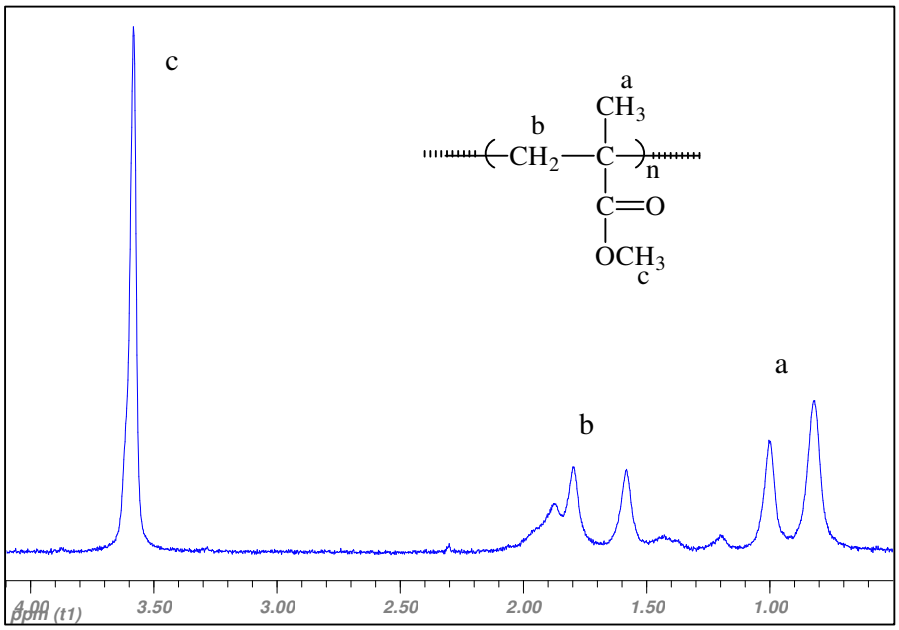


Figure 4.3. ^{1}H NMR spectra of MMA homopolymers.

^{1}HNMR spectra of MMA homopolymers (PMMA1 ve PMMA1-1) in D_2O solution can be seen in Figure 4.3. The three peaks which appear at highest field represent methylmetacrylate methyl groups of varying tacticity[20].

Multiple peaks from different stereoisomerism between 0,8-1,4 δppm belong backbone methylenes(-CH_3) and center methylene groups on the ring. Peaks belong to 0,8 δppm syndiotactic, 1,003-1,009 δppm atactic, 1,2 δppm isotactic methylene groups on the backbone. The corresponding isotactic, atactic and syndiotactic methylene groups absorb in the chemical shift range from 1,4 to 2 δppm. Peaks at 3,6 δppm shows α-$COOCH_3$ group. Syndiotactic rich strucure is more likely to be seen MMA homopolymers obtained.

Comparison of degree of polymerization of MMA polymers can be seen in Table 4.3. PMMA1-1 homopolymer has rather higher molecular weight and lower polydispersity index.

Table 4.3. Comparison of MMA polymers in terms of molecular weight and polydispersity index.

No	Mw	Mn	Polydispersity index
PMMA1	748997	251003	2.984
PMMA1-1	1413726	492513	2.870
PMMA3	767394	234806	3.268
PMC	1201794	308320	3.898
PPEG	636080	215330	2.954

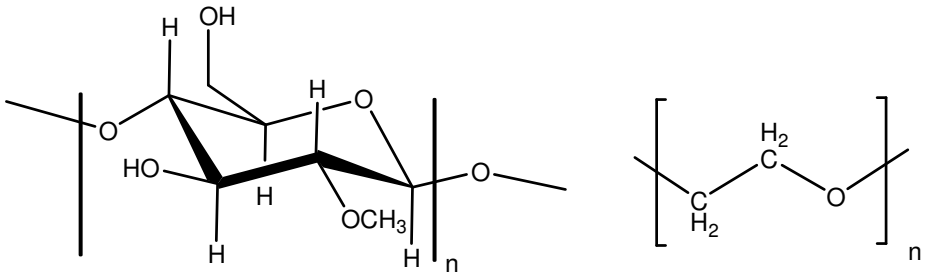
Destabilizing the emulsion and precipitation of the polymer at the end was the general problem for all reactions. Because of being free of additives PMMA1 selected to be used to prepare methyl metacrylate homopolymer composites by in situ method in spite of its low yield. PMMA1-1 was selected to be used □ort he preparation of methyl metacrylate homopolymer composites by solution dispersion method due to its rather high molecular weigt and low polydispersity index.

4.1.2. Preparation and Characterization of MMA Copolymers

All experiments also applied in a three necked flask under nitrogen athmosphere at 80°C and 6h reaction time using APS initiator. The aim was to investigate preparation of MC400 and PEG1500 copolymers with MMA and to obtain copolymers in order to use to prepare composites (Figure 4.4).

MC400 is a type of cellulose of which solubility is higher at low temperatures. Therefore it was added at low temperatures(30 °C) in the aqueous reaction media

and swelled in half an hour. Then another steps were followed. At the end of the reaction, emulsion polymer kept 24h at room temperature and after addition of ethanol, polymer precipitated rapidly. The polymer obtained filtered and washed with water (Code PMC). The yield was %57 (see Table 4.1).



Methyl Cellulose

Poly(Ethylene glycol)

Figure 4.4 General structure of Methyl cellulose and poly(ethylene glycol) polymers

In the next experiment, PEG1500 polymer emulsified in water, then polymerized with MMA monomer in the same conditions. Finally, emulsion polymer kept 24h at room temperature and after addition of excess ethanol(Code PPEG). The yield of copolymer was high (%87, see on p.5, table 4.1).

As seen on Table 4.3 PMC copolymer has a high molecular weight distribution and polydispersity index. However, PPEG copolymer has lower molecular weight than PMC but, also lower polydispersity value attained. As a result, PPEG copolymer has more uniform polymer chain structure than PMC.

FTIR spectra of both PMC and PPEG copolymers is similar with poly(methyl metacrylate) (Figure 4.5) except the change of peaks ±1 cm^{-1} that associated with OH stretching, C-C-O, C-O-C stretching bands. It could easily be seen that especially for methyl metacryate methyl cellulose copolymer, OH stretching band changed from 3441 to 3444 cm^{1} and broadened. This result showed that poly(methyl metacrylate) and methyl cellulose have similar functional groups, and thought that this is caused by low amounts usage of either methyl cellulose and poly(ethylene glycol) against methyl metacrylate.

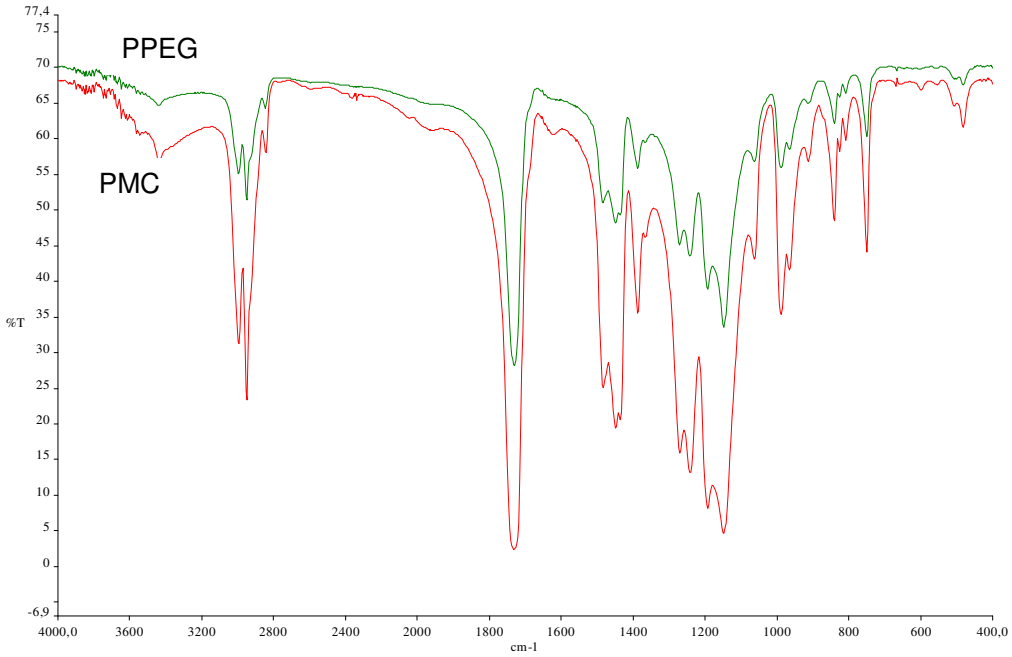


Figure 4.5. FTIR spectra of PMMA-co-MC (Code PMC) and PMMA-g-PEG(Code PPEG).

^{1}HNMR spectra of methyl metacrylate copolymers can be seen in Figure 4.6. Methyl cellulose copolymer of methyl metacrylate (Code PMC) has characteristic peaks of methyl groups on glucose at 3-4,5 δppm[21]. The sharp and single peak at 3,6 δppm assigned to methylene groups on the chain of poly(ethylene glycol) in methyl metacrylate poly(ethylene glycol) copolymer (Code PPEG). Unfortunately, methyl metacrylate polymer has a characteristic peak in the regions mentioned above. Those peaks are similar to characteristic methylene groups on MC and PEG. Therefore, methyl metacrylate copolymers (PMC and PPEG) could not be identified clearly by ^{1}HNMR analysis. Clear increase can be seen on –OCH integral of methyl cellulose in PMMA-co-MC at 3,6 δppm. Besides, as explained before peaks at 0,82 δppm associated with syndiotactic backbone methyls, 1,003 δppm associated with atactic methyl and 1,2 δppm associated with isotactic methyl gruplarına, 1,4-2 δppm associated with methylene groups. It was thought that especially sharp difference on methylene integral at 1,6 δppm proves that poly(ethylene glycol) and particularly methyl cellulose effective on tacticity.

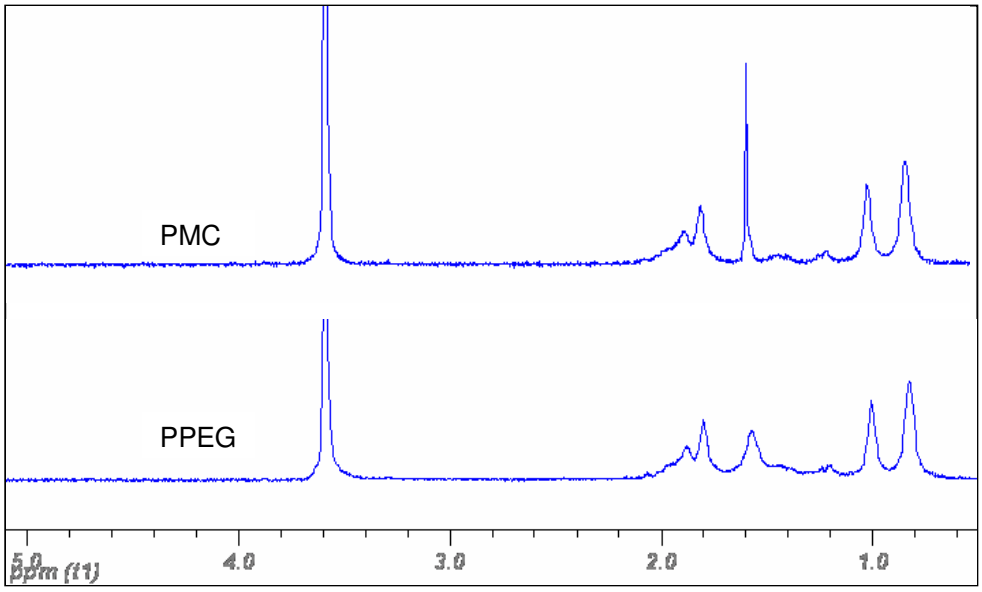


Figure 4.6. [1]HNMR spectra of PMMA-co-MC (Code PMC) and PMMA-g-PEG(Code PPEG) copolymers.

4.2. Preparation and Characterization of Homo and Co-poly(methyl metacrylate) Composites

Montmorillonite (MMT) is a hydrated alumina–silicate clay composed of units made up of two silicatetrahedral sheets with a central alumina octahedral sheet[22]. The Na^+ or Ca^{2+} residing in the interlayers can be replaced by organic cations such as alkylammoium ions via an ion-exchange reaction to make the hydrophilic silicate lipophilic and to render it good dispersion in the organic polymer phase.

The clay from which used to prepare composites received from Edirne-Lalapaşa region[16]. The clay with cation exchange capacity of 135 meq naturally has metals on its interface such as calsium, sodium, and has hydrophylic character. Hydrophobic character had been assigned by modification dodecyl trimethyl ammonium bromide(DTABr) and then purified.

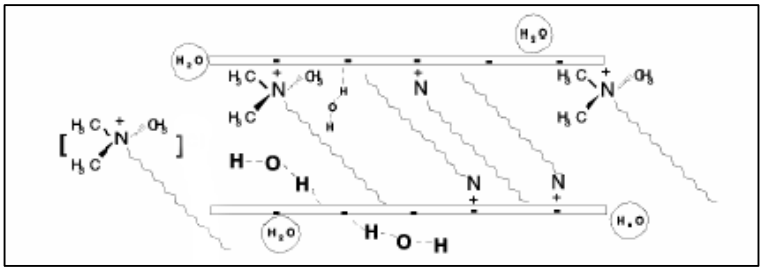


Figure 4.7. The general structure of montnorillonite that has been exchanged with dodecyl trimethyl amonniumbromide(DTABr).

Organophilic montmorillonite (OMMT) dispersed in water and then composites of homo/ co-poly(methyl metacrylate) prepared using homo and co-poly(methyl metacrylate) by polymer intercalation (in solution blending) and composites of homo/ co-poly(methyl metacrylate) prepared by in situ polymerization using MMA monomer with methyl cellulose or poly(ethylene glycol) with initial monomer intercalation(Figure 4.8).

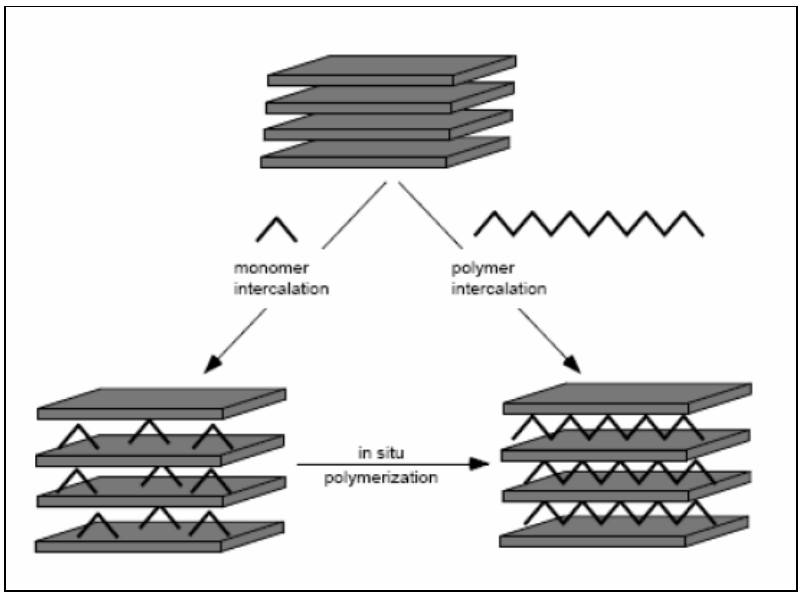


Figure 4.8. Schematic shown of preparation of MMA polymers / clay composites [3].

When preparing polymer–clay nanocomposites via either in situ polymerization or direct intercalation, a very specific temperature is needed in the processing[8]. If the processing temperature to make the polymer layered silicate is higher than that of the thermal stability of organic treatment on the organically modified layered silicates, some decomposition will take place. The onset temperature of decomposition of organic treatment, therefore, is meaningful in the process to make a clay/polymer nanocomposite. All experiment codes can be seen in Table 4.5.

Table 4.5. Codes of MMA polymers / OMMT composites.

PMMA Homopolimer	PMMA-g-MC (PMC)	PMMA-g-PEG (PPEG)	OMMT (%[1])
$N_{insitu}P1$	$N_{insitu}PMC1$	$N_{insitu}PPEG1$	1
$N_{insitu}P3$	$N_{insitu}PMC3$	$N_{insitu}PPEG3$	3
$N_{insitu}P5$	$N_{insitu}PMC5$	$N_{insitu}PPEG5$	5
$N_{blend}P1$	$N_{blend}PMC1$	$N_{blend}PPEG1$	1
$N_{blend}P3$	$N_{blend}PMC3$	$N_{blend}PPEG3$	3
$N_{blend}P5$	$N_{blend}PMC5$	$N_{blend}PPEG5$	5

[1] weight percent with respect to monomer

4.2.1 Preparation of Homo and Co-poly(methyl metacrylate) Composites by In situ Polymerization and Characterization

Organic methylmetacrylate monomer was subsequently intercalated into the interlayer region of organophilic clay hosts, which is prepared by interchange of cations between dodecyltrimethylammonium bromide and montmorrilonite, followed by a typical free radical polymerization (PMMA polymers). The composition of the NP, NPMC, NPPEG materials was varied from 1 to 5 wt.% of organoclay with respect to polymer content as summarized in Table 4.6. Homo and copolymer composites will be investigated in order.

The same polymerization method used with PMMA1 polymer to prepare methyl metacrylate homopolymer composites by in situ polymerization method (Section 4.1). First, organoclay(OMMT), dispersed overnight in water, then stirred to emulsify with MMA monomer during 36h under magnetic stirring at 1100rpm. Reaction carried out at 80°C for 6h under nitrogen atmosphere. At the end of the reaction emulsion composite easily precipitated with ethanol without any additives. Reaction temperature decided to be 80°C, because this temperature is optimum for both MMA monomer and organoclay for their thermal stability.

Table 4.6. Results and conditions of in situ polymerized polymer/clay composites of which 7,5 gr MMA emulsified in 60 ml water and polymerized using 2,5 gr (1,06 mmol/lt) APS initiator during 6h at 80 °C.

Code	OMMT(%)[1]	MC400 gr	PEG gr	yield(%)
$N_{insitu}P1$	1	-	-	53
$N_{insitu}P3$	3	-	-	66
$N_{insitu}P5$	5	-	-	76
$N_{insitu}PMC1$	1	0,5	-	49
$N_{insitu}PMC3$	3	0,5	-	82
$N_{insitu}PMC5$	5	0,5	-	85
$N_{insitu}PPEG1$	1	-	0,5	98
$N_{insitu}PPEG3$	3	-	0,5	25
$N_{insitu}PPEG5$	5	-	0,5	-[2]

As seen in Table 4.6, yields of PMMA composites increased with increased clay content. However, we were experienced with some technical problems such as during dispersion of organoclay in the monomer($N_{insitu}PPEG3$, $N_{insitu}PPEG5$). Those difficulties during dispersion could be caused from very polar structure of MMA monomer. Organoclay should be added slowly into water. On the other hand, MMA monomer should be added slowly into the clay dispersed water. Furthermore,

[1] weight percent with respect to monomer
[2] experienced with technical problems.

agitation speed should be optimum to obtain well dispersed clay and monomer in water. Therefore, the dispersion problem of the MMA monomer which is believed to be caused by polarity, may be limited if unmodified clay used instead of organoclay.

The spectrum of OMMT shows the characteristic bands 3626 cm^{-1} due to O-H stretching (sharp peak), a broad peak centered on 3452 cm^{-1} due to interlayer and intralayer H-bonded O-H, 1638 cm^{-1} due to H-O-H bending, 1032 cm^{-1} with shoulder at 1083 cm^{-1} due to Si-O stretching, 914, 793 and 841 cm^{-1} due to Al-O stretching and 519 and 467 cm^{-1} due to Si-O-Al modes (Figure 4.9).

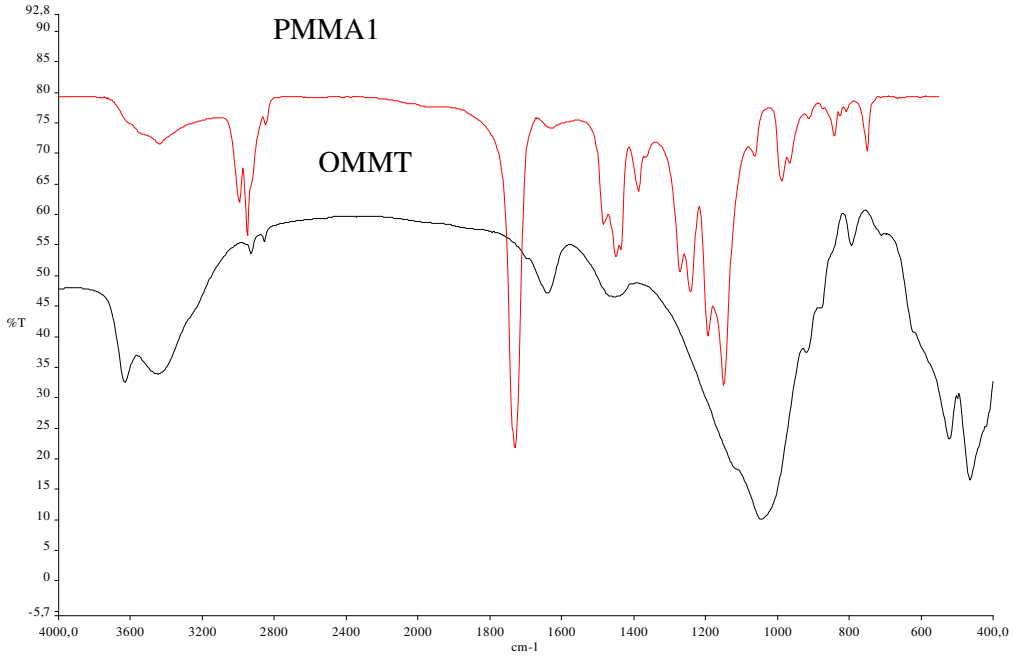


Figure 4.9. FTIR spectra comparison of OMMT and poly(methyl metacrylate).

FTIR-spectra of polymethylmetacrylate adsorbed on OMMT via in situ polymerization was similar to that obtained for poly(methyl metacrylate). But PMMA adsorbed on OMMT, the O-H stretching peak centered on 3441 cm^{-1} was broadened and gave maxima at 3445 cm^{-1} . In addition, methylene C-H asymmetric/ symmetric stretching peak at 2850 cm^{-1} changed to 2844 cm^{-1}, $-CH_3$ symmetric bending peak at 1386 cm^{-1} changed to 1388 cm^{-1} and another C-C-O, C-O-C stretching bands changed -1 cm^{-1}. The peaks at 600-400 cm^{-1} which are associated with Si-O bending changed as clay content increased. Detailed spectra of 2730-3900 cm^{-1} region was shown in Figure 4.10.

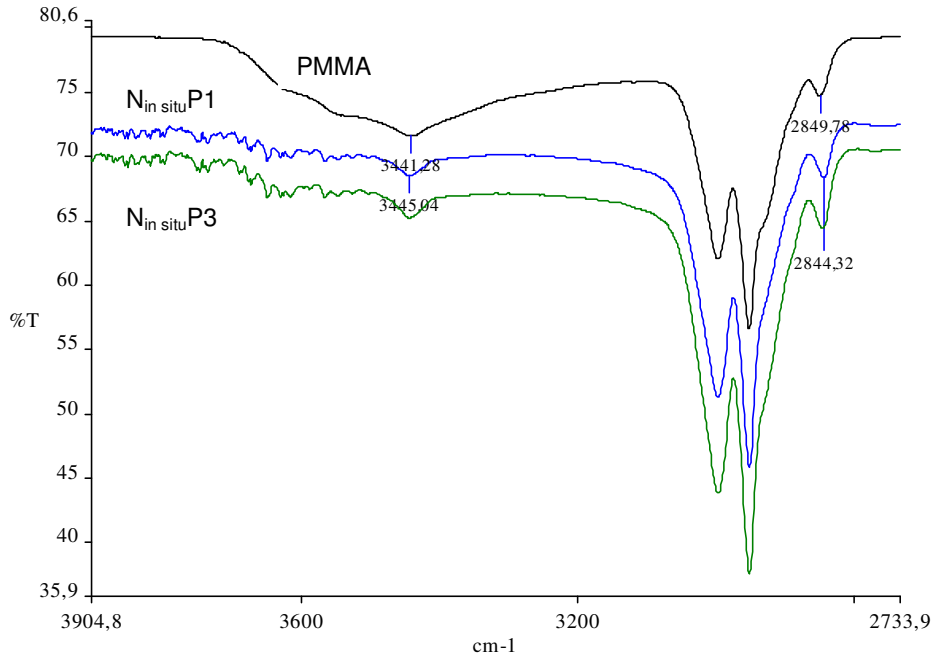


Figure 4.10.. FTIR spectra comparison of poly(methyl metacrylate) composite prepared by in situ method.

As seen in Figure 4.11, the three peaks which appear at highest field represent methylmethacrylate methyl groups of varying tacticity. The band at 0,82 ppm represents syndiotactic methyls, the band at 1,003 ppm arises from atactic methyl and the weak band at 1,2 ppm represents the resonance of the isotactic methyl groups. The corresponding isotactic, atactic and syndiotactic methlene groups absorb in the chemical shift range from 1,4-2,2δppm. The methyl ester protons resonate at lowest field near 3,6 ppm. However, as seen in Figure 4.11, changes on the peaks at 1,6δppm show changes on the tacticity in MMA homopolymer composites.

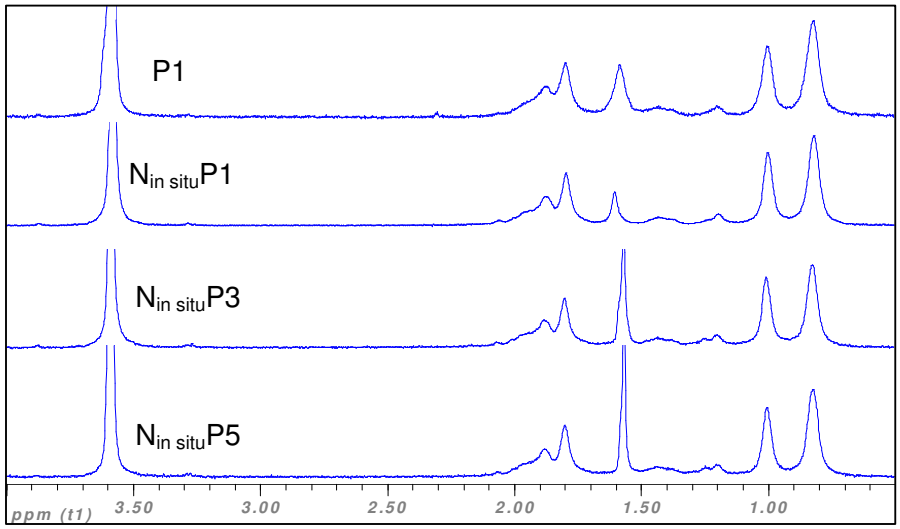


Figure 4.11. ^{1}HNMR spectra of MMA homopolymer composites prepared by in situ method.

XRD spectra of organoclay, MMA homopolymer and MMA homopolymer composites which prepared by in situ method using w/w %1 and 3 organoclay content can be seen in Figure 4.12.

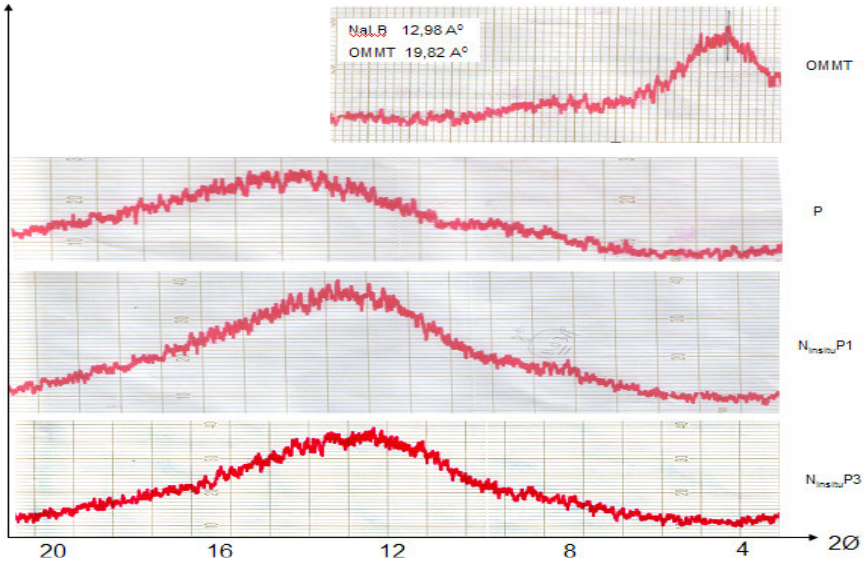


Figure 4.12..XRD spectra of MMA homopolymer composites prepared by in situ method.

Basal spacing of Edirne-Lalapaşa montmorrilonite clay, which has an interlayer spacing of 12,98 A°, increased to 19,82 A° after purification and modification with DTABr. It can easily be seen from XRD data shifts that there is no diffraction peak below 2θ degree which are supposed to belong both composites with different clay loading. This indicated that methyl metacrlate polymer settled interlayer region of OMMT galleries and exfoliated structure gained for composites made by in situ method as shown in Figure 4.13 schematically. Hence, the homopolymer composites can be called as “nano”.

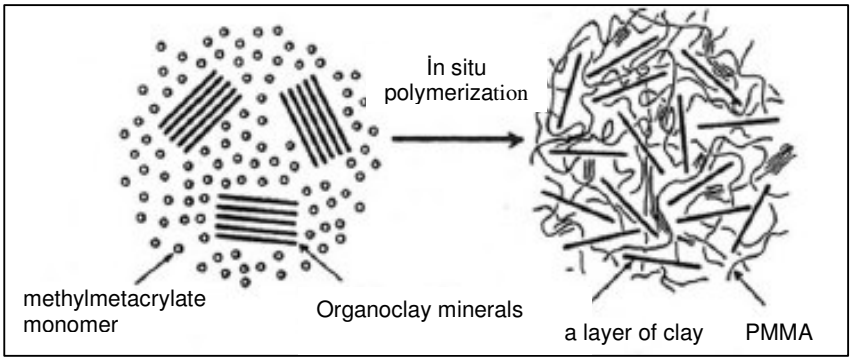


Figure 4.13.. The structure of MMA homopolymer nanocomposites prepared by in situ method.

MMA copolymers invastigated in order to prepare their composites by in situ method and MMA monomer used together with MC400(or PEG1500) at the same reaction conditions in homopolymer composite preparation as explained above. First of all, organoclay dispersed in water , then MC400 added and swelled before MMA monomer. Finally, MMA monomer added, dispersed and polymerized at the same conditions. The same method followed to prepare composites of MMA-co-PEG. After dispersing organoclay in water, PEG1500 and MMA monomer added into flask, emulsified with mixture and finally polymerized at the same conditions explained above.

FTIR and ^{1}HNMR spectra of both copolymer composites show distinct differences. For example, there are some ±1 cm^{-1}differnces on FTIR spectrums of both composites made with MC and PEG,.In addition, characteristic peaks obtained associated with C-H stretching and especially Si-O bending region (600-400 cm^{-1}).

The respectative FTIR spectra of in situ polymerized polymethylmetacrylate-co-methylcellulose composite(N_{insitu}PMC) materials. 600-400 cm^{-1} region is shown in Figure 4.14. Those of 512-517 cm^{-1} and 462-472 cm^{-1} Si-O bending peaks obtained as the loading of MMT increased.

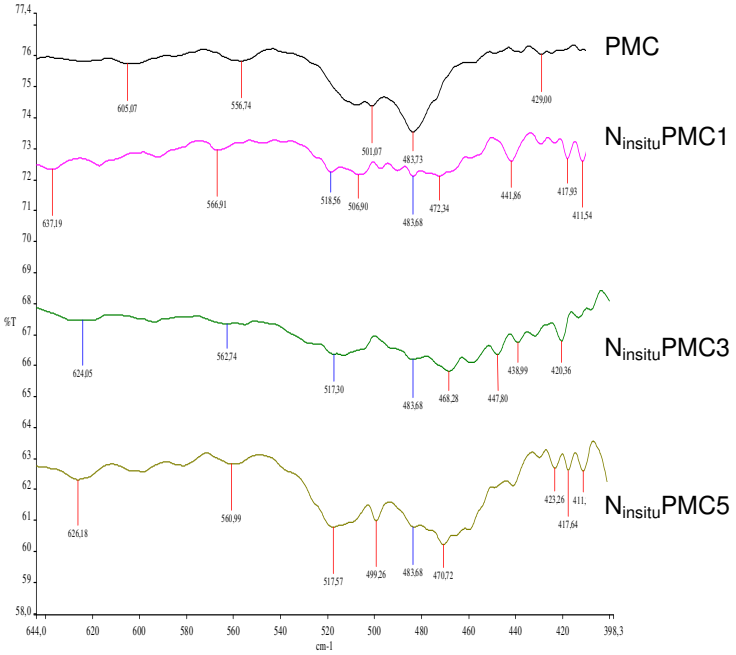


Figure 4.14. FTIR spectra of PMMA-co-MC composites prepared by in situ method.

Differently, as clay content increase C=O stretching band at 1731 cm^{-1} changes and turnes to two different signals at 1738 and 1731 cm^{-1}(Figure 4.15). As clay content increase, peaks of PPEG composites broadened and a different peak obtained at 2926 cm^{-1} associated with –CH stretching.

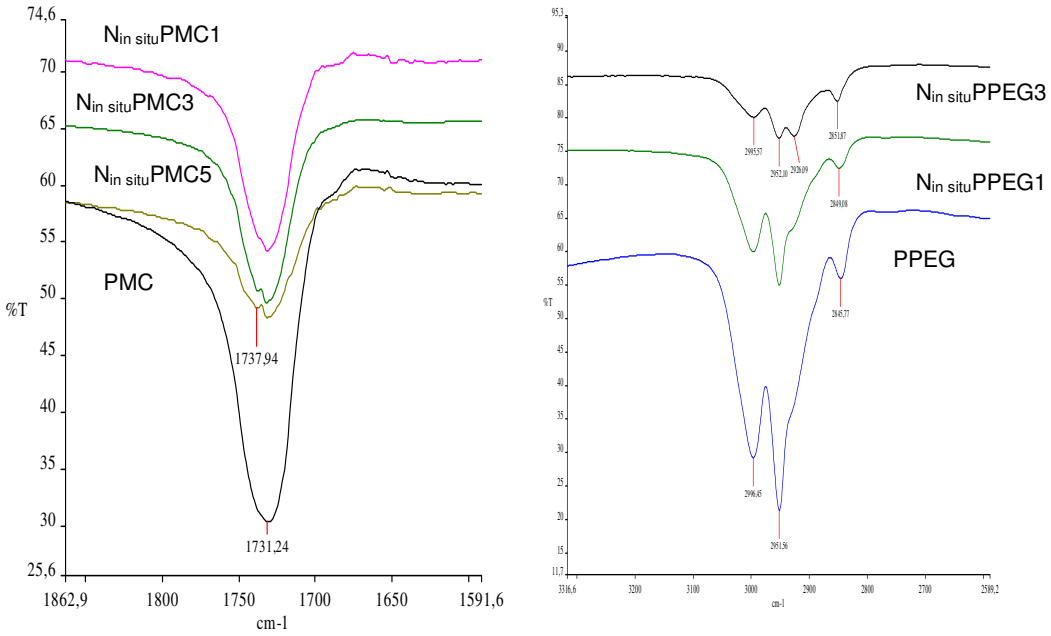


Figure 4.15. FTIR spectra of PMMA-co-MC and PMMA-co-PEG composites prepared by in situ method.

^{1}HNMR spectra of MMA copolymers composites are shown in Figure 4.16 and 4.17. Clear changes on tacticity of the composites of PMMA-co-MC and PMMA-co-PEG prepared by in situ method can be seen from the peaks at 0,8δppm, 1,6δppm, 1δppm similar to homopolymer composites discussed above.

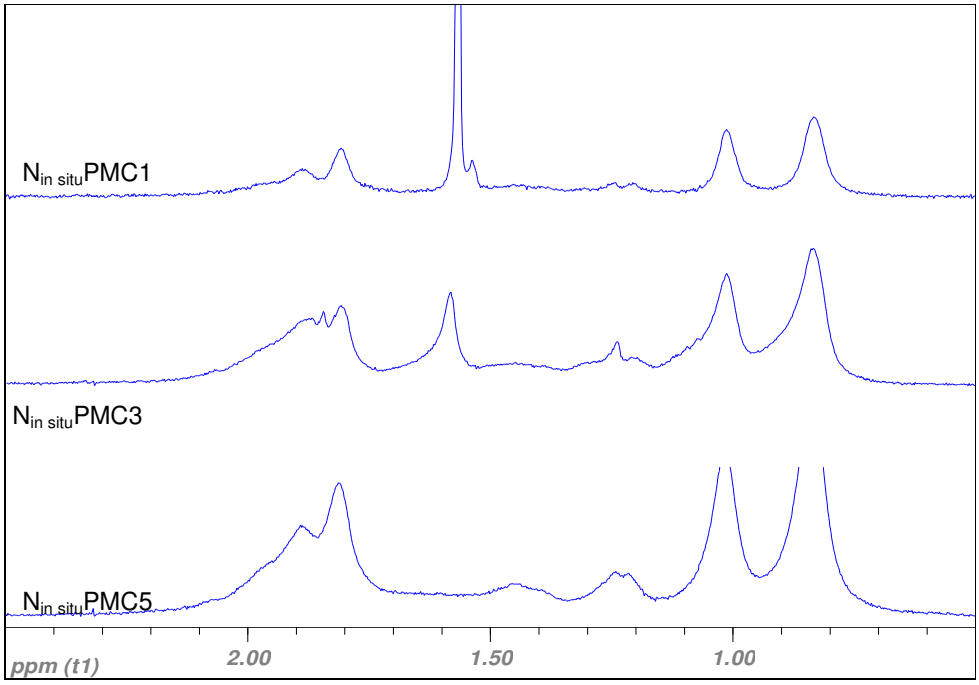


Figure 4.16. ^{1}HNMR spectra of PMMA-co-MC composites prepared by in situ method.

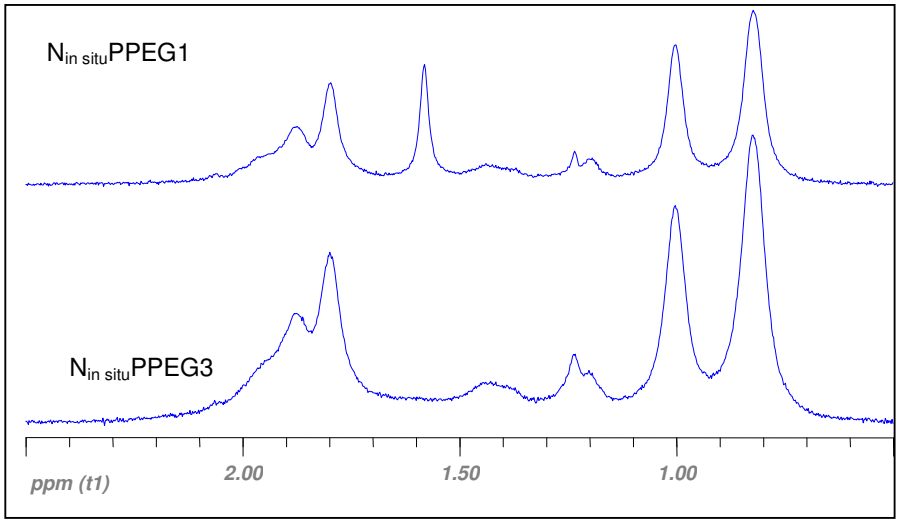


Figure 4.17. [1]HNMR spectra of PMMA-co-PEG composites prepared by in situ method.

It can also easily be seen from the Figure 4.18 that there is no diffraction peak of MMA copolymer composites with different clay loadings in the same region with organoclay (2θ=4,42). This indicated that methyl metacrlate copolymers settled interlayer region of OMMT galleries as homopolymer composites explained above and exfoliated structure obtained for MMA copolymer composites made by in situ method as shown in Figure 4.19 schematically. Therefore, the copolymer composites can also be called as “nano”.

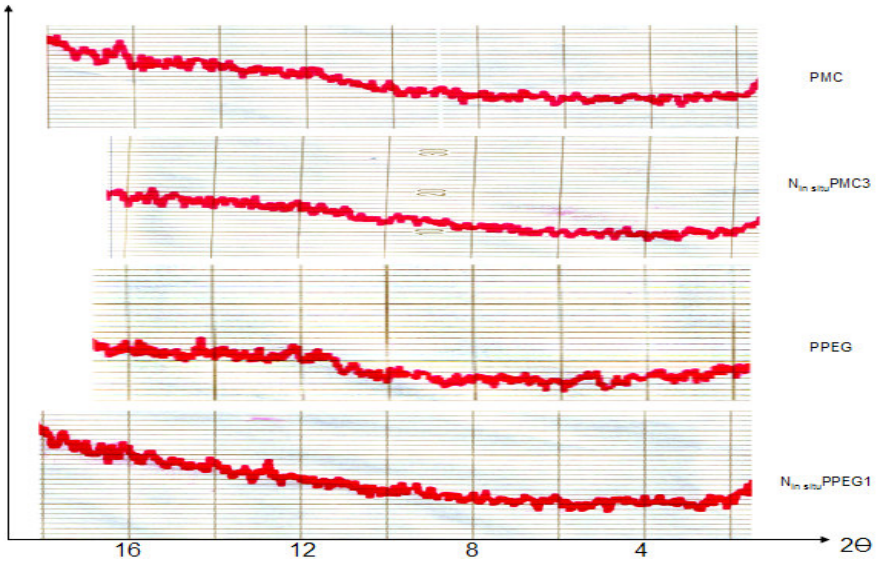


Figure 4.18..XRD spectra of MMA copolymer composites prepared by in situ method.

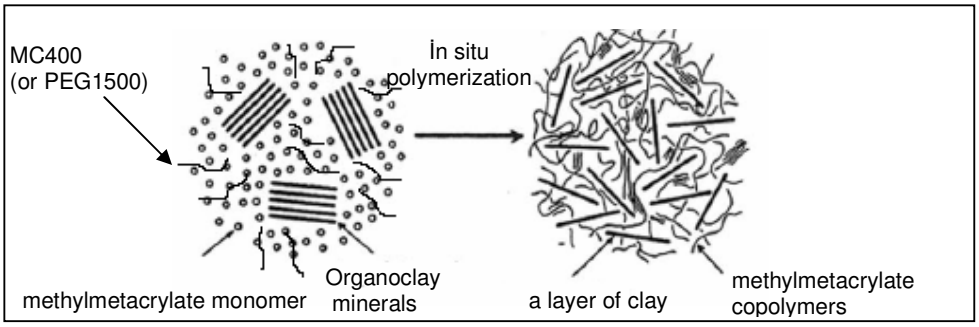


Figure 4.19. The structure of MMA copolymer composites prepared by in situ method.

4.2.2. Preparation of Homo and Co-poly(methyl metacrylate) Composites by Solution Dispersion Method and Characterization

To prepare composites of methyl metacrylate homo and copolymers organophilic clay initially was prepared by cation exchange reaction with DTABr intercalating agent as mentioned section 4.2.1. Since the dispersion of the clay is important in determining the subsequent hybrid materials preparation, it is essential to improve the interaction between the clay and the polymer matrix to produce a useful polymer composite[20]. PMMA homopolymer (PMMA1-1) and copolymers (PMC and PPEG) dispersed in two stages; for 24h at room temperature and for 24h at 80^0 C with addition of certain amounts of OMMT. Dispersion process carried out in a three necked flask and under magnetic stirring at 1100rpm. Reaction temperature determined as 80^0C at which is suitable for both organoclay and homo and copolymers used for this process similar to in situ method. At the end of the experiments, composite solutions directly filtered, washed with water and dried in a vacuum oven. Experiment codes can be seen in Table 4.7.

Table 4.7. The composites obtained after dispersion of 3,75gr polymer each and certain amounts of OMMT for 48h.

Experiment code	OMMT (%)[1]	Polymer type
N_{blend}P1	1	(P)PMMA 1-1
N_{blend}P3	3	(P)PMMA 1-1
N_{blend}P5	5	(P)PMMA 1-1
N_{blend}PMC1	1	PMC
N_{blend}PMC3	3	PMC
N_{blend}PMC5	5	PMC
N_{blend}PPEG1	1	PPEG
N_{blend}PPEG3	3	PPEG
N_{blend}PPEG5	5	PPEG

[1] Weigth percent with respect to MMA

There was no problem experienced during preparation of composites by solution dispersion method. The composites prepared with polymers which prepared before (PMMA1-1, PMC and PPEG). Hence there was no polar interaction on dispersion which is different from in situ method.

As seen on Figure 4.20, as the amount of OMMT increased, characteristic Si-O bending absorption peaks obtained between 467-472 and 512-517 cm^{-1} from FTIR spectra of MMA homopolymer composites that prepared by solution dispersion method. In addition, the peak at 482 cm^{-1} broadened and shortened that belongs to MMA homopolymer(PMMA1-1) shown as P which was used to prepare blend composite.

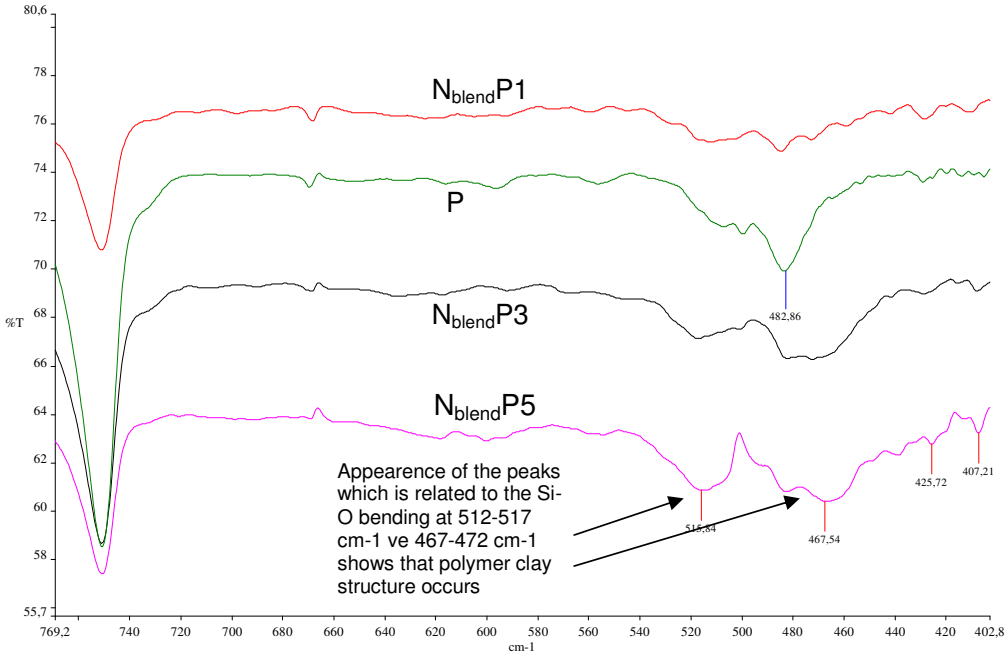


Figure 4.20. FTIR spectra of MMA homopolymer composites prepared by solution dispersion method.

FTIR spectra of MMA copolymer composites seen on Figure 4.21. While the amount of OMMT increases Si-O bending peaks at 471 ve 516 cm^{-1} can be identified clearly similar to those of MMA homopolymer composites.

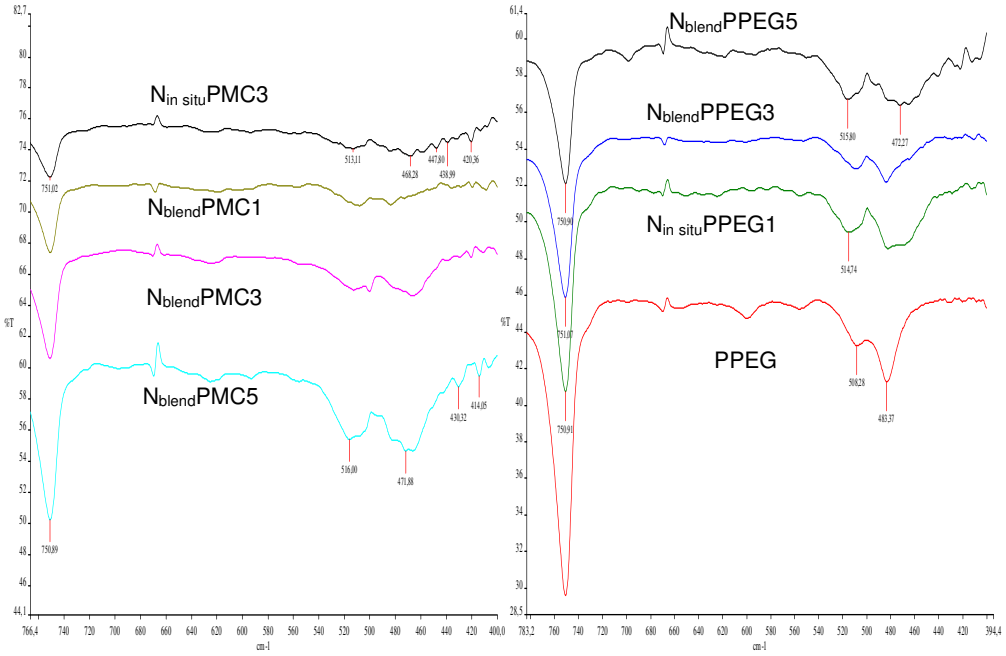


Figure 4.21. FTIR spectra of MMA copolymer composites prepared by solution dispersion method.

It can easily be seen from ^{1}HNMR spectra (Figure 4.22 and 4.23), as the OMMT amount increases sharp changes of the peaks at 0,8δppm, 1δppm 1,6δppm related to varied tacticity of MMA homo and copolymer composites prepared by solution dispersion method.

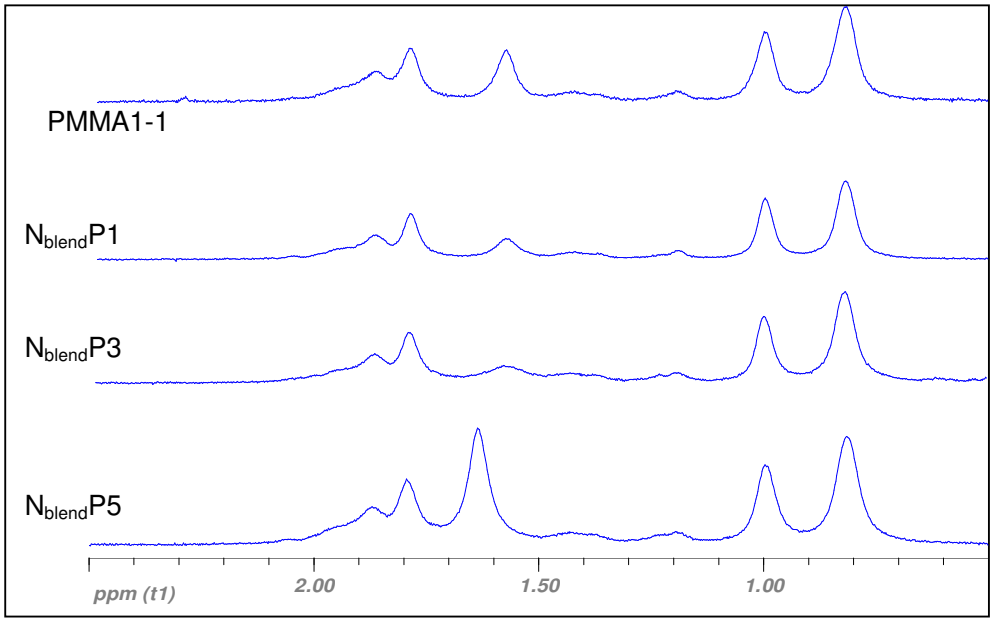


Figure 4.22. ^{1}HNMR spectra of MMA homopolymer composites prepared by solution dispersion method.

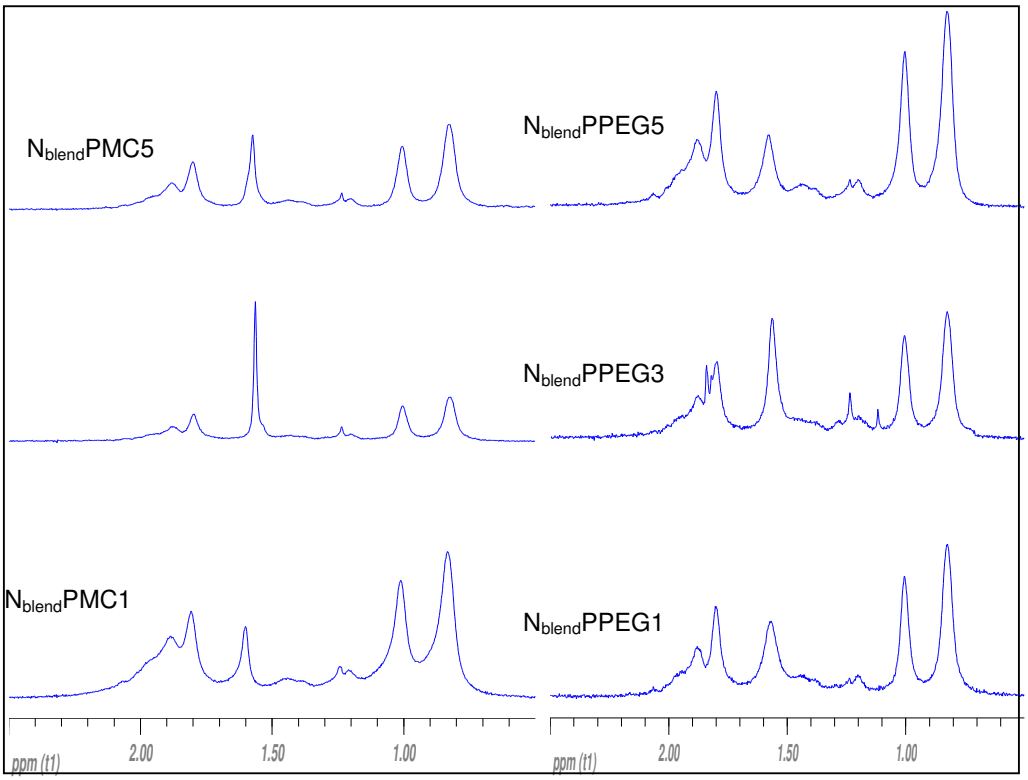


Figure 4.23. [1]HNMR spectra of MMA copolymer composites prepared by solution dispersion method.

Figure 4.24 shows XRD spectra of composites.The similar results obtained from XRD values with composites prepared by in situ method (Section 4.2.4). There is no diffraction peak in the same region with organoclay (2θ=4,42). MMA homo and copolymer composites prepared by solution dispersion method have also exfoliated structure as in situ prepared composites do(Figure 4.25).

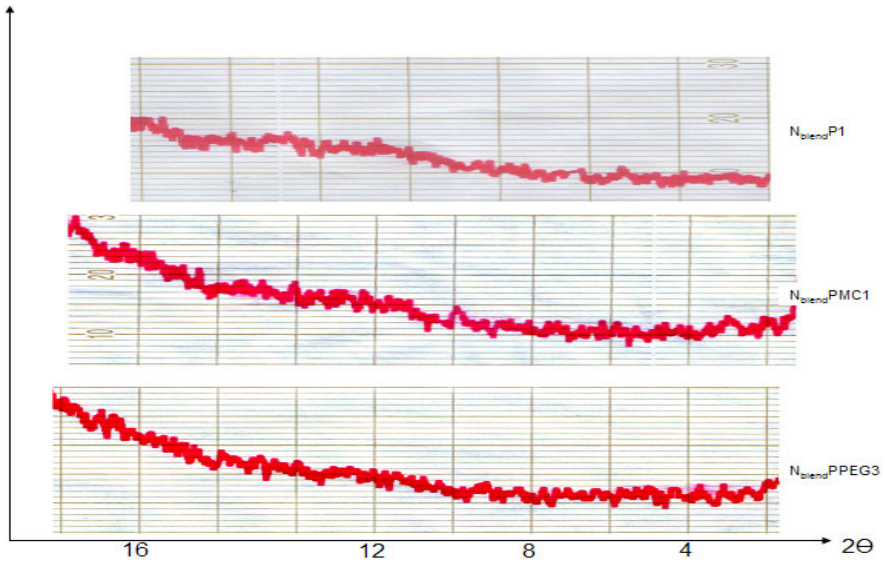


Figure 4.24. XRD spectra of MMA homo and copolymer composites prepared bysolution dispersion method.

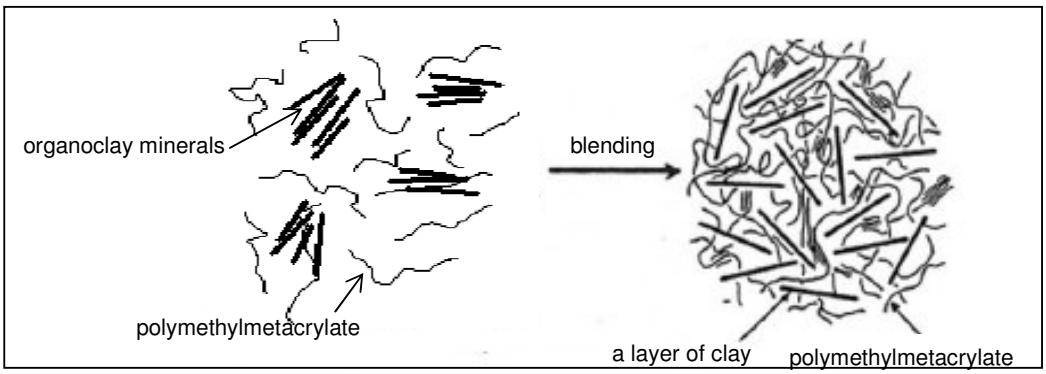


Figure 4.25. The structure of MMA homo and co polymer composites prepared by solution dispersion method.

4.3. Comparison of Polymers and Composites Regarding Their Rheologic, Morphologic and Thermal Properties.

4.3.1. Rheologic Properties

Rheological measurements have been made with Brookfield DV III type low shear rheometer. %2 w/w solution of the samples prepared in methyl ethyl ketone solvent. Rheological curves which belong to methyl metacrylate homopolymer composites prepared by both in situ and solution dispersion methods are shown in Figure 4.26 a and b.

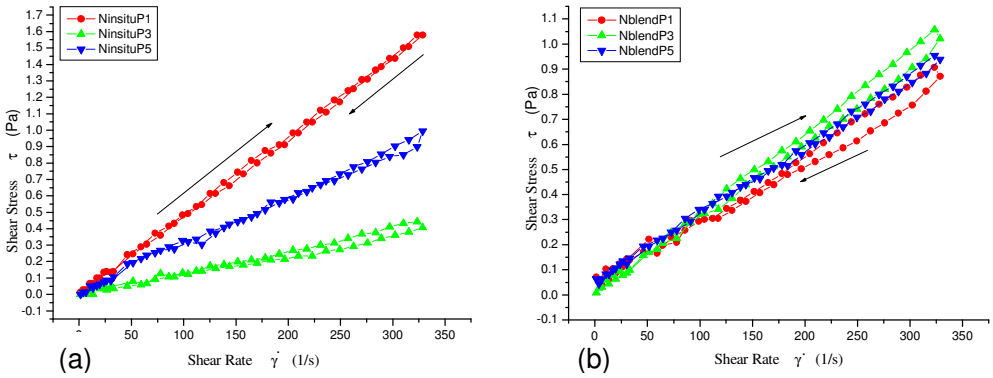


Figure 4.26. Rheological curves of homopolymer composites.

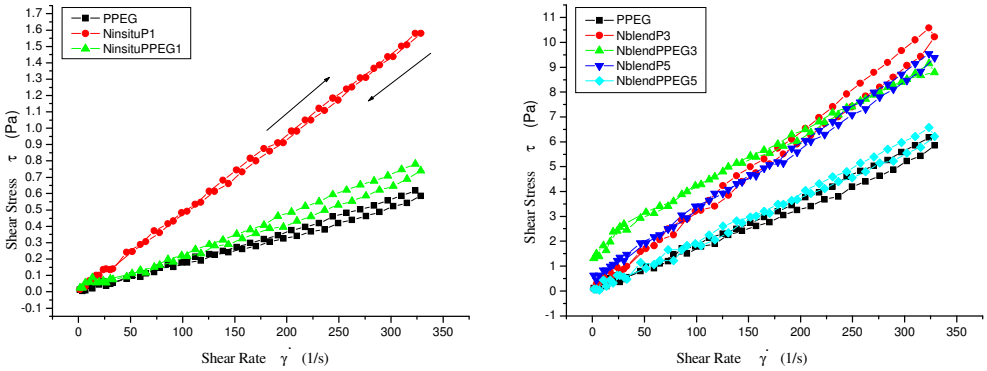
It can easily be seen that incresing yield value and linearity of the line indicates that Bingham Plastic behavior observed (Figure 4.26 a). As the clay content increased, the appearent viscosity of composites increased (Figure 4.26 b). The yield value increased as the clay content increased which had negative value at first sample. This result indicates interactions and bonds between polymer and clay layers. As the clay content increased flow behavior changed and turned to a Bingham Plastic model from Newtonian model.

The results can also be seen in Table 4.8.

Table 4.8. Rheological properties of homopolymer composites.

Sample	Appearent Viscosity ηa (mPa.s) (γ=99 s-1)	Plastic Viscosity η_{pl} (mPa.s)	Yield value τ_B (mPa)	Hysterisis area H.A. (mPa/s)
N_{insitu}P1	4.8790	4.76	18.17	6.9794
N_{insitu}P3	1.3197	1.41	-20.00	7.3897
N_{insitu}P5	3.3193	2.66	43.08	-3.2323
N_{blend}P1	2.9594	2.89	-24.80	9.7493
N_{blend}P3	3.2393	3.21	7.99	12.4642
N_{blend}P5	3.4393	2.83	32.05	6.3889

Comparative rheological curves which belong to methyl metacrylate homo and poly(ethylene glycol) copolymer composites prepared by both in situ and solution dispersion methods are shown in Figure 4.27 a and b.



(a) (b)

Figure 4.27. Comprarative rheological curves of homo and copolymer composites.

Having the greater rheolojic parameters indicates that clay layers have interactions with polymers both composites than the neat polymer (Figure 4.27 a). Increasing of the rheological parameters as the clay content increases indicates that the clay content makes the media more viscous (Figure 4.27 b). The interactions at the highest point at N_{blend}PPEG3 sample among the others, therefore appearent viscosity and plastic viscosity values at maximum. The results can also be seen in Table 4.11 and 4.12.

Table 4.9. Comparative rheological properties of PMMA homo and copolymer composites prepared by insitu method.

Sample	Appearent Viscosity ηa (mPa.s) (γ=99 s-1)	Plastic Viscosity η_{pl} (mPa.s)	Yield value τ_B (mPa)	Hysterisis area H.A. (mPa/s)
PPEG	1.7996	1.95	-22.69	7.8888
N_{insitu}P1	4.8790	4.76	18.17	6.9794
N_{insitu}PPEG1	2.2395	2.50	-26.89	13.8047

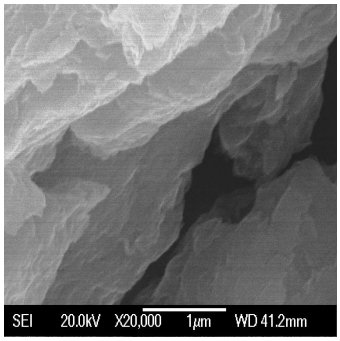
Table 4.10. Comparative rheological properties of PMMA homo and copolymer composites.

Sample	Appearent Viscosity ηa (mPa.s) (γ=99 s-1)	Plastic Viscosity η_{pl} (mPa.s)	Yield value τ_B (mPa)	Hysterisis area H.A. (mPa/s)
PPEG	1.7996	1.95	-22.69	7.8888
N_{blend}P3	3.2393	3.21	7.99	12.4642
N_{blend}PPEG3	4.2791	2.11	220.01	2.2760
N_{blend}P5	3.4393	2.83	32.05	6.3889
N_{blend}PPEG5	1.9196	2.01	-6.01	7.5961

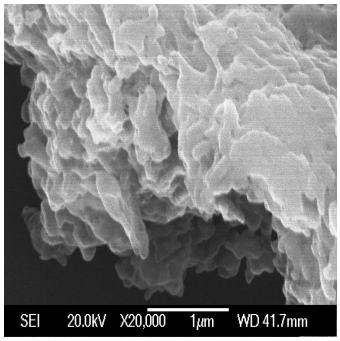
Methyl celulose copolymer composite of methyl metacrylate could not be measured due to insolubility of methyl cellulose in methyl ethyl ketone solvent.

4.3.2. Morphological Properties

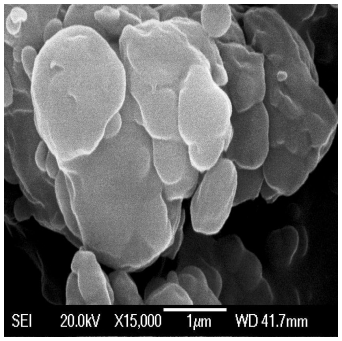
In order to examine morphologies of the nanocomposites prepared by both in situ and solution dispersion methods, scanning electron microscopy (SEM) was used. SEM micrographs can be seen in Figure 4.28, 4.29 and 4.30. Obviously, basal spacing between the OMMT galleries opened with effect of polymers as seen in Figure 4.28. However, OMMT layers are much more opened in the nanocomposites prepared by in situ metod and polymer particles well distributed between layers. Organoclay layers more likely to be surrounded by the polymer in the nanocomposites prepared by solution dispersion method.



(a)Organoclay



(b)N_{blend}PMC1



(c)N_{insitu}PMC3

Figure 4.28. SEM images of organoclay and several nanocomposites.

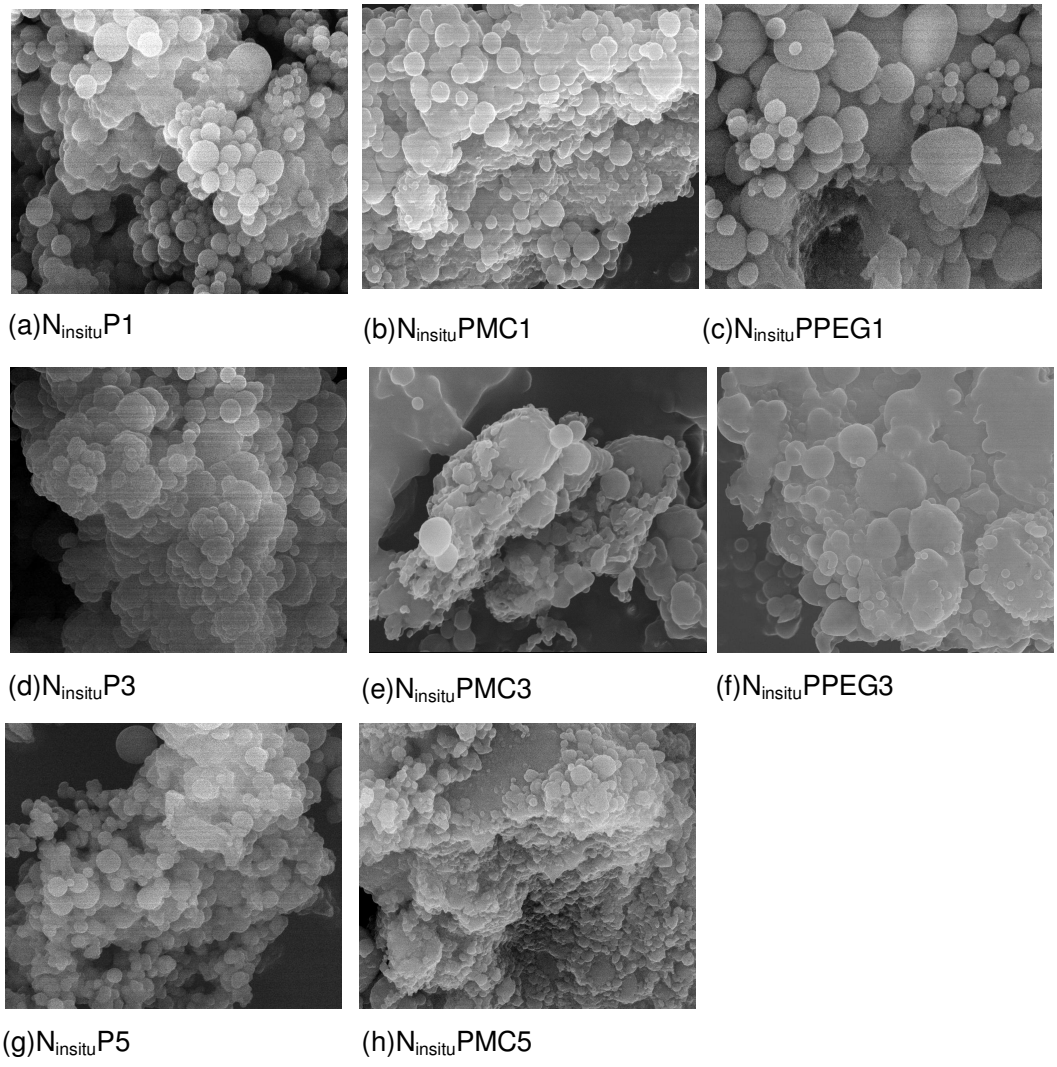


Figure 4.29. SEM images of composites prepared by in situ method.

Methyl cellulose copolymer nanocomposites have smaller size of polymer particles between organoclay layers.

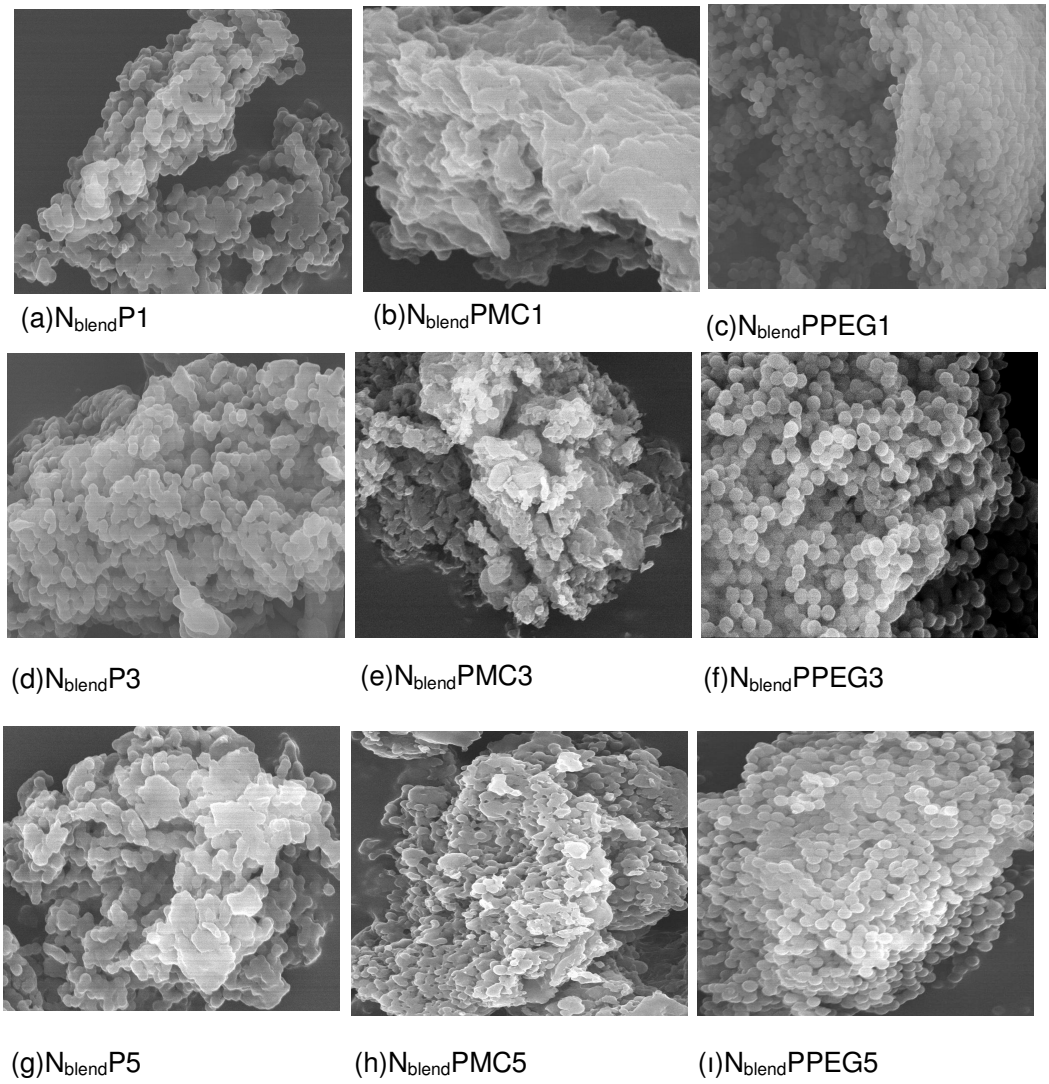


Figure 4.30. SEM images of composites prepared by solution dispersion method.

SEM images of composites supports the XRD results and proves that composites prepared can be called as nanocomposites.

4.3.3. Thermal Properties

The T_g of the PMMA depends strongly on tacticity. In fact, the T_g can vary from 40°C to 140 °C based on the function of isotactic and syndiotactic portion contained within the polymer. Table 4.8 shows thermal properties of polymers and composites prepared by in situ and solution dispersion methods. It can easily be seen that nanocomposites prepared by both methods have an elevated transition temperature(T_g) and 4-15 °C increase compared with that of pure PMC. Melting temperature (T_m) of NP_{insitu}PMC5 is lower than that of NP_{insitu}PMC3 and the same behavior seen between NP_{blend}PMC3 and NP_{blend}PMC5. This may be associated with the dispersion of the clay layers The more disordered dispersion of clay layer causes the higher T_g increase.

Table 4.11. DSC values of PMMA-co-MC composites.

Compound code	Feed composition (wt%)			Thermal properties	
	MMA	MC400	OMMT	Tg(°C)	Tm(°C)
PMC	94,0	6,0	-	112	131
N_{insitu}PMC1	93,4	5,6	0,9	116	135
N_{insitu}PMC3	91,7	5,5	2,8	126	Not clearly determined[1]
N_{insitu}PMC5	90	5,4	4,6	Not clearly determined[1]	134
	PMC				
N_{blend}PMC1	99		1	122	136
N_{blend}PMC3	97		3	124	138
N_{blend}PMC5	95		5	Not clearly determined[1]	136

TGA curves can be seen in Figure 4.26. It can be seen that the thermal stability of the PMMA-co-MC/MMT nanocomposites noticably improved by adding montmorrilonite into the polymer matrix. The residue of the decomposed composite samples increased as the amount of clay increased. From the viewpoint of the thermal decomposition process, thermal decomposition begins from the surface of the nanocomposites[10]. When the molecules at the surface of the nanocomposites decompose, the organoclay content increases and the clay forms a 'protection layer'. Therefore, PMC/MMT nanocomposites exhibit better thermal stability than pure PMC. The second reason may be a decrease in the relative amount of PMC end-capped by carbon–carbon double bond as a result of reduced propensity to disproportionate reactions.

[1] more than one values obtained.

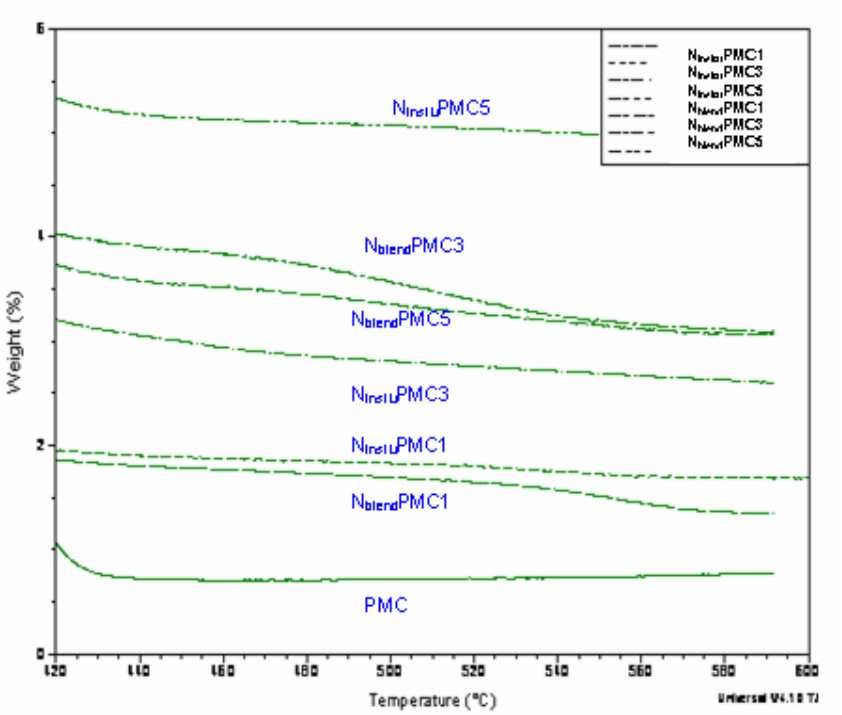


Figure 4.31. TGA curves of PMMA-co-MC composites(420-600 °C).

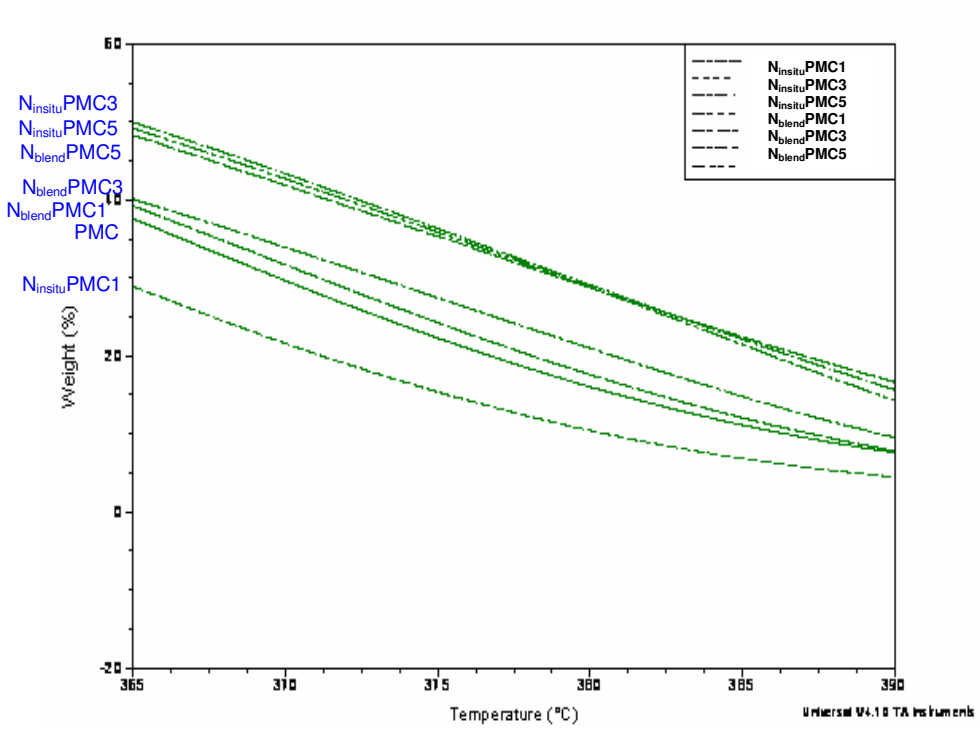


Figure 4.32. TGA curves of PMMA-co-MC composites(365-390 °C).

As seen in Table 4.14 decomposition of composites decreased as the clay content increased. However thermal properties of the composites prepared by in situ

method are much better than the composites prepared by solution dispersion method.

Table 4.12. DSC and TGA values of PMMA-co-MC composites.

Material	W_R^{365} (%)[1]	W_R^{420} (%)[2]	T_g (^oC)	T_m (^oC)
PMC	1,032	36,92	112	131
N_{insitu}PMC1	1,953	28,91	116	135
N_{insitu}PMC3	3,202	49,42	126	Not clearly determined[3]
N_{insitu}PMC5	5,330	48,65	Not clearly Determined[3]	134
N_{blend}PMC1	1,861	38,60	122	136
N_{blend}PMC3	4,025	39,62	124	138
N_{blend}PMC5	3,725	47,79	Not clearly determined[3]	136

4.4. Discussion of The Results

- MMA homopolymer emulsions have been prepared by emulsifier free emulsion polymerization using ammonium persulfate initiator and different precipitation methods have been tried to obtain PMMA powder and finally characterized.
- PMMA copolymers (PMMA-co-MC, PMMA-co-PEG) have been prepared by emulsifier free emulsion polymerization using ammonium persulfate initiator and characterized.
- DTABr modified and hydrophobic character attained OMMT dispersed in water and then composites of homo/ co-poly(methyl metacrylate) prepared using homo and co-poly(methyl metacrylate) by polymer intercalation (solution dispersion) and composites of homo/ co-poly(methyl metacrylate) prepared by in situ polymerization with initial monomer/ organoclay dispersion using emulsifier free emulsion polymerization technique and MMA monomer with methyl cellulose (MC) or poly(ethylene glycol)
- The yield of composites increased as the clay content increased on homopolymer and PMMA-co- MC composites prepared by in situ method.
- The yield of PMMA-co-PEG composite was very high (%98), but increased clay content caused aggregation of OMMT-MMA-PEG mixture.

[1] Weight percent of residue at 365^{o}C
[2] Weight percent of residue at 420^{o}C
[3] More than one value obtained.

- Composite prepared by blend method is convenient and can be suceeded with %100 yield. However, The composites which has prepared by in situ method have better thermal properties.
- Changes on the FTIR peaks at 400-600 cm^{-1} associated with Si-O bending proved that polymers have interactions with clay layers in composites prepared by both methods.
- Changes on the ^{1}HNMR signals of backbone methyl (CH_3) and methylene (CH_2) showed that tacticity changes are associated with composites prepared by both in situ and solution dispersion methods.
- Basal spacing of Edirne-Lalapaşa montmorrilonite clay increased to 19,82 A^{o} after purification and modification with DTABr. It can easily be seen from XRD data shifts that there is no diffraction peak below 2θ degree on the peaks belong to both composites with different clay loading. This indicated that polymer settled interlayer region of OMMT galleries and exfoliated structure gained for composites made by both in situ and solution dispersion methods.
- Rheology measurements indicated that as the clay content increases, rheological properties changes and this result showed the interactions between polymer and clay layers.
- Morphological SEM measurements proved that clay layers opened as a result of interaction with polymer and showed that nanocomposites prepared by in situ method have more likely distributed between clay layers rather than the nanocomposites prepared by solution dispersion method.
- Thermal characterizations showed that thermal properties develops compared to neat polymer and nanocomposites prepared by in situ method have beter properties rather than the nanocomposites prepared by solution dispersion method.
- Finally all of the characterizations supports that composites prepared by both methods are “nanocomposites”.

4.5. Suggestions

- XRD results should be supported with TEM analysis.
- Changes on FTIR and NMR signals should be supported with electrokinetic analysis.
- Composites can be prepared by in situ method without modification of clay.

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RESUME

He was born on 1977 in İstanbul. He started undergraduate education in 1995 in the Department of Chemical Engineering in Osmangazi University after completion of primary, intermediate and high school in İstanbul. He started postgraduate education in 2004 in İstanbul Technical University Faculty of Science and Letters Chemistry Department.