RESULTS AND DISCUSSION

3. RESULTS AND DISCUSSIONS

Organogels are hydrophobic crosslinked networks have strong ability to absorp hydrophobic solvents and petroleum crude oils. The properties of polymeric organogels are highly influenced by crosslink density and also, in the majority of cases, on the functionality of crosslinkers **[Arriola et al., 1997 and Atta and Abdel-Azim, 1998]**. Wide varieties of acrylate crosslinkers have been used to form crosslinked networks. In bulk or solution polymerization the choice of crosslinkers is quite broad. However, the solubility of many crosslinkers in water or oil phase polymerization becomes marginal. Much effort has been expended on attaining high levels of purity in the monomers, but the literature indicates otherwise with regard to the crosslinking agents. In this respect, a simple method was used to synthesize two crosslinkers based on polyfunctional acrylate and methacrylate. The ability to use these new crosslinkers to synthesize novel series of temperature sensitive organogels is the main goal of the present investigation.

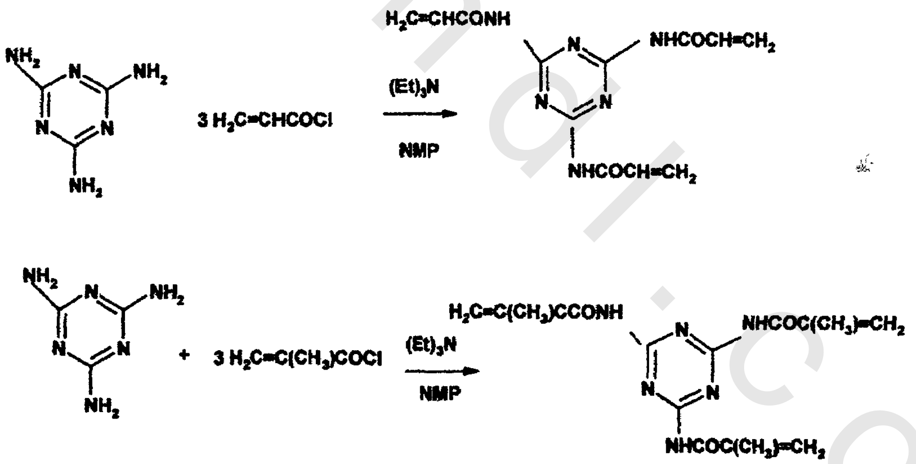
Despite the nation's best efforts to prevent spills, approximately 14,000 oil spills, are reported every year, mobilizing thousands of specially trained emergency response personnel and challenging the best-laid contingency plans. There are different methods can be used to control these spills, such as oil spills skimmers, manual clean up, dispersants, in-situ burning, bioremediation and sorbents. Sorbents come in two basic types: natural organic materials like peat moss and sawdust; and synthetic organic sorbents like polypropylene, polyester foams, polystyrene and polyurethane. Many kinds of polymers have been widely used to absorb oil spilled on water. Among them, alkyl acrylate and aromatic polymers have been attracting much attention of scientific and applied research groups. In the present research, the aim is directed to synthesize new oil sorbers based on hydrophobic monomers (alkyl acrylates and cinnamate moiety) and nonwoven poly(ethylene terephthalate) fibers through copolymerization to control the environmental pollution. Accordingly, the results of the present investigation are divided into the following sections:

- Synthesis of new crosslinkers.
- Synthesis and structure confirmation of cinnamoyloxy ethyl methacrylate monomer (CEMA).
- Synthesis of linear copolymers of CEMA with ODA by radical copolymerization.
- Synthesis of crosslinked copolymers of CEMA with each of ODA, IOA or DDA with high conversion % by bulk polymerization in presence of ABIN initiator and two new different hexafunctinal crosslinkers to produce crosslinked CEMA/acrylates copolymers (oil sorbers).
- Grafting of the synthesized linear copolymers onto poly(ethylene terephthalate) nonwoven fiber, PETNWF, using UV irradiation technique.
- Crosslinking of monomers and new crosslinkers with PETNWF using UV irradiation and temperature.
- Evaluating the efficiency of the synthesized sorbers by measuring swelling and network parameters of the prepared sorbers to determine the best condition to obtain highly swellable polymers in crude oil and toluene.

3.1. SYNTHESIS OF NEW CROSSLINKERS AND MONOMER

3.1.1. Chemical Structure of MAAm and MMAm Crosslinkers

New crosslinkers were prepared by simple reaction of melamine with either methacryloyl- or acryloyl-chloride. This reaction was carried out in presence of 1-methyl-2-pyrrolidone as a solvent and triethyl amine as an acid acceptor. A literature survey revealed that no such modification of melamine with acrylic acid has been reported. The approach aimed to enhance the solubility of melamine in various organic solvents as well as to utilize the synthesized acrylic melamine as a crosslinker. The prepared crosslinkers are NN'N"-trisacryloyl-melanine, MAA$_m$ and NN'N"-trismethacryloyl-melanine, MMA$_m$. The reaction is represented in scheme (1).



Scheme (1): Synthesis of Melamine Crosslinkers

Elemental analysis and physical properties such as boiling points and refractive indices of the prepared MAA$_m$ and MMA$_m$ crosslinkers were measured and shown in **Table (3.1).** The good agreement between the experimental and theoretical values of C, H, O and N reveals that the syntheses of purified MAA$_m$ and MMA$_m$ monomers were performed

Table (3.1): Physicochemical properties of MAA_m and MMA_m Crosslinkers

Charcteristics	MAA_m		MMA_m	
Yeild %	86		78.5	
Rf	0.68		0.71	
Boiling point (K/10 mmHg)	> 343		> 343	
Refractive Indices (n^{30}_D)	1.443		1.441	
Density (g. cm^{-1}at 298 K)	1.131		1.116	
Elemental analysis	Exp.	Cal.	Exp.	Cal.
C	50.02	50	54.51	54.55
H	4.15	4.17	5.48	5.48
N	29.19	29.17	25.4	25.45
O	16.64	16.66	14.61	14.55

successfully. The chemical structure of MAA_m and MMA_m crosslinkers was confirmed by IR, ^{1}H-NMR and ^{13}C-NMR analyses. IR spectra of MAA_m and MMA_m were represented in **Figures (3.1a and b)** respectively. Both crosslinkers show multiple bands at 3350–3200 cm^{-1}, typical of –NH stretching bands of secondary amide due to hydrogen bonding. A strong band at 1680 cm^{-1} is observed in the spectra of both crosslinkers, which is assigned to O=CNH stretching. These peaks indicate the formation of amide linkage in the structure of both MAA_m and MMA_m crosslinkers. The strong peaks at 3075 cm^{-1} (–CH stretching) and 1614 cm^{-1} (C ═ C stretching) confirm the presence of acrylate and methacrylate moieties in the structure of MAA_m and MMA_m. However the presence of bands at 2965–2870 cm^{-1} (CH bending of CH_3) indicates the incorporation of MC with melamine. ^{1}H-NMR and ^{13}C-NMR spectra of these crosslinkers are shown in **Figures (3.2 and 3.3)**. The ^{1}H-NMR spectra of both MAA_m and MMA_m were recorded in **Figure 3.2(a) and (b).** Spectrum of MAA_m **(Figure 3.2a)** shows singlet at 8.1–8.2 ppm for –NH– amide proton and at 5.9–6.2 ppm which confirms protons of C=C of acryloyl groups. The differences in chemical shifts and coupling constants of these protons, which show quartet lines for every H proton of the vinyl groups, can be referred to Ha on the same side of the triazine of melamine; Hb on the opposite side of the ring and Hc is desheilded by NH groups **[Pavia et al., 1979]**. Spectrum of MMA_m **(Figure 3.2b)** shows two signals, one at 4.8 ppm, which reveal H_2C= C splitting and a new singlet signal at 1.15 ppm confirms CH_3 protons. ^{13}C-NMR spectra of MAA_m and MMA_m, **Figure 3.3(a) and (b)**, agree with data recorded on triazine carbons, CONH and vinyl carbons at 165.4, 173 and 126–128 ppm, respectively **[Samaraweera et al., 1992].**

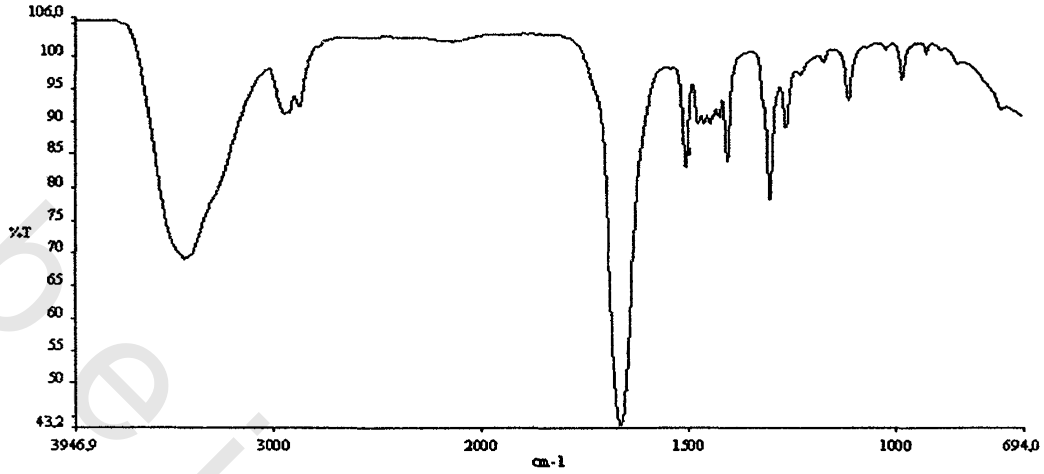


Figure (3.1a): FTIR Spectra of MAA_m Crosslinker

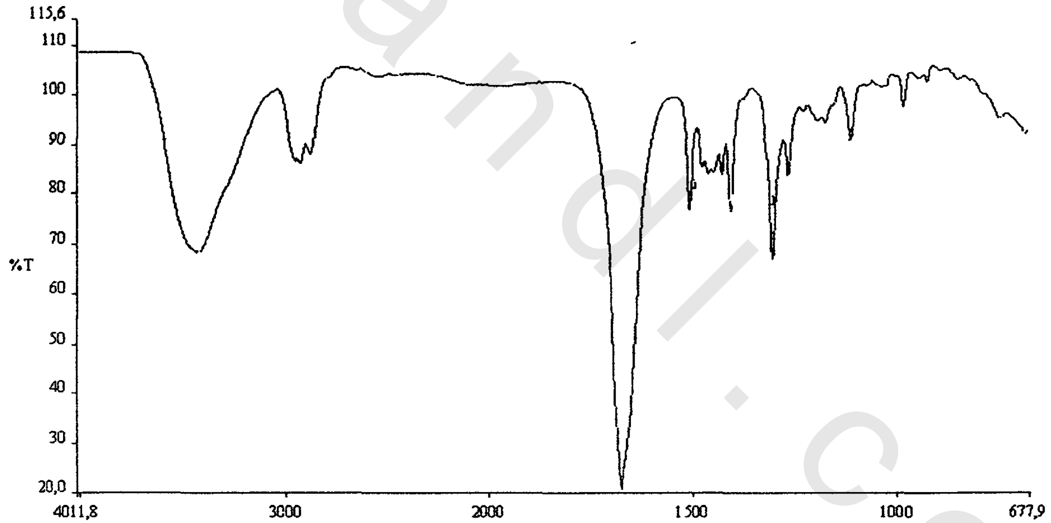


Figure (3.1b): FTIR Spectra of MMA_m Crosslinker

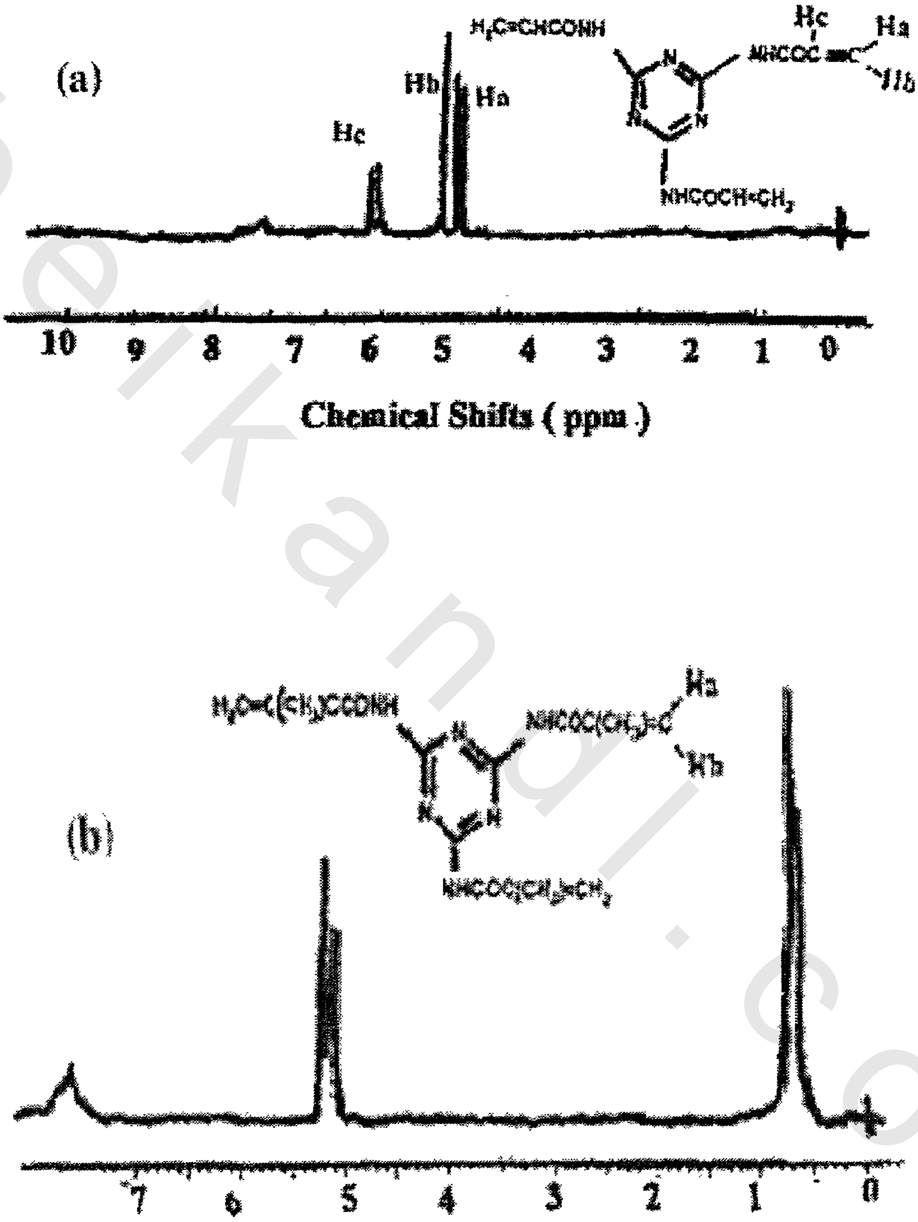
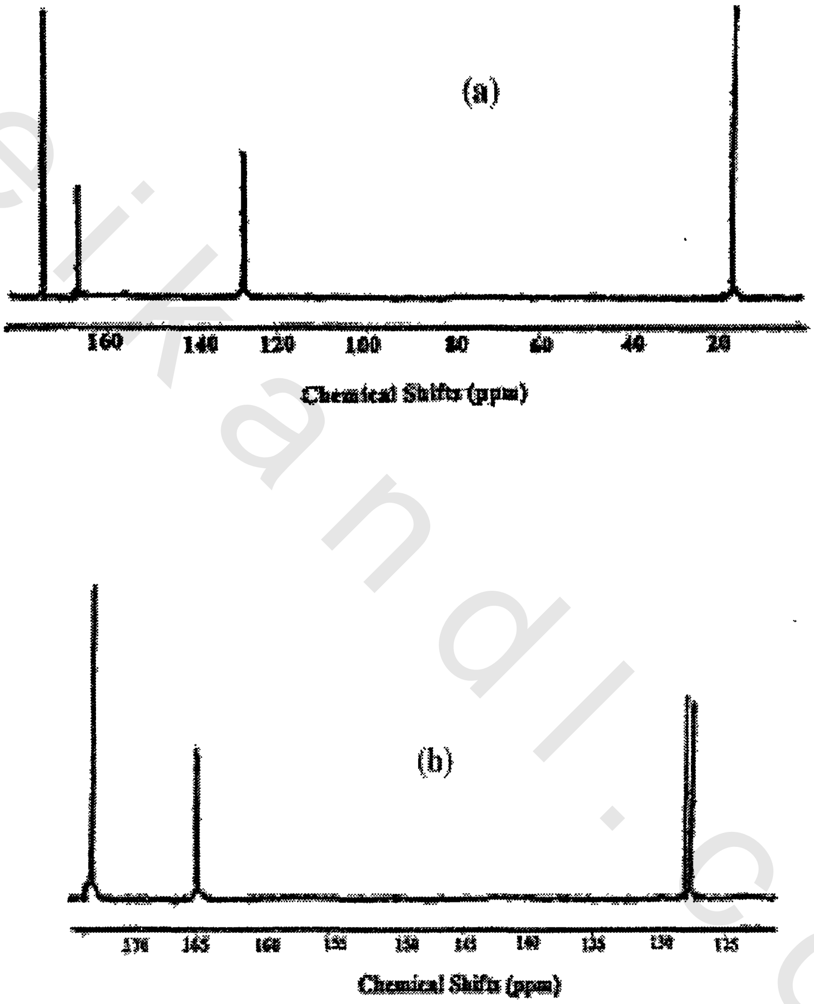


Figure (3.2a): ¹HNMR Spectrum of (a) MAA_m Crosslinker (b) MMA_m Crosslinker



Figures (3.3): ^{13}CNMR Spectra for a) MAA_m and b) MMA_m

3.1.2. Synthesis of Cinnamoyloxy ethyl methacrylate Monomer (CEMA).

It is well known that oil sorbers should have hydrophobic character to swell in oil medium. The present work aims to synthesize new monomer based on hydrophobic moieties such as alkyl or phenyl groups. It is well established that 2-hydroxyethylmethacrylate, HEMA, monomer contains both hydrophilic and hydrophobic moieties. So, it is important to convert it to hydrophobic monomers that will be obtained by reaction of its hydroxyl group. Cinnamoyloxy ethyl methacrylate (CEMA) was prepared and purified as reported in a previous work **[Atta et al., 2005]**. Cinnamoyl chloride was condensed with HEMA to produce CEMA. The synthesized CEMA was characterized by FTIR and ^{1}HNMR spectroscopic analyses **[Atta et al., 2005]**. The chemical structure of the obtained monomer, CEMA, can be evaluated from IR and ^{1}HNMR analyses. In this respect, IR and ^{1}HNMR spectra were represented in **Figures 3.4 and 3.5**, respectively. The IR spectrum of CEMA, Figure **3.4**, exhibits characteristics absorption bands at 2926 cm^{-1} (stretching vibration of the aliphatic C-H bond), 1730 cm^{-1} (stretching vibration of the C=O), 1620 cm^{-1} (stretching vibration of the C=C), 1149 cm^{-1} (stretching of C-O), and 900 – 650 cm^{-1} (out of plane rotational vibration of aromatic C-H). The disappearance of a band at 3200-3500cm^{-1} confirms the completion of the esterification reaction between OH of HEMA and cinnamoyl chloride. In the ^{1}HNMR spectrum, **Figure 3.5**, the peaks of CEMA indicated aromatic protons at 7.2 - 7.8 ppm, vinyl protons at 5.6-6.6 ppm, and methyl protons at 1.9 ppm.

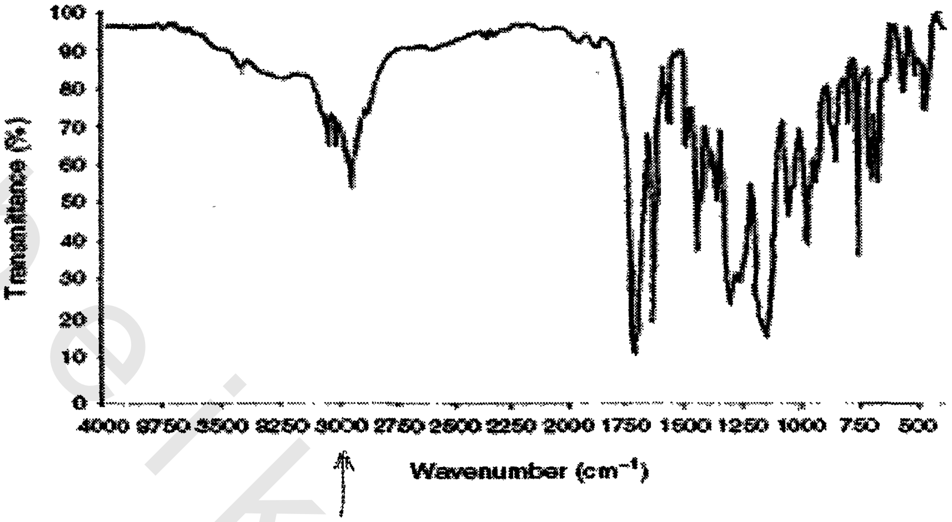


Figure (3.4): FTIR Spectrumf CEMA

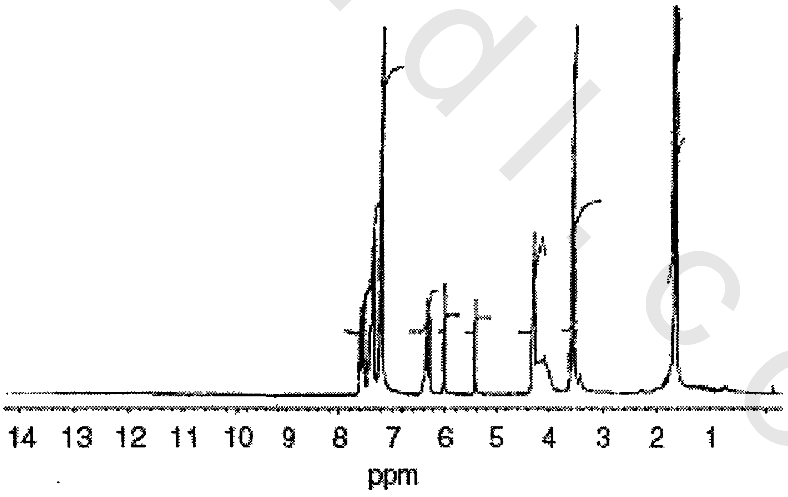


Figure (3.5): ^{1}HNMR Spectrum of CEMA

3.2. PREPARATION OF LINEAR AND CROSSLINKED COPOLYMERS.

3.2.1. Preparation of Linear Copolymers

The radical polymerization mechanism is frequently employed for preparation of copolymers. The overall reaction scheme for radical copolymerization is very similar to the one for homopolymerization: initiation, propagation, termination and transfer reactions are again involved. However, the chemical nature of both monomers plays a role in a number of ways. It is not possible just to mix two monomers, add an initiator, and expect a copolymer to form. While copolymerization may closely follow the kinetics of homopolymerization of the component monomers which are very similar to each other, a small amount of a monomer that is completely different, the copolymerization may proceed much faster than the homopolymerization. Sometimes two monomers that would not homopolymerize can form a copolymer. On the other hand, a small amount of a monomer may totally inhibit the polymerization of the second monomer. A major difference between homopolymerization and copolymerization is in the propagation step.

This difference is based on the nature of the ultimate unit carrying the free radical and the reactivity of this radical. Accordingly, knowledge of the reactivity ratios is the key to predicting the composition of a copolymer. It is therefore very desirable to measure these ratios in order to predict the structure of the produced copolymer. Normally the two monomers will polymerize at different rates, so that the composition of a copolymer isolated before polymerization is complete will depend on the relative reactivity of the first monomer versus the second one. Spectroscopic methods are now widely used in the polymer field as an analytical tool to probe structure and to obtain information on physicochemical changes occurring in polymers and polymer additives. Spectroscopy utilizes the interaction of radiation with matter to provide details of molecular energy levels, energy state life times and transition probabilities. This information in turn may be applied in studying chemical structure, molecular environment, polymer tacticity and conformation, and monitor changes in these properties following external perturbations. In the present study, CEMA monomer has been copolymerized with ODA in the presence of benzene at 70°C using the procedure described in the experimental section. The structure of the prepared linear copolymer was confirmed by ^{1}HNMR analysis. In this respect, ^{1}HNMR spectra of different compositions of CEMA/ODA copolymers were represented in **Figure (3.6).** The ^{1}HNMR spectroscopic analysis of the synthesized copolymers afforded similar spectra, which show bands at 1.1, 7.2-7.8 and 5.6-6.2 ppm that represent, methyl protons in the polymer backbone, aromatic protons of CEMA and vinyl proton in the cinnamoyl moiety, respectively. The appearance of methylene protons band at 1.9 ppm together with the disappearance of vinyl protons in the acryloyl group at 5.6–6.2 ppm indicate the incorporation of alkyl acrylate and CEMA in copolymerization backbone. The reactivity ratios between CEMA and ODA monomer was measured in previous works **[Fineman and Ross, 1950, Kelen and Tudos, 1975, Atta et al., 2005]**. The value of reactivity ratio product for this copolymer reveals that the studied monomers have a tendency to form random copolymers. Several techniques have been developed to determine the reactivity ratios of monomers. The most frequently cited method is that of Fineman-Ross **[Fineman and Ross, 1950]** and Kelen-Tudos **[Kelen and Tudos, 1975]** methods, where monomer feed mixtures of varying composition are polymerized to low conversion and the resultant polymer composition is measured. Determination of reactivity ratios is based mainly on the analysis of the components making up the copolymer molecule. Previous publications demonstrated several techniques used for determining the percentage of the constituents of the copolymers **[Atta et al., 2005]**. The present investigation of CEMA/ODA reactivity ratios used ^{1}HNMR to determine the copolymer composition. The ^{1}HNMR spectra of CEMA/ODA show signal of vinyl proton in the cinnamoyl moiety at 6.4 - 6.8 ppm, and methylene protons at 1.9 ppm together with the disappearance of vinyl protons signal in the acryloyl group at 5.6 – 6.2 ppm. It is useful to use ^{1}HNMR analysis in determining the copolymer compositions **[Atta et al., 2005 and 2006]**. The analysis was carried out by comparing the integrated intensities of resonance signals with chemical shifts, 1.96-2.5 ppm assigned to the –CH proton of ODA repeating units, and from the signals with chemical shifts 6-7 ppm corresponding to the CH=CH protons of the cinnamate moiety of CEMA repeating unit. The above mentioned methods for determining the reactivity ratio were used to measure the reactivity ratio of CEMA, and ODA.

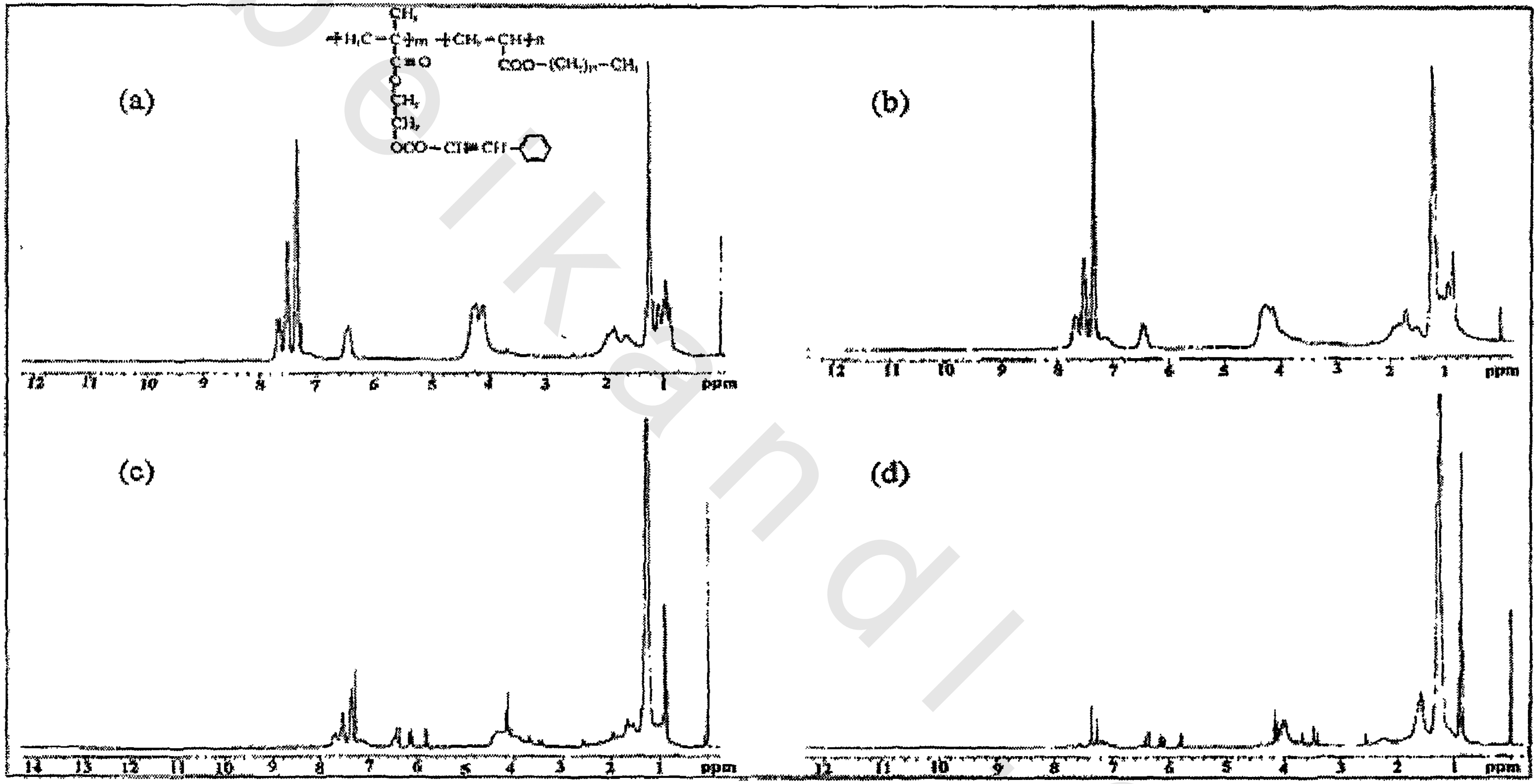


Figure (3.6): HNMR Spectea of CEMA/ODA Linear copolymer having different Composition (a) 90/10 (b) 70/30 (c) 50/50 (d) 10/90

3.2.2. Crosslinked Copolymers

High conversion polymerization was performed for preparing different crosslinked copolymers. The CEMA monomer was copolymerized with different alkyl acrylase monomers using 1, 2 and 4wt% of trimethylolpropane triacrylate (TPT) crosslinker in presence of ABIN as initiator **[Atta et al., 2005 and 2006]**. In the present study, the crosslinked copolymers of CEMA/IOA, CEMA/DDA and CEMA/ODA copolymers were prepared via bulk polymerization in presence of 0.02% ABIN as initiator and different weight percentage of two different crosslinkers MAA_m and MMA_m ranging from 0.5 % to 4%. 90/10, 70/30, 50/50, 30/70 and 10/90 (mole%/mole%) were used in each copolymer. A wide variety of vinyl crosslinkers has been used to form crosslinked networks. The choice of the crosslinkers is quite broad in bulk and solution polymerization. The crosslinker concentrations usually about 0.05-1% are used to provide super absorbents with high swelling capacity and low soluble polymer content. Many side reactions, such as intrachain cyclization, decrease the efficiency of the crosslinker and result in a gel point later in the polymerization than would be predicted by theory and in networks less crosslinked than would be predicted from the number of potential crosslink sites. This deviation from theory can be significant at high crosslinker levels, such as used in styrene divinylbenzene copolymers where intramolecular cyclization is believed to occur. Intramolecular cyclization increases with low monomer content and high copolymer conversion. Because of the high monomer content and low crosslinker levels used in typical gel processes, there is a reduced probability of this inefficient side reaction, especially during the initial part of the polymerization process. To understand the distribution of crosslinks in the network, the reactivity of the various double bonds in the system must be determined. This includes the reactions between double bonds of CEMA and each of alkyl acrylate, the initial double bonds of the crosslinker, and the various double bonds that are pendant to the polymer chain after incorporation of the crosslinker.

The present copolymeric system is composed essentially of CEMA with various amounts of IOA, DDA or ODA comonomer to give certain hydrophibicity, which improves oil affinity. The yield of crosslinking reaction increases very rapidly at some extent of the reaction as the reaction proceeds, and the reaction product begins to form an infinite molecular weight network called gel point. In the gel state, chemical reaction can proceed and chains form the network by crosslinking, the crosslink density or degree of crosslinking is a measure of the total links between chains in a given mass of substance. In a crosslinking system, there are soluble portions and insoluble portion, the former can be extracted with suitable solvents and the latter cannot be extracted with any solvent due to crosslinking. It only swells in good solvent to give a gel.

The data of total conversion (%) for copolymerization of CEMA and IOA, DDA or ODA monomers crosslinked by either MAA_m or MMA_m crosslinker were determined and listed in **Table (3.2).** The data show the variation of conversion (%) for all composition of CEMA and IOA, DDA or ODA monomers with 1% crosslinkers and with different crosslinker weight contents for 50% mole (CEMA) and 50% mole alkyl acrylate. It was found that the crosslinking conversion precentages increase by increasing the amounts of alkyl acrylate. This indicates that the efficiency of crosslinking was increased with increasing alkyl acrylate contents.

Table (3.2): The Percentage Conversion Of The Prepared CEMA/Alkylacrylate Sorbers Crosslinked by Either MAA$_m$ or MMA$_m$ Crosslinker.

Xerogel Compositions	Crosslinker Weight %	Conversion %					
		CEMA/IOA		CEMA/DDA		CEMA/ODA	
		MAA$_m$	MMA$_m$	MAA$_m$	MMA$_m$	MAA$_m$	MMA$_m$
90/10	1	92.35	93.2	89.6	90.4	86.43	87.32
70/30	1	94.72	95.2	91.88	92.33	88.66	89.12
50/50	0.5	93.89	94.7	91.0	91.9	87.93	88.69
	1	95.11	95.9	92.2	93.1	89.03	89.84
	2	96.03	96.8	93.1	93.9	89.87	90.72
	4	97.93	98.7	94.9	95.8	91.63	92.46
30/70	1	96.22	97.19	93.3	94.2	90.06	90.98
10/90	1	97.60	98.4	94.6	95.5	91.36	92.14

3.2.2.1 Soluble Fraction

Some polymer chains are not attached to the infinite network and can be extracted from the gel fraction. The effect of theses chains is difficult to treat and usually neglected in the theories. These chains do not contribute to the modulus but can be solvated and contribute to the swelling. Therefore, it is desirable to eliminate or minimize the content of these extractable molecules. The percentage of this extractble fraction (soluble fraction) depends on: (a) the type and concentration of the monomers, and (b) the type and concentration of crosslinking agent **[Kossmehl et al., 1994]**. In the present investigation the polymer rods were post cured at 378K in an air oven for 24 hours to assure complete polymerization. The sol fractions of these polymeric materials were determined via Soxhlet extraction technique. In this respect, the xerogel discs (gel before extraction of soluble fractions) were exhaustively dried in vaccum at 308K to a constant weight. The dried xerogel discs were transferred into an extraction thimble and were subjected to Soxhlet extraction with chloroform. After extraction for 24 hours, and samples were dried in the atmosphere for several hours and then, dried to a constant weight in vacuum oven at 308K. However, no further extraction was found after 24 hours, and this soxhlet extraction time was adopted for all samples. The reactivity of a crosslinker containing acrylate group (MAA_m) and that with methacrylate group (MMA_m) towards (CEMA-IOA), CEMA-DDA) and (CEMA-ODA) copolymer was investigated from polymerization conversion and SF measurements in chloroform. The cured xerogels were subjected to post curing at high temperature. In this respect the cured rods were subjected to post curing at temperature 378K for 24h before swelling and sol fraction measurements to ensure complete conversion of both monomers and crosslinkers. The total conversion of monomers to cross-linked polymers was estimated using *equation (3.1):*

$$\text{Total conversion } (\%) = W \times 100 / W_0 \qquad (3.1)$$

Where, W and W_0 are total weight of cross-linked polymers after post curing at 378K and weight of reactants, respectively.

a- Copolymerization of CEMA with ODA

Crosslinked CEMA/ODA copolymers were prepared by bulk polymerization in presence of ABIN initiator and hexafunctional crosslinker. The crosslinked copolymers were evaluated for oil-absorbency application. The swelling properties of crosslinked polymers were studied. The data indicate that the formed networks are not porous. In this respect, the formation of porous networks and crosslinking of CEMA with octadecyl acrylate (ODA) are the main goals of the present study to increase the oil absorbency of the prepared copolymers.

Crosslinking is responsible for the three-dimensional network structure that is important for oil to be swelled into sorbers rather to dissolve in it. Elasticity and swelling properties are attributed to the presence of physical or chemical crosslinks within polymer chains. Hydrophobic network polymers are used as absorbents of oil as well as some organic solvents spilled on water in the field of environment. High conversion polymerization was performed for preparing different crosslinked copolymers. The crosslinked copolymers of CEMA/ODA copolymers were prepared via bulk polymerization in presence of 0.02% ABIN as initiator and different weight percentage of MAA_m and MMA_m crosslinkers ranging from 0.5% to 4%. Different molar ratios of CEMA with ODA viz. 90/10, 70/30, 50/50, 30/70 and 10/90 (mole%/mole%) were used in each copolymer. According to Flory's swelling theory

[Flory, 1953], swelling behavior is affected by rubber elasticity, affinity to solution and crosslinking density. The swelling behavior of gels with different amounts of the crosslinkers was studied. Also, the polymer rods were post cured at 378K in an air oven for 24 hours to assure complete polymerization. The sol fractions of these polymeric materials were determined via Soxhlet extraction technique. I the reactivity of MAA_m and MMA_m crosslinkers towards CEMA-ODA copolymer was investigated from polymerization conversion and SF measurements in chloroform. SF% values were determined and listed in **Table (3.3).** The effect of crosslinker concentrations on SF values was determined through crosslinking of CEMA (50 mol%) / ODA (50 mol%) copolymer with different contents of MAA_m and MMA_m crosslinkers 0.5, 1, 2 and 4% (w/w). From data it is obvious that, the percentage of SF for crosslinked copolymers is reduced when crosslinker content increases from 0.5% to 4% (w/w). The effect of copolymer compositions on SF% values were determined by crosslinking different compositions of CEMA-ODA copolymer using 1%(w/w) of either MAA_m or MMA_m crosslinkers and 0.02% (w/w) AIBN as initiator. Regarding the data shown in **Tables (3.3),** it is obvious that, for copolymers crosslinked with MAA_m and MMA_m crosslinkers , SF % decrease with increasing ODA percentage in the copolymer composition. This may be referred to the higher reactivity of ODA homopolymer towards either crosslinkers than that of CEMA/ODA copolymer. In other words, the alkyl acrylate polymers are used up before a significant number of CEMA would incorporate in the network **[Atta et al., 2005]**. It was also determined that the *SF* values for crosslinked CEMA-ODA copolymer with MMA_m are lower

Table (3.3): Soluble fraction values of crosslinked CEMA/ODA copolymers using two different crosslinkers and various crosslinker concentrations

Xerogel composition of (CEMA/ODA)	Crosslinker Content (Wt %)	SF of crosslinked gel in Toluene (%)	
		MAA_m	MMA_m
90/10	1.0	29	22
70/30	1.0	25	20
50/50	0.5	29	25
	1.0	20	15
	2.0	15	10
	4.0	10	8
30/70	1.0	18	12
10/90	1.0	15	8

than the values for that crosslinked with MAA_m. This can be attributed to the high reactivity of the CEMA-ODA copolymer towards methacrylate crosslinker, which is much higher than acrylate crosslinkers.

b- Copolymerization of CEMA with DDA

CEMA monomer was copolymerized with DDA to study the effect of alkyl acrylate chain length on the copolymerization and the crosslinking effeciencies of these monomers. The effect of copolymer composition on gel and sol fraction of the crosslinked CEMA/DDA copolymers with both MMA_m and MAA_m crosslinkers were determined from SF values which represented in **Table (3.4).** The effect of crosslinker concentrations on SF values was determined through crosslinking of CEMA (50 mol%) DDA (50 mol%) copolymer with different contents of MAA_m and MMA_m viz. 0.5, 1, 2 and 4% (w/w). determined SF% values are listed in **Table (3.4).** From data it's obvious that, the percentage of SF for crosslinked copolymers is reduced when crosslinker content increases from 0.5% to 4% (w/w). This indicates that low content of MAA_m or MMA_m crosslinkers reduces the probability of side reactions, which affect the crosslinking activity. It is also observed that SF% values for each of the prepared CEMA/DDA copolymer crosslinked with MMA_m are lower than those crosslinked with MAA_m. This may be attributed to the differences in reactivity ratios of both crosslinkers with the produced polymer **[Atta and Arndt, 2001]**, where the presence of methyl groups in MMA_m would allow it to enter in the crosslinking reaction with CEMA/DDA

Table (3.4): Soluble fraction values of crosslinked CEMA/DDA Copolymers using two different crosslinkers and various crosslinker concentrations

Xerogel composition of (CEMA/DDA)	Crosslinker content (Wt %)	SF of crosslinked gel in Toluene (%)	
		MAA_m	MMA_m
90/10	1.0	21.35	19.03
70/30	1.0	17.08	12.12
50/50	0.5	15.67	13.81
	1.0	10.59	5.85
	2.0	11.43	5.38
	4.0	9.51	3.83
30/70	1.0	11.05	5.87
10/90	1.0	7.90	3.78

comonomer system more readily than MAA_m. It was also noted that the SF values were reduced when DDA copolymerized with CEMA instead of ODA monomer. This indicates that CEMA/DDA copolymers more reactive than CEMA/ODA copolymers towards crosslinkers. Also, the effect of copolymer compositions on SF% values were determined by crosslinking different compositions of CEMA-DDA copolymer using 1%(w/w) of either MMA_m or MAA_m crosslinkers and 0.02% (w/w) AIBN as initiator. Regarding the data shown in **Table (3.4)**, it is obvious that, for copolymers crosslinked with either crosslinker MMA_m or MAA_m, SF % decrease with increasing DDA percentage in the copolymer composition. This may be referred to the higher reactivity of DDA homopolymer towards either crosslinkers than that of CEMA/DDA copolymer. In other words, DDA polymers are used up before a significant number of CEMA would incorporate in the network structure.

c- Copolymerization of CEMA with IOA

SF values of the crosslinked CEMA/IOA copolymers with both MMA_m and MAA_m crosslinkers were determined from Soxhlet extraction and listed in **Table (3.5)**. The data indicate that SF values were decreased with increasing crosslinkers concentrations, IOA composition and incorporation of MMA_m instead MAA_m crosslinker as described in SF values for both CEMA/ODA and CEMA/DDA crosslinked copolymers. It is also observed that, SF % increases as length of alkyl acrylate increases this may be attributed to the lower reactivity of longer alkyl acrylate towards either crosslinkers than that of CEMA/alkyl acrylate copolymer.

Table (3.5): Soluble fraction values of crosslinked CEMA/IOA Copolymers using two different crosslinkers and various crosslinker concentrations

Xerogel composition of (CEMA/IOA)	Crosslinker content (Wt %)	SF of crosslinked gel in Toluene (%)	
		AM	MM
90/10	1.0	17.94	17.41
70/30	1.0	13.83	13.16
50/50	0.5	11.67	10.31
	1.0	6.41	5.51
	2.0	5.40	4.70
	4.0	4.24	3.95
30/70	1.0	4.32	3.15
10/90	1.0	4.37	3.57

3.2.2.2 Thermal characteristics of crosslinked CEMA-alkyl acrylate copolymers

The thermal stability of crosslinked CEMA/ODA copolymers was assessed with initial decomposition temperature (IDT). Thermogravimetric (TG) is a technique to determine weight continuously while heating a sample. Several degradation schemes are proposed for crosslinked polymers based on the principles of the cleavage of simple ethers and the products obtained from the pyrolysis study **[Menard, 2000, Lucas et al., 2001]**. In the present study, TG was used to determine SF values of crosslinked copolymers when the samples were subjected to TG analysis before extraction of SF. The thermal data obtained by TGA for crosslinked CEMA/ODA copolymers were listed in **Tables (3.6-3.9)**. The data of TGA include initial degradation temperature (IDT), 10% weight loss temperature (T_{10}%) and residuum at 600°C (Y_{600}°C). Careful inspection of the thermogram plots, **figure (3.7)**, of crosslinked CEMA/ODA copolymers show two degradation steps, suggesting the coexistence of more than one degradation process whereas; the crosslinked polymers have only one degradation step. The lower temperature loss may be due to the breaking of ester linkages present in the networks, and the second one to the degradation of the crosslinked polymers. This behavior indicates the unextracted SF of linear polymers have different thermal characteristics than that crosslinked by both MAA_m and MMA_m crosslinkers. Accordingly, the determined weight loss values from 25 to 350 °C can be correlated with that determined from Soxhlet extraction method. Careful inspection of data listed in **Table (3.3)** and **Tables (3.6-3.9)** indicates that the good agreement between SF values determined from Soxhlet extraction and thermal decomposition at

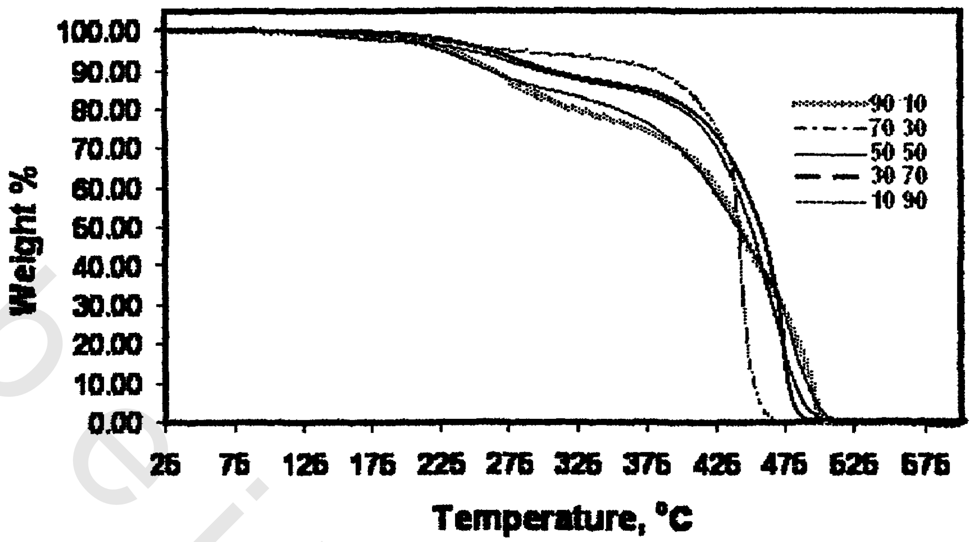


Figure (3.7): TGA curves of CEMA/ODA crosslinked copolymers with different molar ratios for 1 % MMA_m crosslinker.

Table (3.6): Thermal Gravimetric Data of Crosslinked CEMA/ODA at Different Mole Ratios using 1% MMA_m Crosslinker

Mol. Ratios of Crosslinked (CEMA/ODA)	Steps		Weight Loss (%)	IDT (°C)	T_{10}% (°C)	Y_{600} (%)
	Start Temp (°C)	End Temp (°C)				
90/10	0	350	22.87	145.7	260.6	0.74
	350	450	34.02			
	450	600	42.37			
70/30	0	350	20.03	129.5	257.1	0.60
	350	450	36.04			
	450	600	43.33			
50/50	0	350	14.24	115.9	295.2	0.57
	350	450	36.23			
	450	600	48.96			
30/70	0	350	13.59	170.6	300.7	0.30
	350	450	42.21			
	450	600	43.90			
10/90	0	350	7.61	129.8	378.1	0.12
	350	450	80.26			
	450	600	12.01			

Table (3.7) : Thermal Gravimetric Data of Crosslinked CEMA/ODA 50/50 Mol Ratios using different concentrations of MMA_m Crosslinker (0.5-4%)

Mol. Ratios of Crosslinked (CEMA/ODA)	Crosslinker Conc. Wt %	Steps		Weight Loss (%)	IDT (°C)	$T_{10}\%$ (°C)	Y_{600} (%)
		Start Temp (°C)	End Temp (°C)				
50/50	0.5	0	350	24.80	109	291.9	0.02
		350	450	26.90			
		450	600	48.28			
	1.0	0	350	14.24	115	295.2	0.57
		350	450	36.23			
		450	600	48.96			
	2.0	0	350	9.12	145	352.7	0.68
		350	450	36.10			
		450	600	54.10			
	4.0	0	350	8.20	182	355.6	0.80
		350	450	30.0			
		450	600	61.0			

Table (3.8): Thermal Gravimetric Data of Crosslinked CEMA/ODA at Different Mole Ratios using 1% MAA_m Crosslinker

Mol. Ratios of Crosslinked (CEMA/ODA)	Steps		Weight Loss (%)	IDT (°C)	T_{10}% (°C)	Y_{600} (%)
	Start Temp (°C)	End Temp (°C)				
90/10	0	350	27.93	98.4	218.6	0.83
	350	450	57.37			
	450	600	13.87			
70/30	0	350	24.98	105	192.4	0.68
	350	450	58.6			
	450	600	15.74			
50/50	0	350	19.52	150	266.2	0.63
	350	450	22.03			
	450	600	57.82			
30/70	0	350	13.59	164	287.3	0.37
	350	450	72.41			
	450	600	10.57			
10/90	0	350	13.59	175	302.9	0.2
	350	450	30.77			
	450	600	55.44			

Table (3.9): Thermal Gravimetric Data of Crosslinked CEMA/ODA 50/50 Mole Ratios using different concentrations of MAA_m Crosslinker (0.5-4%)

Mol. Ratios of Crosslinked (CEMA/ODA)	Crosslinker Conc. Wt %	Steps		Weight Loss (%)	IDT (°C)	T_{10}% (°C)	Y_{600} (%)
		Start Temp (°C)	End Temp (°C)				
50/50	0.5	0	350	28.50	122	223	0.31
		350	450	42.44			
		450	600	29.06			
	1.0	0	350	19.52	150	266.2	0.63
		350	450	22.03			
		450	600	57.82			
	2.0	0	350	14.21	167	280	0.70
		350	450	43.32			
		450	600	41.89			
	4.0	0	350	11.5	179	348	0.91
		350	450	36.0			
		450	600	51.6			

350°C. Careful inspection of data, **Tables (3.6-3.9)**, indicates that the thermal stability of crosslinked networks increases with increasing of ODA, crosslinker contents and the presence of MMA_m crosslinker. This can be attributed to increase of crosslinking densities of the crosslinked CEMA-ODA copolymers.

Thermal stability data of crosslinked CEMA/DDA and CEMA/IOA copolymers were determined from thermograms and listed in **Table (3.10-3.17)**. Careful inspection of data indicates that the thermal stability of the crosslinked copolymers increases with decreasing alkyl chain lengths, precentage of alkyl acrylate and crosslinker concentrations. This can be attributed to increase alkyl acrylate length increases the probability for thermal degradation.

3.2.2.3 Morphology of the crosslinked polymers

It is well known that, the porous network can be obtained by several techniques **[Zhu and Chen, 1995]** . Submicrometer-sized gel particles respond to the external stimuli more quickly than bulk gels **[Flory, 1953]**. Networks having dangling chains can be easily expand or collapse upon an external stimulus because one side of the dangling chain is free **[Odian, 1981]**. The network having an interconnected pore structure can be formed through the polymerization below lower critical solution temperature and then elevating the temperature above it **[Takahashi and Kuno, 1991]**. It is now well understood that a phase separation during the network formation process is mainly responsible for the formation of porous structure in dried state. In order to obtain macroporous structure, a phase separation must occur during the course of the crosslinking process so that the two-phase structure is fixed by the formation of additional crosslinks.

Table (3.10): Thermal Gravimetric Data of Crosslinked CEMA/DDA at Different Mole Ratios using 1% MAA$_m$ Crosslinker

Mol. Ratios of Crosslinked (CEMA/ODA	Steps		Weight Loss (%)	IDT (^oC)	T_{10}% (^oC)	Y_{600} (%)
	Start Temp (^oC)	End Temp (^oC)				
90/10	0	350	21.71	85.8	258	1.13
	350	450	36.98			
	450	600	40.18			
70/30	0	350	17.37	91.6	274	0.93
	350	450	37.77			
	450	600	43.93			
50/50	0	350	10.77	130.9	314	0.86
	350	450	14.20			
	450	600	74.17			
30/70	0	350	10.24	143.1	339	0.50
	350	450	47.67			
	450	600	41.59			
10/90	0	350	8.03	152.7	357	0.27
	350	450	19.83			
	450	600	71.87			

Table (3.11) : Thermal Gravimetric Data of Crosslinked CEMA/DDA 50/50 Mol Ratios but using different concentrations of MAA_m Crosslinker (0.5-4%)

Mol. Ratios of Crosslinked (CEMA/ODA)	Crosslinker Conc. Wt %	Steps		Weight Loss (%)	IDT (^oC)	$T_{10}\%$ (^oC)	Y 600 (%)
		Start Temp (^oC)	End Temp (^oC)				
50/50	0.5	0	350	15.93	106.5	263	0.42
		350	450	27.36			
		450	600	56.29			
	1.0	0	350	10.77	130.9	314	0.86
		350	450	14.20			
		450	600	74.17			
	2.0	0	350	9.89	145.7	330	0.96
		350	450	27.92			
		450	600	59.69			
	4.0	0	350	9.67	156.0	410	1.24
		350	450	24.56			
		450	600	64.53			

Table (3.12): Thermal Gravimetric Data of Crosslinked CEMA/DDA at Different Mole Ratios using 1% MMA$_m$ Crosslinker

Mol. Ratios of Crosslinked (CEMA/ODA	Steps		Weight Loss (%)	IDT (°C)	T_{10}% (°C)	Y_{600} (%)
	Start Temp (°C)	End Temp (°C)				
90/10	0	350	19.97	150	272	0.98
	350	450	31.03			
	450	600	48.02			
70/30	0	350	15.93	160	315	0.81
	350	450	19.07			
	450	600	64.19			
50/50	0	350	9.94	164	361	0.75
	350	450	28.06			
	450	600	61.25			
30/70	0	350	8.76	176	376	0.44
	350	450	28.24			
	450	600	62.56			
10/90	0	350	6.98	188	425	0.24
	350	450	24.02			
	450	600	62.76			

Table (3.13) : Thermal Gravimetric Data of Crosslinked CEMA/DDA 50/50 Mol Ratios using different concentrations of MMA_m Crosslinker (0.5-4%)

Mol. Ratios of Crosslinked (CEMA/ODA)	Crosslinker Conc. Wt %	Steps		Weight Loss (%)	IDT (°C)	T_{10}% (°C)	Y_{600} (%)
		Start Temp (°C)	End Temp (°C)				
50/50	0.5	0	350	15.32	133	250	0.66
		350	450	26.68			
		450	600	57.34			
	1.0	0	350	9.94	164	361	0.75
		350	450	28.06			
		450	600	61.25			
	2.0	0	350	8.82	183	396	0.83
		350	450	23.18			
		450	600	67.17			
	4.0	0	350	7.54	200	406	0.96
		350	450	21.55			
		450	600	70.04			

Table (3.14): Thermal Gravimetric Data of Crosslinked CEMA/IOA at Different Mole Ratios using 1% MMA_m Crosslinker

Mol. Ratios of Crosslinked (CEMA/ODA	Steps		Weight Loss (%)	IDT (°C)	T_{10}% (°C)	Y_{600} (%)
	Start Temp (°C)	End Temp (°C)				
90/10	0	350	17.38	100.1	249	1.86
	350	450	31.62			
	450	600	49.14			
70/30	0	350	16.64	119.5	297	1.40
	350	450	28.76			
	450	600	54.6			
50/50	0	350	8.72	135	348	1.06
	350	450	27.28			
	450	600	62.94			
30/70	0	350	7.1	151	363	0.9
	350	450	53.6			
	450	600	38.4			
10/90	0	350	4.9	200	400	0.88
	350	450	37.4			
	450	600	56.82			

Table (3.15): Thermal Gravimetric Data of Crosslinked CEMA/IOA 50/50 Mol Ratios using different concentrations of MMA_m Crosslinker (0.5-4%)

Mol. Ratios of Crosslinked (CEMA/ODA)	Crosslinker Conc. Wt %	Steps		Weight Loss (%)	IDT (°C)	$T_{10\%}$ (°C)	Y_{600} (%)
		Start Temp (°C)	End Temp (°C)				
50/50	0.5	0	350	13.32	129	333	0.98
		350	450	36.68			
		450	600	49.02			
	1.0	0	350	8.72	135	348	1.06
		350	450	27.28			
		450	600	62.94			
	2.0	0	350	7.66	155	353	1.14
		350	450	24.34			
		450	600	66.86			
	4.0	0	350	6.53	175	403	1.98
		350	450	24.47			
		450	600	67.02			

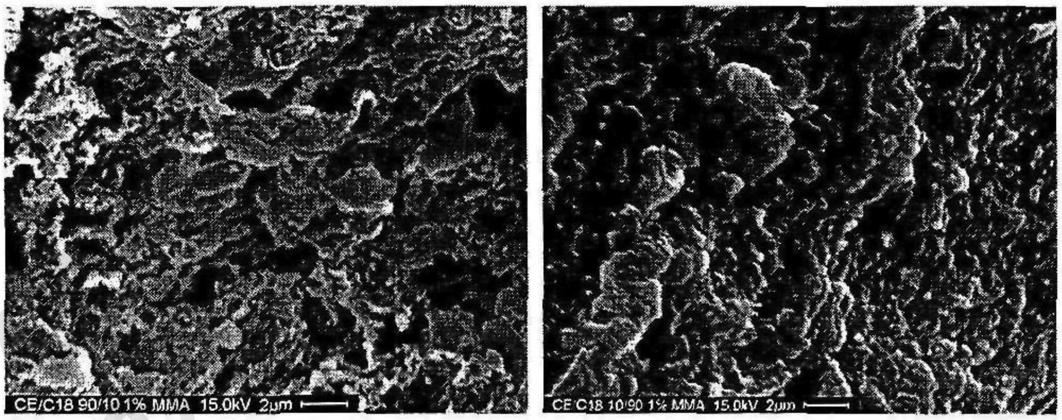
Table (3.16): Thermal Gravimetric Data of Crosslinked CEMA/IOA at Different Mole Ratios using 1% MAA_m Crosslinker

Mol. Ratios of Crosslinked (CEMA/ODA)	Steps		Weight Loss (%)	IDT (°C)	T_{10}% (°C)	Y_{600} (%)
	Start Temp (°C)	End Temp (°C)				
90/10	0	350	18.88	96.5	230	2.12
	350	450	45.02			
	450	600	33.98			
70/30	0	350	18.01	115	279	1.89
	350	450	45.07			
	450	600	34.33			
50/50	0	350	11.18	130	319	1.45
	350	450	46.27			
	450	600	41.1			
30/70	0	350	9.10	145.6	330	0.98
	350	450	43.1			
	450	600	46.82			
10/90	0	350	6.28	192.8	368	0.9
	350	450	41.72			
	450	600	51.1			

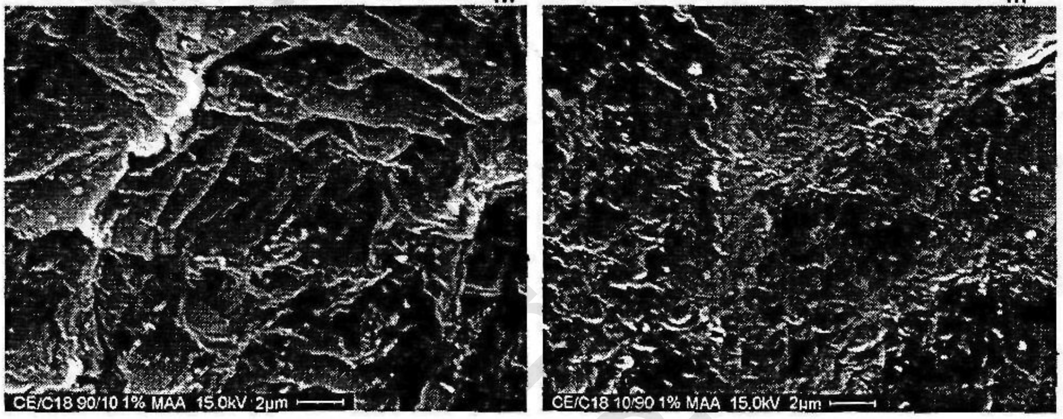
Table (3.17): Thermal Gravimetric Data of Crosslinked CEMA/IOA 50/50 Mole Ratios using different concentrations of MAA_m Crosslinker (0.5-4%)

Mol. Ratios of Crosslinked (CEMA/ODA)	Crosslinker Conc. Wt %	Steps		Weight Loss (%)	IDT (^{o}C)	T_{10}% (^{o}C)	Y_{600} (%)
		Start Temp (oC)	End Temp (oC)				
50/50	0.5	0	350	17.08	124.80	305	1.34
		350	450	40.53			
		450	600	41.05			
	1.0	0	350	11.18	130	319	1.45
		350	450	46.27			
		450	600	41.1			
	2.0	0	350	9.82	149.42	324	1.56
		350	450	40.98			
		450	600	47.64			
	4.0	0	350	8.37	168.70	369	2.71
		350	450	40.63			
		450	600	48.29			

Depending on the synthesis parameters, phase separation takes place on a macroscale or on a microscale. In the first case, when the networks start to form crosslinked structure, the network collapses at the critical point for phase separation and becomes a microsphere. Whereas the separated liquid phase remains as continuous phase in the reaction system. As the reaction proceeds, new microspheres are continuously generated due to the successive separation of the growing polymers. Agglomeration of microspheres leads to formation of a macroporous network consisting of two continuous phases. In the second state, phase separation results in the formation of a dispersion in the reaction system. Thus, the liquid phase during the gel formation process separates in the form of the small droplets inside the gel and become discontinuous. Due to slowness of the volume change of the gel sample, the initiator of the sample is initially under constant volume condition; further polymerization and crosslinking reactions fix the two phase structure in the final material. In the present system, two new crosslinkers were used to prepare porous crosslinked CEMA-Alkyl Acrylates networks. In this respect, the morphology of the prepared networks can be examined with a scanning electron microscope (SEM). The pore size was determined from the SEM picture. The SEM photos were selected for crosslinked CEMA (90 mol %)-ODA (10 mol %) and CEMA (10 mol %)-ODA (90 mol %) with both MMA_m and MAA_m crosslinkers were represented in **Figure (3.8),** to study the effect of copolymer composition and type of crosslinker on the porosity of the networks. While, the effect of crosslinker concentration on the porosity of the prepared CEMA-ODA can be examined from the photo that represented in **Figure (3.9).** Indeed, SEM shown in **figure (3.9)** illustrate the development of the heterogeneity in the networks depending on the crosslinker type and

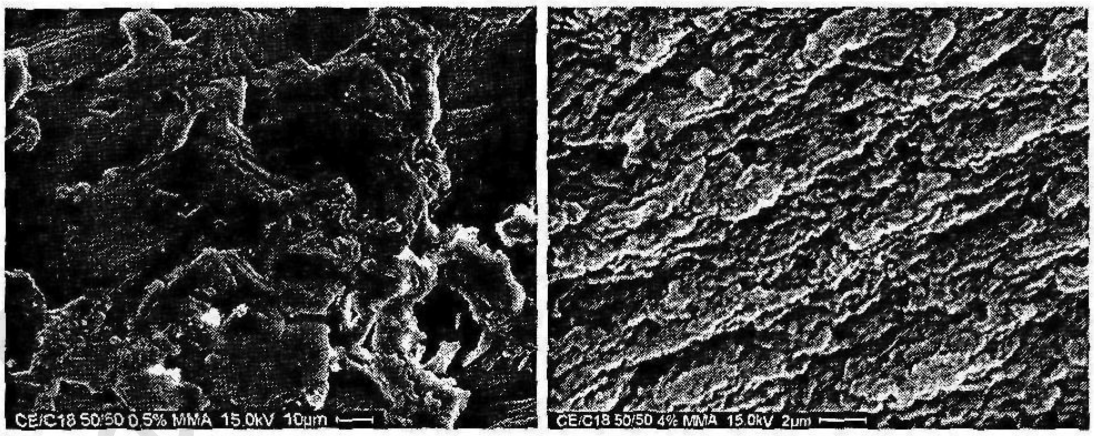


CEMA/ODA 90/10 1 % MMA_m CEMA/ODA 10/90 1 % MMA_m

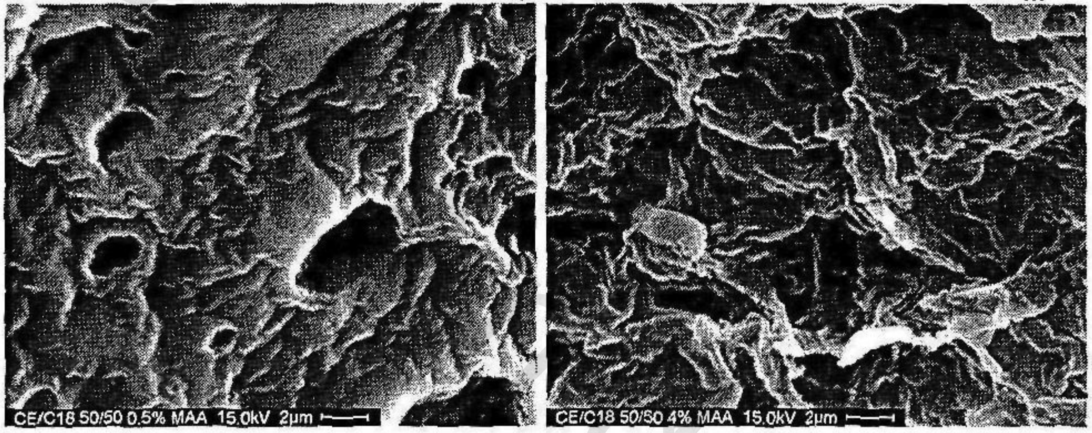


CEMA/ODA 90/10 1 % MAA_m CEMA/ODA 10/90 1 % MAA_m

Figure (3.8): SEM Images for CEMA/ODA



CEMA/ODA 50/50 0.5% MMA$_m$ CEMA/ODA 50/50 4% MMA$_m$



CEMA/ODA 50/50 0.5% MAA$_m$ CEMA/ODA 50/50 4% MAA$_m$

Figure (3.9): SEM Images for CEMA/ODA effect of crosslinker content. At 0.5 wt % of MMA_m, the network consists of large polymer domains; the discontinuities between the domains are also large. If the crosslinker content increase from 0.5 to 2 wt %, the morphology changes drastically and a structure consisting of aggregates of spherical domains appears. As the crosslinker content further increases from 2 to 4 wt %, the morphology changes from a structure of large aggregates of poorly defined microspheres to one consisting of aggregates of 1-2 µm dimensions of well defined microspheres. The microspheres are about 0.1-0.5 µm in diameter. The structure looks like cauliflowers, typical for a macroporous copolymer network. The SEM photographs of CEMA-ODA crosslinked with different weight ratios of MAA_m is different than that crosslinked with MMA_m. It was observed that, the large pores were formed at low MAA_m contents (0.5 wt %). These large pores converted to micropores when the MAA_m content increased up to 4 (wt %). As is known, the lower the concentration of monomer during the gel formation or the higher the crosslinker content, the more heterogeneous is the gel obtained. This behavior can be correlated with data of SF values that obtained from Soxhlet extraction **Table (3.3)** and TGA data **Table 3.6-3.9** which indicate that the crosslinked copolymers with MMA_m have lower SF values than that crosslinked with MAA_m. This can be attributed to increase crosslinking activity of CEMA-ODA with MMA_m than MAA_m crosslinker. SEM photographs, **Figure (3.9)**, indicate that large pores were formed with increasing CEMA content in copolymer when crosslinked with MMA_m crosslinker. While micropores were formed when ODA content was increased in crosslinked copolymers. This can be attributed to the high affinity of copolymer having high content of ODA towards crosslinking which agree with the data of SF values as listed in **Table 3.3**. Accordingly, we can propose the following scheme for the formation of heterogeneous and microsphere CEMA-ODA networks. When the polymerization is initiated by the decomposition of ABIN molecules, the primary radicals formed start to grow by adding the monomers of CEMA and ODA and the crosslinkers either MMA_m or MAA_m. Initially, the primary molecules contain CEMA-ODA, CEMA and ODA units, MMA_m or MAA_m units with two unreacted methacrylate or acrylate (i.e. with pendant vinyl groups) and MMA_m or MAA_m units involved in cycles. As the time goes on, more and more primary molecules are formed so that the intermolecular crosslinking reactions between he primary molecules may also occur during the polymerization.. previous works indicated that, however, importance of cyclization reactions in free radical crosslinking copolymerization **[Hozumi et al., 1992]**. Thus, cyclization clearly dominates over the intermolecular crosslinking reactions. Since every cycle reduces the coil dimension of the molecule as well as the solvent content inside the coil, the structure of the formed polymers is rather compact and can be considered as clusters. The higher the crosslinker contents, the higher is the cyclization density of the clusters. When the cyclization density of the clusters exceeds a critical value, they phase separate and form primary particles called microspheres of about 0.1-0.5 μm in diameter. The microsphere are nonporous and constitute the highly crosslinked region of the network. The agglomeration of the microspheres during crosslinking polymerization through their peripheral pendant vinyl groups and radical ends leads to the formation of large, unshaped, discrete agglomerates of 10-100 μm in diameter, which are further agglomerated to form the final network. Macropores constitute the interstices between the microspheres while the voids between the agglomerates build the large pores in CEMA/ODA network. The morphology of the crosslinked CEMA/DDA copolymers were observed using SEM. Figure (3.10) shows the fractured surfaces of crosslinked CEMA/DDA copolymer crosslinked with 4 wt% of MMAm crosslinker as representative sample. All CEMA/DDA copolymers have a smooth flat surface with some cracks, probably because of its tendency to be more rigid than CEMA/ODA copolymers. On the other hand SEM of crosslinked CEMA/IOA copolymers with different weight percentages of MAAm and MMAm crosslinkers were selected and represented in Figures (3.11) as representative samples. All SEM photographs show skin layer structure and possess homogenous wall-like texture. The formation of homogenous wall-like texture indicates that the crosslinked polymers cannot form porous structure in both crosslinked CEMA/DDA and CEMA/IOA copolymers. By comparing the data of CEMA alkyl acrylate reactivity ratios and SEM photographs, it can be concluded that increasing alkyl acrylate length (ODA) increases the incorporation of CEMA in copolymer composition which increases the porosity of the prepared networks. On the other hand, decreasing the chain lengths of alkyl acrylate (IOA) increases the incorporation of alkyl acrylate in the copolymerization which reflects on the formation of homogenous wall-like texture.

3.2.2.4. Elasticity of CEMA-ODA Networks

Comparing the reactivities of the CEMA and ODA monomers with MMAm or MAAm crosslinkers in free radical copolymerization, the crosslinkers reactivity is at least twice the CEMA and ODA reactivity due to the existence of three vinyl groups on each crosslinker molecule.

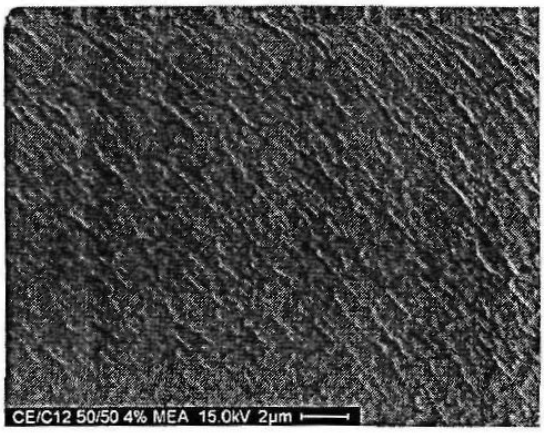
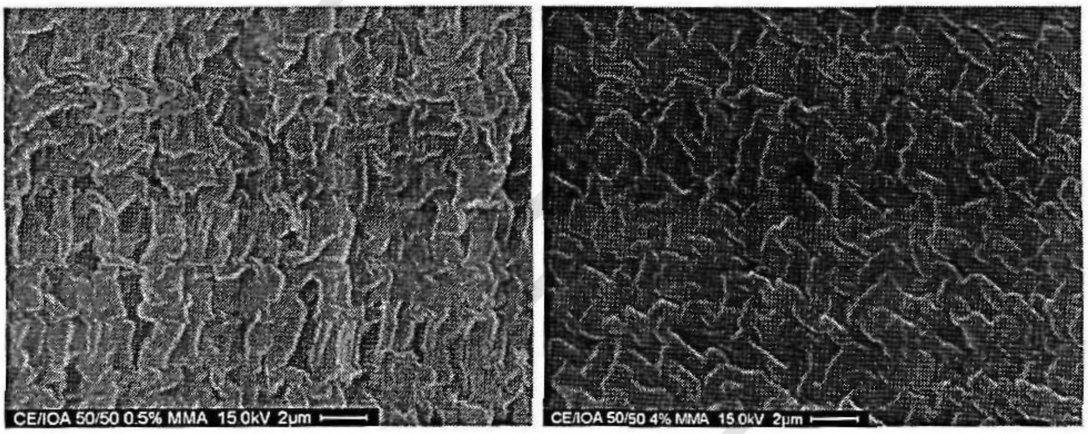
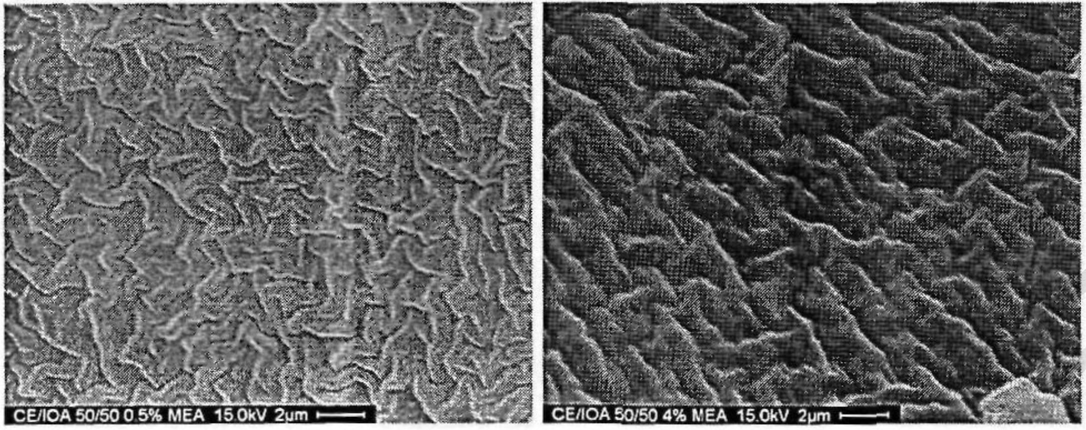


Figure (3.10): SEM Image of Crosslinked CEMA/DDA using 4% MMA_m



CEMA/IOA 50/50 0.5% MMA_m CEMA/IOA 50/50 4% MMA_m



CEMA/IOA 50/50 0.5% MAA_m CEMA/IOA 50/50 4% MAA_m

Figure (3.11): SEM Images of CEMA/IOA with Different Concentrations of MMA_m and MAA_m

Therefore, the molecules formed earlier should contain more MMAm or MAA_m units and therefore highly crosslinked than those formed later. Due to rapid consumption of MMA_m or MAA_m monomer during polymerization, the density of clusters will decrease as the monomer conversion increases and, at high conversion degrees, the structure of the clusters will approach to that of the primary molecules. Thus, the microspheres formed earlier (locating in the interior of agglomerates) probably form the highly crosslinked regions of the final material, which are interconnected with loosely crosslinked regions. The presence of these kinds of regions is well known as spatial inhomogenities which reflects on the rigidity of the networks. In the present work during the copolymerization processes there are three possibilities to form crosslinked copolymer of CEMA-ODA or homopolymers of CEMA and ODA. It is well known hat the behavior and the physical and chemical properties of copolymeric systems depends not only on the chemical compositions of these systems but also on the distribution of the units along the macromolecular chains (microstructure) and on the relative stereochemical configuration of side chains. In this sense, it would be of interest to analyze the influence of these factors on the rigidity or flexibility of the copolymers prepared. In this respect, the reactivity ratios and microstructure of CEMA-ODA copolymers should be analyzed. In previous work **[Atta et al., 2005]**, the reactivity ratios and microstructure of CEMA-ODA copolymers were determined. The data indicated that the prepared copolymer have random distribution sequence. The monomer reactivity ratios for the copolymerization of CEMA with ODA are 0.265 and 0.982, respectively. The product of reactivity ratio suggests a random distribution with longer sequences of ODA units in the copolymer chain. The data of SF values, listed in

Table (3.3), indicate that the crosslinking efficiency increases with increase crosslinker and ODA contents. this means that the formed networks have high crosslink densities when crosslinker and ODA contents were increased in the crosslinked polymers. Accordingly, the rigidity of copolymers increase with increasing crosslinking density of the prepared networks. These speculations can be proved from DMA measurements. The data of DMA were represented in **Figures (12-15)**. On the other hand, it was observed that the tan delta values decreases with incorporation of MAA_m instead of MMA_m in the network structure. This mean that the flexibility of the network increases with incorporation of MMA_m instead of MAA_m crosslinker. DiMarzio **[DiMarzio, 1990]**, has defined the flexibility need not be in the main backbone but can also be in the side groups. Thus, polymethacrylates would have a total of four flexible bonds per monomer unit, polyacrylates would have three flexible bond, but polystyrene would have only two, since the rotation of the benzene ring (CEMA) about the bond connecting it to the polymer backbone does not give a configurationally distinguishable position **[DiMarzio, 1990]**. According to the chemical structure of MMA_m and MAA_m crossklinkers, it can be concluded that the crosslinker based on methacryl group gives more flexible networks than that based on acrylate crosslinker. This observation in harmony with data of DMA of the crosslinked CEMA-ODA copolymers. It was observed that, the height of tan delta decreases with increasing both crosslinker and ODA contents. This fact is due to the strong dipolar interactions between polar groups which correspond to the side substituents and crosslink density of the polymeric chains. DMA of both crosslinked CEMA/DDA and CEMA/IOA copolymers were represented in **figures (3.16-3.23)**. The data indicate that the

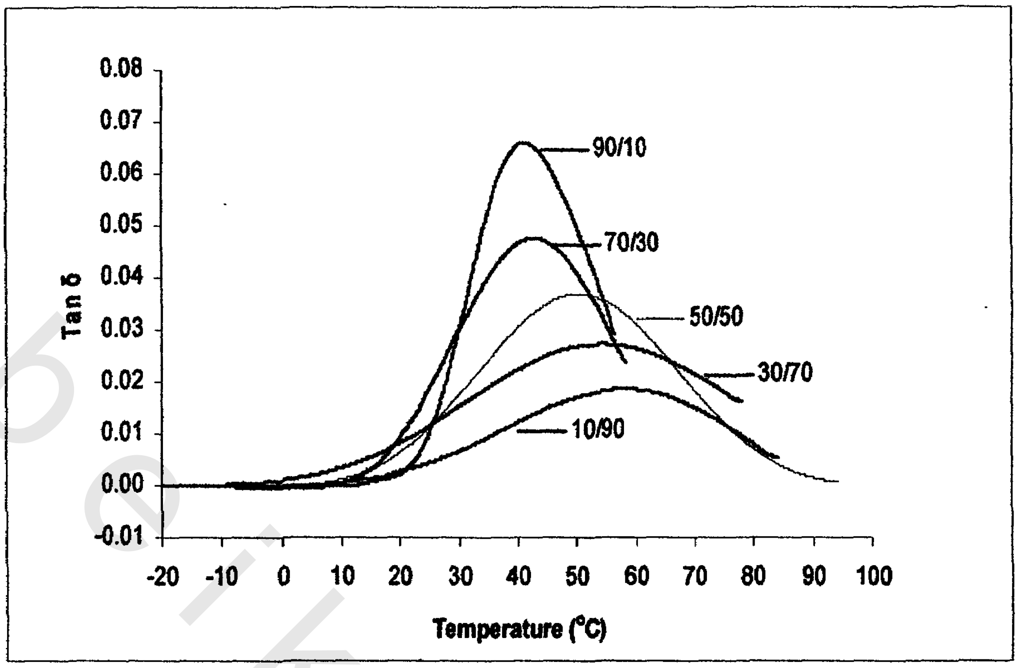


Figure (3.12): Tan δ vs. Temperature for Different Molar Ratios of Crosslinked CEMA/ODA with 1 wt. % of MAA_m crosslinker

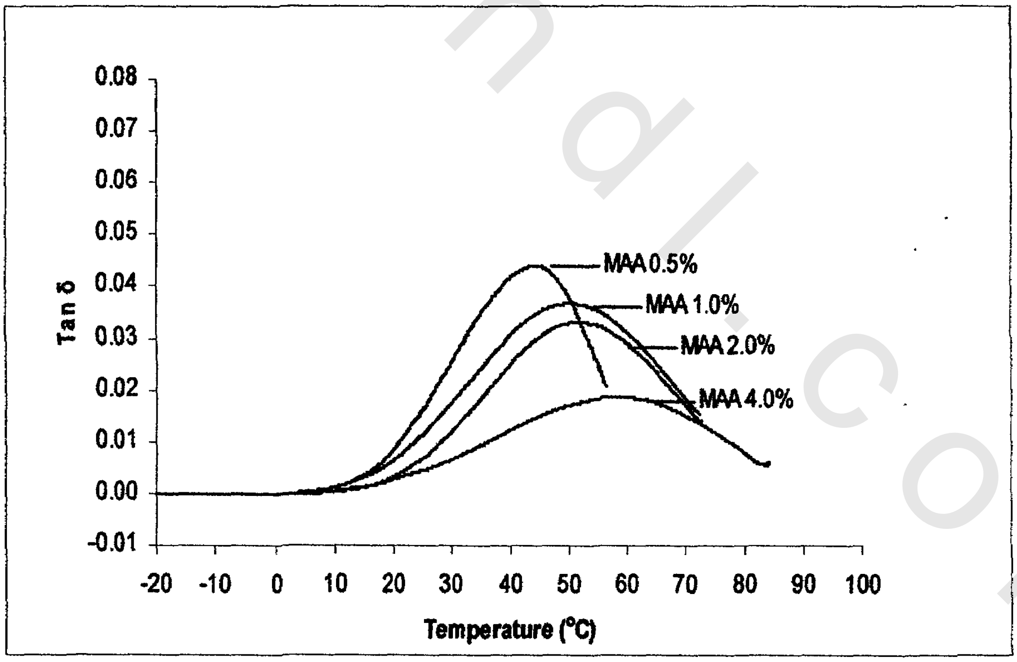


Figure (3.13) :Tan δ vs. Temperature for 50/50 Molar Ratio of Crosslinked CEMA/ODA at Different Concentrations of MAA_m crosslinker

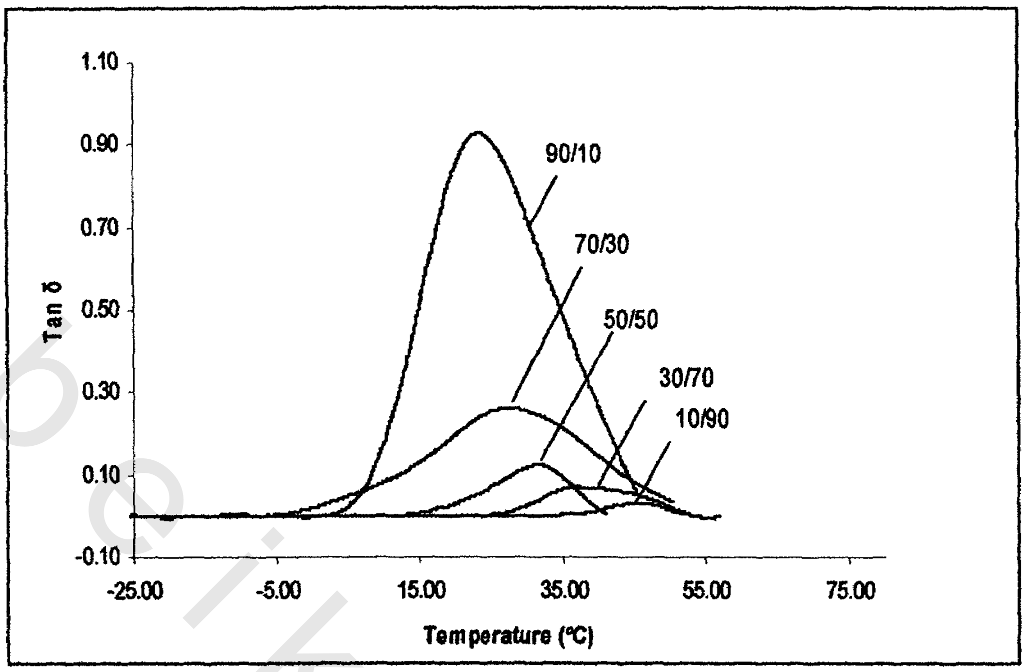


Figure (3.14): Tan δ vs. Temperature for Different Molar Ratios of Crosslinked CEMA/ODA with 1 wt. % of MMA$_m$ crosslinker

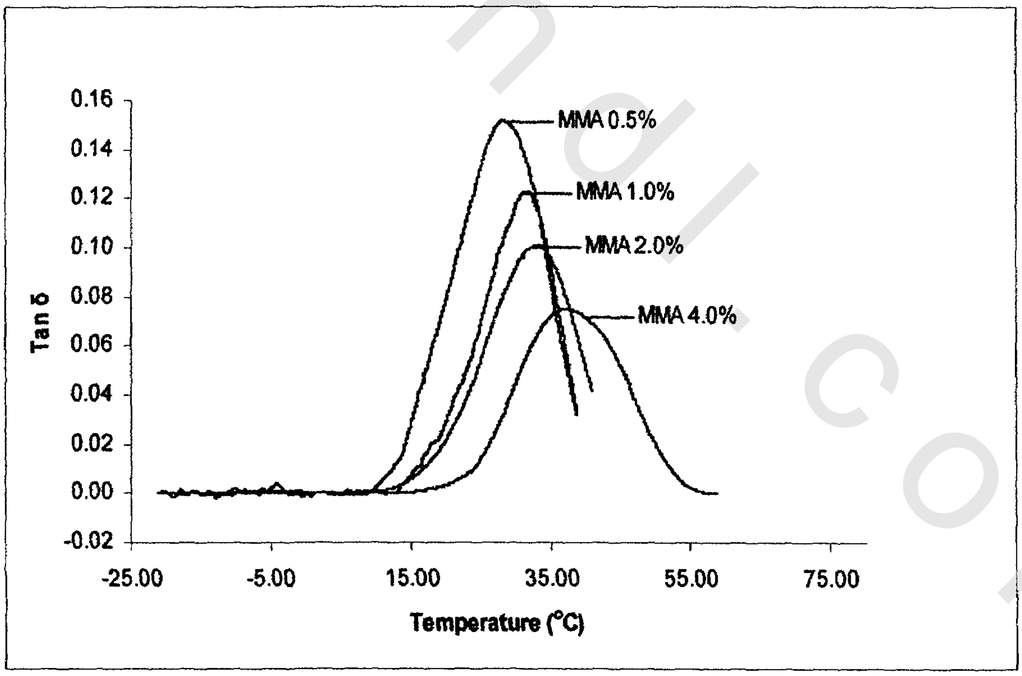


Figure (3.15): Tan δ vs. Temperature for 50/50 Molar Ratio of Crosslinked CEMA/ODA at Different Concentrations of MMA$_m$ crosslinker

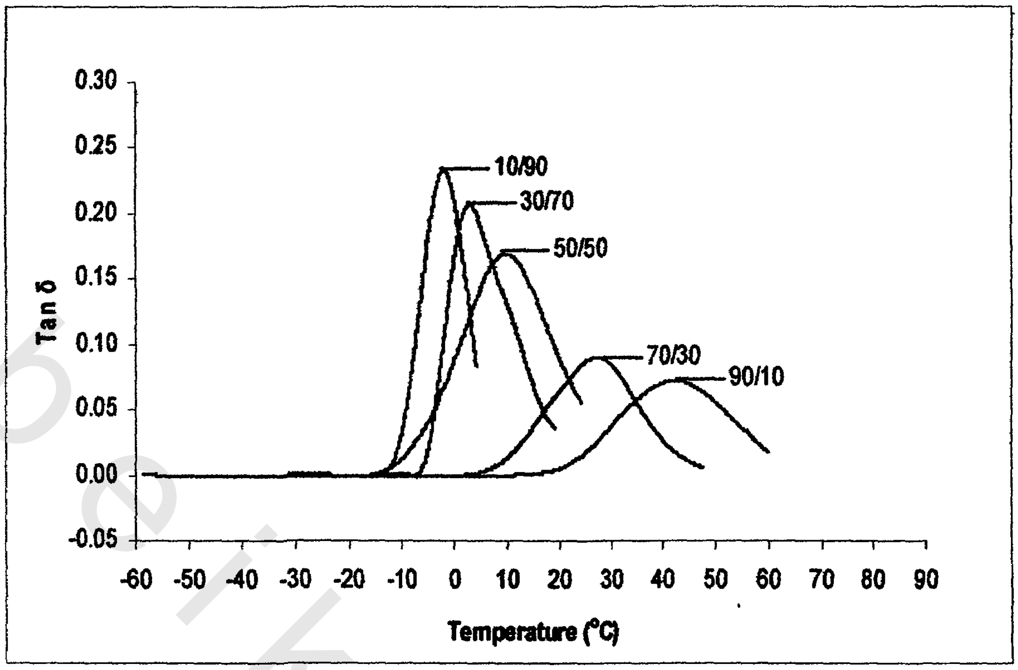


Figure (3.16) : Tan δ vs. Temperature for Different Molar Ratios of Crosslinked CEMA/DDA with 1 wt. % of MAA_m crosslinker

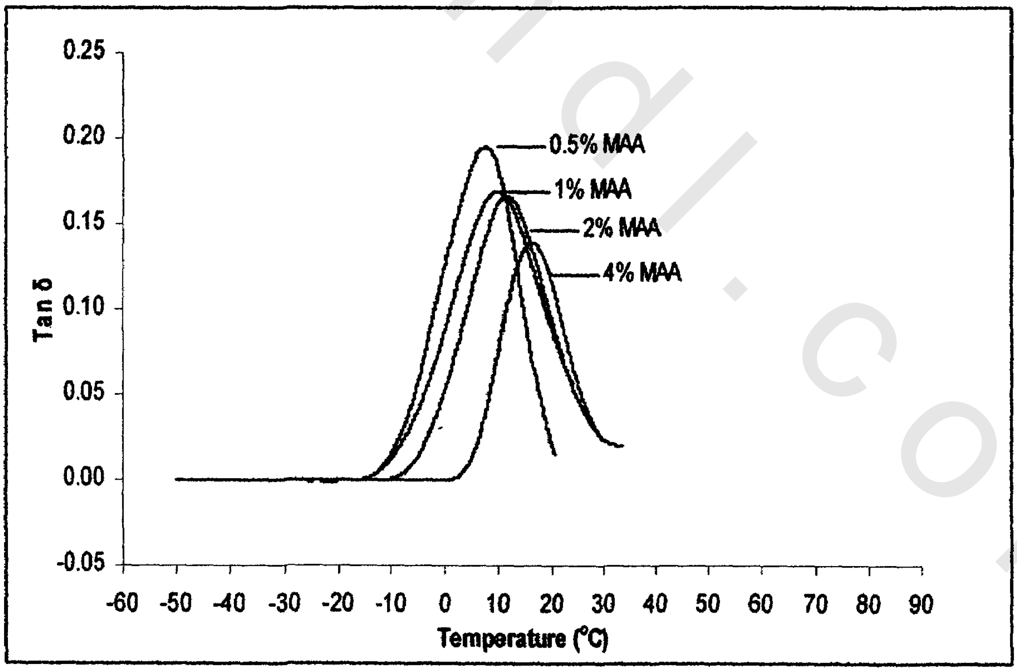


Figure (3.17) : Tan δ vs. Temperature for 50/50 Molar Ratio of Crosslinked CEMA/DDA at Different Concentrations of MAA_m crosslinker

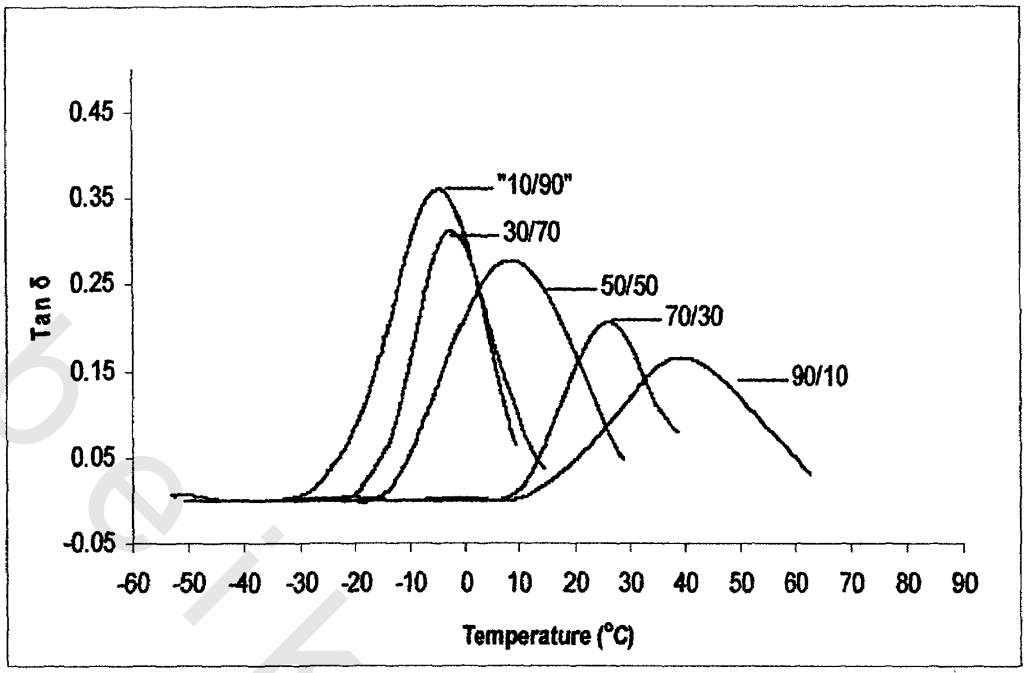


Figure (3.18): Tan δ vs. Temperature for Different Molar Ratios of Crosslinked CEMA/DDA with 1 wt. % of MMA_m crosslinker

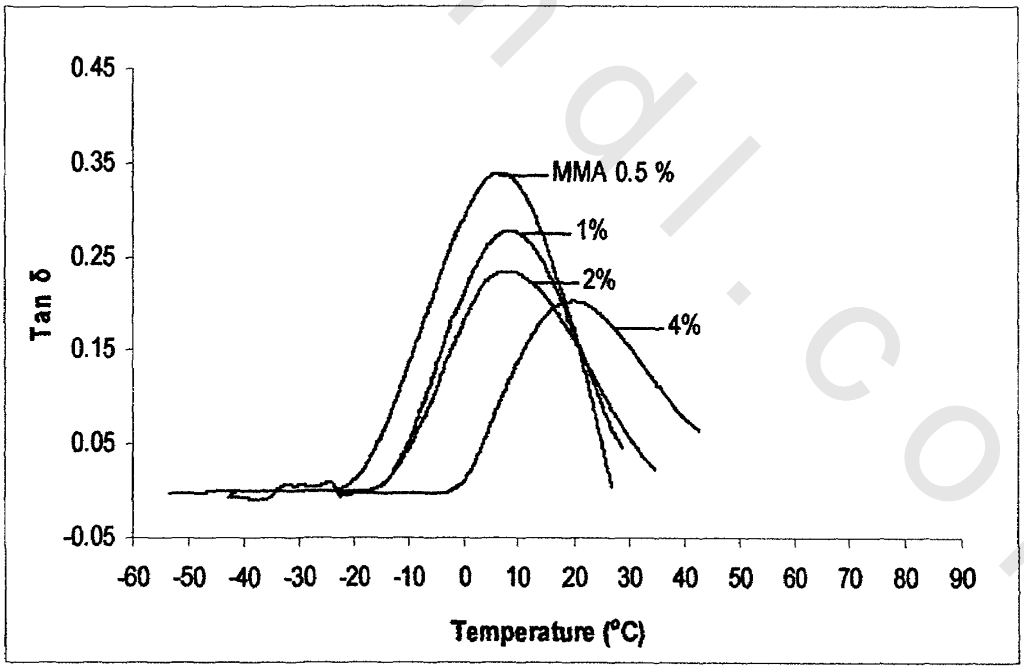


Figure (3.19): Tan δ vs. Temperature for 50/50 Molar Ratio of Crosslinked CEMA/DDA at Different Concentrations of MMA_m crosslinker

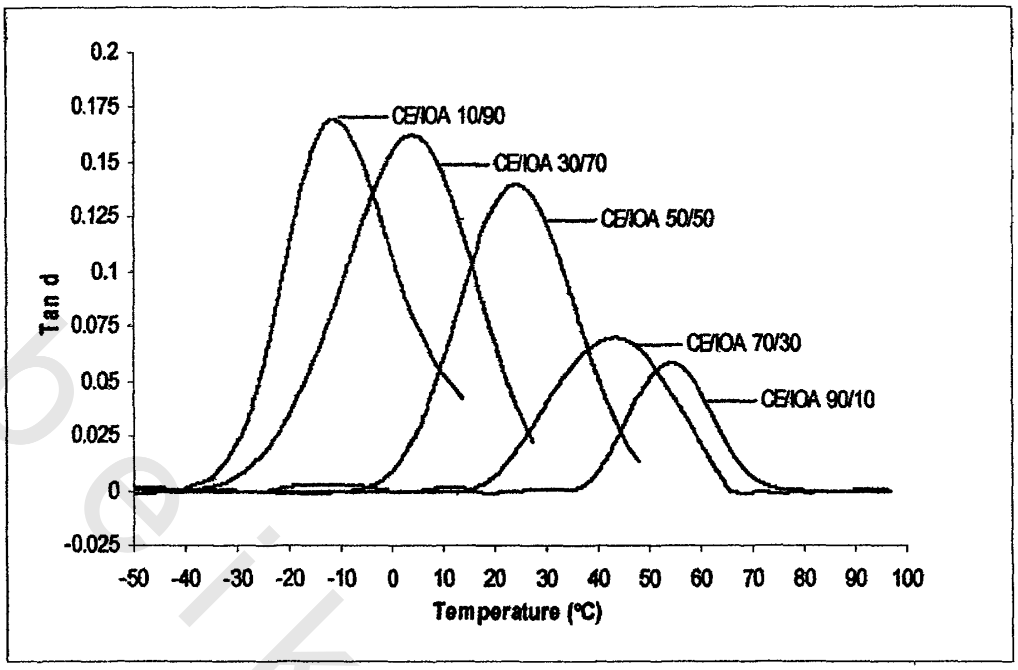


Figure (3.20): Tan δ vs. Temperature for Different Molar Ratios of Crosslinked CEMA/IOA with 1 wt. % of MAA_m crosslinker

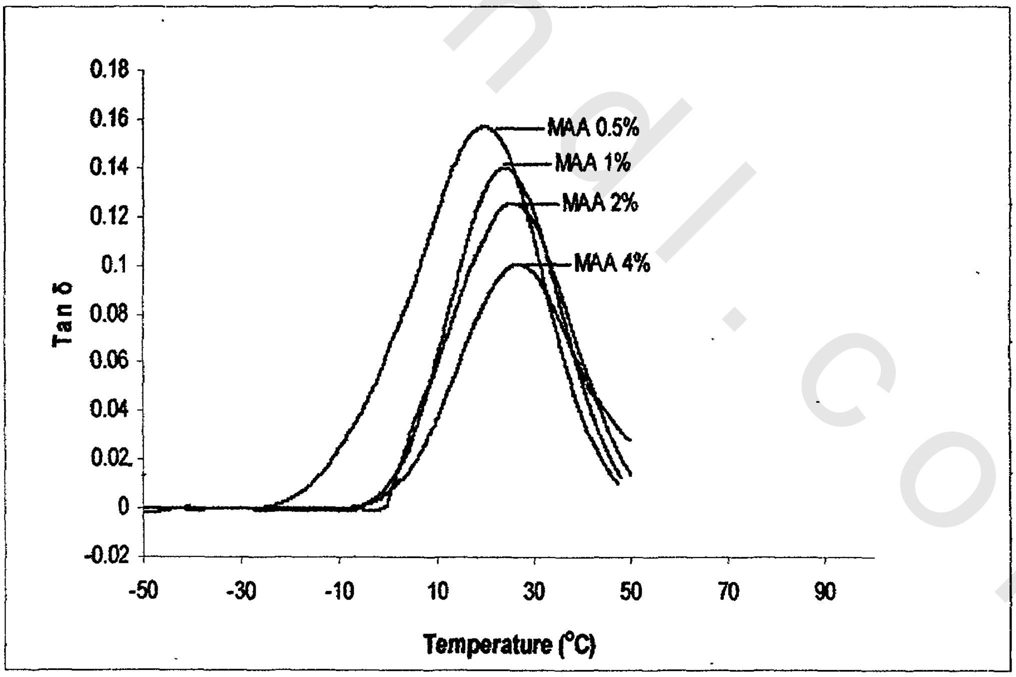


Figure (3.21): Tan δ vs. Temperature for 50/50 Molar Ratio of Crosslinked CEMA/DDA at Different Concentrations of MAA_m crosslinker

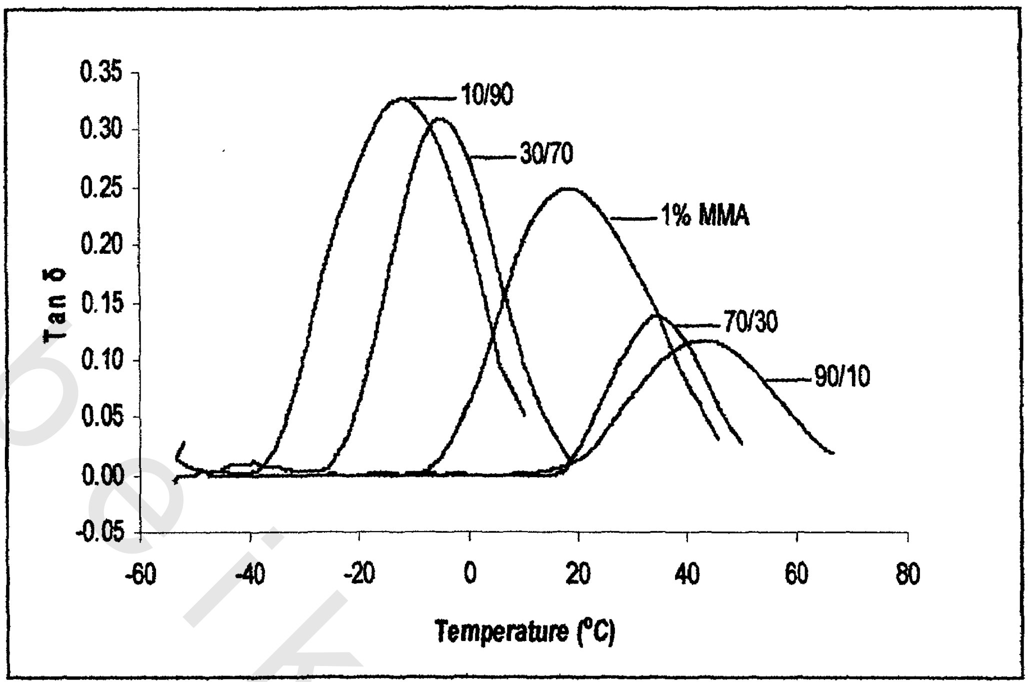


Figure (3.22) : Tan δ vs. Temperature for Different Molar Ratios of Crosslinked CEMA/IOA with 1 wt. % of MMA_m crosslinker

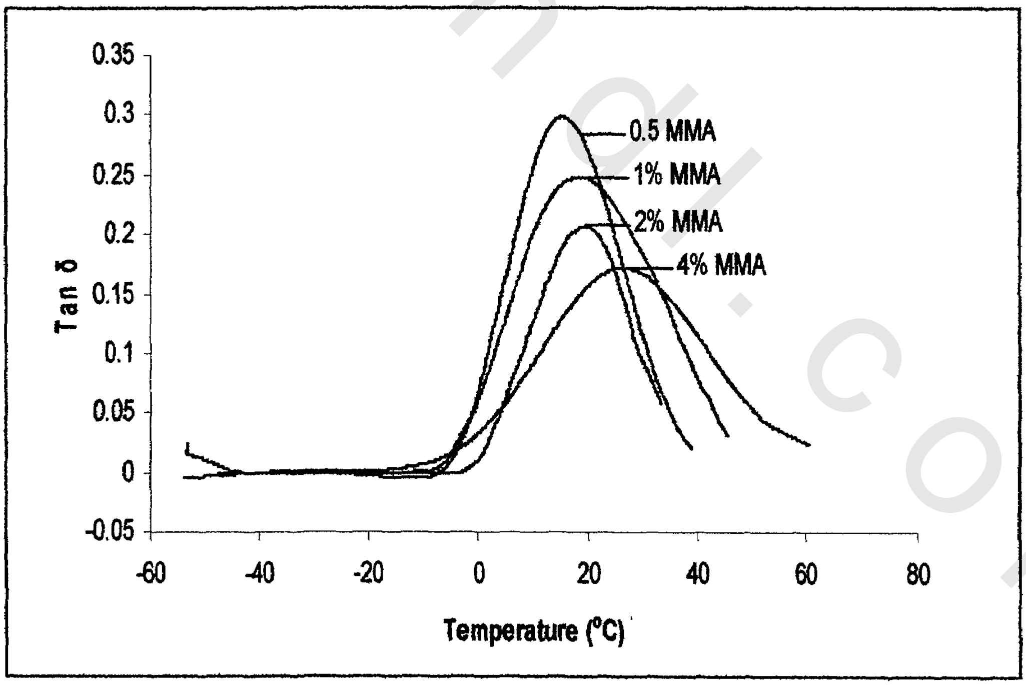


Figure (3.23): Tan δ vs. Temperature for 50/50 Molar Ratio of Crosslinked CEMA/IOA at Different Concentrations of MMA_m crosslinker

flexibility increased with increasing IOA or DDA content and decreasing crosslinker concentrations. It is well known that, the presence of long flexible n-alkyl substituents has a profound effect on flexibility of macromolecules, including polyacrylates and polymethacrylates **[Seung-Hyun et al., 1999]**. As the length of the n-alkyl side chain increases, flexibility increases within each of these families of polymers. This fact indicates that the introduction of the spacer group increases the flexibility of the repeating unit. In the present system, it can be expected that the introduction of the ODA gives rise to a drastic increasing of the flexibility of the polymer segments by decreasing the steric hindrance of the rigid aromatic side groups of CEMA when they are located near the polymer backbone. These facts disagree with the present copolymer system. This can be referred to the fact that, the crosslinking density is the only main factor that can control the degree of flexibility and rigidity of macromolecules.

3.3 CROSSLINKING OF CEMA/ALKYL ACRYLATE COPOLYMERS ONTO NWPET FIBER

Sorbents are materials that soak up liquids. They can be used to recover oil through the mechanisms of absorption, adsorption, or both, absorbents allow oil to penetrate into pore spaces in the materials they are made of while adsorbents attract oil to their surfaces but don't allow it to penetrate into the material. Sorbents are most often used to remove final traces of oil or in areas that cannot be reached by skimmers. Once sorbents have been used to recover oil, they must be removed from the water and properly disposed or cleaned for re-used. Any oil that is removed from sorbent materials must also be properly disposed or recycled. Synthetic sorbent products can be classified into three classes:

polymers, natural materials and treated cellulosic materials. The most often used polymers are polypropylene, polyethylene, polypropylene booms and polyurethane foam, which have highly oleophilic and hydophobic properties and are the most widely used sorbents in the remediation of oil spills **[Zahid et al., 1972, Schrader, 1991]**. Polypropylene fiber **[Sun et al., 2004]** or non-woven fabrics **[Radetic et al., 2003, Wei et al., 2003]**, melt-blown polyesters and polyurthane foam sheets have been used. But these have a serious disadvantage of bulkiness that is, inconvenient shipping and storage. To resolve this disadvantages, an oil-recovery machine was designed, which takes advantage of an on-site foaming method **[Shimizu et al., 1997]**.

The existing oil absorbents polypropylene fiber or fabrics, melt-blown polyesters, polyurethane foam sheets, and so on, have unsatisfactory oil absorbing capability. What is worse, they have difficulty in shipping and storage because of their bulkiness. To overcome these disadvantages, a new concept in manufacturing oil absorbents was suggested. Prior to manufacturing, compressed sponge like materials, base materials with high oil absorption capability, were prepared by copolymerization.

Initiating polymerization by radiation curing is beneficial as it reduces the need for volatile organic solvents, and allows temporal control of initiation and is also more rapid than thermal polymerisation. However, it is difficult and expensive to undertake photopolymerisation in an environment free of molecular oxygen, a well-known inhibitor of free radical polymerisation. Many photosensitive polymers which can be crosslinked by UV light irradiation have been attracting academic and industrial interest because of their oil absorptivity **[Nagamatsu et al., 1979, McGinnes, 1982, Tazuke, 1982, McGinnes, 1979, Green et al.,**

1981, Temiv, 1982]. The polymers containing cinnamoyl moiety can be transformed to a crosslinked structure by UV light irradiation **[Paczkowski, 1996]**. The cinnamate derivatives have been studied for a long time because of their photochemical importance. From the aspect of the photochemistry, for cinnamic acid and cinnamate esters, which have been investigated widely, the [2π + 2 π] photocycloaddition on UV light irradiation occurs at wavelengths over 290 nm, whereas the formed cyclobutane ring is preferentially cleaved to regenerate cinnamate at wavelengths below 260 nm **[Minsk et al., 1959 and Robertson et al., 1959]**. In addition to reactions involving two cinnamate moieties, cinnamates undergo facile *trans–cis* photoisomerization **[Nakayama and Matsuda, 1992]**.

Crosslinking via photodimerization of polymeric systems has been utilized in various applications, such as in paint, adhesive, printing, dental industries, and photoresists **[Green et al., 1981, Temin, 1982, Ichimura and Nisho, 1987 and Cha et al., 1986]**. In spite of the explosive development of photocrosslinking systems, there have been few reports on the preparation of a photocrosslinked poly(stearyl methacrylate-co-cinnamoyloxyethyl methacrylate) (PSCMA) to absorb oil **[Seung-Hyun et al., 1999]**. The aim of this work was to synthesize new oil-absorptive polymers containing the cinnamoyl moiety which can be crosslinked by UV light irradiation. In this respect, CEMA copolymers were photocrosslinked by UV light irradiation onto PET fiber. On the other hand thermal crosslinking of CEMA, alkyl acrylates and crosslinkers were obtained onto nonwoven PET fiber as described in the experimental section. The chemical structures of the prepared copolymers were determined from 1HNMR analyses as described in previous work **[Atta et al., 2005]**. In the present system, the photografting and crosslinking reaction of CEMA/ODA copolymer (50 mol% / 50 mol %) onto NWPET fiber can be illustrated in **Figure (3.24a).** The reaction scheme of photocrosslinking of CEMA, IOA, DDA, ODA and MAA_m or MMA_m monomers onto NWPET fiber was illustrated in **Figure (3.24b).** The reaction mechanism suggests that the cinnamoyl double bonds of CEMA moieties in the polymer or two molecules of CEMA and ODA undergo photochemically initiated dimerization. Since the photochemical reaction of CEMA/ODA should be crosslinked through the intermolecular photodimerization of the CEMA moieties in the polymer **[Hyder and Srinivasan, 1997]**. **[Fechine et al. 2004]** investigated the surface of photograted PET which is based on radical abstraction mechanism. It is well known that, the viscosity in the crosslinking reaction increases very rapidly to some extent as the reaction proceeds, and the reaction product begins to form an infinite molecular weight network called the gel point. In the gel state, chemical reaction can proceed and chains form the network by crosslinking. The crosslink density or degree of crosslinking is a measure of the total links between chains in a given mass of substance. In a crosslinking system, there are a soluble portion and an insoluble portion; the former can be extracted with suitable solvents and the latter cannot be extracted with any solvents due to crosslinking **[Flory, 1953, Shindo et al., 1989]**. In order to clarify, the amounts of soluble CEMA/ODA fractions can be determined from extraction technique using THF solvent. The data of SF measurements of photografting of CEMA, ODA and CEMA/ODA polymers onto NWPET fiber were measured and listed in **Tables (3.18 & 3.19).**

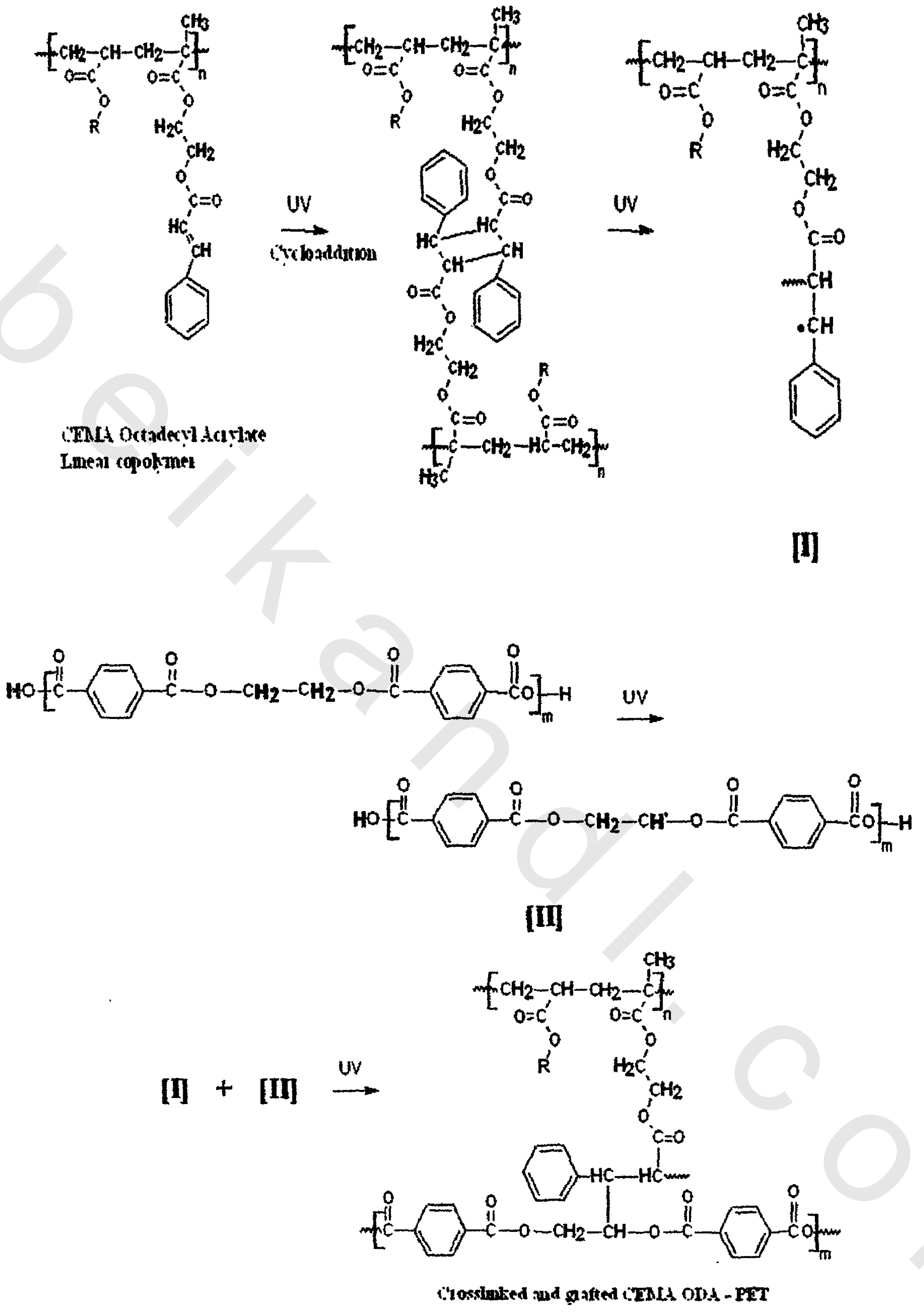


Figure (3.24a): Reaction Scheme of Photocrosslinking of CEMA/ Alkyl Acrylates linear copolymers onto NWPET Fibers

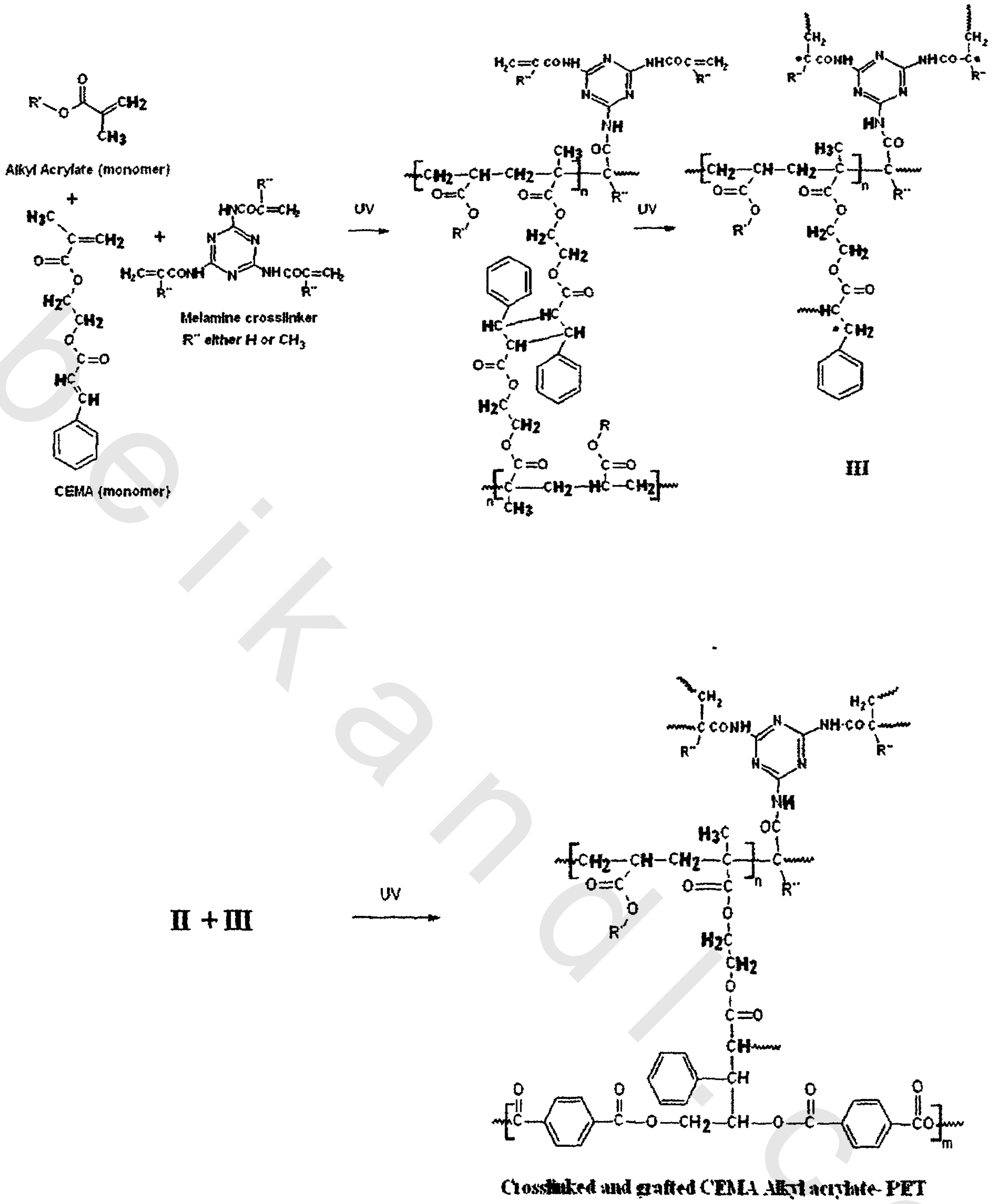


Figure (3.24b): Reaction Scheme of Photocrosslinking of CEMA and Alkyl Acrylates Monomers onto NWPET Fibers in Presence of Melamine Crosslinker

Careful inspection of data reveals that, the crosslinking ratio increased slowly using CEMA, ODA and MAAm or MMAm monomers in the feed. This reveals that the double bond of CEMA in the copolymer participates in the crosslinking **[Shindo et al., 1989, Kim et al., 1996]**. This suggests also that CEMA/ODA is a photocrosslinkable polymer and can be used as a photosensitive group for the preparation of crosslinked polymers.

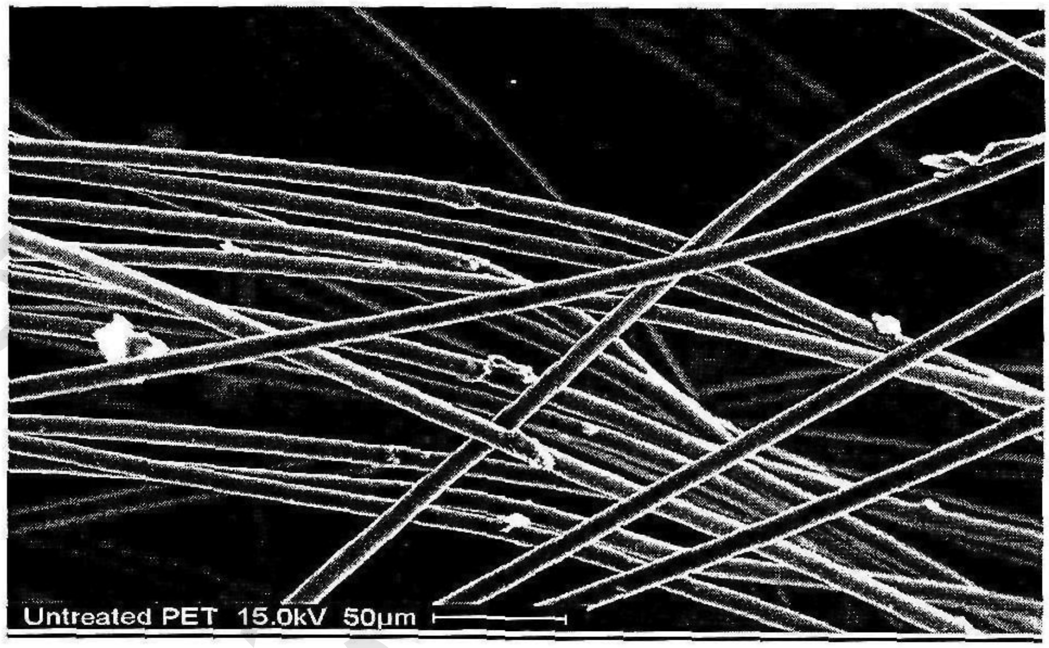
Morphology of the photografted and crosslinked NWPET with CEMA/ODA can be estimated by SEM. **Figure (3.25)** shows scanning electron micrograph of the untreated PET NWF. While scanning electron micrographs of NWPET treated with CEMA/ODA copolymers were represented in **figures (3.26–28)**. Figures show several distinct structures as follows: crossed staples in NWPET, CEMA/ODA incorporated into the crossed staples of NWPET and an extensive pore structure, which was formed by the extraction of uncrosslinked CEMA/ODA and evaporation of THF. Finally it can be concluded that, CEMA/ODA copolymers can be grafted and crosslinked onto NWPET

Table (3.18): The data of grafting ratio and SF measurements of photografted CEMA/ODA linear copolymers onto NWPET fiber

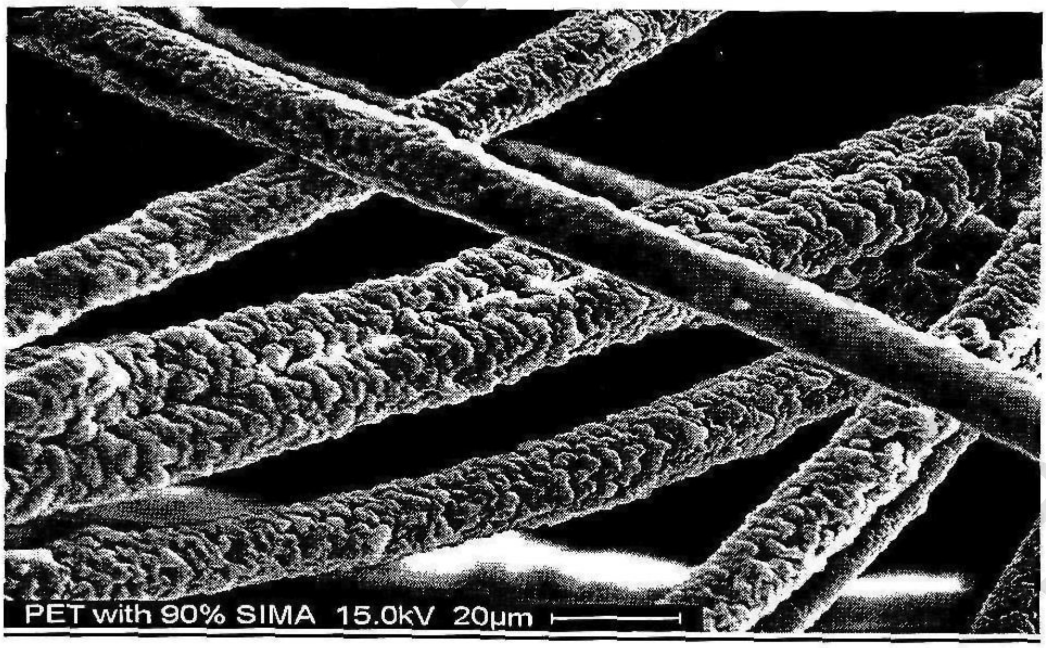
CEMA/ODA Composition	Grafting %	SF %
90/10	25	20
70/30	30	18
50/50	45	8
30/70	35	15
10/90	40	12

Table (3.19): The data of SF measurements of grafted and crosslinked CEMA/ODA monomers onto NWPET fiber in presence of MAA_m and MMA_m crosslinkers

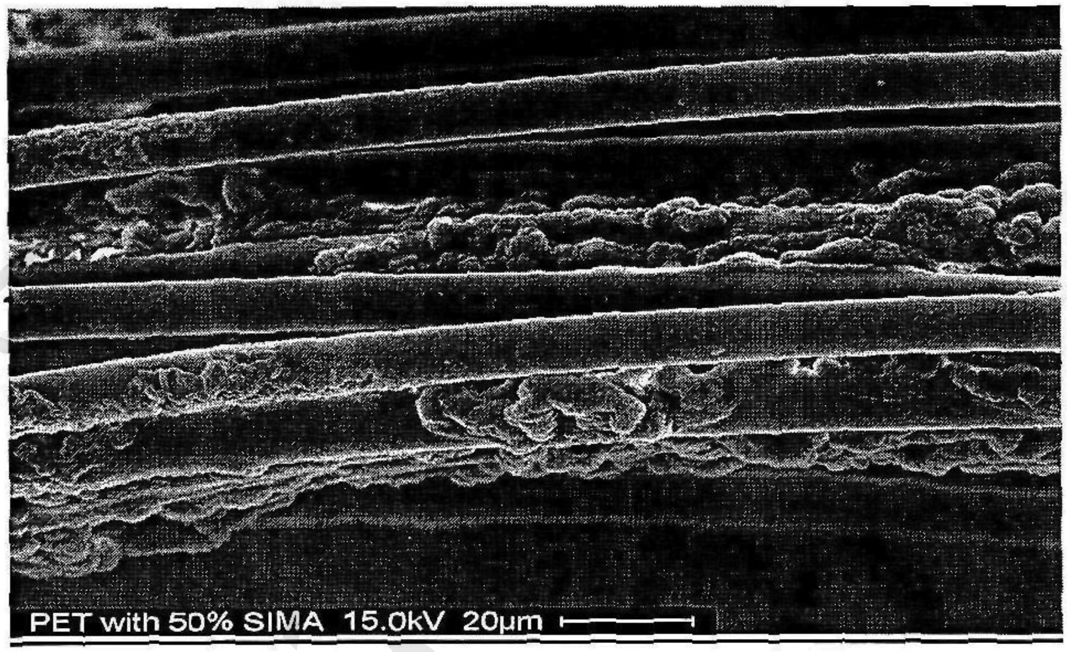
Crosslinker Content	Grafting Method	SF %					
		IOA		DDA		ODA	
		MAA_m	MMA_m	MAA_m	MMA_m	MAA_m	MMA_m
0.5	Thermal	14	12	18	16	20	18
	Photo	16	14	19	18	21	23
1	Thermal	12.3	10.5	15.4	12.1	18.2	15.4
	Photo	14.4	12.1	16.5	14.3	20.1	18.3
2	Thermal	10	9	12	10	14	13
	Photo	12	10	14	12	18	16
4	Thermal	8	7	10	9	12	11
	Photo	10	8	11	10	16	14



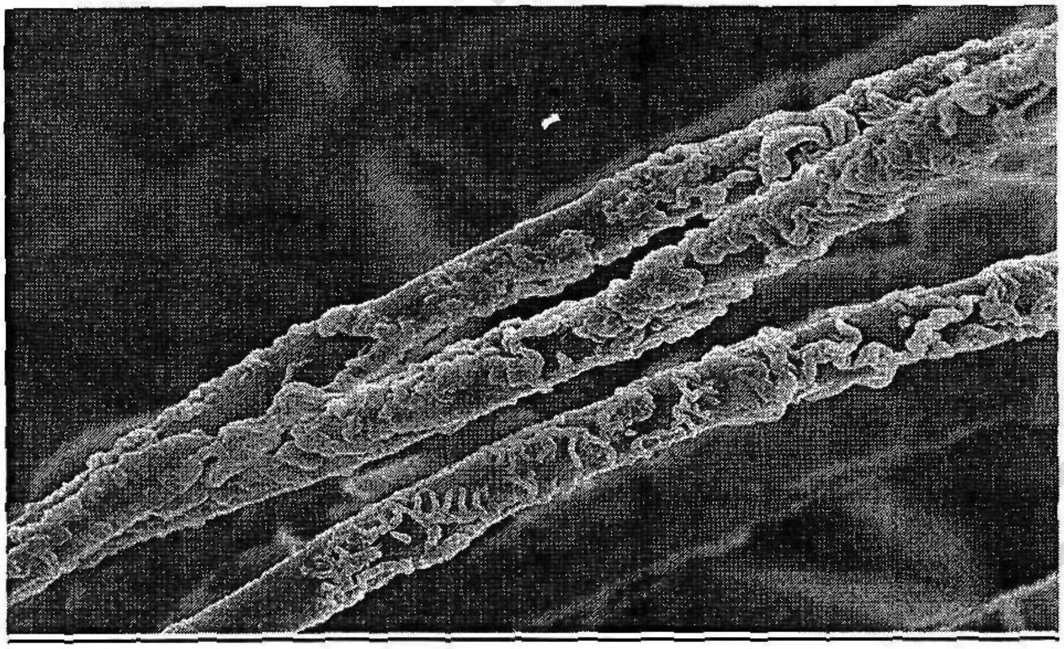
Figures (3.25): Scanning Electron Micrographs of untreated PET NWF.



Figuer (3.26): Scanning Electron Micrographs of PET NWF Treated with 90% CEMA / 10% ODA copolymer



Figuer (3.27): Scanning Electron Micrographs of PET NWF Treated with 50% CEMA / 50% ODA copolymer



Figuer (3.28): Scanning Electron Micrographs of PET NWF Treated with 10% CEMA / 90% ODA copolymer

3.4. SWELLING BEHAVIOR OF THE CROSSLINKED COPOLYMERS

Water preservation implies recovering oils and hydrocarbon oils from water, among other pollutants. Among the main existing techniques, the use of a sorbent seems to be interesting because its function is to induce separation of oil and water so that the oil can easily be recovered [Pete, 1992]. In this respect, the sorbent should have a high oleophilic and hydrophobic property. The sorption capacity is measured by the liquid sorption ratio. It is increased if the sorbent has the capability of drawing the oil into the material matrix, which implies a porous structure. Besides, the faster the oil is trapped, the less likely it will disperse and get away, and the easier the recover operation will be. Its buoyancy and durability in aqueous media are high; it should not retain water and react like a hydrophilic product. Its retention capability should also be high, so that the sorbed oil should not drain too quickly. It should rather be reusable and non-toxic for environment if not reused **[Browers, 1982, Deschamps et al., 2003]**.

It has been reported that, the excellent oil absorptivitiy of materials depends on the bulkiness and length of the alkyl substituents **[Takahashi and Kumo, 1991, Kim, et al., 1999]**, especially the porosity of the microstructure, which can be controlled by crosslinking. Because the driving force for oil absorption is caused mainly by Vander Waals forces between the material and the oil, therefore, the materials with the proper porosity can effectively contain oil in their structures.

The oil used in this experiment is diluted with toluene (10 %). For the real application to clean up an oil spill, the oil absorption test has to be operated using not only light or medium oil but also heavy oil, because the spilt crude oil has a high viscosity. On the other hand, the materials used to absorb the oil do not have a sponge like structure with open pores. It has only a network structure, which formed by the crosslinking reaction. Therefore, heavy oil with high viscosity, like Belayium crude oil, cannot easily diffuse from the surface of the samples into the internal space of network. On the other hand, toluene is the most applicable solvent that used to dissolve asphaltene of crude oil. For these reasons, we have used diluted crude oil with toluene in this experiment so that the swelling behavior of the samples could be easily evaluated. The swelling characteristics of crosslinked networks are controlled by a balance of opposing forces, swelling forces driven by osmotic pressure, and restoring forces from a variety of physical, covalent, or ionic crosslinks. The crosslinks are typically incorporated during the polymerization by the use of copolymerized multifunctional crosslinkers.

The characteristics of sorbents must be considered when choosing sorbents for cleaning up spills:

- Rate of absorption: the rate of absorption varies with the thickness of the oil. Light oils are soaked up more quickly than heavy ones.
- Oil retention: the weight of recovered oil can cause a sorbent structure to sag and deform, and when it is lifted out of the water, it can release oil that is trapped in its pores. Lighter, less viscous oils during recovery of absorbent materials.
- Ease of application, sorbents may be applied to spills manually or mechanically, using blowers or fans. Many natural organic sorbents that exist as loose materials, such as clay and vemiculite, are dusty, difficult to apply in windy conditions, and potentially hazardous if inhaled.

- Good absorption selectivity of oil over water
- Convenient shipping and storage
- Lower density compared to water to float with or without oil absorbed.

Polypropylene fiber **(Sun et al., 2004)** or non-woven fabrics **[Radetic et al., 2003, Wei et al., 2003]**, melt-blown polyesters and polyurthane foam sheets have been used. But these have a serious disadvantage of bulkiness that is, inconvenient shipping and storage. To resolve this disadvantages, an oil-recovery machine was designed, which takes advantage of an on-site foaming method **[Shimizu et al., 1997]**. In other word, two of polyurthane liquid components are transported to the site of the oil spill, and mixing the two components produces polyurthane foams. However, this method also has difficulty in moving the on-site foaming machine to the site of oil spill, and its shipping and storage are very inconvenient **[Jang and Kim, 2000]**.

From the previous discussion, the present works aims to investigate the following:

- Swelling characteristics of the new prepared copolymers based on introducing of new crosslinkers at different temperatures to study the temperature-sensitivy of organogels to reuse oil sorbers.
- Fast and reversible swelling and deswelling changes of these gels in response to oscillating quick temperature changes are also investigated.
- Swelling characteristics of the grafted and crosslinked polymers onto NWPET fiber were measured to produce applicable oil sorber.

3.4.1- Oil absorbencies for CEMA/IOA crosslinked copolymers

The swelling curve is based on plotting the relation between oil absorbancies versus immersion times. In this respect, upon using pure toluene, **Figures (3.29 & 3.30)** show the oil absorbencies for CEMA–IOA copolymers with different mol ratios of CEMA to IOA as a function of immersion time crosslinked by either MAA_m or MMA_m crosslinker respectively. **Figures (3.31 & 3.32)** show the oil absorbencies for CEMA–IOA copolymers with different compositions of CEMA to IOA as a function of immersion time upon using 10% crude as an oil medium crosslinked by either MAA_m or MMA_m crosslinker respectively. In these figures, it is obvious that the oil absorbency increases with increasing the immersion time and leveled off at 3h. Also, it is clear that, the higher the IOA content is the higher the oil absorbency. This may be explained on the basis that, the increase in acrylate ratio in the crosslinked copolymer will increase the hydrophibicity of crosslinked network. It is also observed that, the oil absorbency decreases slightly upon using 10% crude instead of pure toluene. This may be explained that the swelling process of polymer networks may be primarily due to the oil solution penetration into polymeric gel through capillary and diffusion. Therefore, crude oil with higher viscosity cannot easily diffuse from external surface of the sample into the internal space of networks **[Jang and Kim, 2000]**. **Figures (3.33-3.36)** represent the oil absorbencies of poly(CEMA – IOA) xerogels at 50/50 mol% of CEMA to IOA in the presence of different crosslinker contents immersed in pure toluene and 10% crude oil respectively. It is found that, the oil absorbency decreases with increasing the amount of MAA_m or MMA_m crosslinkers.

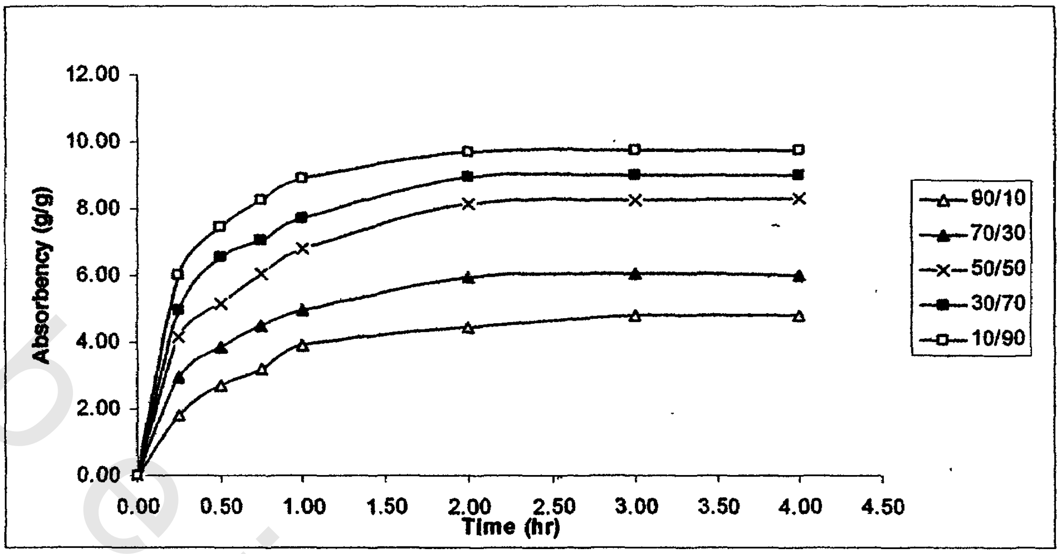


Figure (3.29): Oil Absorbency for CEMA-IOA Copolymer in Toluene with Different Mole Ratios of CEMA to IOA as a Function of Immersion Time Using 1wt% MAA_m at 298 K.

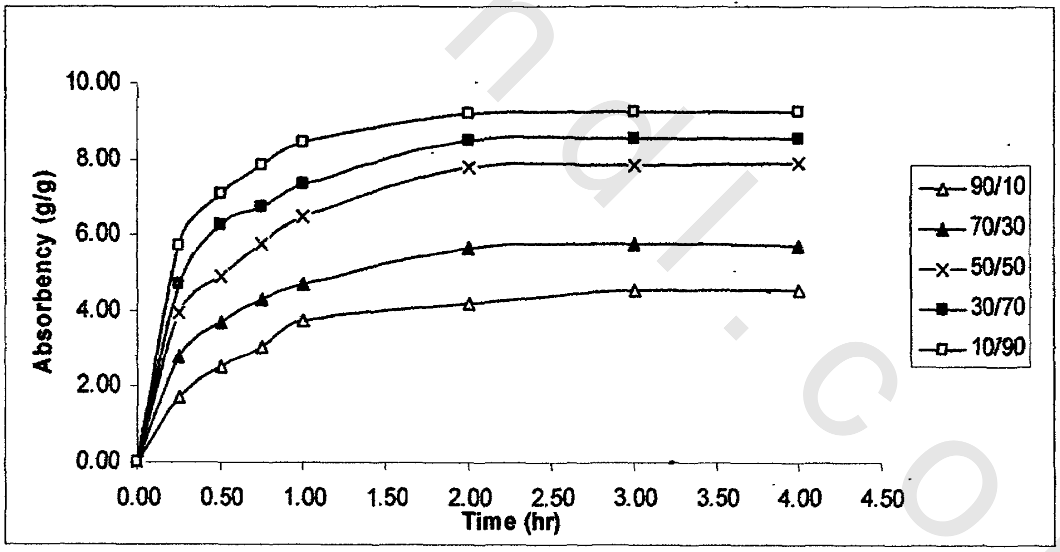


Figure (3.30): Oil Absorbency for CEMA-IOA Copolymer in Toluene with Different Mole Ratios of CEMA to IOA as a Function of Immersion Time Using 1wt% MMA_m at 298 K.

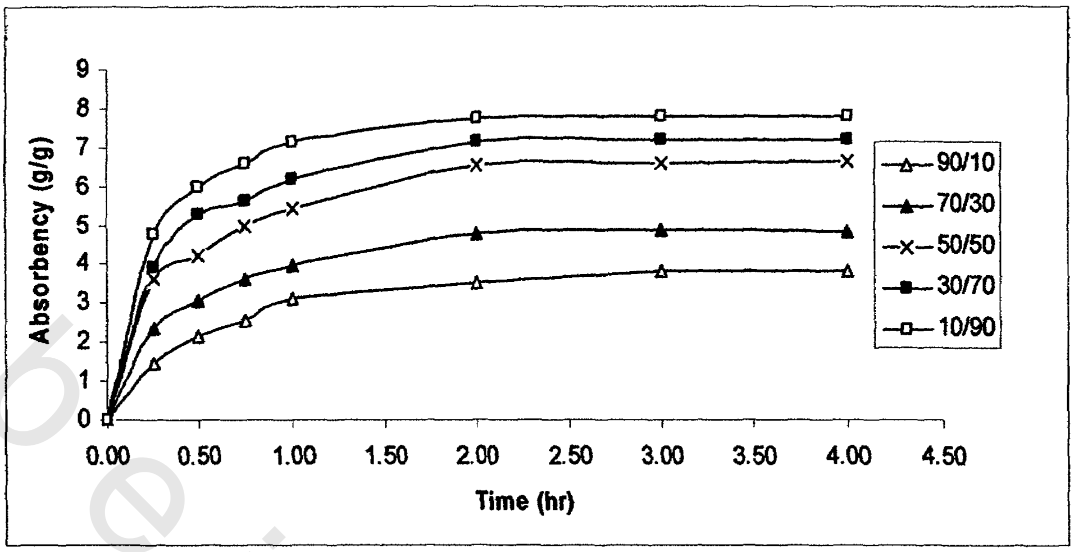


Figure (3.31): Oil Absorbency for CEMA-IOA Copolymer in (10% Crude Oil) with Different Mole Ratios of CEMA to IOA as a Function of Immersion Time Using 1wt% MAA_m at 298 K.

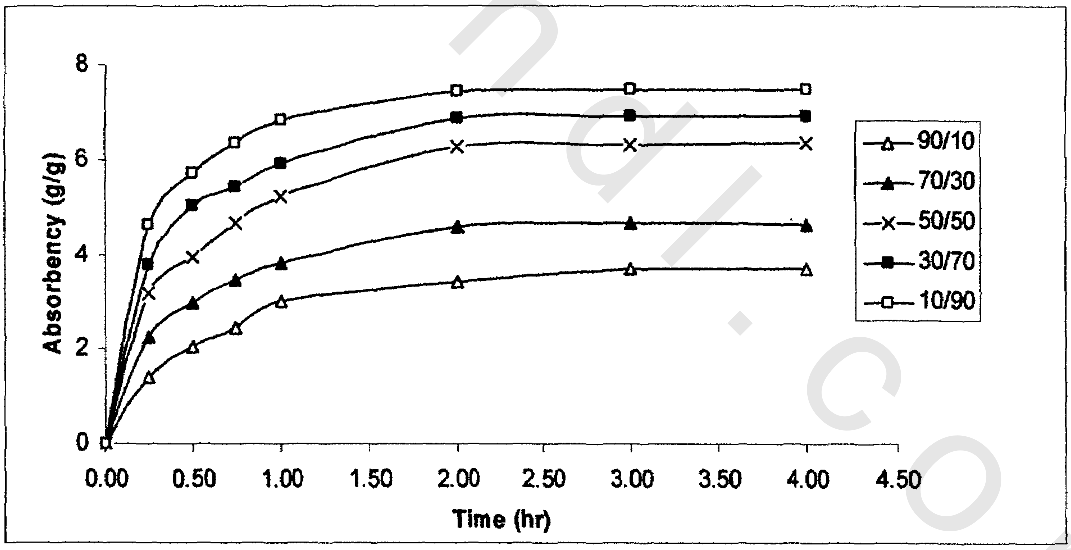


Figure (3.32): Oil Absorbency for CEMA-IOA Copolymer in (10% Crude Oil) with Different Mole Ratios of CEMA to IOA as a Function of Immersion Time Using 1wt% MMA_m at 298 K.

The increment in the amount of the crosslinking agent forms denser network of the copolymer and reduces M_c, (the average molecular weight between crosslinks **[Flory and Rehner, 1943]** i.e., restricted relaxation of the polymeric chain. Generally, the higher M_c decreases the swelling ratio **[peppas and Merrill, 1976]**. By comparing the maximum oil absorbency Q_{max} of poly(CEMA-IOA) crosslinked by MAA_m and those crosslinked by MMA_m, it is found that MAA_m crosslinked sorbers give higher Q_{max} than those of MMA_m based. This is mainly due to lower crosslinking density with MAA_m. **Tables (3. 20 a & b)** list absorption characteristics of the crosslinked CEMA–IOA copolymers upon using pure toluene or diluted crude oil medium respectively, different CEMA/IOA molar compositions and MAA_m or MMA_m crosslinker respectively. Careful inspection of the swelling data indicates that the oil uptake increased with increasing of IOA content. This can be attributed the increment of hydrophobic character of the gel with incorporation of IOA in the crosslinked network.

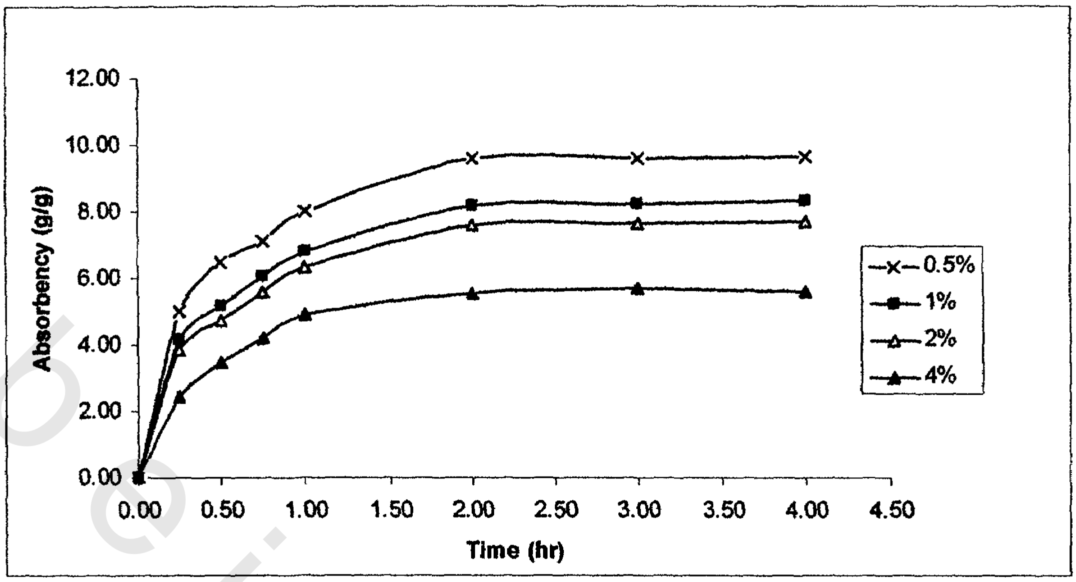


Figure (3.33): Oil Absorbency of CEMA-IOA Xerogels in Pure Toluene at 50/50 Mole% of CEMA to IOA as a Function of MAA_m Crosslinker wt% at 298K.

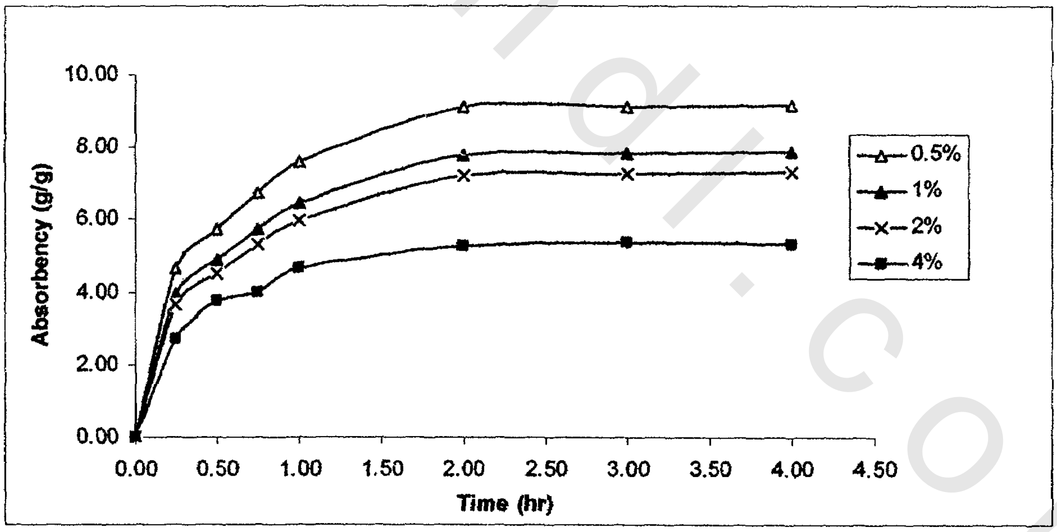


Figure (3.34): Oil Absorbency of CEMA-IOA Xerogels in Pure Toluene at 50/50 mole% of CEMA to IOA as a Function of MMA_m Crosslinker wt% at 298K.

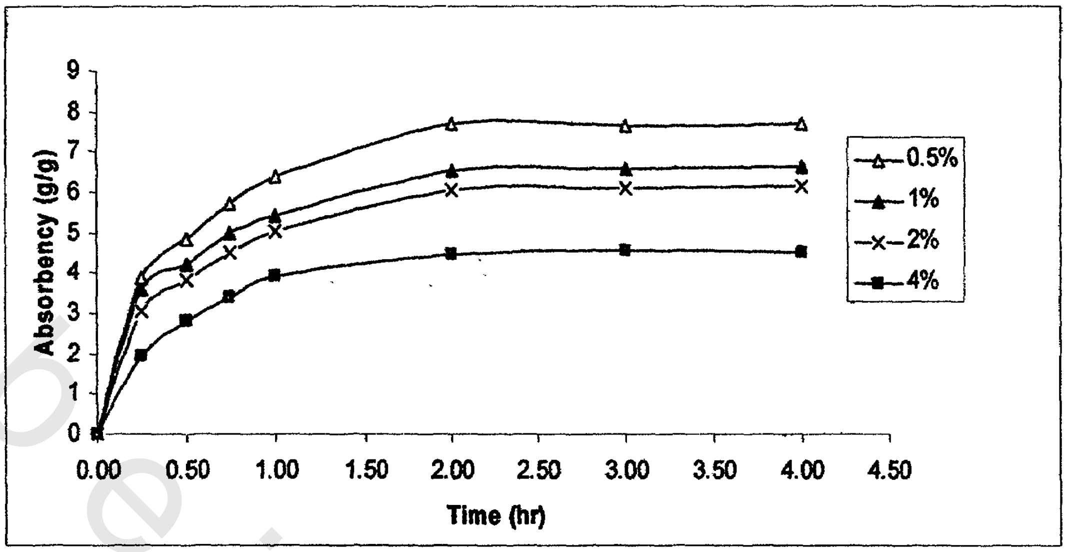


Figure (3.35): Oil Absorbency of CEMA-IOA Xerogels in 10 % Diluted Crude Oil at 50/50 Mole% of CEMA to IOA as a Function of MAA_m Crosslinker wt% at 298 K.

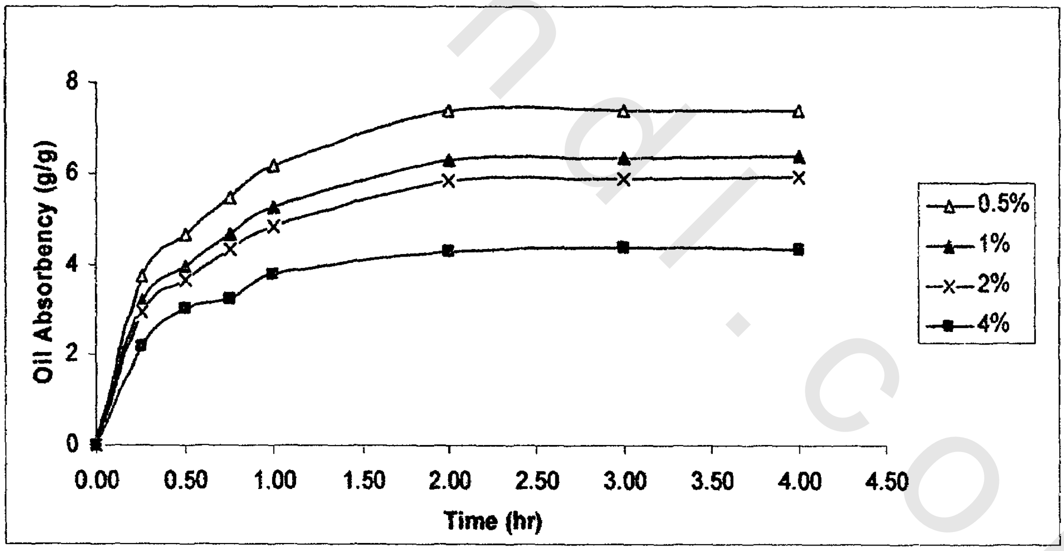


Figure (3.36): Oil Absorbency of CEMA-IOA Xerogels in 10 % Diluted Crude Oil at 50/50 Mole% of CEMA to IOA as a Function of MMA_m Crosslinker wt% at 298 K.

Table (3.20a): Absorption Characteristics of the CEMA/IOA Copolymers Crosslinked With MAA_m Crosslinker at 298 K.

Xerogel composition	Crosslinker content	Qmax (g/g)		ETC		Q (g/g)		T (h)		K (h-1)	
		Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil	Toluene	crude oil
90/10	1	4.80	3.84	79.17	73.96	3.03	1.82	0.66	0.67	1.515	1.492
70/30	1	6.01	4.81	83.36	79.20	2.28	2.28	0.50	0.51	2.020	1.960
50/50	0.5	9.61	7.69	89.59	86.99	3.65	3.65	0.42	0.49	2.380	2.040
	1	8.29	6.63	87.94	84.92	3.15	3.15	0.43	0.50	2.325	1.999
	2	7.67	6.14	86.96	83.70	2.91	2.91	0.51	0.52	1.960	1.922
	4	5.6	4.48	82.14	77.68	2.12	2.12	0.52	0.53	1.922	1.886
30/70	1	8.98	7.18	88.86	86.08	3.41	3.41	0.38	0.39	2.631	2.563
10/90	1	9.75	7.80	89.74	87.18	3.70	3.70	0.27	0.28	3.635	3.570

Table (3.20b): Absorption Characteristics of the CEMA/IOA Copolymers Crosslinked With MMA_m Crosslinker at 298 K.

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil
90/10	1	4.56	3.69	78.07	72.87	2.88	2.33	0.58	0.69	1.724	1.449
70/30	1	5.71	4.62	82.49	78.33	3.61	2.92	0.42	0.48	2.380	2.083
50/50	0.5	9.13	7.38	89.05	86.46	5.77	4.67	0.43	0.45	2.325	2.221
	1	7.88	6.37	87.31	84.29	4.98	4.02	0.44	0.46	2.272	2.173
	2	7.29	5.89	86.28	83.03	4.61	3.72	0.45	0.53	2.221	1.886
	4	5.32	4.30	81.20	76.75	3.36	2.72	0.48	0.54	2.083	1.851
30/70	1	8.53	6.89	88.28	85.50	5.39	4.36	0.30	0.36	3.332	2.777
10/90	1	9.26	7.49	89.20	86.64	5.85	4.73	0.25	0.28	3.999	3.570

3.4.2- Oil absorbencies for CEMA/ DDA or ODA crosslinked copolymers

The oil absorbencies of different compositions of CEMA/DDA and CEMA/ODA crosslinked copolymers as a function of immersion time upon using pure toluene and 10% crude as an oil medium were selected and represented in **Figures (3. 37-3.52)**. In these figures, it is observed that the oil absorbency increases with increasing the immersion time and attain the maximium swelling values during 3h for CEMA-DDA and CEMA-ODA copolymers. This indicates that, the swelling capacities are affected by the hydrophibicity and the crosslinking density of copolymers. Also, it is observed that the higher of the alkyl acrylate content is the higher the oil absorbency. This may be explained on the basis that, the increase in acrylate ratio in the crosslinked copolymer will increase the hydrophibicity of crosslinked network. It is also noticed that, the oil absorbency decreases slightly upon using 10% crude instead of pure toluene. This could be due to the higher viscosity of crude oil can cause two opposite effects: decrease of sorption as the penetration through interior of network is inhibited and improved sorption since the oil is better adhered to the material **[Choi and Cloud, 1992]**. This was noticeable in **Tables (3.21 & 3.22)** which list the absorption characteristics of the crosslinked (CEMA–DDA) and CEMA-ODA) copolymers respectively, upon using pure toluene or diluted crude oil medium respectively, different CEMA/ alkyl acrylate molar compositions and MAA_m or MMA_m crosslinkers. It is clear from theses tables that the sorption of (10% crude oil) has almost slightly increase in viscosity than pure toluene. Initially, a great amount of oil was sorbed to the material, but subsequently it was rapidly drained **[Radetic et al., 2003]**.

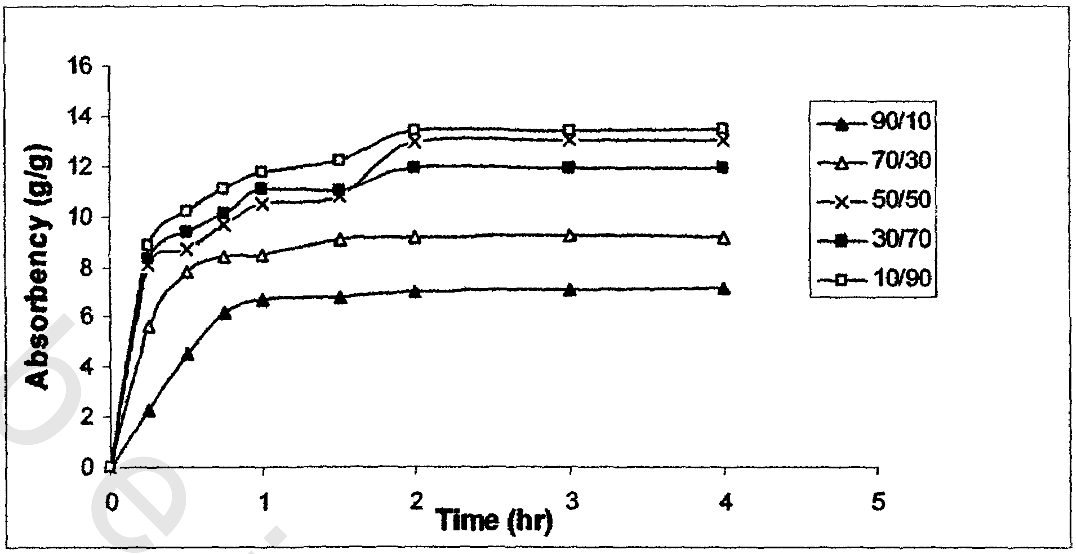


Figure (3.37): Oil Absorbency for CEMA-DDA Copolymer in Toluene with Different Mole Ratios of CEMA to DDA as a Function of Immersion Time Using 1wt% MAA$_m$ at 298 K.

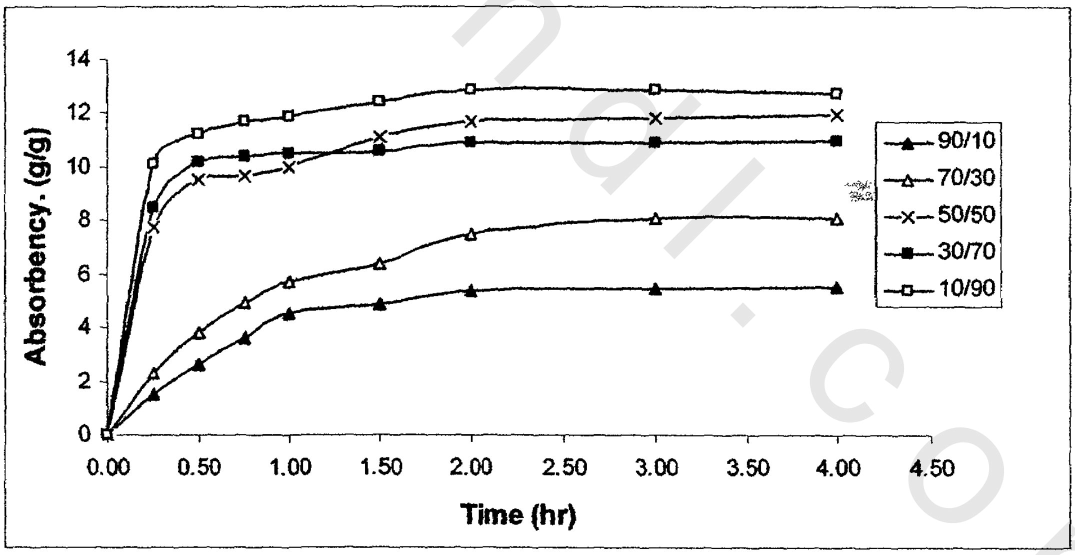


Figure (3.38): Oil Absorbency for CEMA-DDA Copolymer in Toluene with Different Mole Ratios of CEMA to DDA as a Function of Immersion Time Using 1wt% MMA$_m$ at 298 K.

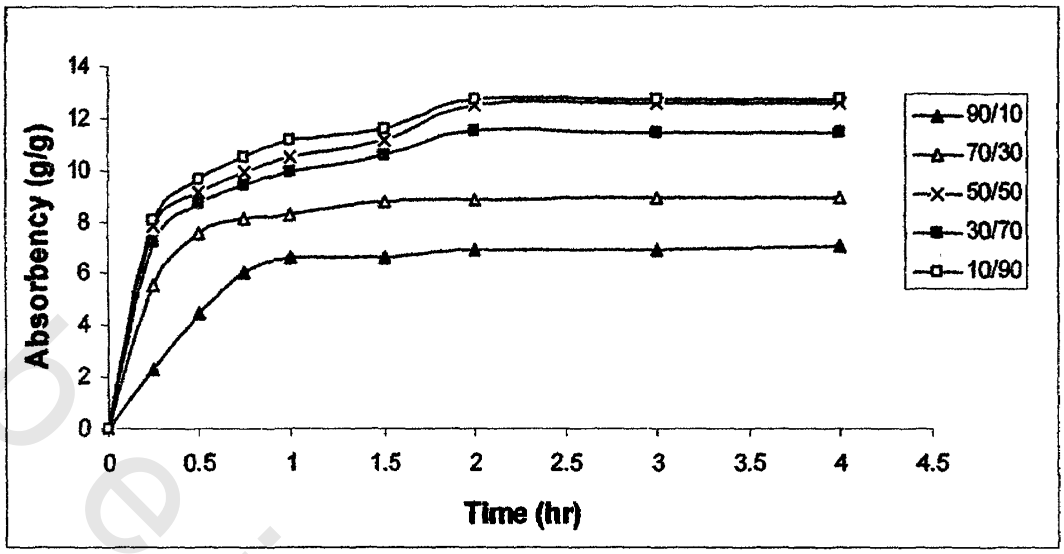


Figure (3.39): Oil Absorbency for CEMA-DDA Copolymer in 10% Crude Oil at Different Mole Ratios of CEMA to DDA as a Function of Immersion Time Using 1 wt% MAA$_m$ at 298 K.

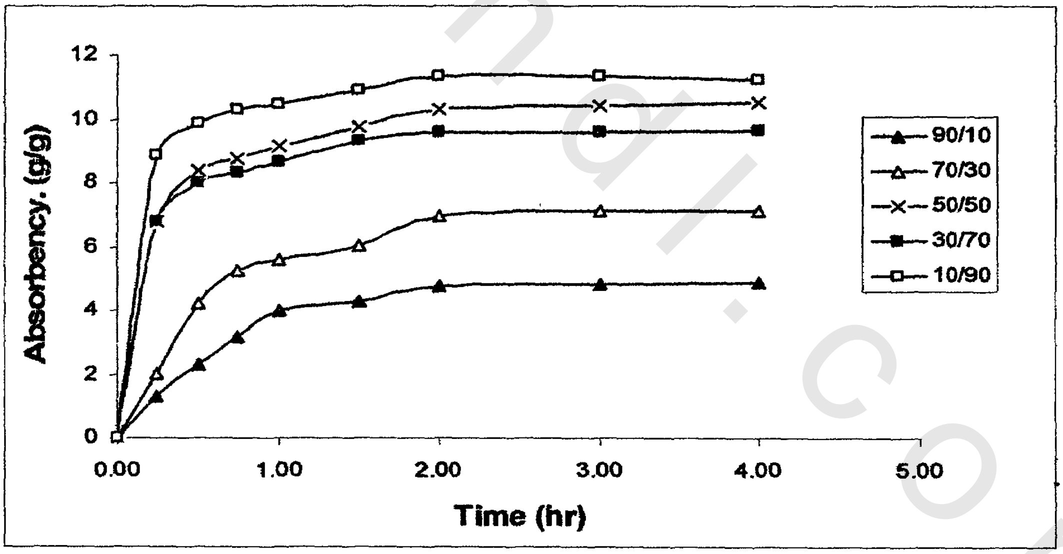


Figure (3.40): Oil Absorbency for CEMA-DDA Copolymer in 10% Crude Oil at Different Mole Ratios of CEMA to DDA as a Function of Immersion Time Using 1 wt% MMA$_m$ at 298 K.

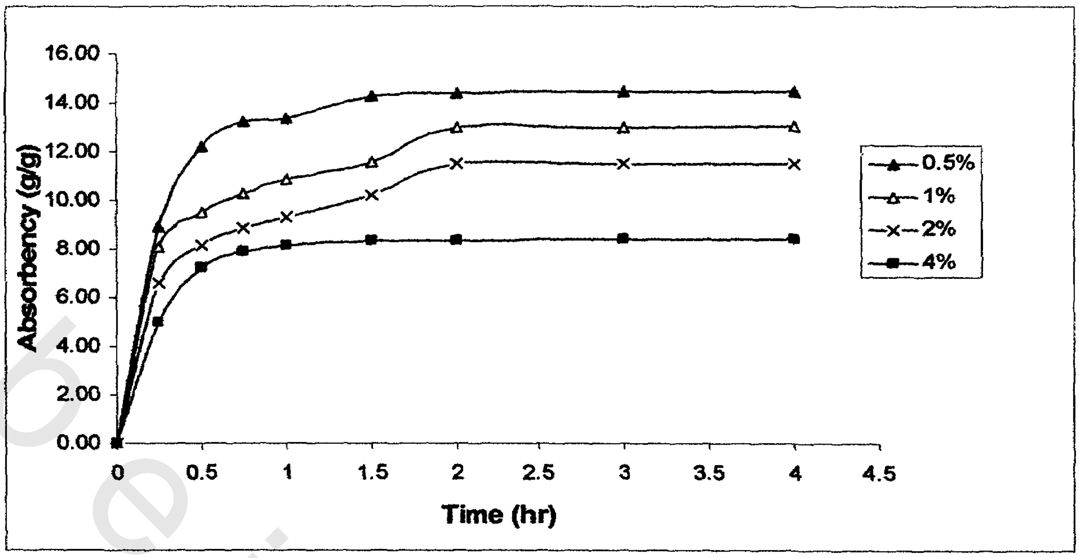


Figure (3.41): Oil Absorbency of CEMA-DDA Xerogels in pure Toluene at 50/50 Mole% of CEMA to DDA as a Function of MAA_m Crosslinker wt% at 298 K.

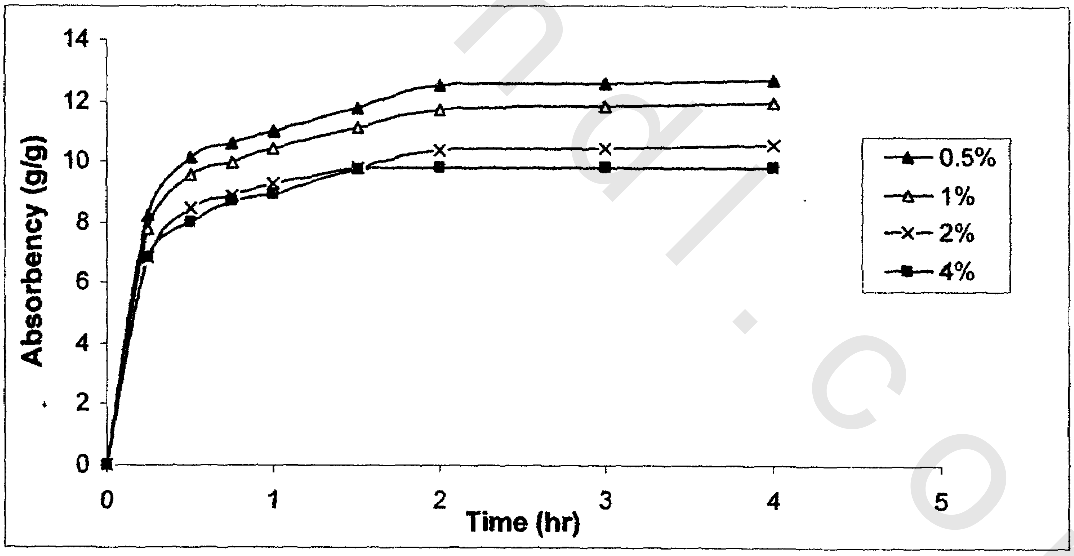


Figure (3.42): Oil Absorbency of CEMA-DDA Xerogels in pure Toluene at 50/50 Mole% of CEMA to DDA as a Function of MMA_m Crosslinker wt% at 298 K.

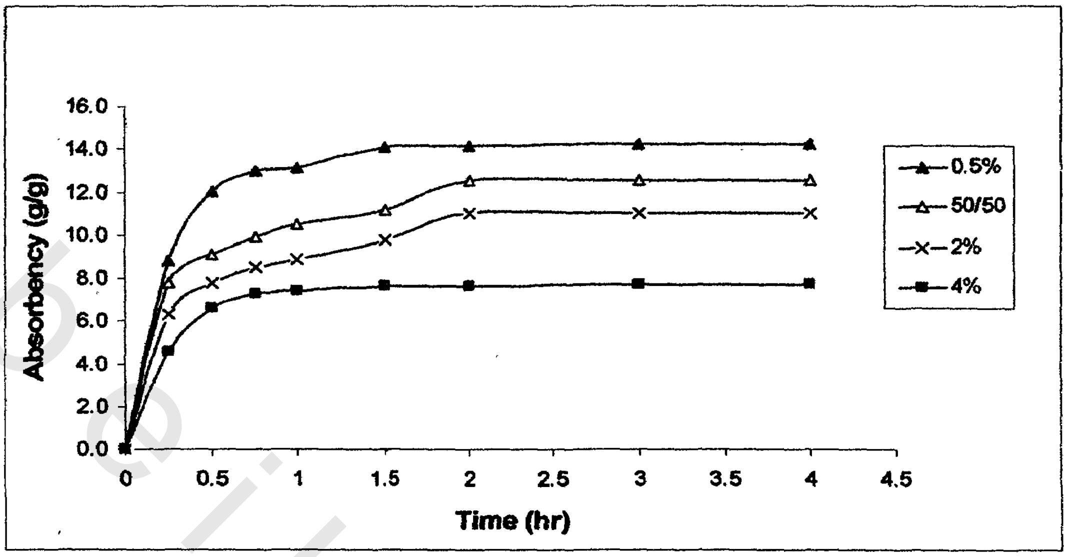


Figure (3.43): Oil Absorbency of CEMA-DDA Xerogels in 10% Crude Oil at 50/50 Mole% of CEMA to DDA as a Function of MAA_m Crosslinker wt% at 298 K.

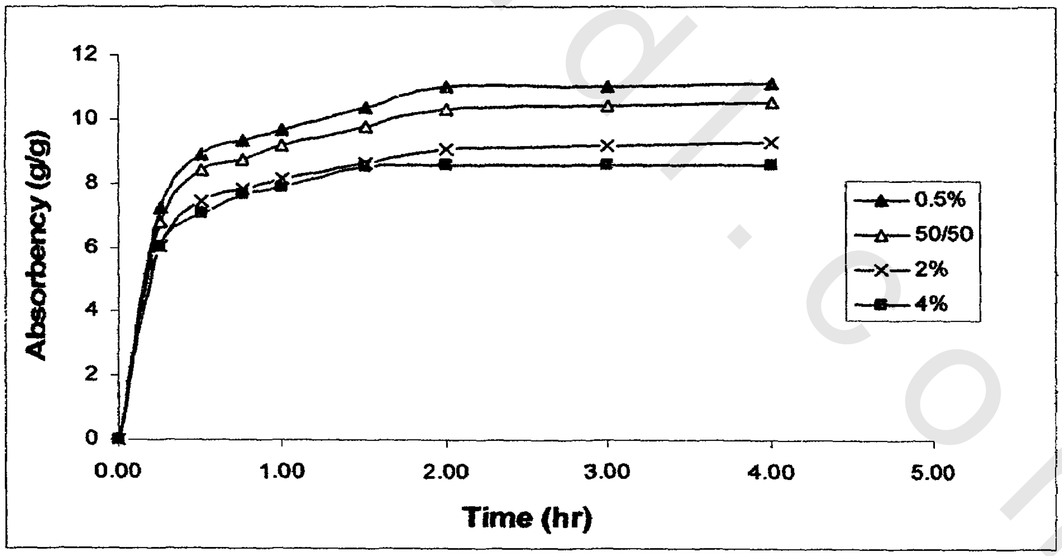


Figure (3.44): Oil Absorbency of CEMA-DDA Xerogels in 10% Crude Oil at 50/50 Mole% of CEMA to DDA as a Function of MMA_m Crosslinker wt% at 298 K.

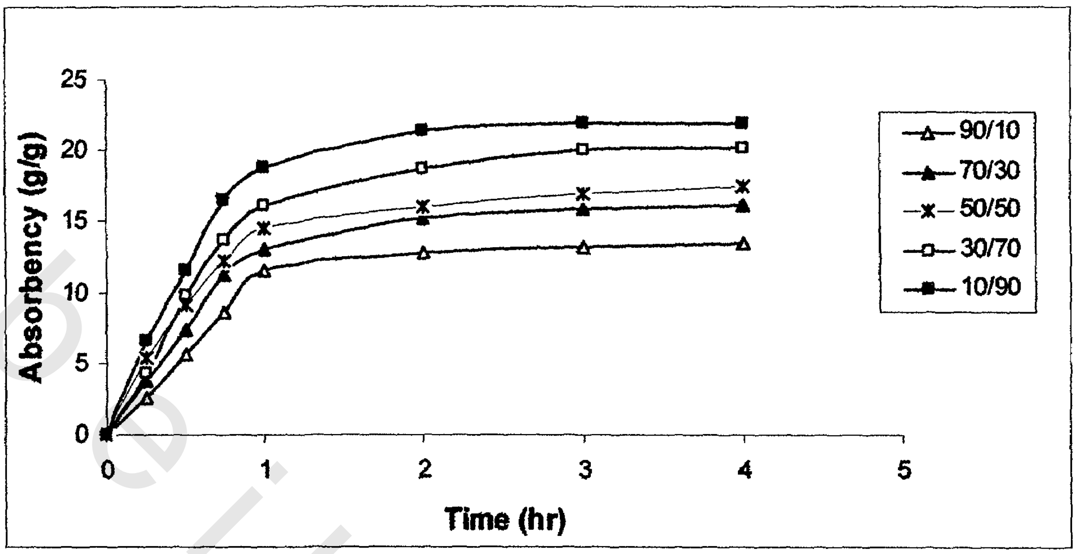


Figure (3.45): Oil Absorbency for CEMA-ODA Copolymer in Toluene with Different Mole Ratios of CEMA to ODA as a Function of Immersion Time Using 1wt% MAA$_m$ at 298 K.

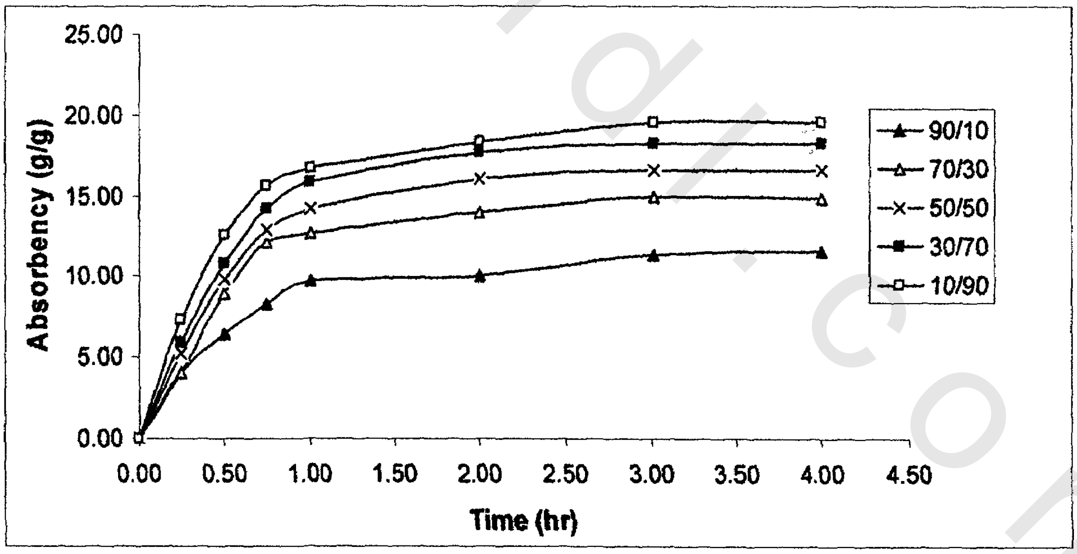


Figure (3.46): Oil Absorbency for CEMA-ODA Copolymer in Toluene with Different Mole Ratios of CEMA to ODA as a Function of Immersion Time Using 1wt% MMA$_m$ at 298 K.

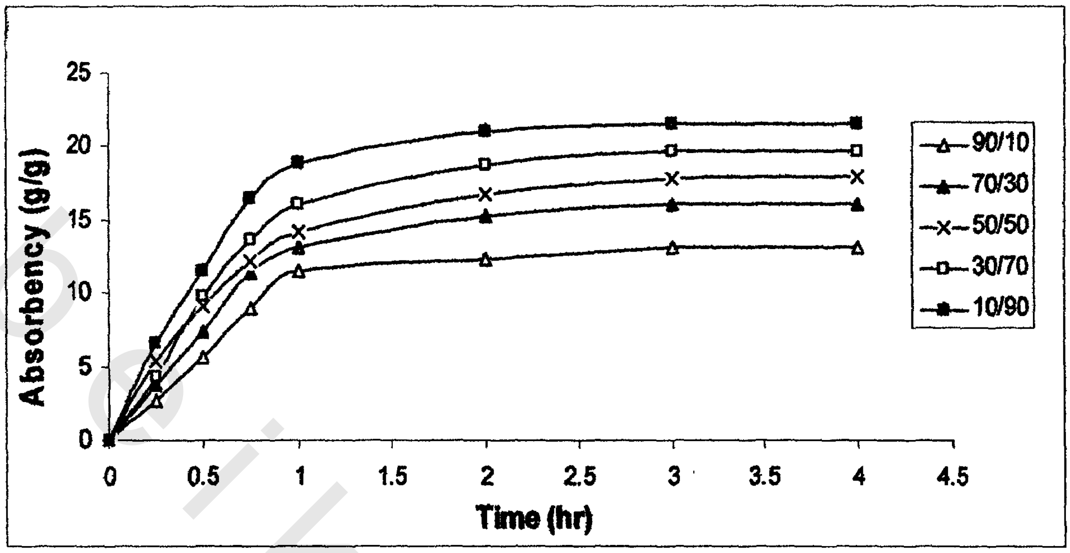


Figure (3.47): Oil Absorbency for CEMA-ODA Copolymer in 10% Crude Oil at Different Mole Ratios of CEMA to ODA as a Function of Immersion Time Using 1wt% MAA_m at 298 K.

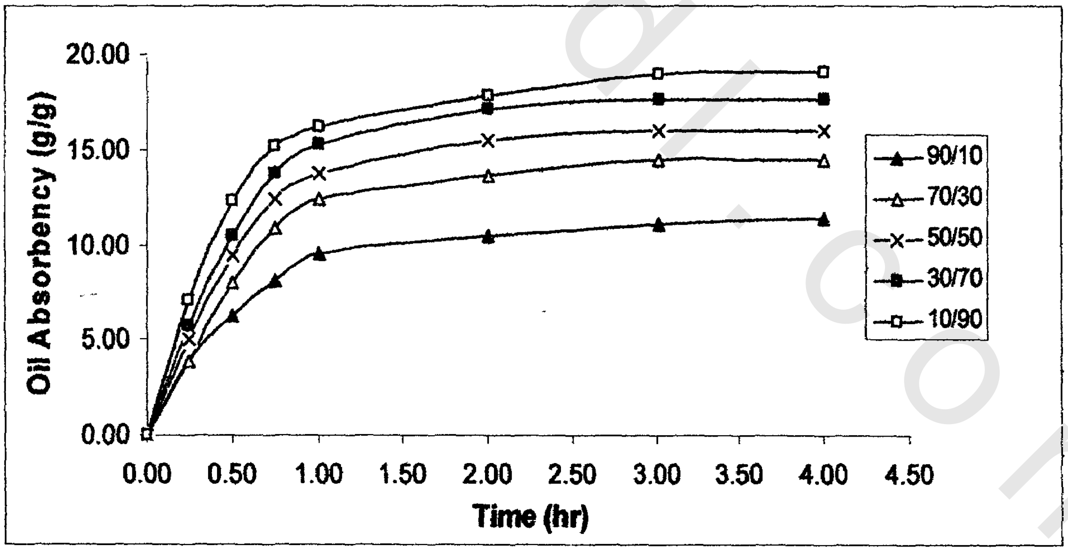


Figure (3.48): Oil Absorbency for CEMA-ODA Copolymer in 10% Crude Oil at Different Mole Ratios of CEMA to ODA as a Function of Immersion Time Using 1wt% MMA_m at 298 K.

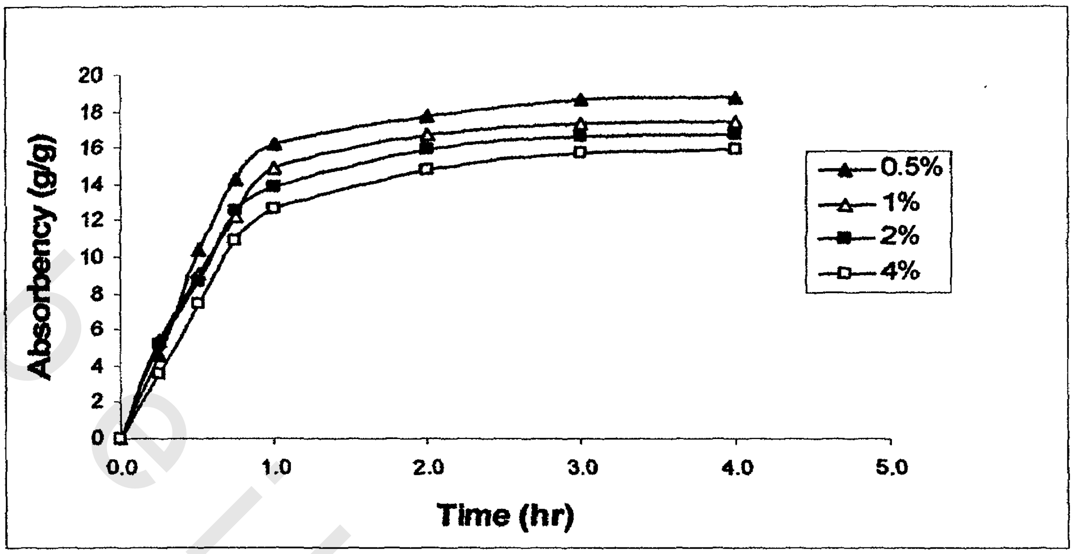


Figure (3.49): Oil Absorbency of CEMA-ODA Xerogels in pure Toluene at 50/50 Mole% of CEMA to ODA as a Function of MAA_m Crosslinker wt% at 298 K.

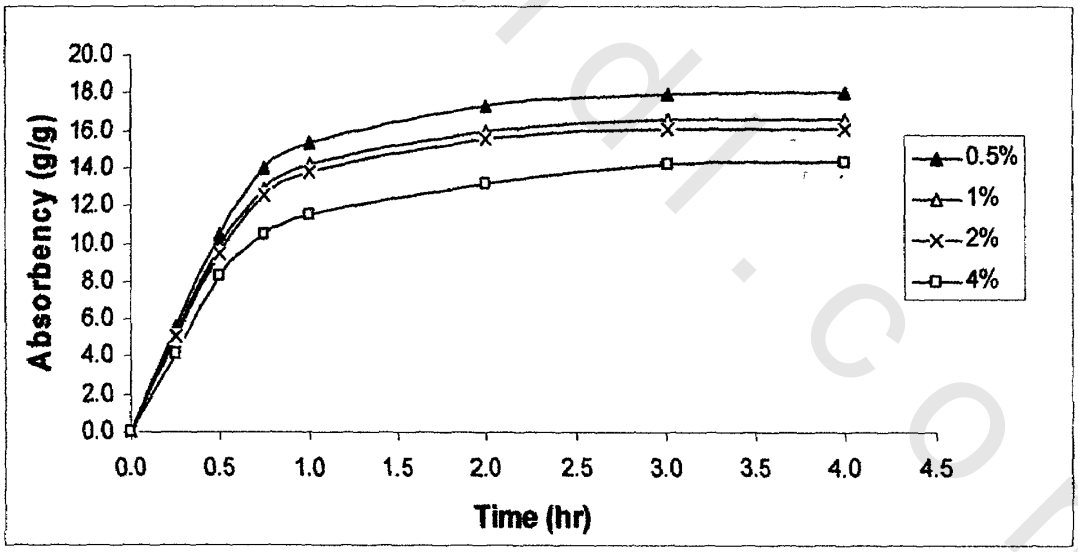


Figure (3.50): Oil Absorbency of CEMA-ODA Xerogels in pure Toluene at 50/50 Mole% of CEMA to ODA as a Function of MMA_m Crosslinker wt% at 298 K.

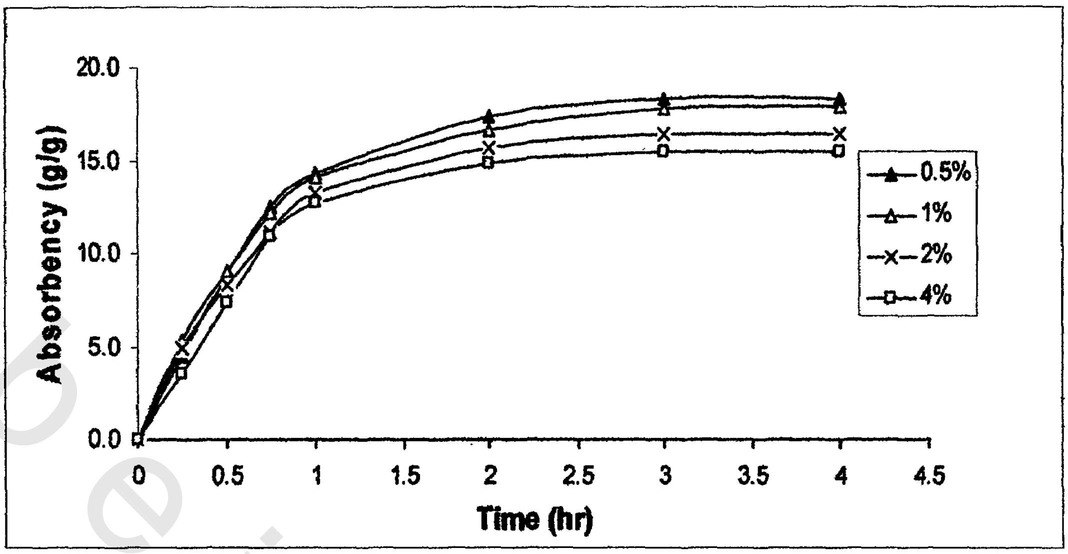


Figure (3.51): Oil Absorbency of CEMA-ODA Xerogels in 10% Crude Oil at 50/50 Mole% of CEMA to ODA as a Function of MAA_m Crosslinker wt% at 298 K.

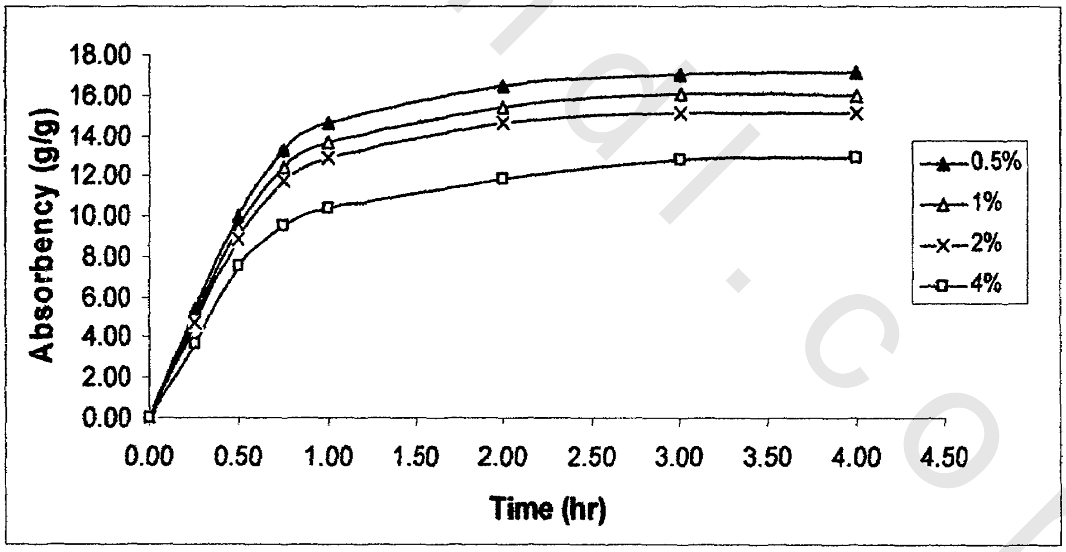


Figure (3.52): Oil Absorbency of CEMA-ODA Xerogels in 10% Crude Oil at 50/50 Mole% of CEMA to ODA as a Function of MMA_m Crosslinker wt% at 298 K.

Table(3.21a): Absorption Characteristics of the CEMA/DDA Copolymers Crosslinked With MAA_mCrosslinker at 298 K.

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil	Toluene	crude oil
90/10	1	7.18	7.02	86.07	85.75	4.54	4.44	0.51	0.52	1.960	1.922
70/30	1	9.18	8.89	89.11	88.75	5.80	5.62	0.26	0.27	3.845	3.702
50/50	0.5	14.42	14.21	93.07	92.96	9.11	8.98	0.26	0.27	3.845	3.702
	1	13.01	12.55	92.31	92.03	8.22	7.93	0.27	0.28	3.702	3.570
	2	11.51	11.03	91.31	90.93	7.27	6.97	0.28	0.3	3.570	3.332
	4	8.4	7.69	88.10	87.00	5.31	4.86	0.29	0.3	3.447	3.332
30/70	1	11.88	11.44	91.58	91.26	7.51	7.23	0.25	0.26	3.999	3.845
10/90	1	13.44	12.72	92.56	92.14	8.49	8.04	0.24	0.25	4.165	3.999

Table (3.21b): Absorption Characteristics of the CEMA/DDA Copolymers Crosslinked With MMA_m Crosslinker at 298 K.

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil
90/10	1	5.52	4.86	81.88	79.41	3.49	3.07	1.41	0.72	1.408	1.388
70/30	1	8.1	7.13	87.65	85.97	5.12	4.50	1.75	0.59	1.754	1.694
50/50	0.5	12.66	11.14	92.10	91.02	8.00	7.04	0.23	0.24	4.346	4.165
	1	11.94	10.51	91.62	90.48	7.55	6.64	4.17	0.25	4.165	3.999
	2	10.54	9.28	90.51	89.22	6.66	5.86	0.25	0.26	3.999	3.845
	4	9.75	8.58	89.74	88.34	6.16	5.42	0.25	0.26	3.999	3.845
30/70	1	10.98	9.66	90.89	89.65	6.94	6.11	4.35	0.24	4.346	4.165
10/90	1	12.78	11.25	92.18	91.11	8.08	7.11	5.26	0.20	5.261	4.998

Table(3.22a): Absorption Characteristics of the CEMA/ODA Copolymers Crosslinked With MAA_m Crosslinker at 298 K.

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil	Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil
90/10	1	13.40	13.06	92.54	92.34	8.47	8.25	0.73	0.7	1.369	1.428
70/30	1	16.10	16.00	93.79	93.75	10.18	10.11	0.68	0.68	1.470	1.470
50/50	0.5	18.80	18.30	94.68	94.68	11.88	11.57	0.65	0.65	1.538	1.538
	1	17.50	17.06	94.29	94.14	11.06	10.78	0.66	0.66	1.515	1.515
	2	16.70	16.40	94.01	93.90	10.55	10.55	0.67	0.67	1.492	1.470
	4	15.90	15.50	93.71	93.55	10.05	10.05	0.69	0.69	1.449	1.449
30/70	1	20.20	19.64	95.05	94.91	12.77	12.41	0.65	0.65	1.538	1.538
10/90	1	21.93	21.52	95.44	95.35	13.86	13.60	0.60	0.6	1.666	1.666

Table (3.22b): Absorption Characteristics of the CEMA/ODA Copolymers Crosslinked With MMA_m Crosslinker at 298 K.

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil
90/10	1	11.60	11.35	91.38	91.19	7.33	7.17	0.64	0.63	1.562	1.587
70/30	1	14.90	14.50	93.29	93.10	9.42	9.16	0.60	0.6	1.666	1.666
50/50	0.5	17.98	17.1016	94.44	94.15	11.36	10.81	0.54	0.56	1.851	1.785
	1	16.60	.02	93.98	93.76	10.49	10.12	0.56	0.57	1.785	1.754
	2	16.10	15.13	93.79	93.39	10.18	9.56	0.58	0.58	1.724	1.724
	4	14.3	12.92	93.01	92.26	9.04	8.17	0.59	0.59	1.694	1.694
30/70	1	18.20	17.64	94.51	94.33	11.50	11.15	0.50	0.55	1.999	1.818
10/90	1	19.55	19.03	94.88	94.75	12.36	12.03	0.47	0.48	2.127	2.083

By comparing the maximum oil absorbency Q_{max} for all CEMA/alkyl acrylates crosslinked with MAA_m and those crosslinked by MMA_m, it is found that the crosslinked sorbers with MAA_m have higher Q_{max} than that crosslinked with MMA_m. This is mainly due to lower crosslinking density of network when MMA_m is used as crosslinker.

It was also observed that, the oil absorbency is found to be in the order CEMA/ ODA > CEMA/DDA> CEMA/IOA. This can be attributed to formation of elastic and porous networks when ODA was used instead of IOA and DDA monomers to copolymerize with CEMA as described in previous sections. Finally, it can be concluded that oil absorbency increases with increase of the length of alkyl groups. It can be easily explained that the longer the aliphatic side group exists, the more hydrophobic property can be introduced to the copolymer and hence promotes the oil absorption capacity **[Jang and Kim, 2000]**.

3.4.3. Swelling kinetics of the synthesized crosslinked CEMA/ alkyl acrylate copolymers

The sorption and diffusion of organic solvents through crosslinked polymer networks has been a subject of great interest **[Errede, 1986, Poh etal., 1987, Berens and Hopfenbergh, 1978]**. The sorption behavior gives an idea about the permeability, and diffusion coefficient of pentrant through polymers, which are used in various applications such as, gel permeation chromatography, ion-exchangers and controlled-release of drugs. As, such there is a growing interest in the study of the kinetics of gel swelling.

Swelling kinetics of the prepared crosslinked copolymers were determined according to **[Yao and Zhou, 1994]** in which the swelling rate can be described by the following experimental equation:

$$\frac{dQ}{dT} = K\,(Q_{max} - Q) \qquad (3.\ 7)$$

where Q_{max} and Q are the maximum and the characteristic oil absorbency respectively. While K is the swelling kinetic constant. Integration from eq.(3.8) gives:

$$-\ln\,(Q_{max} - Q) = Kt + C \qquad (3.\ 8)$$

where, t is the characteristic swelling time and the integration constant. As a consequence of $t = 0$, $Q = 0$, and $-\ln Q_{max} = C$, therefore

$$\ln(Q_{max} / (Q_{max} - Q)) = kt \qquad (3.9\ )$$

For an example, the characteristic swelling time is defined at $Q = 0.632\ Q_{max}$ **[Lee and Wu, 1996]**.

Swelling kinetic constant (k), listed in **Tables (3.20-3.21)**, increases with increasing alkyl acrylate mole ratio and with decreasing crosslinker wt.%. This result may be explained by the fact that the more crosslinker content, the stiffer the crosslinked polymer is, and the smaller cavities produce. Considering that the swelling kinetics may be dependent not only on the surfaces of the polymer but also on the number and volume of the pores in the polymer. The smaller cavities will provide larger absorption surfaces, which give higher swelling rate of the polymeric network, namely larger value of k. In other words, the polymer with higher swelling rate may have suitable structure for oil absorption **[Zhou and Ha, 2001]**.

The data reveal also that, the absorption rate constant increase by increasing alkyl acrylate length. This may be attributed to the longer the aliphatic side group exists, the more hydrophobic property can be introduced to the copolymer and hence promotes the oil absorption capacity rate.

The equilibrium toluene content (ETC), listed in **Tables (3.20-3.22),** increases with increasing alkyl acrylates mol%. This high oil absorptivity of the polymer depends on the blockness of the alkyl constituent.. The ability of the swelled gels to undergo several cycles of swelling and deswelling is shown in **Figure (3.53)**. In this respect, the swelling behavior of crosslinked and grafted CEMA/IOA onto PET NWF in both toluene and crude oil, at 50/50 mol% of CEMA to IOA crosslinked with 0.5% MAA_m crosslinker, was selected as representative sample. We can see that after the first cycle the gel did not achieve the original swollen state but that in all of the following cycles it swelled back to its previous swollen state. This indicates that small amount of soluble fractions still remains in the crosslinked gels which could have leached out upon deswelling, reducing the degree of successive swelling **[Atta, 2002]**.

3.4.4. Effect of Temperature on Swelling Characteristics of Crosslinked CEMA/Alkyl Acrylate Copolymers

Intelligent polymers are soluble, surface coated or crosslinked polymeric materials capable of undergoing sharp physical or chemical modifications in response to external stimuli such as temperature or pH **[Bignotti et al., 2000]**. Crosslinked polymers are one such class of intelligent or smart material. They are used in a variety of applications including diagnostic, therapeutic, and implantable devices, particularly in controlled release drug delivery systems, where they have been studied extensively **[Devine and Higginbotham, 2003, Kishida and**

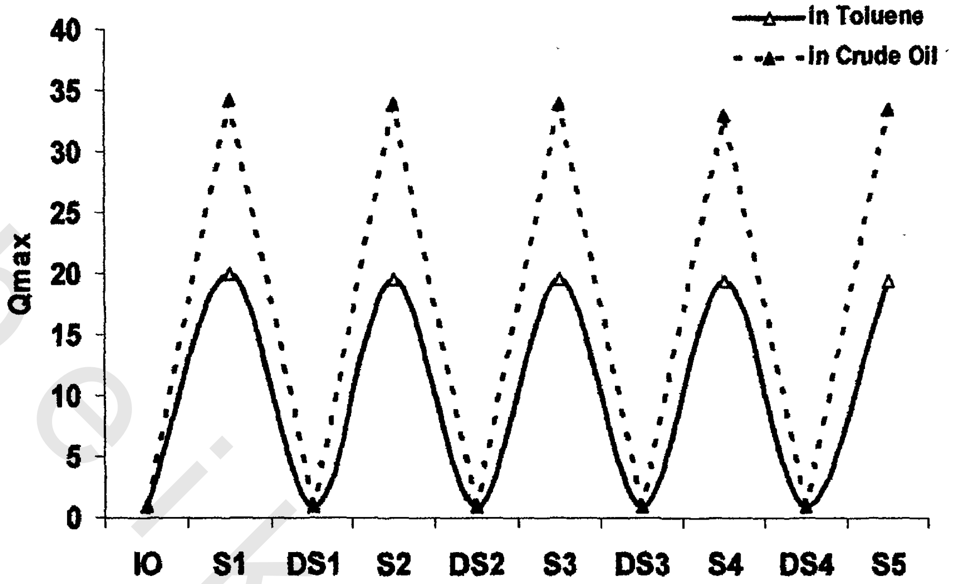
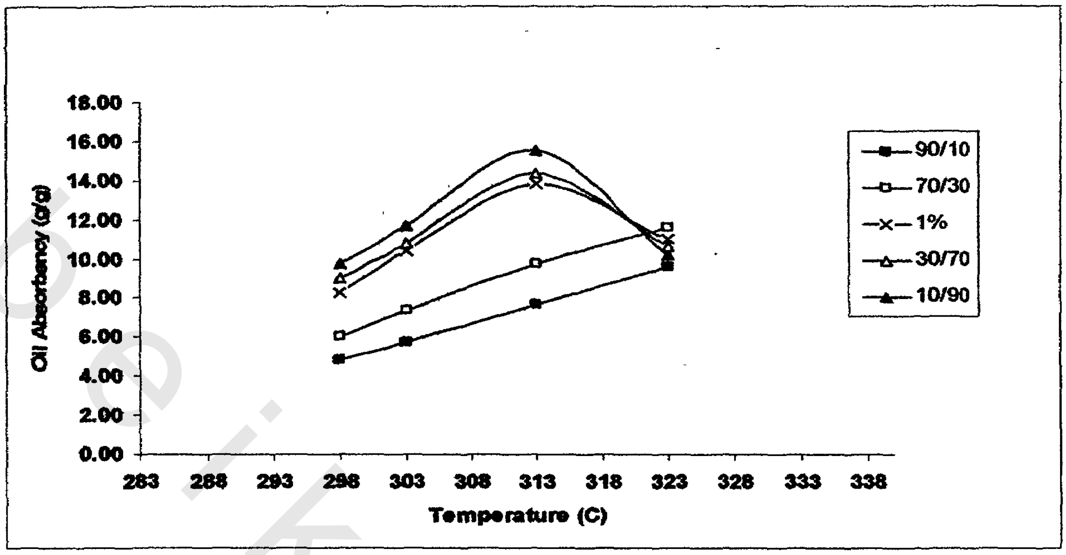


Figure (3.53): Swelling Reversibility of CEMA (50%)/IOA (50%) Monomers Photocrosslinked and grafted onto PET NWF with 0.5 % of MAA_m in Toluene and Crude Oil: IO indicates initial condition, S1-5 = swelling cycle equilibrium condition and DS 1-4 = deswelling cycle equilibrium condition.

Ikada, 2002, Ravichandran and Shantha, 1997, Peppas et al., 2000, Risbud et al., 2000, LaPorte, 1997, Brazel and Peppas, 1996, Grass et al., 2000, Murata et al., 2000, Ruel-Garie'py et al., 2000]. Chemical crosslinking is a highly versatile method of creating crosslinked gels with good mechanical stability. Thermosensitive gels can be classified as positive or negative temperature-sensitive systems. A positive temperature- sensitive hydrogel has an upper critical solution temperature (UCST). Such gels contract upon cooling below the UCST. Most gels belong to this category. The swelling increases with temperature indicating that the process is endothermic. Negative temperature-sensitive gels have a lower critical solution temperature (LCST). These gels contract upon heating above the LCST, and are known as thermoreversible gels as the phenomenon is totally reversible upon cooling **[Peppas et al., 2000]**. Generally, in the case of temperature sensitive polymers, incorporation of a hydrophilic comonomer leads to an increase in LCST, whereas incorporation of a hydrophobic comonomer leads to a decrease **[Liu et al., 2004, Eeckman et al., 2002]**. There is a combined effect of swelling decreasing with temperature, down to a minimum value and thereafter increasing at higher temperatures. Of particular interest to the present study is the negative temperature sensitive properties of these gels, which offers great possibilities for use in oil sorber systems.

The swelling characteristics of CEMA/IOA, CEMA/DDA and CEMA/ODA copolymer crosslinked with MAAm and MMAm crosslinkers at different temperature were measured and represented in Figures, (3.54), (3.55) and (3.56), respectively. As can be seen in these figures, the swelling characteristics show two different behaviours

(a)



(b)

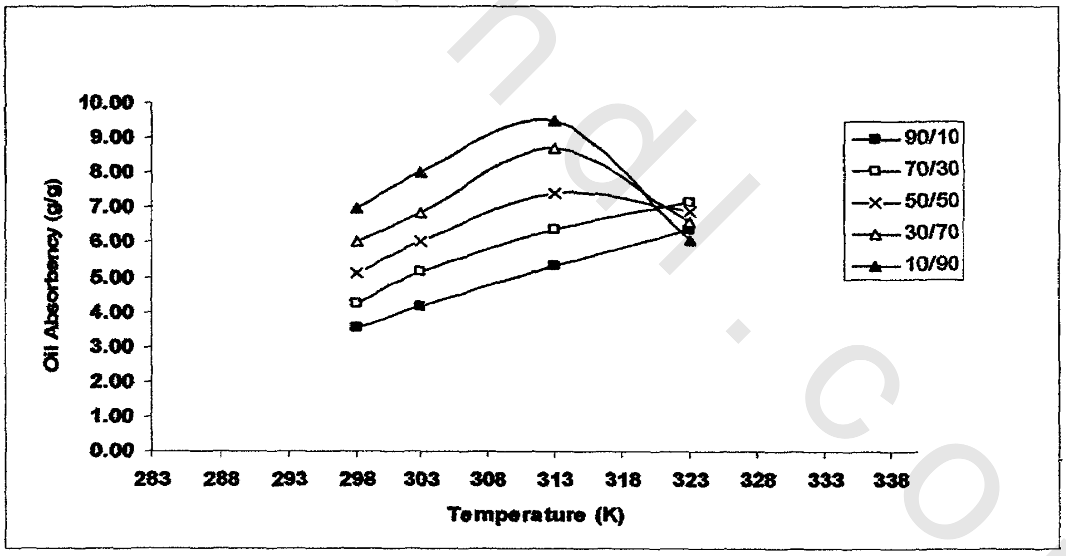
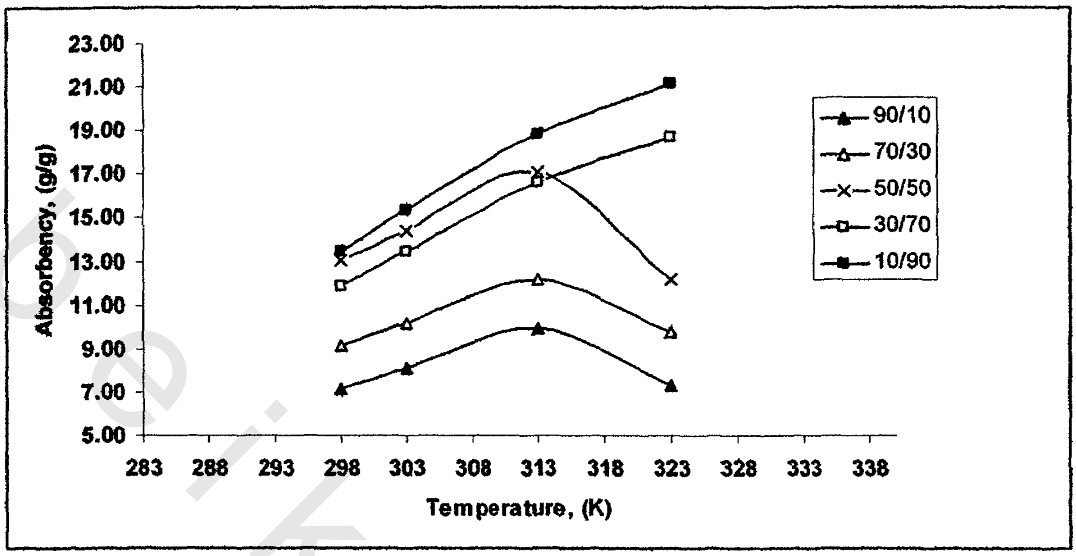


Figure (3.54): Effect of Temperature on the Toluene uptake for Crosslinked CEMA/IOA Copolymers with a) MAA_m and b) MMA_m Crosslinkers

(a)



(b)

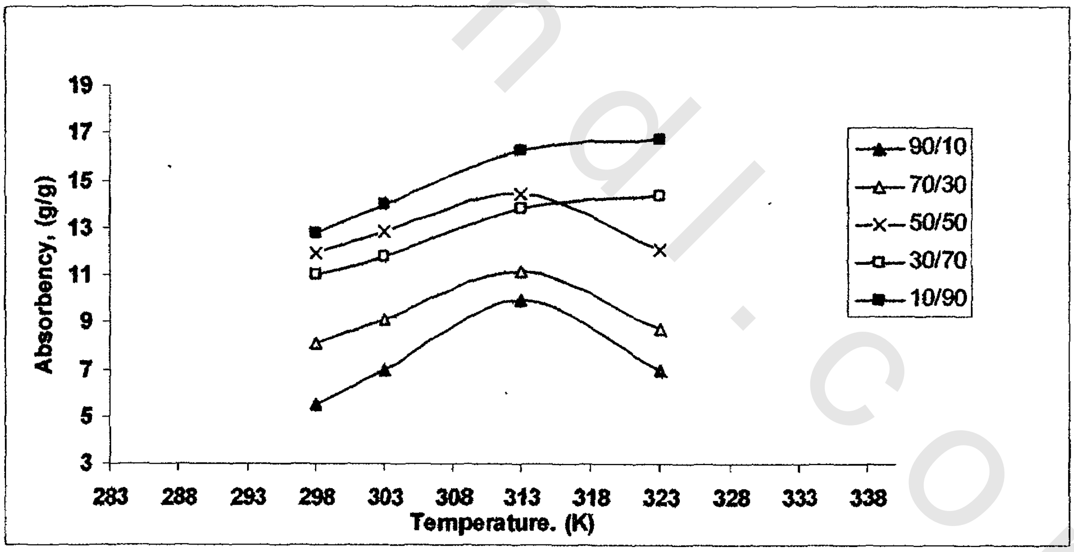
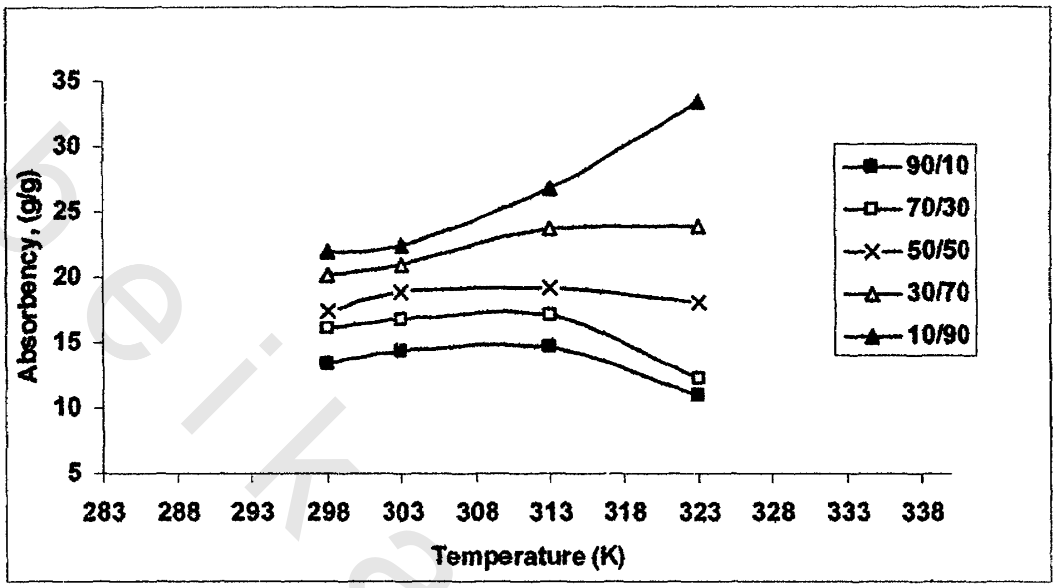


Figure (3.55): Effect of Temperature on the Toluene uptake for Crosslinked CEMA/DDA Copolymers with a) MAA_m and b) MMA_m Crosslinkers

(a)



(b)

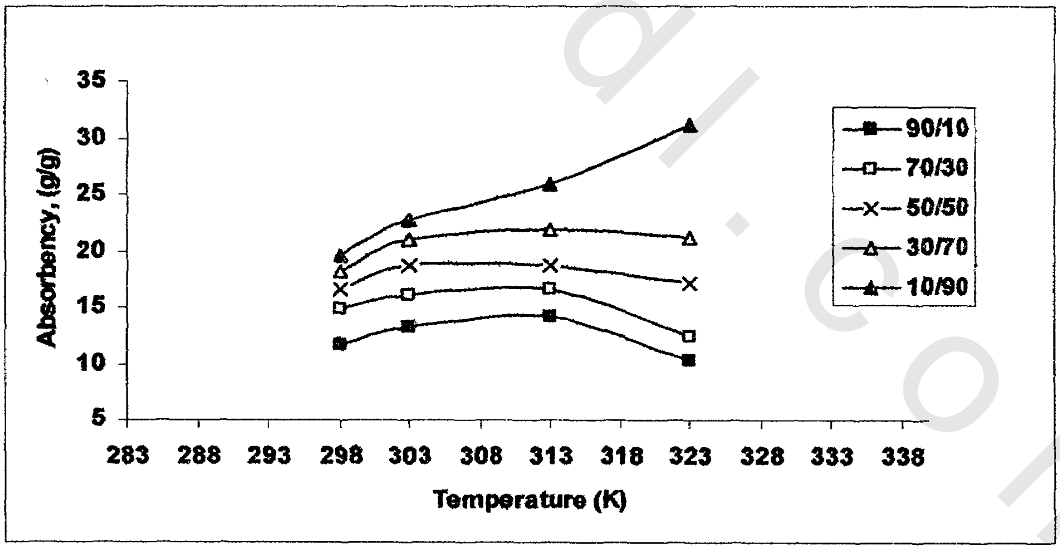


Figure (3.56): Effect of Temperature on the Toluene uptake for Crosslinked CEMA/ODA Copolymers with a) MAA_m and b) MMA_m Crosslinkers

positive and negative temperature dependance. These charactersitics based on copolymer compositions. It was observed that, the toluene uptake was increased with temperature increment upto 30% of IOA content for both crosslinked CEMA/IOA copolymer either with MAA_m or MMA_m crosslinkers. Positive effect is indicative that the process is endothermic. This positive effect is not attributed to hydrophobic interaction as in case of hydrogel negative effect, but it depends on the interaction of the polymer with the organic liquid. This indicates that the toluene is good solvent for these polymers. While increment of IOA from 50 upto 90 mol %, the toluene uptake show negative swelling behavior with increasing of temperatures. This behaviour indicates that the toluene is not good solvent for these polymers. On the other hand, increasing alkyl chain lengths of DDA and ODA increases polymer toluene interaction. This was observed from positive temperature swelling dependence of CEMA/DDA and CEMA/ODA copolymers when the DDA and ODA contents increased from 50 upto 90 mol% in these copolymers. The polymer solvent interaction parameters will be determine from network parameters in the next section.

3. 5. NETWORK PARAMETERS OF CROSSLINKED CEMA/ACRYLATE COPOLYMERS.

The theoretical crosslinking density υ_t is given in terms of concentration C (mol dm^{-3}) of crosslinking agent of functionality f as explained in experimental section (equation 2.5). The values of C were calculated from the known weights (*mc*) of crosslinkers MAA_m or MMA_m in the feed mixture, the mass *mx* of xerogel, in conjunction with the density ρ ($kgdm^{-3}$) of xerogel. This value of ρ is the average of densities obtained from direct weights and micrometrically measured dimensions of all the dried discs and pellets used, and was virtually independent of the concentration of crosslinker over the range used here. C is given by the following Eqation.:

$C = mc/Mw(mx/\rho)$ **(3.10)**

The value of density was virtually independent of the concentration of crosslinker over the range used here. Their values were calculated for crosslinked CEMA and alkyl acrylate copolymers with both MAA_m and MMA_m crosslinkers. The network parameters υ_e, M_c and χ were determined from the swelling measurements of copolymers with toluene and listed in **Tables (3.23-3.28)** As described in the experimental section. From the values of $\boldsymbol{\upsilon_e}$ and $\boldsymbol{\rho}$ the molar mass per crosslinked unit $\mathbf{M_c}$ was calculated. Before considering the network parameters it will be useful at this juncture to supplement on the basis of Eq. (2. 11) the previous discussion on the values of χ. Isolation of χ depends mainly on the mixing contribution, i.e. the three terms of Eq. (2.11). Numerically, it is found that the elastic contribution, i.e. remaining terms, have only a slight effect on the derived value of χ. Because in the present system where in Φ_p and v_e are small, this is especially true and Eq. (2.11) can be reduced as follows to an excellent approximation:

$$\ln(1-\Phi_p)+\Phi_p+\chi\Phi_p{}^{2}\approx 0 \qquad \textbf{(3.11)}$$

Expansion of the logarithmic series, followed by funcation of terms in $\Phi_p{}^{4}$, $\Phi_p{}^{5}$ and $\Phi_p{}^{6}$ etc. and rearrangement yields

$$\chi=1/2+\Phi_p{}^{1/3} \qquad \textbf{(3.12)}$$

Of course full implementation of Eq. (2.11) does allow in principle the values of χ to be <0.50. However, Eq. (3.11) indicates that $\chi > 0.5$. In fact use of Eq. (3.12) in conjunction with the values of Φ_p affords values of χ that lie in close accord with those listed in **Tables (3.23– 3.28)**. It should be noted that the application of equation (3.12) **[Huglin and Rego, 1991, Flory, 1953, Rego, 1993]** is based on the acceptance that the entropy of mixing is given entirely by the configurationally entropy; this assumption implies that other contributions to the entropy derived from specific interaction between neighboring components are neglected. The values of χ are all <0.500 and toluene remains a moderately good solvent thermodynamically over the whole temperature region. χ comprises enthalpic (χH) and entropic (χS) components:

$$X=\chi H+\chi s$$

$$\chi H=-T\,d\chi/dT$$

$$\chi s=\chi+T\,d\chi/dT$$

Because $d\chi/dT = 0$, it follows that $\chi = \chi S$ and the swelling process is entropically dominated, which lends support to the previously mentioned comment on the assumptions implicit in Eq. (3.12). It is interesting to note that for protein gels the situation is entirely different and the swelling is enthalpically controlled **[Clark and Ross-Murphy, 1987]**. The compression moduli G_T values were obtained via following Eq.

$$G_T=RT\upsilon e\,\Phi p^{1/3}(Vu/Vf)^{2/3} \qquad (3.13)$$

Where, R is the gas constant, T is absolute temperature.

Table (3.23a): Network Parameters of Different Compositions CEMA/IOA Copolymers Crosslinked with Various Concentrations of MAA_m Crosslinker at 298K.

Xerogel composition	Crosslinker content	υ_t mol/dm^3	$\upsilon_e \times 10^3$ (mol/dm^3)		$M_c x 10^{-3}$ (g/mole)		χ	
			Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.860	415.11	452.20	1.98	1.82	0.691	0.770
70/30	1	0.810	310.14	343.53	2.49	2.25	0.581	0.672
50/50	0.5	0.752	106.31	182.00	6.98	4.08	0.425	0.480
	1	0.789	209.33	277.52	3.60	2.72	0.426	0.534
	2	0.810	312.38	401.08	2.48	1.93	0.433	0.574
	4	0.840	651.17	686.50	1.23	1.17	0.657	0.796
30/70	1	0.789	178.61	184.04	4.22	4.10	0.396	0.510
10/90	1	0.759	122.05	137.48	5.94	5.28	0.402	0.492

Table (3.23b): Follow Network Parameters of Different Compositions CEMA/IOA Copolymers Crosslinked with Various Concentrations of MAA_m Crosslinker at 298K

Xerogel composition	Crosslinker content	Density (ρ_p) Kg/dm^3	Φ_p		G_T MN.m^{-2}	
			Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.82	0.208	0.260	238.09	324.19
70/30	1	0.77	0.166	0.208	142.07	196.70
50/50	0.5	0.74	0.104	0.130	30.44	65.15
	1	0.75	0.121	0.151	69.52	115.20
	2	0.77	0.131	0.163	112.08	179.87
	4	0.80	0.179	0.223	320.12	421.86
30/70	1	0.75	0.111	0.139	54.77	70.55
10/90	1	0.73	0.103	0.129	34.47	48.54

Table(3.24a): Network Parameters of Different Compositions CEMA/IOA Copolymers Crosslinked with Various Concentrations Of MMA_m Crosslinker at 298K.

Xerogel composition	Crosslinker content	υ_t mol/dm^3	$\upsilon_e \times 10^3$ (mol/dm^3)		$M_c \times 10^{-3}$ (g/mole)		χ	
			Toluene	Crude oil	Toluene		Toluene	Crude oil
90/10	1	0.869	615.65	648.20	1.55	1.473	0.767	0.852
70/30	1	0.842	453.88	490.75	2.039	1.885	0.620	0.726
50/50	0.5	0.834	115.59	145.01	7.921	6.314	0.440	0.509
	1	0.710	220.63	384.71	4.238	2.431	0.452	0.551
	2	0.869	347.53	434.56	2.747	2.197	0.462	0.600
	4	0.887	710.90	753.28	1.370	1.293	0.704	0.834
30/70	1	0.816	184.40	244.88	4.86	3.659	0.424	0.518
10/90	1	0.798	132.26	175.24	6.628	5.002	0.418	0.495

Table (3.24b): Follow Network Parameters of Different Compositions CEMA/IOA Copolymers Crosslinked with Various Concentrations of MMA_m Crosslinker at 298K.

Xerogel composition	Crosslinker content	Density (ρ_p) Kg/dm^3	Φ_p		G_T MN.m^{-2}	
			Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.95	0.219	0.271	371.69	484.08
70/30	1	0.93	0.175	0.217	218.85	292.71
50/50	0.5	0.92	0.110	0.135	34.86	54.07
	1	0.94	0.127	0.157	77.13	166.35
	2	0.95	0.137	0.170	131.30	203.01
	4	0.97	0.188	0.233	367.88	482.19
30/70	1	0.90	0.117	0.145	59.51	97.78
10/90	1	0.88	0.108	0.134	39.31	64.45

Table (3.25a): Network Parameters of Different Compositions CEMA/DDA Copolymers Crosslinked with Various Concentrations Of MAA_m Crosslinker at 298K

Xerogel composition	Crosslinker content	υ_t mol/dm^3	υ_e x 10^3 (mol/dm^3)		M_c (g/mole)		χ	
			Toluene	Crude oil	Toluene		Toluene	Crude oil
90/10	1	0.743	709.37	805.83	1.002	0.882	0.392	0.406
70/30	1	0.754	242.78	245.75	2.975	2.939	0.325	0.350
50/50	0.5	0.689	68.34	74.15	9.905	9.129	0.281	0.270
	1	0.743	97.58	103.11	7.234	6.847	0.262	0.275
	2	0.795	137.97	156.96	5.537	4.867	0.267	0.269
	4	0.806	452.79	727.76	1.709	1.063	0.271	0.277
30/70	1	0.795	120.37	134.44	6.347	5.682	0.277	0.279
10/90	1	0.764	96.98	101.56	7.478	7.141	0.239	0.269

Table (3.25b): Follow Network Parameters of Different Compositions CEMA/DDA Copolymers Crosslinked with Various Concentrations of MAA_m Crosslinker at 298K.

Xerogel composition	Crosslinker content	Density (ρ_p) Kg/dm^3	Φ_p		G_T MN.m^{-2}	
			Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.711	0.139	0.142	271.99	316.02
70/30	1	0.722	0.109	0.112	72.81	76.10
50/50	0.5	0.677	0.069	0.070	13.05	14.37
	1	0.706	0.077	0.080	20.65	22.62
	2	0.764	0.086	0.091	33.00	39.18
	4	0.774	0.119	0.130	148.40	260.54
30/70	1	0.764	0.084	0.087	27.89	32.35
10/90	1	0.725	0.074	0.079	19.87	21.98

Table (3.26a): Network Parameters of Different Compositions CEMA/DDA Copolymers Crosslinked with Various Concentrations Of MMA_m Crosslinker at 298K.

Xerogel composition	Crosslinker content	υ_t mol/dm^3	$\upsilon_e \times 10^3$ (mol/dm^3)		M_c (g/mole)		χ	
			Toluene	Crude oil	Toluene		Toluene	Crude oil
90/10	1	0.771	357.09	567.68	2.37	1.49	0.624	0.725
70/30	1	0.736	117.48	253.50	6.88	3.19	0.486	0.606
50/50	0.5	0.718	87.33	99.81	9.03	7.90	0.308	0.359
	1	0.710	97.51	111.49	8.49	7.43	0.322	0.374
	2	0.789	110.41	120.40	7.85	7.20	0.374	0.428
	4	0.834	121.91	127.68	7.51	7.17	0.402	0.458
30/70	1	0.692	112.43	147.02	6.76	5.17	0.346	0.379
10/90	1	0.665	93.76	103.38	7.79	7.07	0.285	0.347

Table (3.26b): Follow Network Parameters of Different Compositions CEMA/DDA Copolymers Crosslinked with Various Concentrations of MMA_m Crosslinker at 298K.

Xerogel composition	Crosslinker content	Density (ρ_p) Kg/dm^3	Φ_p		G_T MN.m^{-2}	
			Toluene	Crude oil	toluene	Crude oil
90/10	1	0.847	0.181	0.206	178.10	321.73
70/30	1	0.808	0.123	0.140	39.93	97.91
50/50	0.5	0.789	0.079	0.090	18.99	24.66
	1	0.828	0.084	0.095	22.48	29.21
	2	0.867	0.095	0.108	28.84	35.74
	4	0.916	0.103	0.117	34.42	40.97
30/70	1	0.760	0.091	0.103	28.19	41.89
10/90	1	0.731	0.078	0.089	20.20	25.31

Table (3.27a): Network Parameters of Different Compositions CEMA/ODA Copolymers Crosslinked with Various Concentrations of MAA_m Crosslinker at 298K.

Xerogel composition	Crosslinker content	υ_t mol/dm^3	$\upsilon_e \times 10^3$ (mol/dm^3)		$M_c \times 10^{-3}$ (g/mole)		χ	
			Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.659	67.502	64.142	9.312	9.799	0.328	0.351
70/30	1	0.628	45.147	45.822	13.280	13.084	0.310	0.310
50/50	0.5	0.516	37.939	40.337	13.356	12.562	0.262	0.263
	1	0.691	39.039	39.405	17.017	16.859	0.296	0.308
	2	0.764	41.413	41.005	17.699	17.875	0.309	0.320
	4	0.795	47.709	45.627	16.012	16.743	0.305	0.327
30/70	1	0.607	32.309	32.953	17.958	17.607	0.260	0.272
10/90	1	0.544	30.357	30.461	17.201	17.143	0.226	0.237

Table (3.27b): Follow Network Parameters of Different Compositions CEMA/ODA Copolymers Crosslinked with Various Concentrations of MAA_m Crosslinker at 298K.

Xerogel composition	Crosslinker content	Density (ρ_p) Kg/dm^3	Φ_p		G_T MN.m^{-2}	
			toluene	Crude oil	toluene	Crude oil
90/10	1	0.63	0.075	0.077	13.868	13.521
70/30	1	0.60	0.062	0.063	7.720	7.884
50/50	0.5	0.51	0.053	0.055	5.556	6.068
	1	0.66	0.057	0.059	6.141	6.359
	2	0.73	0.060	0.061	6.827	6.883
	4	0.76	0.063	0.065	8.261	8.104
30/70	1	0.58	0.050	0.051	4.403	4.619
10/90	1	0.52	0.046	0.046	3.811	3.897

Table (3.28a): Network Parameters of Different Compositions CEMA/ODA Copolymers Crosslinked with Various Concentrations of MMA_m Crosslinker at 298K.

Xerogel composition	Crosslinker content	υ_t mol/dm^3	$\upsilon_e \times 10^3$ (mol/dm^3)		$M_c \times 10^{-3}$ (g/mole)		χ	
			Toluene	Crude oil	Toluene		Toluene	Crude oil
90/10	1	0.701	71.59	76.14	10.75	10.11	0.390	0.392
70/30	1	0.665	48.81	49.47	14.97	14.77	0.334	0.345
50/50	0.5	0.621	36.69	39.19	18.58	17.39	0.296	0.308
	1	0.710	44.15	45.69	17.65	17.05	0.298	0.309
	2	0.771	45.15	49.73	18.77	17.03	0.309	0.323
	4	0.798	60.32	74.73	14.53	11.73	0.314	0.328
30/70	1	0.621	40.85	42.04	16.69	16.22	0.263	0.274
10/90	1	0.576	36.20	36.91	17.49	17.15	0.250	0.261

Table (3.28b): Follow Network Parameters of Different Compositions CEMA/ODA Copolymers Crosslinked with Various Concentrations of MMA_m Crosslinker at 298K

Xerogel composition	Crosslinker content	Density (ρ_p) Kg/dm^3	Φ_p		G_T MN.m^{-2}	
			Toluene	Crude oil	toluene	Crude oil
90/10	1	0.77	0.086	0.088	16.989	18.469
70/30	1	0.73	0.067	0.069	9.018	9.392
50/50	0.5	0.68	0.056	0.058	5.618	6.310
	1	0.78	0.060	0.062	7.322	7.851
	2	0.85	0.062	0.066	7.720	9.049
	4	0.88	0.070	0.077	11.613	15.922
30/70	1	0.68	0.055	0.057	6.178	6.560
10/90	1	0.63	0.051	0.053	5.098	5.340

For the present systems, a solvent was included within the reaction medium and hence the correction factor $(Vu/Vf)^{2/3}$ is required **[Davis and Huglin 1990]** in Eq. (3.13), where Vu and Vf are the volumes of the dry unstrained xerogel and the network at its formation (i.e. the feed mixture) respectively.

The value of Vu was calculated from Eq.

$$V u = (mt/\rho) x \theta \qquad (3.14)$$

Where, mt and θ are the weight of total monomers in the feed and fractional conversion in preparation of xerogel respectively. Alternatively, Vu can be calculated as Vu = mx/ ρ. Vf can be obtained directly by using a volumetric cylinder; Vf can also be obtained from a calibration curve of [total monomers (g)/solvent (g)] against [total volume (ml) of solution/volume of solvent (ml)]. In the present system, water was included within the reaction medium and therefore Vu < Vf. Note that if no solvent is used, Vu/Vf = 1. In this respect G_T values were calculated for the copolymeric gels and listed in **Tables (3.23-3.28)** It is well known that the lower G_T values indicate that the prepared gels have elastic network **[Toblosky et al., 1961]**. This will increases the interaction between toluene and the copolymer networks. Bastide et al. **[Bastide et al, 1979]** showed that the presence of dangling chains or pendant chains in the polymeric network affected the compression moduli of elasticity. They found that the values of moduli decrease drastically when the proportion of pendant chains increase. The lower values of G_T and υ_e for crosslinked copolymers by MAA_m than that crosslinked with MMA_m crosslinkers, listed in **Tables (3.23-28)**, indicate the formation of dangling chain that was increased by using MAA_m than MMA_m crosslinker. This can be proved from measuring polymer-solvent interaction parameter (χ). The values of χ were calculated for all copolymers and listed in **Tables (3.23-28).** The data of χ values for crosslinked copolymers by MAA_m show lower values than that determined for crosslinked copolymers by MMA_m crosslinker. The decreasing of χ values indicates the good interaction between the crosslinked copolymers with toluene. This indicates that crosslinking with MAA_m introduces hydrophobic groups to network at crosslinking **[Atta and Arndt, 2003, Mehnert et al., 1993, Heger, 1990, Atta and Arndt, 2001]**.

The values of υ_t, υ_e and Mc are listed in **Tables (3.23-3.28).** In general υ_e varies with υ_t according to follwing Eq.

$$\upsilon_e = \alpha + \beta\, \upsilon_t \tag{3.15}$$

in which the value of effective crosslinking in the absence of any included chemical crosslinker may arise from physical crosslinking. The parameter β is a measure of crosslinking efficiency ($\beta = \upsilon_e/\upsilon_t$ when $\alpha = 0$) and its magnitude is usually **[Davis and Huglin, 1990, Huglin et al., 1987, Davis and Huglin, 1989, Collett et al., 1981]** ≤ 1.0, although one unusual case has been reported **[Davis and Huglin, 1990]** where $\beta \geq 1$. Plots (not reproduced here) according to Eq. (3.15) display linearity for the prepared organogels of CEMA and alkyl acrylate copolymers and values of α and β were calculated and listed in **Table (3.29).** In this respect, α values for CEMA/ODA copolymer crosslinked with different concentrations of MAA_m and MMA_m have values ranging from 0.1259 to 0.0286. While CEMA/IOA copolymers possess high α values than other copolymers. It is well known that poly(acrylates) and their copolymers have a high tendency to crosslink under irradiation **[Atta and Abdel-Azim,1998, Chapiro, 1975, Huglin and Richard 1980]** and, moreover, acrylic acid undergoes chain transfer and crosslinking when polymerized by irradiation **[Huglin and**

Richard 1980]. On the other hand the ability of physical crosslinking was increased in both CEMA/IOA and CEMA/DDA than CEMA/ODA copolymers. So, CEMA deactivates the crosslinking efficiency of ODA > DDA >IOA polymers in absence of crosslinkers. On the other word, this can be also referred to the increasing probability of crosslinking in bulk system due to increment in the rate of chain transfer of the polymerization and crosslinking reactions. The crosslinking and polymerization of the present systems were carried out in bulk without diluent. This agrees with the finding that the crosslinking decreases with decreasing content of diluent **[Janacek and Hasa, 1966]**. So, the ability of copolymers to form physical crosslinks increases with IOA > DDA > ODA copolymers. Accordingly,

the oil swelling will increases for CEMA/ODA copolymers due to their low affinity to form physical crosslinks. It was also observed that the β values for crosslinking of CEMA/alkyl acrylate were decreased when ODA used instead of IOA and DDA copolymers. This finding reveals that the reactivity of MAA_m or MMA_m crosslinkers is less efficient for crosslinking of CEMA/ODA copolymers. On the other hand, crosslinked CEMA/ alkyl acrylate copolymers with MMA_m have higher β values than that crosslinked with MAA_m crosslinker. Compared to β obtained from using MAA_m in CEMA/alkyl acrylate with that crosslinked with MMA_m organogels, the crosslinking efficiency is much higher for MMA_m used in organogels, but there is still quite a large proportion of MAA_m wasting during the crosslinking polymerization, probably due to a low reactivity ratio of MAA_m with CEMA/alkyl acrylate. This conclusion is supported by the data of M_C for the crosslinked copolymer by both crosslinkers. **Tables (3.23-3.28)**,

Table(3.29): The values of β and α for CEMA/alkyl acrylat copolymer crosslinked with different wt % of either MAA_m or MMA_m crosslinker using pure toluene as swelling medium.

COPOLYMERS	α		β		Correlation coefficient	
	MAA_m	MMA_m	MAA_m	MMA_m	MAA_m	MMA_m
CEMA/IOA	0.1146	0.1259	0.1738	0.1913	0.91	0.944
CEMA/DDA	0.1093	0.0751	0.1194	0.117	0.96	0.99
CEMA/ODA	0.0336	0.0286	0.0032	0.0072	0.97	0.98

show that M_C values of MMA_m networks are always smaller than the corresponding values when MAA_m is used as the crosslinking agent. Since M_C is used to determine the distance between two successive crosslinks. The smaller its value indicates the higher crosslinking density networks. As the crosslinking density increases, the oil sorber capacities are reduced ***(see Tables 3.23-28)***. It was also observed that the β values are less than unity. It is due to the fact that toluene is a better swelling agent for this system. This is because β is not only a measure of chemical crosslinking but also of physical interaction between the chains when the values are greater than unity **[Yokota et al., 1978]**.

3.6. SWELLING CHARACTERISTICS OF GRAFTED AND CROSSLINKED NWPET

The present section extended to apply crosslinked CEMA and alkyl acrylate copolymers on fiber to be easily handled to use as oil sorbers. In this respect, CEMA/ODA linear copolymer having different compositions was photografted onto NWPET fiber. Their swelling characteristics of the treated and untreated fiber in toluene and diluted crude oil and their swelling curves at 25 °C were recorded and listed in **Table (3.30)** and represented in **Figure (3.57)**. The photocrosslinked CEMA/ODA linear copolymer was not soluble in toluene. The highest oil absorptivity of photocrosslinked CEMA/ODA linear copolymer than both untreated fiber and crosslinked CEMA/ODA copolymers indicates that the photografting technique successes to prepare more efficient oil sorbers. Also, the oil absorptivity for PET NWF photocrosslinked with CEMA/ODA linear copolymer increased to about 10 min and thereafter leveled off. The higher oil absorptivity for crosslinked CEMA/ODA linear copolymer than for the photocrosslinked PET NWF may be ascribed to the size of the microporosity which cannot preferably contain oil. It has been reported **[Takahashi and Kuno, 1991, Hozumi et al., 1992, Hozumi and Uno, 1993, Kitamura and Hayami, 1993]** that the excellent oil absorptivity of materials depends on the bulkiness and length of the alkyl substituents, especially the porosity of the microstructure which can be controlled by crosslinking and the foaming agent. Because the driving force for oil absorption is caused mainly by Van der Waals forces between the material and the oil, therefore, the materials with the proper porosity can effectively contain oil in their structures. This result may be interpreted as an interaction between CEMA/ODA linear copolymer and oil in the porous structure of the photocrosslinked polymer coated on the NWF PET, as manifested in the micrograph **Figure (3.26)**. On the other hand it was observed that the best composition to obtain efficient oil sorbers is 50 mol% of CEMA to 50 mol% ODA copolymers. It was also observed that the swelling characteristics of grafted polymer with diluted crude oil higher than toluene. These behaviors can be attributed to the variation of polymer solvent interaction with copolymer and solvent compositions. This means that diluted crude oil is good solvent for grafted NWPET fiber and can easily penetrate into fiber and increases the swelling characteristics.

From the previous discussion the appropriate mol ratios between CEMA and alkyl acrylate monomers is 50 mol% to 50 mol%. In this respect, this ratio was used to crosslink CEMA/alkyl acrylate monomers thermally and photochemically in the presence of different concentrations of both MAA_m and MMA_m crosslinkers (0.5-4 wt %). In

Table (3.30): Absorption Characteristics at 298 K for Linear CEMA/ODA grafted onto PET NWF by UV radiation .

Xerogel composition	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil
90/10	13.53	14.6	92.61	93.15	8.55	5.40	0.09	0.24	10.945	4.224
70/30	14.07	20.09	92.89	95.02	8.89	5.62	0.08	0.22	12.266	4.639
50/50	20.40	39	95.10	97.44	12.89	8.15	0.06	0.21	15.910	4.876
30/70	15.00	22.35	93.33	95.53	9.48	5.99	0.08	0.21	12.983	4.798
10/90	16.63	32.9	93.99	96.96	10.51	6.64	0.07	0.21	14.281	4.822
Untreated	11.19	13.34	91.06	92.50	7.07	4.47	0.10	0.2415	10.166	4.139

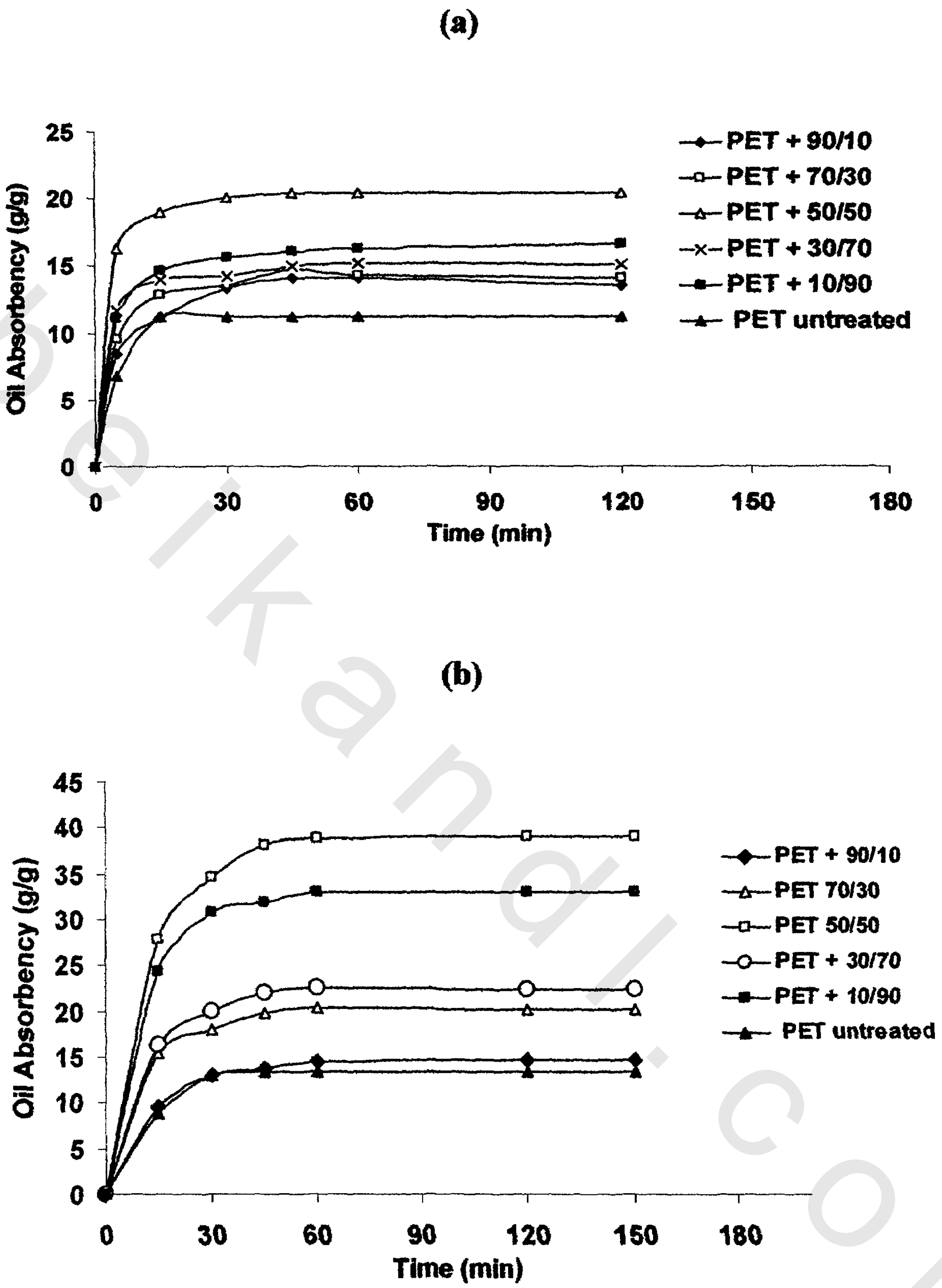


Figure (3.57): Oil Absorbency for CEMA-ODA linear Copolymer grafted onto PET NWF a) in Pure Toluene b) in 10% Crude Oil at Different Mole Ratios of CEMA to ODA as a Function of Immersion Time at 298 K.

the present work AIBN was used as thermal initiator to produce crosslinked polymer in the presence of NWPET fiber. On the other hand, there is no any thermal or photo initiator used to prepare crosslinked polymers using UV irradiation technique. The swelling kinetics of the crosslinked CEMA/IOA, CEMA/DDA and CEMA/ODA using photo or thermal techniques in the presence of NWPET fiber were calculated and listed in **tables (3.31-3.36).** The swelling curves at 25 °C of these copolymers were represented in **figures (3.58-63)** Careful inspection of data indicates that the swelling decreases with increasing concentrations of both MAA_m and MMA_m which indicates that the monomers were crosslinked efficiently in the presence of both MAA_m and MMA_m crosslinkers. The data indicate that the best concentration to obtain maximum swelling for crosslinked CEMA/ODA copolymer in the presence of NWPET using both MAA_m and MMA_m crosslinker is 1 (wt%). While, the best concentration for both MAA_m and MMA_m crosslinkers is 0.5 (wt %) in case of crosslinked CEMA/DDA and CEMA/IOA copolymers. The lower swelling capacities of the thermal crosslinked CEMA/alkyl acrylate monomers using NWPET fiber than that crosslinked using UV irradiation indictes that there are dangling chains formed during photochemical initiation **[Atta and Arndt, 2005]**. The dangling chain was increased by irradiation than chemical initiation. Also, this result may be explained by the fact that the crosslinked gels produced via UV irradiation are stiffer than that crosslinked with chemical initiation. The stiffer crosslinked polymers have small cavities. At the same time, the smaller cavities will provide larger absorption surfaces, which give higher swelling rate of the polymeric network **[Zhou et al., 2001]**. It has been reported **[Kitamura and Hayami, 1993]** that the excellent oil

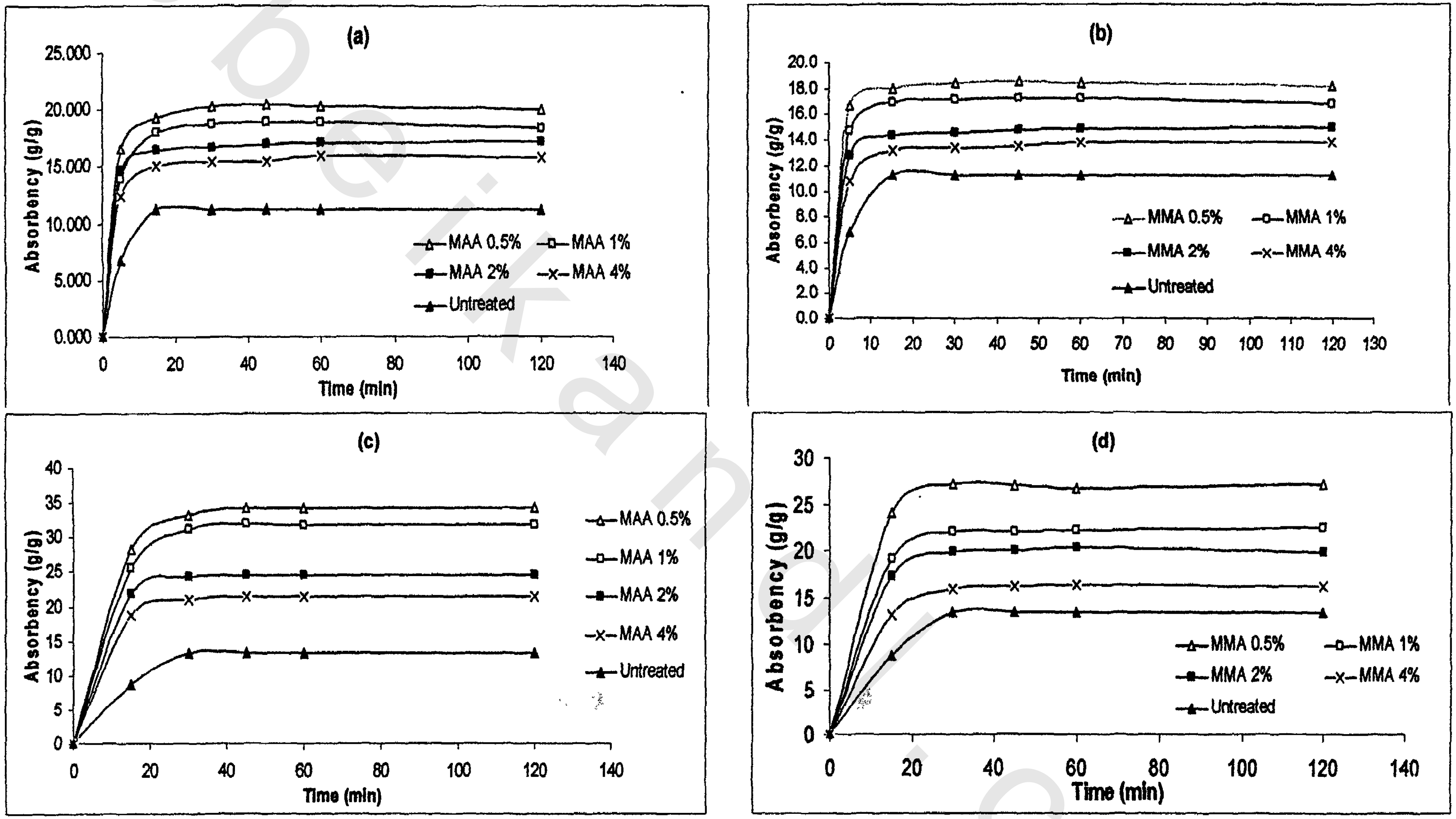


Figure (3.58): Oil Absorbency of 50 mol% CEMA / 50 mol% IOA monomers Photochemically Crosslinked onto PET NWF at Different Concentrations of Crosslinker (0.5-4%) as a Function of Immersion Time at 298K a) In Pure Toluene and Using MAA_m. b) In Pure Toluene and Using MMA_m c) In 10% crude Oil and Using MAA_m d) In 10% crude Oil and Using MMA_m

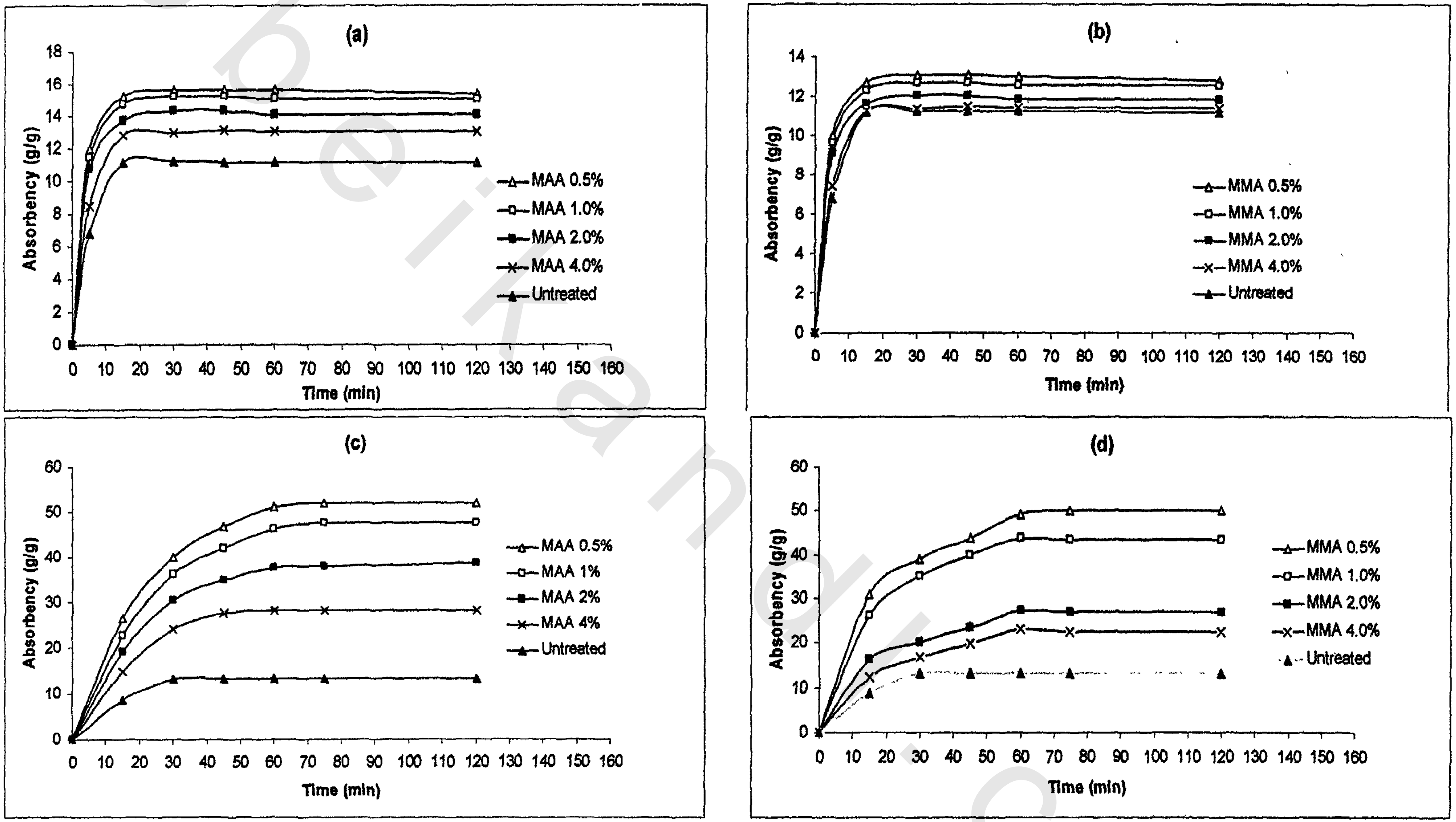


Figure (3.59): Oil Absorbency of 50 mol% CEMA / 50 mol% IOA monomers Thermally Crosslinked onto PET NWF at Different Concentrations of Crosslinker (0.5-4%) as a Function of Immersion Time at 298K a) In Pure Toluene and Using MAA_m. b) In Pure Toluene and Using MMA_m c) In 10% crude Oil and Using MAA_m d) In 10% crude Oil and Using MMA_m

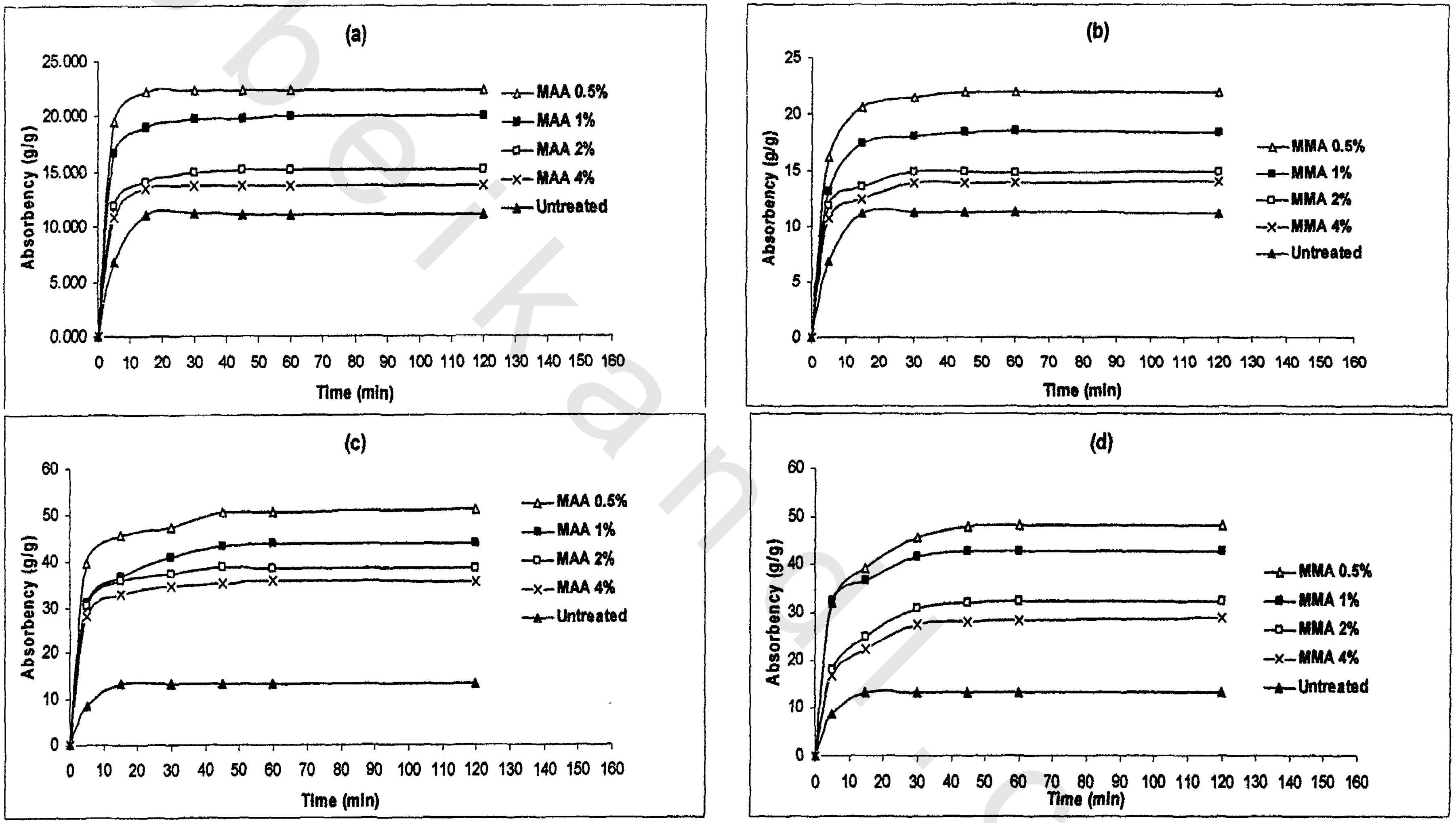


Figure (3.60): Oil Absorbency of 50 mol% CEMA / 50 mol% DDA monomers Photochemically Crosslinked onto PET NWF at Different Concentrations of Crosslinker (0.5-4%) as a Function of Immersion Time at 298K a) In Pure Toluene and Using MAA_m. b) In Pure Toluene and Using MMA_m c) In 10% crude Oil and Using MAA_m d) In 10% crude Oil and Using MMA_m

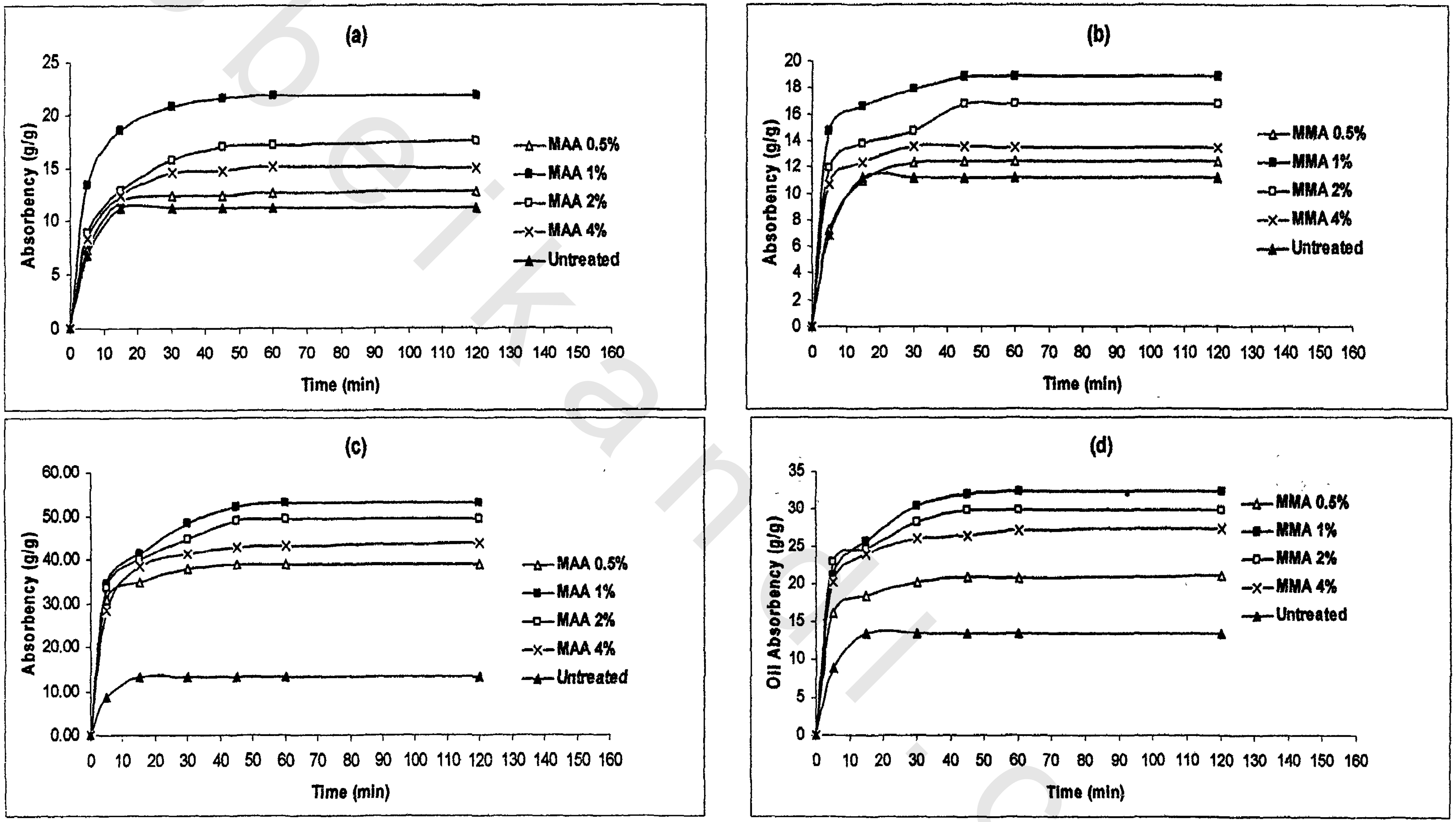


Figure (3.61): Oil Absorbency of 50 mol% CEMA / 50 mol% DDA monomers Thermally Crosslinked onto PET NWF at Different Concentrations of Crosslinker (0.5-4%) as a Function of Immersion Time at 298K a) In Pure Toluene and Using MAA_m. b) In Pure Toluene and Using MMA_m c) In 10% crude Oil and Using MAA_m d) In 10% crude Oil and Using MMA_m

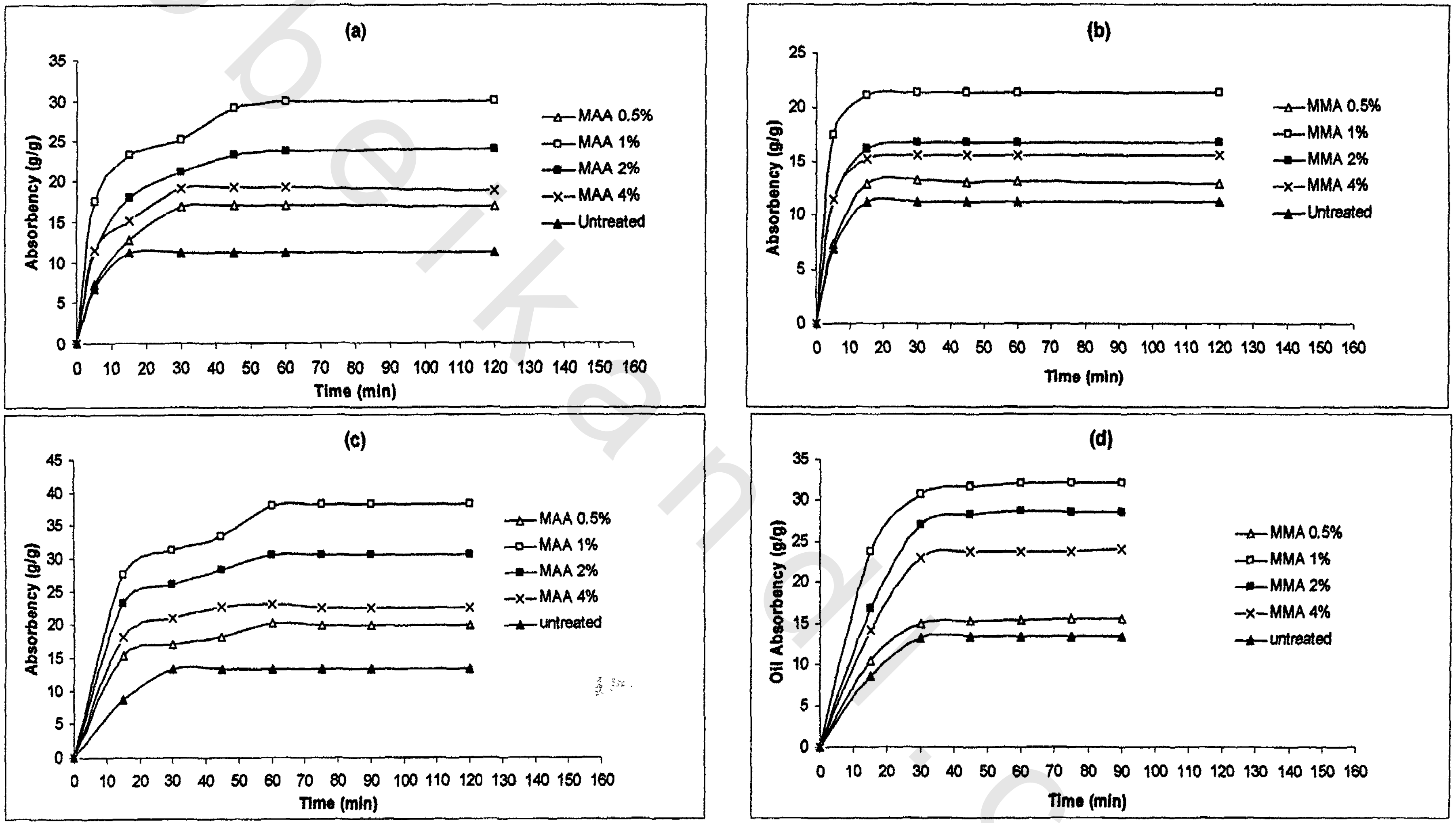


Figure (3.62): Oil Absorbency of 50 mol% CEMA / 50 mol% ODA monomers Photochemically Crosslinked onto PET NWF at Different Concentrations of Crosslinker (0.5-4%) as a Function of Immersion Time at 298K a) In Pure Toluene and Using MAA_m. b) In Pure Toluene and Using MMA_m c) In 10% crude Oil and Using MAA_m d) In 10% crude Oil and Using MMA_m

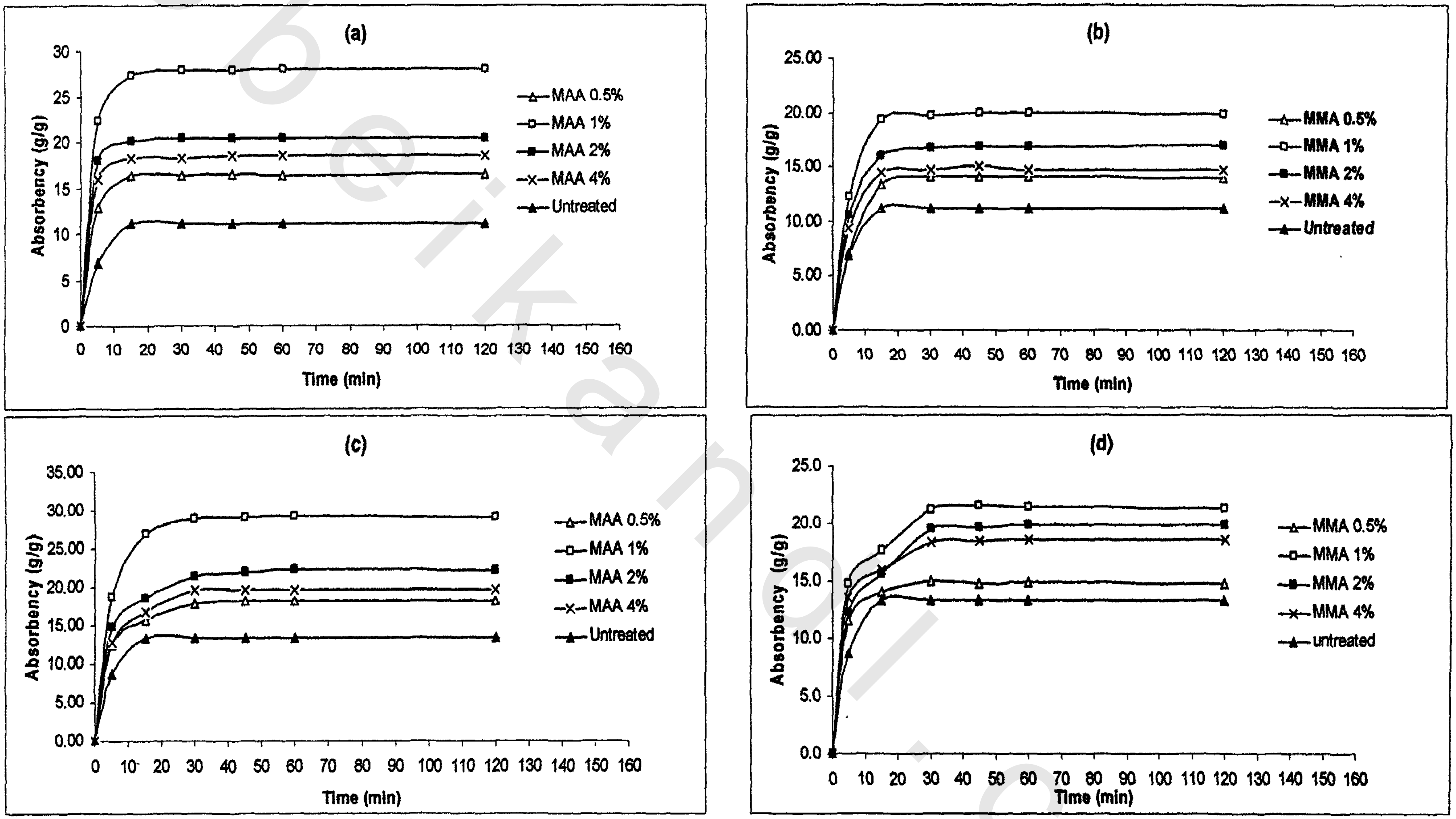


Figure (3.63): Oil Absorbency of 50 mol% CEMA / 50 mol% ODA monomers Thermally Crosslinked onto PET NWF at Different Concentrations of Crosslinker (0.5-4%) as a Function of Immersion Time at 298K a) In Pure Toluene and Using MAA_m. b) In Pure Toluene and Using MMA_m c) In 10% crude Oil and Using MAA_m d) In 10% crude Oil and Using MMA_m

Table (3.31a): Absorption Characteristics at 298 K for 50/50 mol% CEMA/ODA Copolymers Thermally Crosslinked and /or Grafted onto PET NWF in Presence of 0.5-4% of MAA_m Crosslinker

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil
50/50	0.5	16.50	18.29	93.94	94.53	10.43	11.56	0.071	0.09	14.014	11.761
	1	28.09	29.19	96.44	96.57	17.75	18.45	0.066	0.08	15.147	12.266
	2	20.48	22.20	95.12	95.50	12.94	14.03	0.062	0.08	16.211	12.093
	4	18.59	19.61	94.62	94.90	11.75	12.39	0.063	0.08	15.995	11.996
Untreated	0	11.19	13.34	91.06	92.50	7.07	8.43	0.098	0.24	10.166	4.139

Table (3.31b): Absorption Characteristics at 298 K for 50/50 mol% CEMA/ODA Copolymers Thermally Crosslinked and /or Grafted onto PET NWF in Presence of 0.5-4% of MMA_m Crosslinker

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil
50/50	0.5	14.00	14.80	92.86	93.24	8.85	9.35	0.106	0.07	9.431	14.281
	1	19.80	21.36	94.95	95.32	12.51	13.50	0.076	0.06	13.154	16.388
	2	17.00	19.90	94.12	94.97	10.74	12.58	0.081	0.06	12.342	15.620
	4	14.70	18.58	93.20	94.62	9.29	11.74	0.090	0.07	11.107	15.147
Untreated	0	11.19	13.34	91.06	92.50	7.07	8.43	0.098	0.24	10.166	4.139

Table (3.32a):Absorption Characteristics at 298 K for 50/50 mol% CEMA/DDA Copolymers Thermally Crosslinked and /or grafted onto PET NWF in Presence of 0.5-4% of MAA_m Crosslinker

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil
50/50	0.5	12.70	38.70	92.13	97.42	8.03	24.46	0.105	0.07	9.521	13.509
	1	21.80	52.88	95.41	98.11	13.78	33.42	0.093	0.07	10.749	14.701
	2	17.50	49.20	94.29	97.97	11.06	31.09	0.173	0.07	5.778	13.884
	4	15.00	43.60	93.33	97.71	9.48	27.56	0.122	0.07	8.194	13.509
Untreated	0	11.19	13.34	91.06	92.50	7.07	8.43	0.098	0.24	10.166	4.139

Table (3.32b): Absorption Characteristics at 298 K for 50/50 mol% CEMA/DDA Copolymers Thermally Crosslinked and /or Grafted onto PET NWF in Presence of 0.5-4% of MMA_m Crosslinker

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil
50/50	0.5	12.45	21.10	91.97	95.26	7.87	13.34	0.074	0.071	13.509	14.080
	1	19.80	32.30	94.95	96.90	12.59	20.41	0.062	0.065	16.124	15.380
	2	16.74	29.80	94.03	96.64	10.58	18.83	0.068	0.069	14.701	14.488
	4	13.50	27.30	92.59	96.34	8.53	17.25	0.072	0.070	13.884	14.281
Untreated	0	11.19	13.34	91.06	92.50	7.07	8.43	0.098	0.24	10.166	4.139

Table (3.33a): Absorption Characteristics at 298 K for 50/50 mol% CEMA/IOA Copolymers Thermally Crosslinked and /or grafted onto PET NWF in Presence of 0.5-4% of MAA_m Crosslinker

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil
50/50	0.5	15.420	52.00	93.51	98.08	9.75	32.86	0.065	0.360	15.380	2.777
	1	15.072	47.50	93.37	97.89	9.53	30.02	0.068	0.380	14.701	2.631
	2	14.054	38.60	92.88	97.41	8.88	24.40	0.071	0.320	14.080	3.124
	4	13.087	28.00	92.36	96.43	8.27	17.70	0.077	0.330	12.983	3.029
Untreated	0	11.19	13.34	91.06	92.50	7.07	8.43	0.098	0.24	10.166	4.139

Table (3.33b): Absorption Characteristics at 298 K for 50/50 mol% CEMA/IOA Copolymers Thermally Crosslinked and /or Grafted onto PET NWF in Presence of 0.5-4% of MMA_m Crosslinker

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil
50/50	0.5	12.850	50.02	92.22	98.00	8.12	31.61	0.064	0.270	15.620	3.702
	1	12.560	43.39	92.04	97.70	7.94	27.42	0.069	0.280	14.488	3.570
	2	11.850	27.04	91.56	96.30	7.49	17.09	0.072	0.290	13.884	3.447
	4	11.430	22.39	91.25	95.53	7.22	14.15	0.076	0.350	13.154	2.856
Untreated	0	11.19	13.34	91.06	92.50	7.07	8.43	0.098	0.24	10.166	4.139

Table (3.34a): Absorption Characteristics at 298 K for 50/50 mol% CEMA/ODA Copolymers Photochemically Crosslinked and /or Grafted onto PET NWF in Presence of 0.5-4% of MAA_m crosslinker

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil
50/50	0.5	16.80	19.96	94.05	94.99	10.62	12.61	0.190	0.20	5.261	4.998
	1	29.90	38.20	96.66	97.38	18.90	24.14	0.100	0.21	9.997	4.760
	2	23.90	30.53	95.82	96.72	15.10	19.29	0.140	0.20	7.141	4.998
	4	18.70	22.41	94.65	95.54	11.82	14.17	0.150	0.19	6.664	5.261
Untreated	0	11.19	13.34	91.06	92.50	7.07	8.43	0.098	0.24	10.166	4.139

Table (3.34b): Absorption Characteristics at 298 K for 50/50 mol% CEMA/ODA Copolymers Photochemically Crosslinked and /or Grafted onto PET NWF in Presence of 0.5-4% of MMA_m Crosslinker

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil
50/50	0.5	12.90	15.50	92.25	93.55	8.15	9.80	0.098	0.23	10.201	4.346
	1	21.29	32.00	95.30	96.88	13.46	20.22	0.064	0.27	15.620	3.702
	2	16.80	28.51	94.05	96.49	10.62	18.02	0.070	0.26	14.281	3.845
	4	15.60	24.00	93.59	95.83	9.86	15.17	0.075	0.28	13.329	3.570
Untreated	0	11.19	13.34	91.06	92.50	7.07	8.43	0.098	0.24	10.166	4.139

Table (3.35a): Absorption Characteristics at 298 K for 50/50 mol% CEMA/DDA Copolymers Photochemically Crosslinked and /or Grafted onto PET NWF in Presence of 0.5-4% of MAA_m crosslinker

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil
50/50	0.5	22.40	51.10	95.54	98.04	14.16	32.30	0.058	0.060	17.236	16.661
	1	20.09	43.75	95.02	97.71	12.70	27.65	0.063	0.063	15.868	15.868
	2	15.22	38.46	93.43	97.40	9.62	24.31	0.067	0.063	14.920	15.868
	4	13.70	35.53	92.70	97.19	8.66	22.45	0.073	0.069	13.694	14.488
Untreated	0	11.19	13.34	91.06	92.50	7.07	8.43	0.098	0.24	10.166	4.139

Table (3.35b): Absorption Characteristics at 298 K for 50/50 mol% CEMA/DDA Copolymers Photochemically Crosslinked and /or Grafted onto PET NWF in Presence of 0.5-4% of MMA_m Crosslinker

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil
50/50	0.5	21.912	48.11	95.44	97.92	13.85	8.75	0.066	0.072	13.509	14.080
	1	18.414	42.74	94.57	97.66	11.64	7.35	0.068	0.077	16.124	15.380
	2	14.85	32.42	93.27	96.92	9.39	5.93	0.070	0.122	14.701	14.488
	4	13.926	28.80	92.82	96.53	8.80	5.56	0.072	0.123	13.884	14.281
Untreated	0	11.19	13.34	91.06	92.50	7.07	8.43	0.098	0.24	10.166	4.139

Table (3.36a): Absorption Characteristics at 298 K for 50/50 mol% CEMA/IOA Copolymers Photochemically Crosslinked and /or Grafted onto PET NWF in Presence of 0.5-4% of MAA_m crosslinker

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil
50/50	0.5	20.011	34.23	95.00	97.08	12.65	21.63	0.060	0.189	16.661	5.289
	1	18.414	31.7	94.57	96.85	11.64	20.03	0.065	0.195	15.380	5.127
	2	17.187	24.4	94.18	95.90	10.86	15.42	0.070	0.175	14.281	5.712
	4	15.809	21.4	93.67	95.33	9.99	13.52	0.071	0.178	14.080	5.616
Untreated	0	11.19	13.34	91.06	92.50	7.07	8.43	0.098	0.24	10.166	4.139

Table (3.36b): Absorption Characteristics at 298 K for 50/50 mol% CEMA/IOA Copolymers Photochemically Crosslinked and /or Grafted onto PET NWF in Presence of 0.5-4% of MMA_m Crosslinker

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	Crude oil
50/50	0.5	18.192	27.23	94.50	96.33	11.50	17.21	0.060	0.176	5.680	16.661
	1	16.740	22.50	94.03	95.56	10.58	14.22	0.062	0.180	5.554	16.124
	2	14.946	19.90	93.31	94.97	9.45	12.58	0.065	0.182	5.493	15.380
	4	13.747	16.20	92.73	93.83	8.69	10.24	0.071	0.199	5.023	14.080
Untreated	0	11.19	13.34	91.06	92.50	7.07	8.43	0.098	0.24	10.166	4.139

absorptivity of materials depends on the bulkiness and length of alkyl constituents, especially the porosity of the microstructure, which can be controlled by crosslinking techniques.