

Crosslinked Poly(octadecene-*alt*-maleic anhydride) Copolymers as Crude Oil Sorbers

Ayman M. Atta,¹ Sabrnal H. El-Hamouly,² Ahmed M. AlSabagh,¹ Moataz M. Gabr³

¹Egyptian Petroleum Research Institute, Petroleum Application Department, Nasr City 11727, Cairo, Egypt

²Chemistry Department, Faculty of Science, Menoufia University, Menoufia, Egypt

³Qarun Petroleum Company, Safety Department, Cairo, Egypt

Received 3 August 2006; accepted 29 December 2006

DOI 10.1002/app.26326

Published online 3 May 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Crosslinked octadecene (OD) and maleic anhydride (MA) copolymer MA/OD (50 : 50 mol ratios) was prepared by condensation of the prepared linear copolymer with different glycols. Ethylene glycol and polyethylene glycols having different molecular weights were used as crosslinking agents. The crosslinked copolymers were evaluated for oil-absorbency application. The effect of glycol type, composition; crosslinker wt % and type of oil on swelling properties of crosslinked polymers were studied through

the oil absorption tests. The swelling parameters, such as the maximum oil absorbency (Q_{\max}), characteristic oil sorbency (Q), characteristic swelling time (T), and swelling rate constant (k), were evaluated for the synthesized sorbers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2113–2120, 2007

Key words: crosslinking; organogel; copolymerization; swelling kinetics; network parameters; octadecene

INTRODUCTION

Oil spills skimmers and sorbents are effective tools used to alleviate oil spill pollution.^{1,2} There are different kinds of polymers that have been widely used to absorb oil spilled on water.^{3,4} The most often used polymers are polypropylene, polyethylene, polypropylene booms, and polyurethane foam, which have highly oleophilic and hydrophobic properties.⁵ Among them, alkyl acrylate and aromatic polymers, which have hydrophobicity and gel-type structure consisting of an elastic network and interstitial space, have been attracting much interest in the field of environmental studies.^{6–12}

The copolymerization of acrylate monomers was carried out by electron-beam irradiation at different dose rates in a previous article.¹³ Furthermore, the crosslinking of these polymers by a high dose electron-beam irradiation in the presence of crosslinkers have been studied.¹³ Synthesis and characterization of linear and crosslinked cinnamoyloxy ethyl methacrylate and alkyl acrylate copolymers for oil absorbency application were studied in a previous article.^{14–16} In the present research, the aim is directed to synthesize new oil sorbers based on hydrophobic monomers (α -olefine monomers) through copolymerization with maleic anhydride (MA) to produce reactive polymers that crosslinked in the presence of ethylene glycol and polyethylene glycol to control the environmental pol-

lution. In this respect, the copolymerization and crosslinking of octadecene (OD) with MA, are the main goals of the present study to increase the oil absorbency of the prepared copolymers. On the other hand, the present study aims to use MA to introduce ester moieties with glycol to increase its solubility in crude oil and to increase oil swelling capacities. Determination of swelling and kinetic parameters of the prepared gels is another goal of the present work.

EXPERIMENTAL

Materials

Octadecene (OD) and maleic anhydride (MA) were obtained from Aldrich Chemical, Germany. The OD was purified by washing with 5% aqueous sodium hydroxide, dried over anhydrous CaCl_2 , and distilled under vacuum. Ethylene glycol (EG), polyethylene glycol₆₀₀ (PEG₆₀₀), polyethylene glycol₂₀₀₀ (PEG₂₀₀₀), and polyethylene glycol₆₀₀₀ (PEG₆₀₀₀) were obtained from Aldrich Chemical Benzoyl peroxide recrystallized from ethanol was used as a thermal polymerization initiator. The Belayium crude oil and condensates were produced from PETROBEL and Rashid Petroleum Companies (Egypt), respectively.

Synthesis of crosslinked MA/OD copolymers

The crosslinked MA/OD copolymers were performed through stepwise polymerization. The copolymer (50/50 mol %) was mixed together with the calculated

Correspondence to: A. M. Atta (khaled_00atta@yahoo.com).

weight percentages of EG and PEG with different weight ratios of polyurethane foam. The stepwise polymerization reactions were performed in Petri dishes at 373 K for 3 h. The time of reaction was extended to assure complete reaction of all monomers. The constituents of the synthesized crosslinked copolymers were calculated according to molar ratios. The crosslinked copolymer foams were post cured at 378 K in air oven. The foams were cut to thin discs, which were used to determine the soluble fraction (SF) and swelling parameters.

Characterization of the prepared polymers

The chemical structure of MA/OD copolymer was determined from FTIR data. FTIR spectra were obtained with Mattson-infinity series bench tab 961 model using KBr discs.

For the crosslinked discs, SF were extracted with chloroform until constant weights were achieved.^{13–16}

Oil absorption test

Oil absorbency of copolymers crosslinked with EG and PEG was determined by ASTM (F726-81) : 0.1 g of blended composite was put in a stainless steel mesh ($4 \times 4 \times 2 \text{ cm}^3$). The sample was immersed in pure toluene, petroleum condensate, or in crude oil solution (crude oil diluted with toluene, 10% oil). The sample and the mesh were together picked up from oil, drained for 30 s, tapped with filter paper to remove excess oil from the bottom of the mesh, and then weighted. The oil absorbency (Q) and equilibrium toluene content (ETC) were calculated as described in a previous article.¹³

The swelling kinetics of oil absorption was studied by repeating the previous measurements at different time intervals. The swelling parameters, Q and ETC, of the prepared gels were calculated from five measurements. To study the kinetics of swelling, gel samples in triplicate were immersed in crude oil. After swelling equilibrium, gel samples were placed in an oven at 318 K for 12 h, which caused gels to deswell. The deswelling was then followed by weighing the gel at various time intervals.

RESULTS AND DISCUSSIONS

The present work aims to prepare copolymers based on hydrophobic moieties. In this respect, OD was selected as the hydrophobic monomer to obtain crosslinked oil sorbers. In previous work,¹³ octene was copolymerized of alkyl acrylate to prepare crosslinked copolymers. In the present investigation, we have extended our work to synthesize copolymers having high oil absorptive capacities. This can be achieved by increasing the lengths of the alkyl substituent

of octene monomers. In this respect, OD monomer was used to copolymerize with the MA monomer. The radical polymerization mechanism is frequently employed for the preparation of copolymers.

High conversion and crosslinked copolymerization

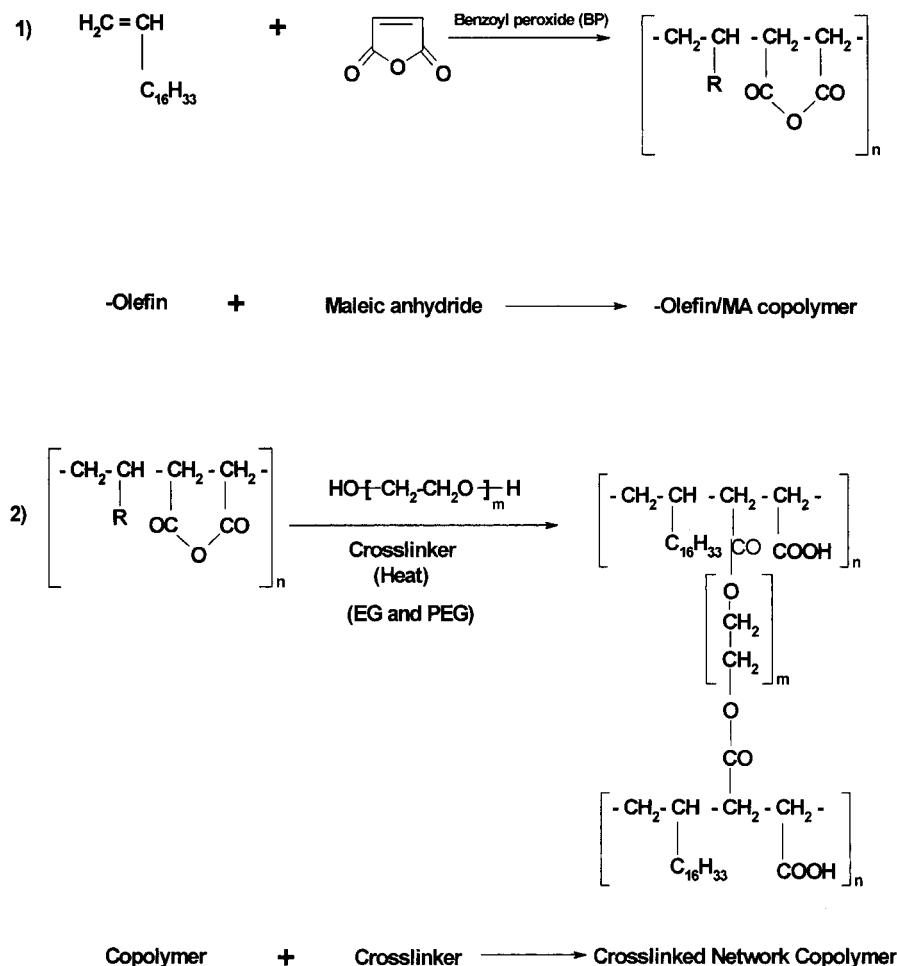
Hydrophobic network polymers are used as absorbents of oil as well as some organic solvents spilled on water in the field of environment. Crosslinking is responsible for the three-dimensional network structure that is important for oil to be swelled into sorbers rather to dissolve in it. Elasticity and swelling properties are attributed to the presence of physical or chemical crosslinks within polymer chains. High conversion polymerization was performed for preparing different crosslinked copolymers. The crosslinked MA/OD copolymer (50/50 mol ratio) was prepared via bulk polymerization in presence of 0.02% BP as an initiator. EG and PEG having different molecular weights were used to form crosslinked polymers through esterification reactions between hydroxyl groups of PEG and anhydride groups of the prepared copolymers. Reaction scheme of the prepared crosslinked copolymers was represented in Scheme 1.

The composite technique is one of the available methods for reinforcing oil sorbers.¹⁷ Fibers, sponges, and nonwoven fabrics were used as reinforces. The sponge was used through two different techniques. The first technique is based on immersion during polymerization of monomers. The second technique is based on coating of sponge with polymer solution. In this respect, the reaction was conducted on PU foam by the second technique.

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 substrate. In a crosslinking system, there are soluble portions and insoluble portions, the former can be extracted with suitable solvents and the latter cannot be extracted with any solvent because of crosslinking. It only swells in good solvent to give a gel. According to Flory's swelling theory,¹⁸ swelling behavior is affected by rubber elasticity, affinity to solution and crosslinking density. Generally, the crosslinker concentrations affect swelling capacity and soluble polymer fractions.

Soluble fraction

Some polymer chains are not attached to the infinite network can be extracted from the gel fraction. The effect of these chains is difficult to treat, and usually



Where;

EG = Ethylene Glycol

PEG = Polyethylene Glycol

Where as;

R = C₁₆H₃₃, the copolymer is MA/OD [EG, PEG600, PEG2000 and PEG 6000].

Scheme 1 Synthesis of crosslinked network copolymers.

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 extractable fraction (soluble fraction) depends on: (a) the type and concentration of the monomers, and (b) the type and concentration of crosslinking agent.¹⁹ In the present investigation the polymers were post cured at 378 K in an air oven for 24 h to assure complete polymerization. The sol fractions of these polymeric materials were determined via Soxhlet extraction technique. In this respect, the dried crosslinked polymers were transferred into an extraction thimble and were subjected to Soxhlet extraction with chloroform. After extraction for 24 h, the samples were dried in atmosphere for several hours and then dried to a constant weight in vacuum oven at 308 K. However, no further extraction was found after 24 h, and this Soxhlet extraction time was

adopted for all samples. The determined SF% values for MA/OD copolymer with EG, PEG600, PEG2000, and PEG6000 are 30.66, 23.14, 20.32, and 16.33, respectively. The data of SF% values for MA/OD copolymer crosslinked with EG is higher than those crosslinked with PEG. This can be attributed to the lower affinity of EG to crosslink MA/OD copolymer. This may be attributed to the differences in reactivity of both EG and PEG crosslinkers with the produced polymer.²⁰

Swelling behavior of the crosslinked copolymers

Water clean up implies recovering oils and hydrocarbon oils from water, among other pollutants. 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.²¹ In this respect, the sorbent should have a high oleophilic or hydrophobic property. The sorption capacity is measured by the

TABLE I
Absorption Characteristics of the MA/OD Copolymers Crosslinked with EG Crosslinker

XCLP : PU	Q_{\max} (g/g)		Q (g/g)		ECC, %		EOC, %		T_{\max} (h)		K (h ⁻¹)	
	Cond.	Oil	Cond.	Oil	Cond.	Oil	Cond.	Oil	Cond.	Oil	Cond.	Oil
1 : 1	54.1	61.5	34.2	38.9	98.2	98.4	0.42	0.3	2.40	3.00		
1 : 3	53.9	57.8	33.8	36.5	98.2	98.3	0.67	0.6	1.48	1.71		
1 : 5	49.2	57.6	31.1	36.4	98.0	98.3	1.0	0.8	1.00	1.20		
1 : 10	47.2	56.1	29.9	35.5	97.9	98.3	1.3	1.17	0.75	0.86		
1 : 5	44.4	49.3	28.1	31.2	97.8	98.0	1.7	1.42	0.66	0.71		

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 recovery operation will be. Sorbents buoyancy and durability in aqueous media are high; it should not retain water or react like a hydrophilic product. Their oil retention capability should also be high, so that the sorbed oil should not drain too quickly. It should rather be reusable and nontoxic for environment if not reused.²² It has been reported that, the excellent oil absorbability of materials depends on the bulkiness and length of the alkyl substituents²³ and especially the permeability of the microstructure, which can be controlled by crosslinking. Because the driving force for oil absorption is caused mainly by the van der Waals force between the material and the oil, therefore, the materials with the proper permeability can effectively absorb more oil in their structures.

The oil used in this experiment is diluted with toluene (10% oil). 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. So that, toluene is the most applicable solvent that used to dissolve asphaltene of crude oil. For these reasons, the diluted crude oil by toluene was used in this experiment. As a result of 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.

Oil absorbencies for composite crosslinked copolymers

In the present investigation the oil absorbency of the crosslinked MA/OD foam composites crosslinked with EG and PEG were determined according to ASTM F 726 81 using paraffin condensate and 10% crude oil. The soluble fractions were extracted from composites using Soxhlet before swelling measurements. The maximum oil absorbencies of composites containing different crosslinked polymers to foam content was calculated and recorded in Tables I–IV. On the other hand, the swelling capacities of used sponge without crosslinked polymers using diluted crude oil and condensate were 12 and 20 g/g, respectively. Previous works^{22–26} showed that for 10% crude oil sample the dry wool-based nonwoven sample sorbs 11.2 g/g sample. Deschamps et al.²² also observed the sorption capacity of different cotton-based materials. They found a maximum sorption of 23 g/g sample for raw cotton and 19 g/g sample for treated cotton in 28% fuel (v/v%) at 20°C. In other words, lower capacities were accomplished by synthetic fibers than by natural ones. Choi et al.²⁴ demonstrated that cotton and milkweed have 1.5–3 times better sorption properties than polypropylene fibers.

TABLE II
Absorption Characteristics of the MA/OD Copolymers Crosslinked with PEG-600 Crosslinker

XCLP : PUFS ^a	Q_{\max} (g/g)		Q (g/g)		ECC, %		EOC, %		T_{\max} (h)		K (h ⁻¹)	
	Cond.	Oil	Cond.	Oil	Cond.	Oil	Cond.	Oil	Cond.	Oil	Cond.	Oil
1 : 1	21.50	24.06	13.59	15.20	95.6	96.00	0.67	0.50	1.50	2.00		
1 : 3	17.78	18.40	11.24	11.63	94.67	94.85	1.17	0.92	0.86	1.09		
1 : 5	17.57	18.21	11.10	11.51	94.61	94.80	1.75	1.50	0.57	0.67		
1 : 10	16.14	17.24	10.20	10.89	94.17	94.52	2.00	1.75	0.50	0.57		
1 : 15	14.35	14.41	9.07	9.11	93.48	93.51	2.50	2.25	0.40	0.44		

^a XCL : PU, weight ratios between crosslinked polymer and polyurethane foam.

TABLE III
Absorption Characteristics of the MA/OD Copolymers Crosslinked with PEG-2000 Crosslinker

XCLP : PUFS*	Q_{\max} (g/g)		Q (g/g)		ECC, %		EOC, %		T_{\max} (h)		K (h ⁻¹)	
	Cond.	Oil	Cond.	Oil	Cond.	Oil	Cond.	Oil	Cond.	Oil	Cond.	Oil
1 : 1	19.64	20.04	12.41	12.67	95.15	95.25	0.83	0.67	1.20	1.50		
1 : 3	16.99	17.89	10.74	11.31	94.44	94.71	1.33	1.17	0.75	0.86		
1 : 5	16.63	17.31	10.51	10.94	94.33	94.54	2.00	1.75	0.50	0.55		
1 : 10	15.66	16.21	9.89	10.25	94.00	94.23	2.33	2.17	0.43	0.46		
1 : 15	13.98	14.19	8.89	8.97	93.33	93.42	2.83	2.67	0.35	0.38		

Zhou and Cho²⁵ and Zhou and Ha²⁶ reported that, the highest Q_{\max} observed for 4-*tert* butylstyrene-SBR-divinylbenzene was 57.76 g/g polymer at a solvent amount of 15.0 mL/g after being immersed in oil solution for 48 h. The oil absorbency of 4-*tert*-butylstyrene-ethylene-propylene-divinylbenzene (PBED) graft terpolymer was reported by Zhou and Cho.²⁵ They have got maximum oil absorbency (84.0 g/g) for the treated PBED.

On the other hand, the swelling curve is based on plotting the relation between oil absorbencies versus immersion times. In this respect, the oil absorbencies for MA/OD foam composites crosslinked with EG and PEG upon using 10% crude as an oil as a function of immersion time was also calculated and listed in the same Tables I–IV. This relation was also represented upon using paraffin condensate and crude oil as shown in Figures 1–4. In these figures, it is obvious that the oil absorbency increases with increasing the immersion time and leveled off at 2 h. It is also observed that, the oil absorbency decreases slightly upon using condensate instead of 10% crude toluene solution. This may be explained as follow; the swelling process of polymer networks may be primarily due to the oil solution penetrate into the polymeric gel through capillary and diffusion. Therefore, the diluted crude oil with toluene can be easily diffused from external surface of the sample into the internal space of networks.²⁷ The molecular mechanism of solvent transfer is dependent on the properties of the components. The large mass, chain structure, and flexibility of macromolecules affect the nature of diffusion in polymer-solvent systems. The properties of the system are function not only of the nature of the components

but also of their composition. Mixing of a polymer with a solvent involves change in the energy of interaction and in the number of direct contacts between the polymer chains. Intermolecular interaction changes little when polymer–polymer contacts are replaced by polymer-solvents contacts, but the mobility of the segments of the polymer molecules increases. The thermal motion of molecules under the influence of a concentration gradient is associated with cooperative movement of neighboring molecules. The probability of this process is dependent on the mobility of the molecules of the medium. The higher solvent content of the system the greater is the mobility and the less the energy required for movement of the diffusing molecules. Assuming an exponential dependence of this energy on composition it is possible to find the relationship connecting the unidirectional coefficient of diffusion with the solvent concentration.²⁸ When a molecule moves under the influence of a concentration gradient the molecule is orientated in the direction of movement,²⁹ and is subjected to two types of resistances, namely “lateral” and “frontal” resistances. The first is determined by the amount of movement that the moving molecule transmits to the surrounding medium. It is dependent on the interaction of the medium molecules with the diffusing molecules, and is proportional to the size or to the first approximation of mass of the molecule. The second is associated with the necessity for movement of the molecules of the diffusion medium for the formation of gaps of the required dimensions. This resistance is on the one hand proportional to the minimal cross-sectional area of the diffusing molecule, that is, it is determined by its structure. Also, it is dependent on

TABLE IV
Absorption Characteristics of the MA/OD Copolymers Crosslinked with PEG-6000 Crosslinker

XCLP : PUFS*	Q_{\max} (g/g)		Q (g/g)		ECC, %		EOC, %		T_{\max} (h)		K (h ⁻¹)	
	Cond.	Oil	Cond.	Oil	Cond.	Oil	Cond.	Oil	Cond.	Oil	Cond.	Oil
1 : 1	16.43	16.98	10.38	10.73	94.26	94.44	1	0.92	1.00	1.09		
1 : 3	15.98	16.56	10.10	10.46	94.11	94.30	1.5	1.33	0.67	0.75		
1 : 5	15.44	16.01	9.76	10.12	93.92	94.12	2.25	2.00	0.44	0.50		
1 : 10	14.82	15.65	9.37	9.89	93.68	93.99	2.5	2.33	0.40	0.43		
1 : 15	13.95	14.85	8.82	9.38	93.31	93.69	3	2.83	0.33	0.35		

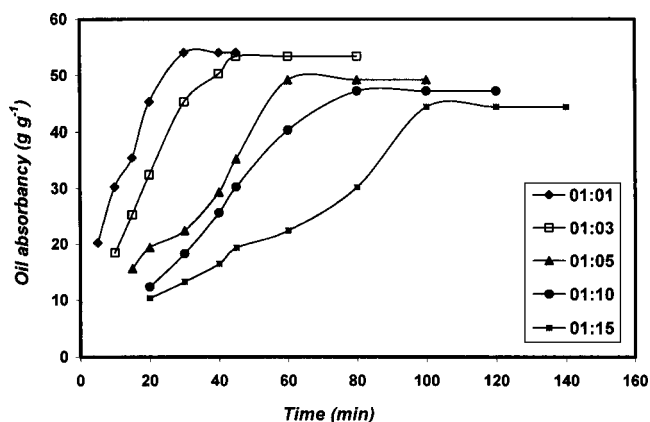


Figure 1 Oil absorbency for MA/OD-EG copolymer in parffin condensate at different polymer/foam ratios.

the molecular interaction between the molecules of the medium and on the compressibility of the latter. Both types of resistance are determined to a considerable extent by the viscosity of the medium.³⁰

Careful inspection of the listed data in Tables I–IV, in respect to effect of crosslinker type on the oil absorbencies of MA/OD foam composites, it was found that the oil absorbency decreased with increasing the molecular weight of crosslinkers. These can be attributed to the increasing of probability for formation of highly crosslinked polymer when the molecular weight of PEG increased that is, restricted relaxation of the polymeric chain.³¹ By comparing the maximum oil absorbency Q_{max} of MA/OD foam composites crosslinked with EG and those crosslinked with PEG 6000, it was found that the crosslinked sorbers with EG give higher Q_{max} than those crosslinked with PEG 600, 2000, and 6000. This is mainly due to lower crosslinking density with EG. These results run in harmony with SF% data which confirm that PEG 6000 is more efficient as a crosslinker than EG. On the other hand, this can be also attributed to decreasing the hydropho-

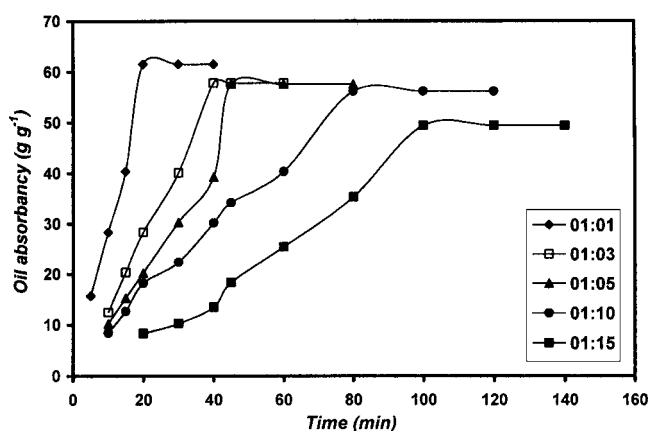


Figure 2 Oil absorbency for MA/OD-EG copolymer in parffin crude Oil at different polymer/foam ratios.

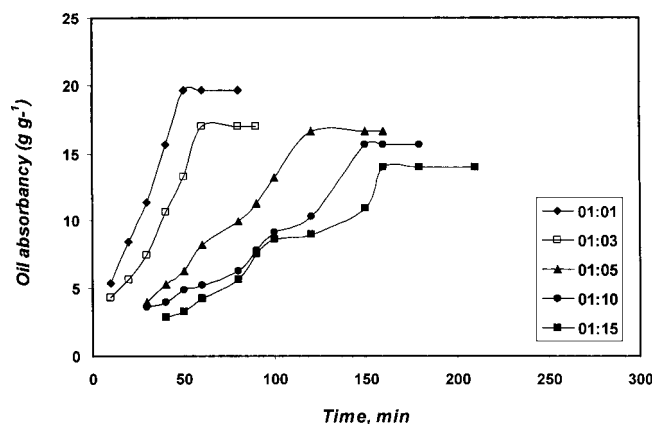


Figure 3 Oil absorbency for OD/MA-PEG 2000 copolymer in parffin condensate at different polymer/polyurethane ratios.

bicity of polymeric network when the molecular weight of PEG was increased. This indicates that, the swelling capacities increases with increasing of hydrophobicity of copolymers and *vice versa* with increasing of hydrophilicity. From the data listed in Tables I–IV, it is observed that the oil absorbency is increased for MA/OD copolymers. This can be attributed for two reasons based on the reactivity ratios between monomers and crosslinkers and also to hydrophobicity of copolymers. The reactivity ratios of copolymer, which discussed previously, indicate that the MA have a tendency to form alternating copolymer with OD monomer.³² Accordingly the probability for reaction of EG and PEG can be arranged in the same order but the steric hindrance of C-18 α -olefin will inhibit the reaction of PEG with MA.

The effect of foam to crosslinked copolymers ratios with oil absorbance capacities was determined and represented in Figures 1–4. It was observed that, the best swelling ratios were obtained when the ratio between foam and crosslinked copolymers was 1 : 1

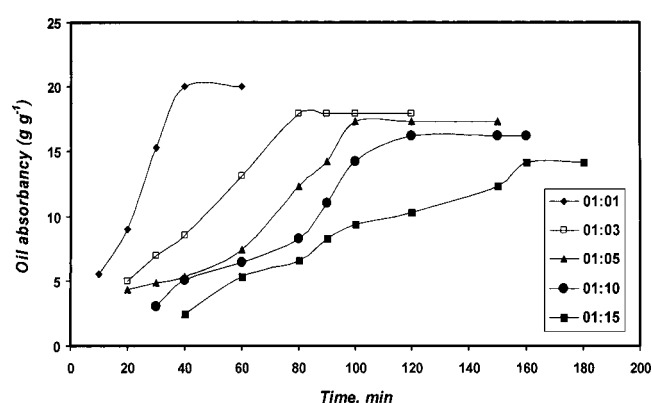


Figure 4 Oil absorbency for OD/MA-PEG 2000 copolymer in parffin crude oil at different polymer/polyurethane ratios.

and decreased when the wt % of crosslinked increased to 1 : 15 wt %. This phenomenon may be explained by considering that oil absorption of composites is probably synergized by the supporter. Probably, too much crosslinked copolymers will stuff many pores that exist in the sponge and give large specific surface area. In contrast, the crosslinked polymers in the pores may not swell freely.³³

Swelling kinetics of the synthesized crosslinked copolymers

The sorption and diffusion of organic solvents through crosslinked polymer networks has been a subject of great interest.³⁴ The sorption behavior gives an idea about the permeability and diffusion coefficient of penetrant through polymers, which are used in various applications, such as, gel permeation chromatography, ion-exchangers, and controlled-release of drugs. Consequently, 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 Ref. 35 in which the swelling rate can be described by the following experimental equation:

$$\frac{dQ}{dT} = K(Q_{\max} - Q) \quad (1)$$

where Q_{\max} and Q are the maximum and the characteristic oil absorbency, respectively, while K is the swelling kinetic constant. Integration of eq. (2) gives:

$$-\ln(Q_{\max} - Q) = Kt + C \quad (2)$$

where, t is the characteristic swelling time and C is the integration constant.

As a consequence of $t = 0$, $Q = 0$, and $-\ln Q_{\max} = C$, therefore

$$\ln(Q_{\max}/(Q_{\max} - Q)) = kt \quad (3)$$

For an example, the characteristic swelling time is defined at

$$Q = 0.632 Q_{\max} \quad (4)$$

According to Yao and Zhou,³⁵ the swelling kinetic of the investigated crosslinked polymers MA/OD was studied. The swelling parameters were determined from the swelling curves are shown in Figures 1–4 as representative samples. Tables III and IV show the equilibrium condensate content (ECC %) and the equilibrium oil content (EOC %), oil content characteristic time required for the swelling (T), maximum swelling time (T_{\max}) required to reach equilibrium and swelling kinetic constant (k) for the prepared reactive crosslinked copolymers. Swelling kinetic constant values (k) are also listed in these Tables III and IV. The (k)

values increase with decreasing the molecular weight of crosslinker (EG and PEG). This may be due to increase of crosslinker (wt %) leads to stiffens of the obtained crosslinker polymer, further small swelling was obtained because of resulting low polymer solvent interaction. Considering that the swelling kinetics may be depend not only on the surfaces of the polymer but also on the elasticity of the polymer network. The more elastic network will provide larger absorption surfaces, which give higher swelling rate of the polymeric network, namely large value of (k). In other words, the polymer with higher swelling rate may have suitable structure for oil absorption.²⁶

Regarding T_{\max} values in either oil medium or condensate cases (condensate and 10% diluted crude oil toluene solution), generally it is noticeable that as the ethyloxy chain length of crosslinker increases the T_{\max} increase. This behavior may be due to increase of molecular weight of PEG leading to increase the hydrophilic nature of the polymer matrix. The swelling rate constant (k) increases with decreasing the molecular weight of the PEG crosslinkers as cleared in Tables I–IV. This may be explained on the basis of swelling mode, which indicates that, the swelling process of polymeric networks is primarily due to oil solution penetrating into the polymeric gel through diffusion. Here, increasing the ethyloxy chain length increases the hydrophilicity of the polymeric networks, thus increasing the difficulty of oil diffusion. In other words, low compatibility between oil and the polymeric networks hinders oil diffusion. Comparing the swelling rate constants between the gels swelled in 10% crude oil and those which swelled in condensate, the former always shows higher values than the later. This behavior can be easily explained on the basis of different viscosity of either 10% diluted crude oil with toluene and condensate that cannot easily diffuse from the surface of the gels into the internal space of the network.

CONCLUSIONS

The conclusion of this work can be stated in the following:

1. The prepared crosslinked copolymers exhibited a higher absorption capacity of crude oil than which obtained for paraffin condensate.
2. The polyurethane foam used as a supporter to the crosslinked copolymer. The ratio 1 : 1 polyurethane foam to crosslinked copolymer exhibited the maximum oil absorption capacity.
3. The data indicate that the copolymer crosslinked with ethylene glycol (EG) exhibited higher absorption efficiency than that crosslinked with olyethylene glycol. Meanwhile the low molecular

weight PEG600 exhibited higher absorption among PEG2000 or PEG6000.

References

1. Davis, S. C.; Hellens W. V.; Zahalka H. A. In *Polymeric Materials Encyclopedia*, Vol. 4; Salamone, J. C., Ed.; CRC Press: New York, 1996; pp 2264–2271.
2. Liu, Y.; Mao R.; Huglin, M. B.; Holmes, P. A. *Polymer* 1996, 37, 1437.
3. Bertrand, P. A. *J Mater Res* 1993, 8, 1749.
4. Anthony, W. S. *Appl Eng Agric* 1994, 10, 357.
5. Schrader, E. L. *Environ Geol Water Sci* 1991, 17, 156.
6. Zhou, M. H.; Cho, W. *J Polym Int* 2000, 49, 17.
7. Martel, B.; Morcellet, M. J. *J Appl Polym Sci* 1994, 51, 443.
8. Monji, N.; Hoffman, A. S. *Appl Biochem Biotechnol* 1987, 14, 107.
9. Saito, S.; Kanno, M.; Inomoto, H. *Adv Polym Sci* 1993, 109, 207.
10. Sayil, C.; Okay, O. *Polymer* 2001, 42, 7637.
11. Okano, T. *Adv Polym Sci* 1993, 110, 180.
12. Atta, A. M. *Polym Adv Technol* 2002, 13, 567.
13. Atta, A. M.; Arndt, K.-F. *J Appl Polym Sci* 2005, 97, 80.
14. Atta, A. M.; Rasha, A. M.; Farag, R. K.; El-Kafrawy, A. F.; Abdel-Azim, A. A. *Polym Int* 2005, 54, 1088.
15. Atta, A. M.; Rasha, A. M.; Farag, R. K.; Abdel-Azim, A. A. *React Funct Polym* 2006, 66, 931.
16. Atta, A. M.; Rasha, A. M.; Farag, R. K.; Abdel-Azim, A. A. *J Polym Res* 2006, 13, 257.
17. Zhou, M. H.; Cho, W. *J Polym Int* 2001, 50, 1193.
18. Flory, P. J. In *Principles of Polymer Chemistry*; Baker, G. F., Ed.; Cornell University Press: Ithaca, New York, 1953; Chapter 13.
19. Kossmehl, T. M.; Abdel-Bary, E. M.; Sarhan, A. A.; Abdelaal, M. *Die Angew Makromol Chem* 1994, 215, 59.
20. Atta, A. M.; Arndt, K. F. *Polym Int* 2001, 50, 1360.
21. Pete, J. *Nonwovens Ind* 1992, 6, 32.
22. Deschamps, G.; Caruel, H.; Borredon, M. E.; Bonnin, C.; Vignoles, C. *Environ Sci Technol* 2003, 37, 1013.
23. Kim, S.; Chung, I.; Ha, C.; Kim, K.; Cho, W. *J Appl Polym Sci* 1999, 73, 2349.
24. Choi, H. M.; Kwon, H. J.; Moreau, J. P. *Text Res J* 1993, 63, 211.
25. Zhou, M. H.; Cho, W. *J Appl Polym Sci* 2002, 85, 2119.
26. Zhou, M. H.; Ha, C. S. *J Appl Polym Sci* 2001, 81, 2119.
27. Jang, J.; Kim, B. S. *J Appl Polym Sci* 2000, 77, 914.
28. Vasenin, R. M. *Vysokomole* 1960, 2, 885.
29. Aitkin, A.; Barrer, R. *Trans Faraday Soc* 1955, 5, 116.
30. Vasenin, R. M. *Vysokomole* 1960, 2, 1220.
31. Flory, P. J.; Rehner, J. *J Chem Phys* 1943, 11, 512.
32. Davies, M. C.; Dawkins, J. V.; Hourston, D. J.; Meehan, E. *Polymer* 2002, 43, 4311.
33. Zhou, M. H.; Hao, C. S.; Cho, W. *J Appl Polym Sci* 2001, 81, 1277.
34. Poh, B. T.; Adachi, K.; Kotaka, T. *Macromolecules* 1987, 20, 2563.
35. Yoa, K. J.; Zhou, W. *J Appl Polym Sci* 1994, 53, 1533.