



Swelling and network parameters of crosslinked porous octadecyl acrylate copolymers as oil spill sorbers

Abdel-Azim A. Abdel-Azim,¹ A. Mahmoud Abdul-Raheim,^{1 2} Ayman Mohamady Atta,^{1*} Witold Brostow,² Tea Datashvili²

^{1*}Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt; fax +20-2-274-7443; e-mail: khaled00atta@yahoo.com

²Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering, University of North Texas, 1150 Union Circle # 305310, Denton, TX 76203-5017, USA; e-mail: wbrostow@yahoo.com, tea0033@marta.phys.unt.edu; <http://www.unt.edu/LAPOM/>

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Abstract: In previous work crosslinked copolymers were prepared from cinnamoyloxy ethyl methacrylate (CEMA) and several monomers feed ratios of octadecyl acrylate (ODA). Networks so produced are both flexible and porous; we now report their swelling efficacies as a function of temperature in toluene and in crude petroleum. Network characteristics is presented including the polymer + solvent interaction parameter χ , effective crosslink density ν_e , equilibrium modulus of elasticity E , average molecular weight between crosslinks M_c and the theoretical crosslink density ν_t . These parameters are correlated with structures of the synthesized sorbers.

Keywords: petroleum sorbers; copolymerization; acrylate crosslinkers; smart polymers; polymer networks; porous polymers

Introduction

Pollution by petroleum spills is one of the most dangerous threats to environment. Therefore, various kinds of polymers have been used to absorb oil spilled on water [1, 2]. Polypropylene (PP), polyethylene (PE) and polyurethane (PU) foams have strong oleophilic and hydrophobic properties and are widely used as sorbents in remediation of oil spills [3]. Among such materials, alkyl acrylate and aromatic polymers with hydrophobicity and gel-type structures consisting of an elastic network and interstitial space have attracted interest [4 - 10].

Jang and Kim [11] performed copolymerization of styrene monomers with various long-chain alkyl acrylate monomers; acrylate monomers with long-chain alkyl groups are generally known as hydrophobic materials. Earlier publications [12, 13] describe synthesis of cinnamoyloxy ethyl methacrylate (CEMA) monomer to be used in preparation via different types of chemical crosslinkers of new oil-absorbing polymers containing alkyl acrylate. In this work, swelling properties of the crosslinked copolymers and swelling parameters such as maximum oil absorbency $Q_{\max}$, characteristic oil sorbency Q , characteristic swelling time t_s and swelling rate constant k were evaluated. These values were used to determine the efficiency of each sorber to absorb oil or toluene. Effects of temperature change, type of the crosslinking agent and monomer feed composition were evaluated via oil absorption tests. Network

parameters such as polymer + solvent interaction parameter χ , effective crosslink density ν_e , equilibrium modulus of elasticity E , average molecular weight between crosslinks M_c and theoretical crosslink density ν_t were determined and correlated with the structure of the synthesized sorbers.

Results and Discussion

Crosslinked copolymers

We have reported before synthesis of crosslinked CEMA/ODA copolymers [13]. Their thermal stability, mechanical properties and morphology have been evaluated. The copolymers so prepared have porous and elastic networks. Since the copolymers are based on hydrophobic moieties such as alkyl or phenyl groups, efficient petroleum sorbers were expected. Therefore, we have now evaluated the swelling efficacy and the network parameters of CEMA/ODA copolymers. To study the effect of composition on swelling properties different mole ratios of CEMA and ODA were copolymerized in presence of 1.0 wt. % of either MA or MM crosslinker. We have also investigated the effect of crosslinker and temperature variation.

According to the Flory swelling theory [15 - 17], swelling behavior is affected by rubber elasticity, affinity to solution, and crosslinking density. Some polymer chains, called soluble fractions, are not attached to the infinite network and can be extracted from the gel fraction. The effect of these chains is difficult to be treated, and is usually neglected in the models. Such short chains do not contribute to the modulus - but can be solvated and can contribute to the swelling. Therefore, it is desirable to eliminate or minimize the content of these extractable molecules. The percentage of the soluble fraction depends on: (a) the type and concentration of the monomers and (b) the type and concentration of the crosslinking agent [22].

Tab. 1. Soluble fraction (SF) and conversion percentage.

Xerogel composition (CEMA/ODA)	Crosslinker content (Wt. %)	Conversion %		SF of crosslinked gel in toluene (%)	
		AM	MM	AM	MM
90/10	1.0	86.4	87.3	29	22
70/30	1.0	88.7	89.1	25	20
	0.5	87.9	88.7	29	25
50/50	1.0	89.0	89.8	20	15
	2.0	89.9	90.7	15	10
	4.0	91.6	92.5	10	8
30/70	1.0	90.1	91.0	18	12
10/90	1.0	91.4	92.1	15	8

In our case polymer rods were post-cured at 378 K in an air oven for 24 h to assure complete polymerization. The sol fractions in these polymeric materials were determined via the Soxhlet extraction technique similarly as in earlier work [23 – 26]. Thus, dry xerogel was subjected to extraction of soluble fraction with chloroform) for 24 h. Then the samples were dried in air atmosphere for several hours, and finally dried to a constant weight in a vacuum oven at 308 K. We investigated the reactivity of a crosslinkers containing acrylate groups (MA) and those with methacrylate groups (MM) towards CEMA/ODA copolymers from polymerization conversion and SF

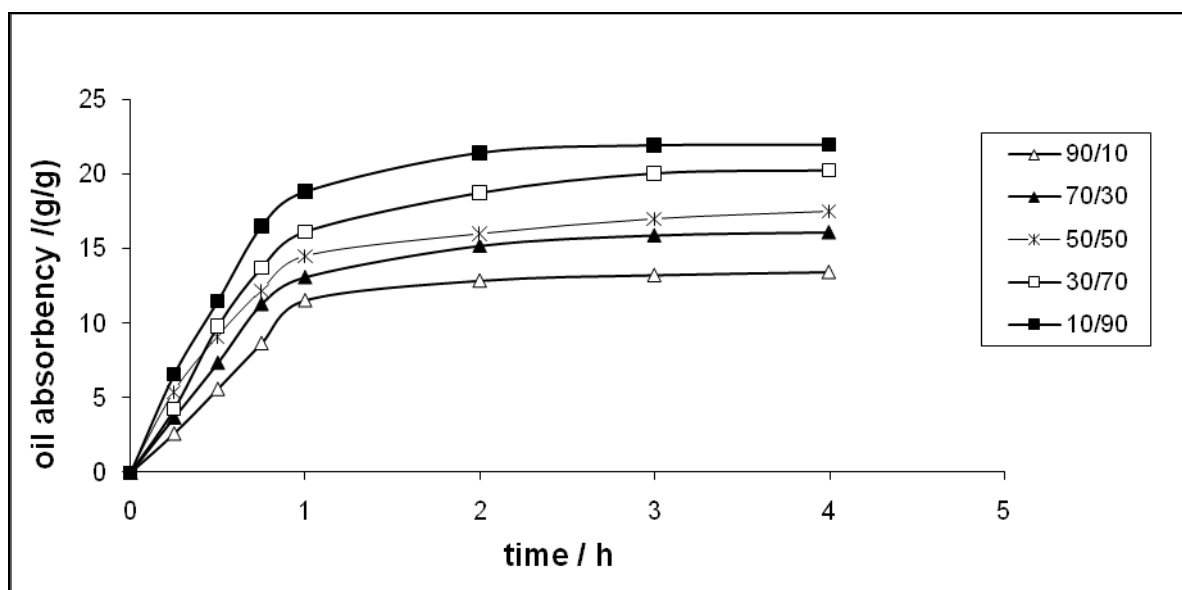
measurements in chloroform. The degree of conversion of monomers to crosslinked polymers was calculated as $= (W \cdot 100 / W_0) \%$; here W and W_0 are the total weights of the crosslinked polymers after post-curing and the weight of the reactants, respectively. The results are listed in Table 1.

Table 1 shows variation of the percentage of conversion for all compositions of CEMA and ODA monomers with 1 % crosslinker and with different crosslinker weight contents for 50 % mole (CEMA) and 50% mole ODA. We find that the crosslinking conversion percentages increase as the amount of ODA increase. This indicates that the efficiency of crosslinking increased with increasing acrylate content. The effect of the crosslinker concentrations on the SF values was determined through the crosslinking of CEMA (50 mole %)/ODA (50 mole %) copolymer with different contents of MA or MM: 0.5 %, 1.0 %, 2.0 % and 4.0 wt. %. We see that the percentage of SF for crosslinked copolymers is reduced when the crosslinker content increases from 0.5 % to 4.0 wt. %. This indicates that a low content of MA or MM crosslinkers reduces the probability of side reactions since they affect the crosslinking activity.

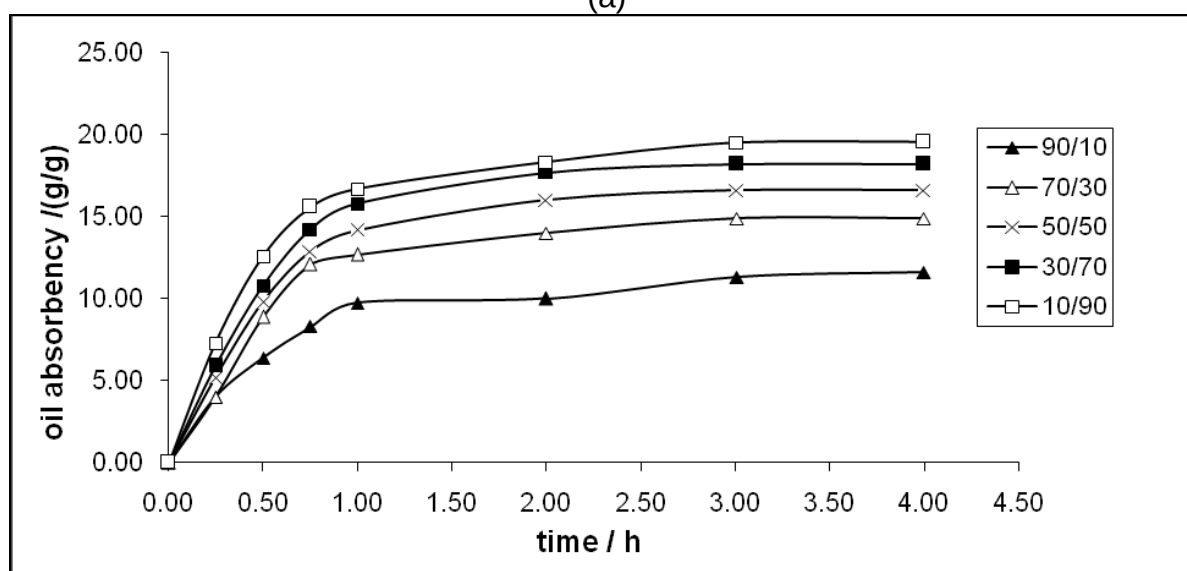
We also see that SF values for each of our copolymers crosslinked with MM are lower than those for crosslinked with MA. This may be attributed to differences in the reactivity ratios of both crosslinkers with the produced polymer [13]; the presence of methyl groups in MM allows participation in the crosslinking reaction of CEMA/ODA more readily than MA. Effects of copolymer compositions on SF values were determined by crosslinking different compositions of CEMA/ODA copolymer using 1.0 wt. % of crosslinker (either MA or MM) and 0.2 wt. % of AIBN as initiator. We find that SF decreases with increasing alkyl acrylate percentage in the copolymer composition. This is related to higher reactivity of octadecyl acrylate homopolymer towards either crosslinker compared to that of CEMA/ODA copolymer. In other words, the octadecyl acrylate polymers are consumed before a significant number of CEMA units would incorporate in the network structure.

Swelling behavior of crosslinked copolymers

Water cleanup implies recovering petroleum and hydrocarbon oils from water. While several techniques exist, the use of a sorbent allows separation of petroleum from water so that petroleum can easily be recovered [27]. In this respect, the oil sorber should be highly oleophilic and hydrophobic. The petroleum retention capability should also be high, so that the sorbed petroleum should not drain too quickly. Kim and coworkers reported that petroleum absorptivity depends on bulkiness and length of alkyl substituents [28] and especially on porosity of the microstructure. The porosity can be controlled by crosslinking. The driving force for petroleum absorption is mainly created by van der Waals interactions between the material and petroleum. Thus, materials with high porosity can effectively contain petroleum in their structures. Materials used to absorb petroleum should *not* have a sponge-like structure with widely open pores. Therefore, heavy petroleum with high viscosity – such as Belayium crude oil - cannot easily diffuse from the surface of the samples into the internal space of the network. On the other hand, toluene is the most applicable solvent that is used to dissolve asphaltenes in crude petroleum. We have determined petroleum absorbencies of different compositions of CEMA/ODA crosslinked copolymers as a function of immersion time using pure toluene and 10% crude oil medium. The results are presented in Figures 1 and 2.



(a)

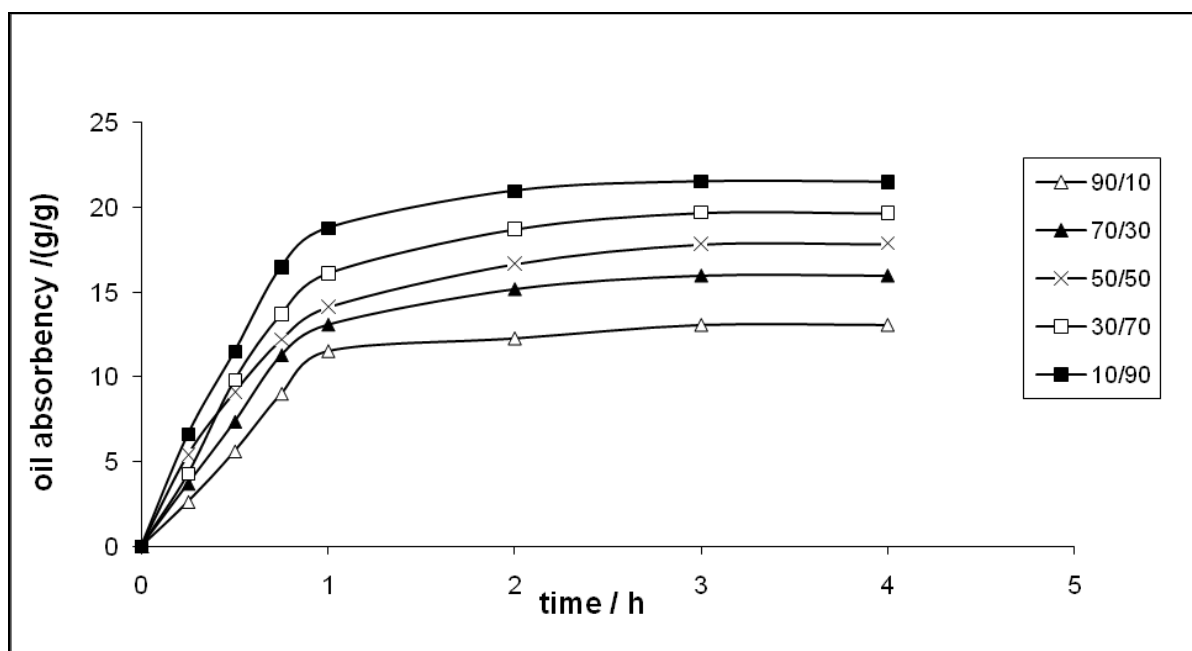


(b)

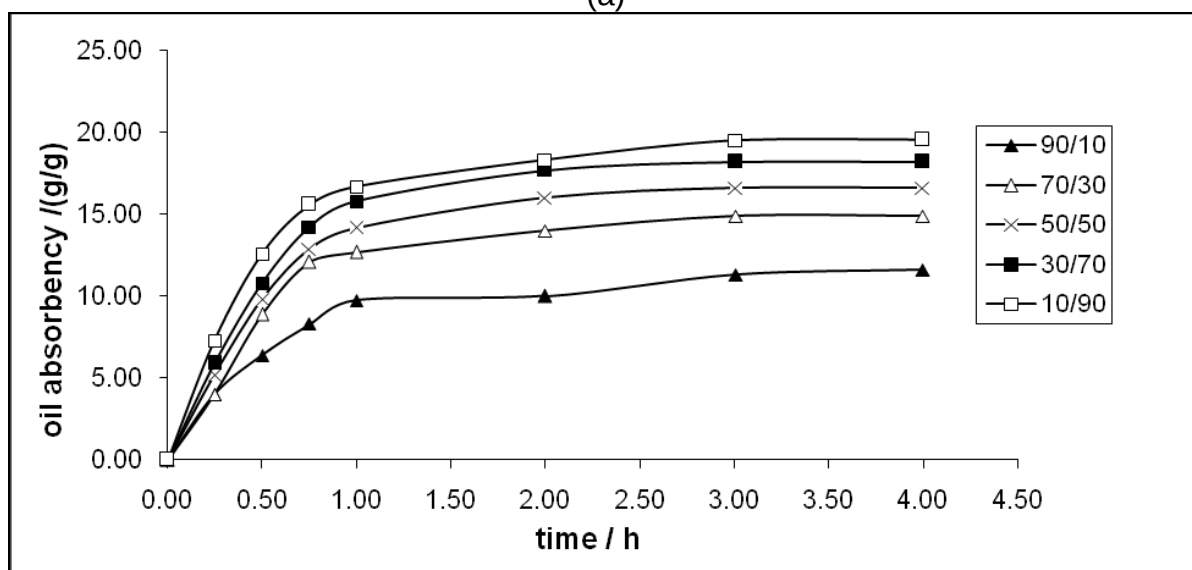
Fig. 1. Petroleum absorbency vs. time curves at 298 K for CEMA/ODA copolymers in toluene at different mole ratios of CEMA and ODA: (a) 1.0 wt. % MACrosslinker; (b) 1.0 wt. % MM crosslinker.

We find that the oil absorbency increases with increasing the immersion time – as expected. The maximum swelling values are attained in 3 h. Clearly the swelling capacities are affected by the hydrophobicity and the crosslinking density of copolymers. We also observe that the oil absorbency increases with increasing alkyl acrylate content. An increase in acrylate ratio in the crosslinked copolymer increases the hydrophobicity of crosslinked network. Further we note that the oil absorbency decreases slightly upon using 10 % crude oil instead of pure toluene. This could be due to higher viscosity of crude petroleum which causes two opposite effects: decrease of sorption as the penetration through interior of network is inhibited and improved sorption since petroleum adheres better to the sorbent – as discussed by Choi and Cloud [29]. This was noticeable upon using pure toluene or diluted crude oil medium respectively, different CEMA/ODA molar compositions and MA or MM

crosslinkers. Radetic and coworkers [30] report that a large amount of petroleum was sorbed originally, but later drained fairly rapidly. In our materials we see an initial increase in absorption followed by establishment of an approximately horizontal plateau. This applies to both toluene and 10 % crude oil in toluene.



(a)



(b)

Fig. 2. Petroleum absorbency vs. time curves at 298 K for CE/MA copolymers in 10 wt. % crude oil diluted with toluene at different mole ratios of CE and MA: (a) 1.0 wt. % MA crosslinker; (b) 1.0 wt. % MM crosslinker.

Effect of temperature on swelling

As discussed by Bignotti and coworkers [31], crosslinked polymers are intelligent or smart materials. Thus, they are capable of undergoing sharp physical or chemical modifications in response to external stimuli such as temperature or pH. Smart materials are used in a variety of applications including diagnostic, therapeutic, and

implantable devices, and in particular in controlled release drug delivery systems where they have been studied extensively [32 - 36]. We recall that another option in drug delivery systems consists in using uncrosslinked polymers as a medium slowing drug delivery; a measure of success of this operation is a change of the glass transition temperature T_g as compared to the neat polymer [37].

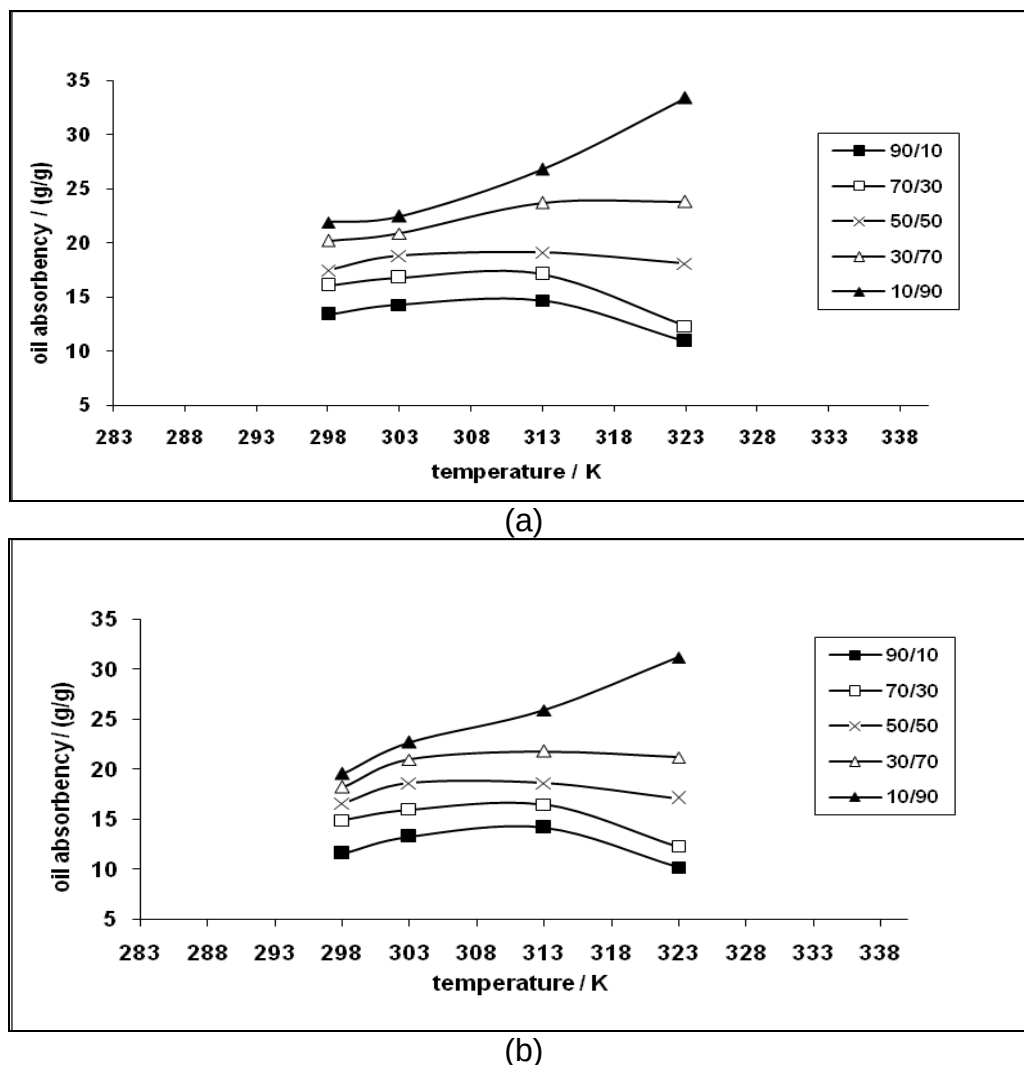


Fig. 3. Effect of temperature on toluene uptake for crosslinked CEMA/ODA copolymers with a) MA and b) MM crosslinkers.

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 increasing 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 [35]. For more discussion of both UCST and LCST see for instance Gedde [38]. Generally, in temperature sensitive polymers, incorporation of a hydrophilic comonomer leads to an increase in LCST, whereas incorporation of a hydrophobic comonomer leads to a decrease in LCST [39 - 41]. There is a combined effect of swelling decreasing with temperature, down to a minimum value and

thereafter increasing at still higher temperatures. Of particular interest to us is the negative temperature sensitive property of these gels, which offers significant possibilities for use in petroleum sorber systems. Therefore, swelling characteristics of our CEMA/ODA copolymers crosslinked with MA and MM crosslinkers were measured at several temperatures. The results are shown respectively in Figure 3a and b.

We see that the swelling characteristics show two different behaviors, positive and negative temperature dependence, depending on copolymer compositions. The toluene uptake increases with temperature with increasing ODA content from 50 to 90 mol. %, hence the process is endothermic. This process depends on the polymer + organic liquid interactions; toluene is good solvent for these polymers. In the case of a negative effect, the cause is hydrophobic character of the hydrogel.

Network characteristics

The network parameters: crosslinking density ν_e , molecular weight between crosslinks M_c , polymer + solvent interaction parameter χ , theoretical crosslinking density ν_t , and mass densities ρ in $\text{kg}\cdot\text{dm}^{-3}$ of xerogels were determined from the swelling measurements of copolymers with pure toluene or 10 % crude oil + toluene by using equations provided above. The results are presented in Tables 2 – 5.

Tab. 2. Network parameters at 298 K for several compositions of CEMA/ODA copolymers crosslinked with varying concentrations of MA.

Xerogel composition	Crosslinker content	ν_t mol/dm ³	$\nu_e \cdot 10^3$ (mol/dm ³)		$M_c \cdot 10^{-3}$ (g/mole)		χ	
			Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.659	67.5	64.1	9.31	9.80	0.328	0.351
70/30	1	0.628	45.1	45.8	13.28	13.08	0.310	0.310
	0.5	0.516	37.9	40.3	13.36	12.56	0.262	0.263
50/50	1	0.691	39.0	39.4	17.02	16.86	0.296	0.308
	2	0.764	41.4	41.0	17.70	17.88	0.309	0.320
	4	0.795	47.7	45.6	16.01	16.74	0.305	0.327
30/70	1	0.607	32.3	32.9	17.96	17.61	0.260	0.272
10/90	1	0.544	30.4	30.5	17.20	17.14	0.226	0.237

Tab. 3. Further network parameters.

Xerogel composition	Crosslinker content	Density ρ_p /(kg/dm ³)	Φ_p		E/(MN·m ⁻²)	
			Toluene	crude oil	Toluene	crude oil
90/10	1	0.63	0.075	0.077	13.87	13.52
70/30	1	0.60	0.062	0.063	7.72	7.88
	0.5	0.51	0.053	0.055	5.56	6.07
	1	0.66	0.057	0.059	6.14	6.36
	2	0.73	0.060	0.061	6.83	6.88
50/50	4	0.76	0.063	0.065	8.26	8.10
30/70	1	0.58	0.050	0.051	4.40	4.62
10/90	1	0.52	0.046	0.046	3.81	3.90

The compression modulae were calculated as

$$E = RT v_e \Phi_p^{1/3} \quad (1)$$

Here as usual R is the gas constant, T the thermodynamic temperature in K; Φ_p is defined below in Eqs. (5) and (6).

Tab. 4. Network parameters at 298 K for several compositions of CEMA/ODA copolymers crosslinked with varying concentrations of MM

Xerogel composition	Crosslinker content	u_t mol/dm ³	$u_e \cdot 10^3$ (mol/dm ³)		$M_c \cdot 10^{-3}$ (g/mole)		χ	
			toluene	crude oil	toluene	crude oil	toluene	crude oil
90/10	1	0.701	71.6	76.1	10.75	10.11	0.390	0.392
70/30	1	0.665	48.8	49.5	14.97	14.77	0.334	0.345
	0.5	0.621	36.7	39.2	18.58	17.39	0.296	0.308
50/50	1	0.710	44.2	45.7	17.65	17.05	0.298	0.309
	2	0.771	45.2	49.7	18.77	17.03	0.309	0.323
	4	0.798	60.3	74.7	14.53	11.73	0.314	0.328
30/70	1	0.621	40.9	42.0	16.69	16.22	0.263	0.274
10/90	1	0.576	36.2	36.9	17.49	17.15	0.250	0.261

Tab. 5. Further network parameters.

Xerogel composition	Crosslinker content	Density $\rho_p/(\text{kg/dm}^3)$	Φ_p		$E/\text{MN}\cdot\text{m}^{-2}$	
			toluene	Crude oil	toluene	crude oil
90/10	1	0.77	0.086	0.088	16.99	18.47
70/30	1	0.73	0.067	0.069	9.02	9.39
	0.5	0.68	0.056	0.058	5.62	6.31
50/50	1	0.78	0.060	0.062	7.32	7.85
	2	0.85	0.062	0.066	7.72	9.05
	4	0.88	0.070	0.077	11.61	15.92
30/70	1	0.68	0.055	0.057	6.18	6.56
10/90	1	0.63	0.051	0.053	5.10	5.34

The compression modulae E calculated from Eq. (1) are listed in Tables 3 and 5. Bastide and coworkers [42] report that the values of the modulae decrease dramatically when the proportion of pendant chains increase. We see that formation of dangling chains increased when using MA instead of MM as the crosslinker.

Similarly, values of E and v_e decrease with increasing the alkyl acrylate proportion in the copolymers, and increase with increasing crosslinker weight content. This can be seen analyzing the Flory-Huggins-Staverman interaction parameters χ listed in Tables 2 and 4. χ values for copolymers crosslinked by MA are lower than for the MM crosslinker. By definition, the lower χ is, the stronger the polymer + solvent interaction [43 - 45]; negative values of χ are also possible when interactions still stronger than for $\chi = 0$ are present. Thus - and as expected from the above results - crosslinking with MA increasing the concentration of the dangling groups reinforces the copolymer + solvent interactions.

M_c results for both crosslinkers are listed in Tables 2 and 4. We see that M_c values for the MM networks are always smaller than for MA-crosslinked networks. These results agree with those discussed above: more dangling chains in MA networks cause larger M_c values. As the crosslinking density increases (smaller M_c), the petroleum sorber capacities are reduced; MA as the crosslinking agent is preferred from this point of view.

A survey of results

The following general conclusions can be listed: Higher SF values for CEMA/ODA copolymers crosslinked with MA compared to those crosslinked with MM show that MM is more efficient than MA as a crosslinker. Petroleum absorbency increases by using a higher incorporation of hydrophobic acrylate units and by decreasing the amount of either crosslinking agent, MA or MM. Toluene uptake increases with increasing temperature and with increasing ODA content from 50 to 90 mol %, an endothermic process. The strength of polymer + solvent interactions as represented by decreasing χ is enhanced by increasing concentration of the hydrophobic octadecyl acrylate units and by decreasing the amount of either crosslinking agent, MA or MM. The average molecular weight between crosslinks M_c for our copolymers crosslinked by MM is lower than when crosslinked with MA. Moreover, M_c increases when increasing the ODA fraction in the copolymers. The use of MA results in lower

E values than MM, a consequence of more dangling chains; the result is a better sorber capacity.

Experimental

Materials

N,N,'N"-Trisacryloyl-melamine (MA), N,N,'N"-trismethacryloyl-melamine (MM) and cinnamoyloxy ethyl methacrylate (CEMA) were prepared and characterized as reported previously [12]. Octadecyl acrylate (ODA) was obtained from Aldrich Chemical Co., USA, and purified by washing with 5 % aqueous sodium hydroxide, dried over anhydrous CaCl₂, and distilled under vacuum. 2, 2' Azobis isobutyronitrile (ABIN) was obtained from Aldrich Chemical Co., recrystallized from ethanol and used as a thermal polymerization initiator. Petroleum crude oil was obtained from Petrobel, Cairo. Its physicochemical characteristics are given in Table 6.

Crosslinked copolymers

Copolymerization and crosslinking of CEMA and ODA monomers were performed through bulk polymerization. The monomers were mixed together with 0.02 wt. % ABIN initiator. Different weight ratios of MA or MM crosslinkers, ranging from 0 % to 4 wt. % were applied.

The reaction mixture was bubbled with nitrogen. This procedure was repeated with different monomer feed ratios (mole % CEMA/mole % acrylate): 90/10, 70/30, 50/50, 30/70, and 10/90 in preparation of crosslinked copolymers. The copolymerization reactions were performed in siliconized test tubes at 333 K for 3 h; the crosslinked copolymer rods were post-cured at 378 K in an air oven. The rods were cut to thin discs that were used for determining the soluble fraction (SF) and swelling parameters.

Tab. 6. Physicochemical Properties of the Petroleum Crude used.

Test	Method	Value
Specific gravity at 60°F	IP 160/87	0.875
API gravity	Calculated	21.70
Pour Point in °C	IP 15/67(86)	14.00
Kinematic viscosity at 60°F (cSt)	IP 71	762.8
Wax content (wt. %)	UOP 46/64	2.45
Asphaltene content (wt. %)	IP 143/84	8.80

Determination of soluble fractions

Soluble fractions (SFs) of crosslinked polymers were extracted with chloroform until constant weights were achieved [12, 13]. The SF values were calculated as

$$SF = [(W_0 - W) \cdot 100/W_0] \% \quad (2)$$

where, W_0 and W are respectively the weights of the discs before and after extraction.

Petroleum absorption evaluation

Petroleum absorbency of CEMA/ODA copolymers crosslinked with either MA or MM was determined according to the ASTM F726-81 standard used before [12 - 14]. 0.1 g polymer was put in a pure stainless steel mesh (4 x 4 x 2 cm) that had been immersed in pure toluene or with crude oil diluted with toluene (10 % oil) and weighed beforehand. The sample and the mesh were together picked up from petroleum, drained for 30 s, tapped with filter paper to remove excess oil from the bottom of the mesh, and then weighed on a balance. The oil absorbency Q and equilibrium toluene content (ETC) were calculated as:

$$Q = (\text{weight of absorbed oil in sample})/(\text{weight of sample before oil absorption}) \quad (3)$$

$$ETC = [(\text{wt. of gel} - \text{wt. of xerogel})/\text{wt. of gel}] \cdot 100\% \quad (4)$$

The value of the swelling equilibrium is related to the nature of the polymer solvent system and provides information concerning the nature of the crosslinking and reinforcement. In order to determine the final swollen equilibrium and polymer volume fraction, it is necessary to place a sample of known density in the chosen solvent until weight measurements indicate the saturation of the polymer by liquid. Assuming that no extractable are present, and that all the absorbed solvent causes swelling.

The volume fraction of polymer within xerogel Φ_p is given at any temperature by:

$$\Phi_p = (D_o/D)^3 \quad (5)$$

where, D_o and D are the diameters of dry and swollen discs, respectively. D_o was measured at 298 K with a micrometer. Values of D were obtained at different temperatures within the range 298 – 313 K.

Values representing the swelling equilibrium reflect the nature of the polymer + solvent system. Practically, one places a sample of known density in the solvent chosen until weight measurements indicate the saturation of the polymer by liquid. Assuming that no extractable are present, and that all the absorbed solvent causes swelling, the polymer volume fraction Φ_p is:

$$\Phi_p = (W_1 - W_0) \rho_p / W_0 \rho_s \quad (6)$$

Here W_0 is the sample weight before swelling, W_1 is the sample weight after swelling, ρ_p is the density of polymer sample and ρ_s is the density of the solvent. We note that in view of the above definitions Φ_p can also be calculated from Q values, namely $\Phi_p = 1/Q$.

Swelling kinetics of petroleum absorption

The swelling kinetics of petroleum absorption was determined by repeating the previous measurements at several time intervals. The swelling parameters Q and ETC of our gels were averaged from five repeated measurements. The maximum oil absorbency was determined by performing the tests after 24 h. To study the kinetics of swelling, gel samples in triplicate were immersed in crude petroleum. After equilibration, swollen gel samples were placed into an oven at 318 K for 12 h to achieve de-swelling. De-swelling was followed by weighing the gel periodically until a constant weight was achieved. The reversibility of swelling and de-swelling was determined using the same samples in consecutive swelling and de-swelling experiments.

Network parameters

Network parameters of crosslinked polymers include the theoretical crosslink density v_t , the Flory-Huggins-Staverman interaction parameter χ , effective crosslink density v_e and molar mass between crosslinks M_c . The theoretical crosslink density v_t has been calculated as

$$v_t = Cf/2 \quad (7)$$

where C in mol dm^{-3} is the concentration of crosslinking agent of functionality f . For MA and MM crosslinkers we have $f = 6$. The value of C was determined from the weight amounts of MA and MM and the mass density ρ_p of the xerogel. The latter was determined by direct weighing and from micrometrically measured dimensions of the dried discs and pellets used.

The Flory-Rehner swelling model [15 - 17] has been used in the literature to predict the molar mass between crosslinks M_c . This requires accurate values of χ [17]. Several groups [18, 19] have attempted to compute it from the solubility parameter developed by Hildebrand [20]. However, this approach is known not to provide accurate predictions for χ . Also, while mathematics of diffusion is well developed, for some penetrants it would be difficult to find reliable solubility parameters [21]. Instead, we suggested using an alternative phenomenological theory to calculate χ .

Thus, starting from the Flory-Rehner equation [15, 16], the temperature change of volume fraction ($d\Phi_p/dT$) may be obtained as:

$$(d\Phi_p/dT) = \chi \Phi_p T^{-1} \{ 2\Phi_p \chi - \Phi_p(1 - \Phi_p) - [\ln(1 - \Phi_p) + \Phi_p + \chi \Phi_p^2] N \}^{-1} \quad (8)$$

where

$$N = (1/3 \Phi_p^{2/3} - 2/3) (\Phi_p^{1/3} - (2/3)\Phi_p)^{-1} \quad (9)$$

Solving Eq. (6), we obtain the value of χ as follows:

$$\chi = [\Phi_p(1 - \Phi_p)^{-1} + N \ln(1 - \Phi_p) + N\Phi_p] \times [2\Phi_p - N\Phi_p^2 - \Phi_p^2 T^{-1} (d\Phi_p/dT)^{-1}]^{-1} \quad (10)$$

The molar mass between crosslinks can then be calculated as:

$$M_c = -\rho_p v_s \Phi_p^{1/3} [\ln(1 - \Phi_p) + \Phi_p + \chi \Phi_p^2]^{-1} \quad (11)$$

Here, v_s is the molar volume of the solvent. v_e was calculated [16] from:

$$\ln(1 - \Phi_p) + \Phi_p + \chi \Phi_p^2 + v_e v_s (\Phi_p^{1/3} - 2\Phi_p f^{-1}) = 0 \quad (12)$$

where v_s is the molar volume (in $\text{dm}^3 \text{mole}^{-1}$) of toluene at different temperatures T and calculated from the molecular weight of toluene; in obvious notation:

$$v_s = M_{\text{toluene}} / \rho_s \quad (13)$$

while ρ_s is represented by a linear function of T . Determination of χ thus allowed the effective crosslinking density v_e to be evaluated, thereby yielding the molar mass between crosslinks M_c via:

$$M_c = \rho_p / v_e \quad (14)$$

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