

Synthesis and Characterization of Oil Sorbers Based on Docosanyl Acrylate and Methacrylates Copolymers

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ABSTRACT: Docosanyl acrylate (DCA) monomer was copolymerized with different monomer feed ratios of cinnamoyloxy ethyl methacrylate (CEMA) or methyl methacrylate (MMA) monomer to produce different compositions for DCA/CEMA or DCA/MMA copolymer with low conversions. ^1H NMR spectroscopy was used to confirm the copolymer structure. DCA was crosslinked with different mol % of CEMA or MMA using dibenzoyl peroxide as initiator and various weight percentages of either 1,1,1-trimethylolpropane triacrylates or 1,1,1-trimethylolpropane trimethacrylates crosslinkers. The effects of monomer feed composition, crosslinker concentration, and the hydropho-

bicity of the copolymer units on swelling properties of the crosslinked polymers were studied through the oil absorbency tests. The network parameters, such as polymer solvent interaction (χ), effective crosslink density (ν_e), equilibrium modulus of elasticity (G_T), and average molecular weight between crosslinks (M_c), were determined and correlated with the structure of the synthesized copolymers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3704–3713, 2008

Key words: oil sorber; alkyl acrylate; copolymerization; swelling parameters

INTRODUCTION

The use of oil sorbers is the most widely employed and immediately effective method of combating oil pollution. The most urgent technique of elimination of emergency spread of oil and petroleum products is collecting of thin layers from the water surface with the help of sorbents. They can be used to recover oil through the mechanisms of absorption, adsorption, or both. Sorbents need to be oleophilic or hydrophobic although they may be used as sole cleanup method in small spills.

It was known that an effective mean to obtain oil absorbent is to synthesize the crosslinked polymer, which does not dissolve in oil.¹ Other kinds of polymers have been widely used to absorb oil spilled on water.^{2,3} 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 environment.^{4–14} These hydrophobic network polymers were used as absorbents of oil or some organic solvents spilled on water.

Jang and Kim¹⁵ studied the copolymerization of styrene monomer with various long chain alkyl acrylate monomers like, 2-ethylhexyl acrylate (EHA),

lauryl acrylate (LA), lauryl methacrylate (LMA), and stearyl acrylate (SA). These acrylates with long chain alkyl groups are generally known as hydrophobic materials. Therefore, a highly oil absorbing property can be obtained by controlling the composition and the crosslinking density of the copolymer. EHA, LA, and SA were chosen to evaluate the effect of hydrophobic chain length of alkyl groups. LMA, on the other hand, was chosen to find the difference between acrylate and methacrylate. Various crosslinked styrene/alkylacrylate copolymers were synthesized. They were prepared by adding (DVB) as a crosslinking agent.

Jang and Kim¹⁶ conducted a detailed study on the swelling properties of the crosslinked copolymers. The influence of synthetic variables (monomer feed ratio, amount of crosslinking agent, amount of initiator, polymerization temperature, and type of acrylate monomer) of the crosslinked copolymers on the oil absorbency capacity were examined. The effect of moisture was also investigated through a series of oil absorption tests. Sponge-like materials using crosslinked styrene-acrylate copolymers were prepared and their oil absorption capacity was evaluated.

Atta and Arndt^{17,18} synthesized new oil-absorptive polymers containing alkyl acrylate via different types of chemical crosslinkers and irradiation techniques. They conducted a detailed study on the swelling properties of the crosslinked 1-octene-isodecyl acrylate copolymers.

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In our previous publications,^{19,20} we have synthesized cinnamoyloxy ethyl methacrylate (CEMA) monomer that used for preparing oil-absorptive polymers containing alkyl acrylates via different types of chemical crosslinkers. We have also prepared crosslinked reactive macromonomers based on octadecyl acrylate and modified polyisobutylene with maleic anhydride and cinnamoyl moieties.²¹

In this study, long chain docosanyl acrylate was copolymerized with different mol % of either cinnamoyloxy ethyl methacrylate or methyl methacrylate and crosslinked with different percentages of either 1,1,1-trimethylolpropane trimethacrylate (TPT_m) or 1,1,1-trimethylolpropane triacrylate (TPT) as crosslinkers. The main goal of this article is to increase the oil absorbency of the synthesized copolymers by using long chain hydrophobic alkyl acrylate and to introduce aromatic moieties to increase its solubility in crude oil. The swelling parameters were also measured and discussed.

EXPERIMENTAL

Materials

Cinnamoyloxy ethyl methacrylate (CEMA) was prepared and purified as reported in previous article,¹⁹ acrylic acid Aldrich No. 48,723-0, docosanol Aldrich No. 16,910-2, methylmethacrylate Aldrich No. 44,884-2, dibenzoyl peroxide Aldrich No. 22,887-7, tetrahydrofuran (THF) Aldrich No. 18,656-2, triethylamine (TEA) Aldrich No. 47,128-3, and benzene Aldrich No. 17,587-0, were obtained as analytical reagents from Aldrich Chem., Germany. Xylene was obtained from Adweic Chem., Egypt. Petroleum crude oil was obtained from PETROBEL, Egypt, with specifications listed in Table I.

Synthesis of docosanyl acrylate monomer

The reaction was carried out in four-necked reaction flask fitted with mechanical stirrer, reflux condenser, thermometer, and Dean Stark trap. A solution of 66 mmol of acrylic acid and 66 mmol of docosanol was refluxed in 100 mL toluene in presence of 0.4 g of *p*-toluene sulfonic acid as catalyst, and 0.25 g of hydro-

quinone as a polymerization inhibitor. The reaction was carried out at the reflux temperature until the theoretical amount of water of the reaction was collected azeotropically in Dean Stark trap. The synthesized monomer was washed with water to remove the catalyst, inhibitor, and any unreacted materials. The solvent was distilled off using cuprous chloride to inhibit polymerization. The chemical structure of the prepared monomer was confirmed by ¹H NMR spectroscopic analysis.

Linear copolymerization

The detailed procedures to synthesize linear DCA/MMA and DCA/CEMA copolymers are described as follows: A mixture of MMA or CEMA and DCA with different monomer feed ratios (mol % DCA/mol %methacrylate viz, 80/20, 60/40, 50/50, 40/60, and 20/80) was dissolved in 100 mL toluene and the solution was poured into a round-bottom flask under N₂ atmosphere. The monomers were mixed together with ABIN initiator 0.02% (w/w). The solution was then heated to 70°C until ≈10% of low conversion copolymerization was obtained. The products were poured into excess methanol with stirring.

The obtained precipitate was filtered and dried in vacuum at 30°C to a constant weight. The time required for low conversion was estimated by monitoring the weight of the linear copolymer precipitated in excess methanol after different time intervals.

Synthesis of crosslinked DCA/methacrylates copolymers

The crosslinked copolymers of DCA/MMA and DCA/CEMA were performed in bulk polymerization. The monomers were mixed together with dibenzoyl peroxide initiator 0.01% (w/w), and different weight ratios of TPT or TPT_m crosslinker ranging from 0.5 to 4% (w/w) and the mixture were bubbled with nitrogen. This procedure was repeated with different monomer feed ratios (mol % DCA/mol %methacrylate) viz, 80/20, 60/40, 50/50, 40/60, and 20/80 to prepare different compositions of crosslinked copolymers. The copolymerization reactions were performed in siliconized test tubes at 333 K for 3 h. The time of reaction was extended to assure complete reaction of all monomers. The crosslinked copolymer rods were post cured at 378 K in air oven. The rods were cut to thin discs that were used for determining the soluble fraction (SF) and swelling parameters.

Characterization of the prepared copolymers

¹H NMR spectroscopy

The prepared copolymers were analyzed using ¹H NMR spectroscopic technique for determining the

TABLE I
Physicochemical Properties of the Used
Petroleum Crude Oil

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

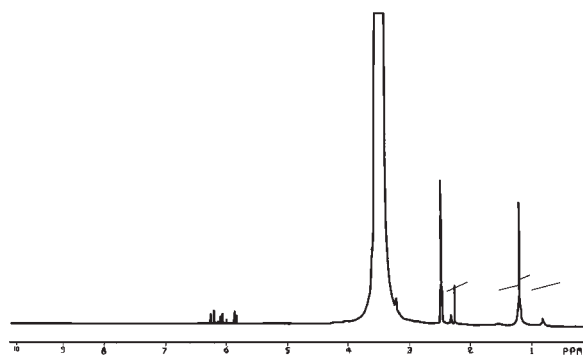


Figure 1 ^1H NMR spectrum of docosanyl acrylate monomer (DCA).

chemical structure of the prepared linear DCA/methacrylate copolymers. ^1H NMR spectra were obtained at 300 MHz on a Varion NMR-300 spectrometer (Jeol NMR spectrometer model JNM-EX) using CDCl_3 as a solvent and TMS as an internal reference.

Extraction of soluble fraction materials

The polymer rods were post cured at 378 K in an air oven for 24 h to ensure complete polymerization. These rods were cut to thin discs and exhaustively dried in vacuum at 308 K to a constant weight. The soluble fractions of these polymeric materials were determined via Soxhlet extraction technique. In this respect, the soluble fraction (SF) was expressed as the fractional loss in weight of xerogel. SF values were calculated according to the following equation

$$\text{SF}\% = \frac{(W_0 - W)}{W_0} \times 100$$

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

Oil absorption test

Oil absorbency of synthesized crosslinked copolymers with either TPT or TPT_m were determined at 298, 303, and 308 K through ASTM (F726-81): 0.1 g of polymer was put in a pure stainless steel mesh (4 cm × 4 cm × 2 cm) that had been immersed in pure toluene or with crude oil diluted with toluene, 10% oil, and weighted beforehand. 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 weighed on a balance. The oil absorbency (Q), equilibrium toluene content (ETC) were calculated as described in our previous works.^{19–21}

RESULTS AND DISCUSSION

It is well known that oil sorbers should have hydrophobic character to swell in oil medium. In our previous works,^{19–21} CEMA monomer which has hydrophobic moieties such as alkyl or phenyl groups has been crosslinked with IOA, DDA, and ODA to be applied as oil sorbers.

In this study, we have extended our search to synthesize copolymers having higher oil absorption capacities than previous work. This can be achieved by increasing alkyl acrylate chain length monomers. In this respect, we prepare long chain alkylacrylate (DCA) monomer by reacting docosanol with acrylic acid. The structure of the prepared DCA monomer was confirmed by IR and ^1H NMR spectroscopic analysis. In this respect, the ^1H NMR spectrum of DCA monomer using CDCl_3 as a solvent and TMS as an internal reference is represented in Figure 1, which shows bands at 5.6–6.6 ppm assigned for vinyl protons of acrylate moiety, bands at 1.2 ppm represent methyl protons in docosanol moiety. And band at 2.5 ppm for methylene protons adjacent to methyl protons. Chemical shifts at 3–4 ppm represents methylene protons bands of long docosanyl acrylate ($\text{O}-(\text{CH}_2)_n$ length. The disappearance of COOH and OH protons peaks confirms the preparation of DCA monomer.^{22,23}

On the other hand, the IR spectrum of DCA representing in Figure 2 shows characteristic absorption bands at 2926 cm^{-1} (assigned for stretching vibration of the aliphatic C–H bond), 1750 cm^{-1} (assigned for stretching vibration of the C=O group) and 1620 cm^{-1} (assigned for stretching vibration of the C=C), 1143 cm^{-1} (assigned for stretching of C–O). The lack of a band at $3200\text{--}3500\text{ cm}^{-1}$ confirms the completion of the esterification reaction between OH of docosanol and acrylic acid.^{22,23}

DCA monomer has been linear copolymerized with different feed ratios of either methyl methacrylate (MMA) or CEMA monomer as described in the experimental section. In this respect, the synthesized

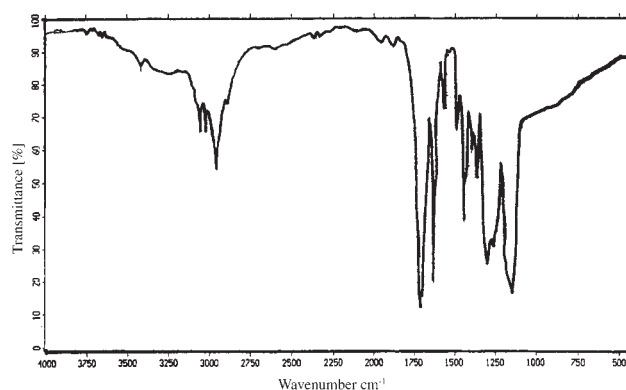


Figure 2 IR spectrum of DCA monomer.

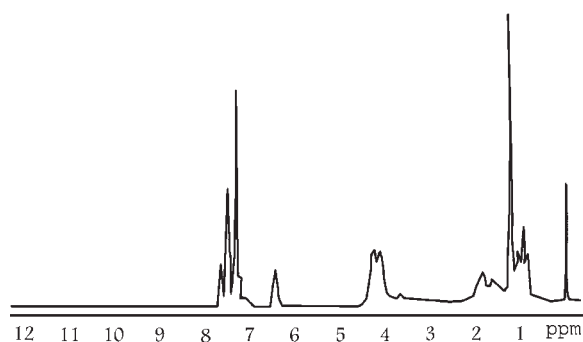


Figure 3 ^1H NMR spectrum of DCA/CEMA copolymer at molar ratio 50/50.

linear copolymers afforded similar NMR spectra, which show bands at 1.1 ppm that represent, methyl protons in the polymer backbone. 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 DCA and MMA in copolymerization backbone, however, for DCA/CEMA copolymers aromatic bands appear at 7.2–7.8 ppm and vinyl protons in the cinamoyl moiety at 6.2–6.6 ppm.^{22,23} Figure 3 represents ^1H NMR spectrum of DCA/CEMA copolymer at molar ratio of 50/50.

Crosslinked copolymers

The early history of crosslinking polyolefins was presented by Dole.²⁴ Sultan and Palmlof²⁵ reviewed the advances in crosslinking technology. Chodok has recently reviewed²⁶ the properties of crosslinked polyolefin-based materials.

Crosslinking is the general term meaning the process of forming covalent bonds or relatively short sequences of chemical bonds joining two polymeric chains. Crosslinking with chemical covalent bonds linking the crystalline and amorphous domains is responsible to three-dimensional network structures that characterize these materials. The crosslinking efficiencies DCA/MMA and DCA/CEMA copolymers were determined from the SF values which were determined from soxhlet extraction of the prepared xerogels with chloroform after 24 h of extraction. The extraction period of 24 h was confirmed to be enough to remove all the oil extractable materials from the gels. The unreacted fractions that fail to incorporate to the network were leached and their values were determined.²⁰ In this work, the reactivity of a crosslinker containing acrylate group (TPT) and that with methacrylate group (TPT_m) towards (DCA/CEMA) and (DCA/MMA) copolymers was investigated from SF measurements in chloroform. Table II shows the effect of crosslinker concentrations on SF values which determined through cross-

linking of DCA (50 mol %)/(CEMA or MMA 50 mol %) copolymer with different contents of TPT or TPT_m viz. 0.5, 1, 2, and 4% (w/w). From the 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). This indicates that low content of TPT or TPT_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 DCA/methacrylates copolymers crosslinked with TPT_m are lower than those crosslinked with TPT. This may be attributed to the differences in reactivity ratios of both crosslinkers with the produced polymer,²⁷ where the presence of methyl groups in TPT_m would allow it to enter in the crosslinking reaction of DCA/methacrylate comonomer system more readily than TPT. Also, the effect of copolymer compositions on the solubility fraction (SF%) values were determined by crosslinking different compositions of DCA/methacrylates copolymers using 1% (w/w) of either TPT or TPT_m crosslinkers and 0.01% (w/w) dibenzoyl peroxide as initiator. Regarding the data shown in Table II, it is obvious that, for copolymers crosslinked with either crosslinkers TPT or TPT_m, SF % decrease with decreasing DCA percentage in the copolymer composition. This may be referred to the higher reactivity of DCA homopolymer towards either crosslinkers than that of DCA/CEMA or DCA/MMA copolymer. It is also observed that, SF % in case of DCA/CEMA is higher than that of DCA/MMA sorber in all percentages crosslinked under same conditions. This may be attributed to the lower reactivity of the longer alkyl group of (DCA) acrylate towards either crosslinkers than that of copolymers.

Oil absorbency

Transportation of petroleum from oil fields to consumers may require 10 to 15 transfers. Tankers, pipelines, trains transport petroleum, and tank trucks

TABLE II
Soluble Fraction of the Crosslinked DCA/methacrylates Copolymers Having Different Crosslinker Contents

Xerogel composition	Crosslinker content (wt %)	SF %			
		DCA/CEMA		DCA/MMA	
		TPT	TPT _m	TPT	TPT _m
80/20	1	24.51	20.66	22.57	18.41
60/40	1	22.11	18.14	20.55	16.54
50/50	0.5	23.00	20.32	24.91	15.41
	1	18.78	16.33	16.89	13.89
	2	15.76	13.54	13.6	11.12
	4	11.32	10.53	10.25	8.54
40/60	1	15.35	12.02	13.57	11.25
20/80	1	12.89	10.89	10.25	8.52

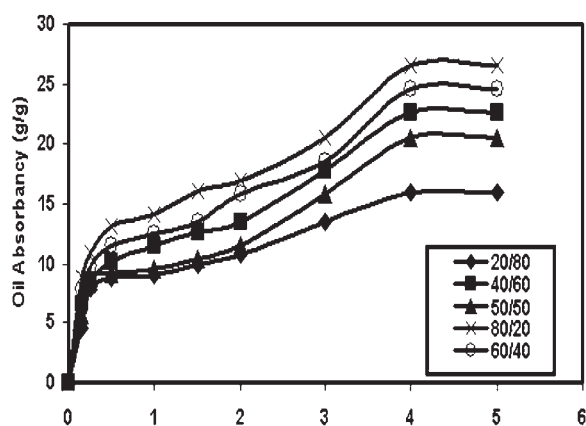


Figure 4 Oil absorbency for DCA/MMA copolymer in pure toluene with different mole ratios of DCA to MMA as a function of immersion time using 1 wt % TPT.

stored temporarily in a cultivator of facilities. Accidents may occur during each of these transportation and storage steps. Offshore and shoreline waters can be polluted by runoff from offshore oil exploration and production and spills from ship transport of oil. Water can be polluted by runoff from oil fields and refinery areas and, in some cases process effluent from petroleum and petrochemical plants.²⁸ As environmental pollution by oil spills increases, oil absorbents have gained considerable interest.^{29–31} In this respect, different molar ratios of DCA/CEMA and DCA/MMA oil absorbents were synthesized as described in experimental sections. The oil absorbencies of the synthesized sorbers which crosslinked with different concentrations of either TPT or TPT_m as crosslinker are measured upon using pure toluene or 10% crude oil. Figures 4 and 5 represent the swelling kinetic curves for different molar ratios of DCA/CEMA and DCA/MMA sorbers crosslinked at 1% TPT crosslinker immersed in toluene as a sol-

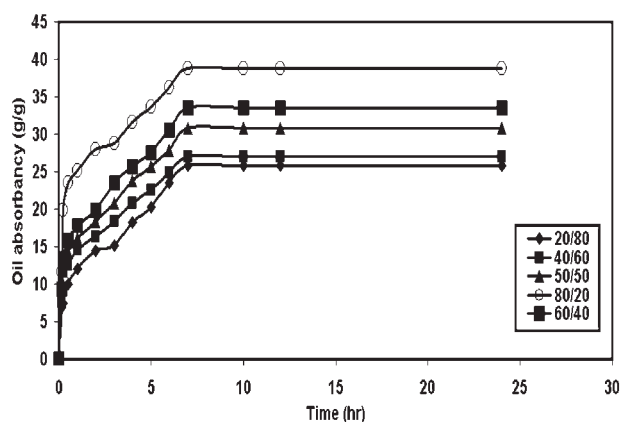


Figure 5 Oil absorbency for DCA/CEMA copolymer in pure toluene with different mole ratios of DCA to CEMA as a function of immersion time using 1 wt % TPT.

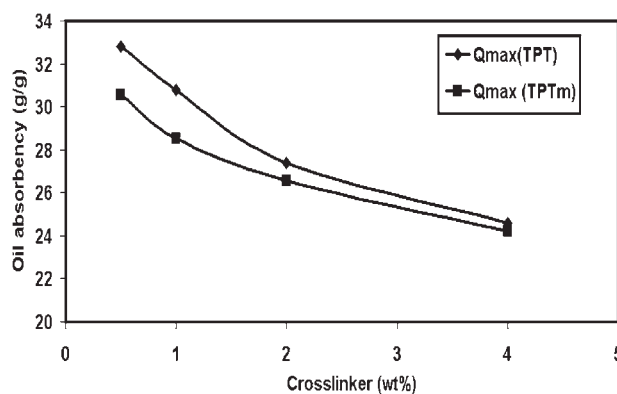


Figure 6 Oil absorbencies of DCA/CEMA xerogels in pure toluene at 50/50 mol % of DCA to CEMA versus crosslinker wt %.

vent. From these Figures, it is observed that the oil absorbency increases with increasing immersion time and attain maximum swelling capacity during few hours. Also, the higher DCA content the higher the oil absorbency. This may be explained based on that, the high DCA content in the crosslinked copolymer increases the hydrophobicity of crosslinked network. On the other hand, Q_{\max} values are largely affected by the type and concentrations of either TPT or TPT_m. Figures 6 and 7 show maximum oil absorbency for 50 mol % DCA/50 mol % CEMA and 50 mol % DCA/50 mol % MMA as a function of crosslinker weight content of either %TPT or TPT_m, respectively, using dibenzoyl peroxide as initiator at 298 K. It was found that oil absorbency increase by decreasing amount of TPT or TPT_m crosslinker. The reasons may be that the increase in the amount of crosslinker led to the formation of denser network of the copolymer, i.e. restricted relaxation of polymeric chain.³²

According to Yao and Zhou,³³ the swelling kinetic of the investigated synthesized sorbers DCA/CEMA or DCA/MMA was studied. The swelling param-

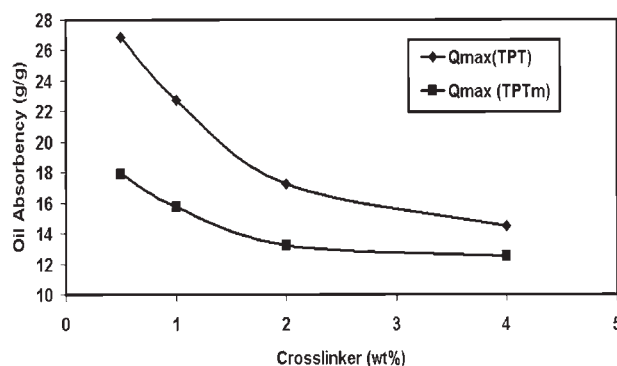


Figure 7 Oil absorbencies of DCA/MMA xerogels in pure toluene at 50/50 mol % of DCA to MMA versus crosslinker wt %.

TABLE III
Absorption Characteristics of the DCA/CEMA Copolymers Crosslinked with TPT Crosslinker at 298 K

Xerogel composition	Crosslinker content	Q_{\max} (g/g)		Q (g/g)		T (h)		K (h^{-1})		ETC	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil
80/20	1	38.8	35	24.521	22.12	0.6	1	1.666	0.999	97.487	97.222
60/40	1	36	32.55	22.752	20.571	1.5	1	0.666	0.999	97.29	97.019
50/50	0.5	32.8	30.56	20.729	19.313	2.2	0.8	0.454	1.249	97.041	96.831
	1	30.8	28.56	19.465	18.049	1.5	1	0.666	0.999	96.85	96.61
	2	27.38	25.45	17.304	16.084	1	1	0.999	0.999	96.47	96.219
	4	24.242	22.64	15.320	14.308	1	1	0.999	0.999	96.03	95.769
40/60	1	27.03	25.342	17.082	16.014	2	1	0.499	0.999	96.432	96.203
20/80	1	25.81	21.56	16.311	13.625	2.2	1	0.454	0.999	96.270	95.567

ters were determined from the swelling curves as described in our previous works^{19–21} and listed in Tables III–VI. These tables show the equilibrium toluene content, (ETC) characteristic time required for the swelling (T), and swelling kinetic constant (k) for the prepared crosslinked copolymers. Regarding T values in 10% crude oil, it is noticeable that generally as the DCA content increases the T decrease. This behavior can be explained easily by considering the increase in the hydrophobic nature of the polymer chain length by increasing the DCA content. Tables III–VI show also that the swelling rate constant (k) decreases with increasing the concentrations of either TPT or TPT_m crosslinker from 0.5 to 4%. This result may be explained by the fact that the higher crosslinker content, the stiffer the crosslinked polymer is, and the smaller the cavities produced. On the other hand, the rate constant values increase with increasing the DCA concentrations. This may be explained on the basis of swelling mode. The swelling process of polymeric networks is primarily due to oil solution penetrating into the polymeric gel through diffusion. Here, increasing the DCA content increases the hydrophobicity of the polymeric networks, thus increasing the facility of oil diffusion. In other words, high compatibility between oil and the polymeric networks facilitate oil diffusion.

A comparison of rate constant values for DCA/CEMA with those of DCA/MMA copolymers at same molar ratio and crosslinked with the same crosslinker content in pure toluene and 10% crude oil was held. It was observed that in all molar ratios a rate constant and maximum oil absorbencies values for DCA/CEMA were higher than those for DCA/MMA. As an example, $k = 1.666 \text{ h}^{-1}$ for 80% DCA/20% CEMA, whereas $k = 2.499 \text{ h}^{-1}$ for 80% DCA/20% MMA using 1% TPT crosslinker in toluene. This show increased absorption capacity for DCA/CEMA sorbers than that for DCA/MMA copolymer. The larger surface areas the higher will be the swelling rate and hence the smaller will be the swelling kinetic constant. This behavior can be easily explained based on, in case of DCA/CEMA copolymer, more hydrophobic chain nature due to the presence of cinnamate moiety which enhances oil diffusion than that of DCA/MMA copolymer (less hydrophobic moieties).

Network studies

One of the important structural parameters characterizing crosslinked polymers is M_c , the average molar mass between crosslinks, which is directly related to the crosslink density. The magnitude of

TABLE IV
Absorption Characteristics of the DCA/CEMA Copolymers Crosslinked with TPT_m Crosslinker at 298 K

Xerogel composition	Crosslinker content	Q_{\max} (g/g)		Q (g/g)		T (h)		K (h^{-1})		ETC	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil
80/20	1	36.832	28.472	23.277	17.994	1.4	1.5	0.714	0.666	97.356	96.606
60/40	1	32.89	26.356	20.786	16.656	1.5	1.6	0.666	0.624	97.049	96.344
50/50	0.5	30.56	24.982	19.313	15.788	1.5	1.8	0.666	0.555	96.831	96.151
	1	28.54	22.034	18.037	13.925	1.7	1.8	0.588	0.555	96.61	95.658
	2	26.58	20.662	16.798	13.058	1.7	1.8	0.588	0.555	96.37	95.383
	4	24.58	18.572	15.534	11.737	1.8	2	0.555	0.499	96.090	94.890
40/60	1	26.398	22.342	16.683	14.120	2	2.2	0.499	0.454	96.35	95.715
20/80	1	23.242	20.214	14.688	12.775	2.2	2.5	0.454	0.399	95.87	95.286

TABLE V
Absorption Characteristics of the DCA/MMA Copolymers Crosslinked with TPTm Crosslinker at 298 K

Xerogel composition	Crosslinker content	Q_{\max} (g/g)		Q (g/g)		T (h)		K (h ⁻¹)		ETC	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil
80/20	1	20.898	18.653	13.207	11.788	0.4	0.5	2.499	1.999	95.433	94.911
60/40	1	19.3353	16.458	12.219	10.401	0.4	0.5	2.499	1.999	95.082	94.271
50/50	0.5	17.866	14.56	11.291	9.201	0.9	1	1.110	0.999	94.699	93.573
	1	15.7112	12.45	9.929	7.868	1	1.1	0.999	0.908	94.015	92.565
	2	13.22	10.564	8.355	6.676	1.4	1.3	0.714	0.768	92.967	91.352
	4	12.5	8.5	7.9	5.372	1.8	2	0.55	0.499	92.592	89.473
40/60	1	15.791	13.56	9.979	8.569	1.2	1.3	0.833	0.768	94.044	93.131
20/80	1	11.66	10.56	7.369	6.673	1.3	1.4	0.768	0.714	92.101	91.349

M_c significantly affects the physical and mechanical properties of the crosslinked copolymers and its determination has great practical significance.³⁴ Equilibrium swelling is widely used for determination of M_c . According to the theory of Flory-Rehner, the following equation could be obtained for a perfect network:

$$M_c = V_1 \rho_p \left(\Phi_p^{1/3} - \Phi_p / 2 \right) / \left(\ln(1 - \Phi_p) + \chi (\Phi_p^2 + \Phi_p) \right)$$

where M_c is the number average molar mass of the chain between crosslinks, V_1 is the molar volume (mL/g), ρ_p is the polymer density (g/mol), Φ_p is the volume fraction of polymer in swollen gel, and χ is the polymer-solvent interaction parameter.³⁵ The swelling ratio Q is equal to $1/\Phi_p$. here, the crosslink density q , is defined as the mole fraction of crosslinked units³⁶: $q = M_0/M_c$ where M_0 is the molar mass of the repeating units. Other authors defined a crosslink density, ν_e , as the number of elastically effective chains, totally included in a perfect network, per unit volume. ν_e is simply related to q :

$$\nu_e = \rho_p N / M_c$$

where N is Avogadro number.

The values of ν_1 , χ , ρ_p were taken from related literature.³⁶ The equilibrium moduli G_T values were obtained via the following equation $G_T = RT\nu_e\Phi_p^{1/3}$, where R , Φ_p , and T are the gas constant, polymer volume fraction, and absolute temperature.

Swelling process of DCA/CEMA and DCA/MMA were investigated in pure toluene and in crude oil diluted with 10% toluene. Tables VII–X show effective crosslink density (ν_e), theoretical crosslink density (ν_t), molecular weight of the chains between two successive crosslinks (M_c), polymer-solvent interaction parameter (χ), volume fraction of the polymeric material in the xerogels (Φ_p), equilibrium moduli of elasticity for xerogels (G_T), and density of the xerogels. The data reveal that χ have values always < 0.5 for DCA/CEMA at 80/20 M ratios, where $\chi = 0.259$ for DCA/CEMA whereas for DCA/MMA $\chi = 0.317$ at the same crosslinker concentration (1% TPT) where the samples are swelled in toluene. However, the lower the values of χ , the higher the polymer-solvent interaction are. This behavior runs in harmony with the equilibrium swelling results, where Q_{\max} values are shifted to higher values as χ decreases. In other words, toluene is a thermodynamically good solvent for these polymers when χ is always less than 0.5. It is also observed from Tables VII–X that, the lowest value of χ was exhibited at

TABLE VI
Absorption Characteristics of the DCA/MMA Copolymers Crosslinked with TPT Crosslinker at 298 K

Xerogel composition	Crosslinker content	Q_{\max} (g/g)		Q (g/g)		T (h)		K (h ⁻¹)		ETC	
		Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil
80/20	1	26.898	22.653	16.999	14.316	0.4	0.5	2.499	1.999	96.415	95.772
60/40	1	24.3353	20.458	15.379	12.929	0.5	0.6	1.999	1.666	96.052	95.339
50/50	0.5	26.866	24.56	16.979	15.521	1	1.1	0.999	0.908	96.411	96.087
	1	22.7112	18.45	14.353	11.660	1.2	1.3	0.833	0.768	95.782	94.858
	2	17.22	15.564	10.883	9.836	1.4	1.4	0.714	0.714	94.5113	93.962
	4	14.5	12.5	9.164	7.9	1.8	2.1	0.555	0.476	93.548	92.592
40/60	1	20.791	18.56	13.139	11.729	1.2	1.3	0.833	0.768	95.410	94.88
20/80	1	16.66	14.56	10.529	9.201	1.3	1.5	0.768	0.666	94.337	93.576

TABLE VII
Network Parameters of Different Compositions of DCA/CEMA Copolymers Crosslinked with Various Concentrations of TPT Crosslinker at 298 K

Xerogel composition	Crosslinker content	Density (ρ_p) kg/dm ³	$v_e \times 10^3$ (mol/dm ³)		M_c (g/mole)		χ		Φ_p		G_T (MN m ⁻²)	
			Crude		Crude		Crude		Crude		Crude	
			Toluene	oil	Toluene	oil	Toluene	oil	Toluene	oil	Toluene	oil
80/20	1	0.82	8.121	9.515	100.968	86.176	0.259	0.271	0.025	0.028	5.819	7.056
60/40	1	0.78	9.004	10.020	86.621	77.836	0.271	0.293	0.027	0.030	6.615	7.613
50/50	0.5	0.75	10.342	11.905	72.516	62.995	0.282	0.283	0.030	0.032	7.837	9.237
	1	0.7	11.183	13.015	62.590	53.782	0.294	0.295	0.032	0.035	8.654	10.328
	2	0.65	13.492	14.870	48.173	43.709	0.306	0.318	0.036	0.039	10.859	12.263
	4	0.75	16.445	18.981	45.603	39.511	0.319	0.321	0.041	0.044	13.784	16.276
40/60	1	0.7	12.441	14.193	56.262	49.319	0.327	0.329	0.036	0.039	10.056	11.721
20/80	1	0.65	12.893	18.753	50.414	34.659	0.339	0.343	0.038	0.046	10.582	16.344

the lowest TPT (crosslinker) content for all synthesized sorbers polymer swelled in toluene. A similar behavior for χ parameter and its effects was observed for samples swelled in 10% crude oil. A comparison of χ parameter values of the DCA/CEMA with those of DCA/MMA copolymers crosslinked with the same crosslinker content and the same mole ratio in 10% crude oil was held. The data reveal that χ values for DCA/CEMA were lower, than those for DCA/MMA. This shows increased polymer-solvent interaction for DCA/CEMA than that for DCA/MMA copolymer. This in turn affects on the swelling behavior of either cases. In this respect, the swelling is shifted to higher values of Q_{max} for DCA/CEMA = 38.8 g/g polymer where as for DCA/MMA Q_{max} = 26.89 g polymer at molar ratio 80/20 upon using 1% TPT in toluene solvent. This increased swelling efficiency may be attributed to the hydrophobic nature of the cinnamate moiety.

Values of Φ_p listed in Tables VII–X measured at 298 K using pure toluene as oil medium increases with increasing content of crosslinking agent (from

0.5 to 4 wt %). Also, Φ_p increase with decreasing DCA content which may be explained as previously mentioned explanation for χ values. Increase in Φ_p values is also observed upon using 10% crude oil instead of pure toluene (Tables VII–X).

The densities of the prepared sorbers (ρ_p) crosslinked with 0.5, 1, 2, or 4 wt % TPT or TPT_m crosslinker were determined and the results indicate the increase of the densities of the prepared sorber with the increase in the crosslinker weight content and the DCA concentration. This may be due to the decreased probability of forming dangling chain or pendant groups as increasing crosslinker weight content or DCA concentration. The presence of pendant chains or dangling chains in the polymeric network affects the compression moduli. The values of moduli decrease drastically when the proportion of pendant chains increase.³⁷ The lower G_T and v_e values for synthesized DCA/CEMA polymers than that for DCA/MMA sorbers in all the copolymer composition crosslinked at the same conditions indicate that the prepared DCA/CEMA gel have more elastic network. This will increase interaction between tolu-

TABLE VIII
Network Parameters of Different Compositions of DCA/CEMA Copolymers Crosslinked with Various Concentrations of TPT_m Crosslinker at 298 K

Xerogel composition	Crosslinker content	Density (ρ_p) kg/dm ³	$v_e \times 10^3$ (mol/dm ³)		M_c (g/mole)		χ		Φ_p		G_T (MN m ⁻²)	
			Crude		Crude		Crude		Crude		Crude	
			Toluene	oil	Toluene	oil	Toluene	oil	Toluene	oil	Toluene	oil
80/20	1	0.87	8.238	13.729	105.600	63.367	0.281	0.285	0.027	0.035	6.006	10.906
60/40	1	0.83	9.817	15.329	84.545	54.143	0.293	0.296	0.030	0.037	7.432	12.495
50/50	0.5	0.81	10.814	15.451	74.8997	52.421	0.304	0.319	0.032	0.040	8.390	12.821
	1	0.85	11.776	20.106	72.179	42.274	0.316	0.322	0.035	0.045	9.347	17.397
	2	0.89	12.873	21.811	69.133	40.804	0.328	0.3348	0.037	0.048	10.463	19.280
	4	0.94	14.252	25.930	65.954	36.25	0.340	0.348	0.040	0.053	11.890	23.751
40/60	1	0.78	13.795	18.456	56.538	42.262	0.317	0.332	0.037	0.044	11.239	15.895
20/80	1	0.75	16.983	21.53	44.159	34.826	0.331	0.345	0.043	0.049	14.436	19.176

TABLE IX
Network Parameters of Different Compositions of DCA/MMA Copolymers Crosslinked with Various Concentrations of TPTm Crosslinker at 298 K

Xerogel composition	Crosslinker content	Density (ρ_p) kg/dm ³	$v_e \times 10^3$ (mol/dm ³)		M_c (g/mole)		χ		Φ_p		G_T (MN m ⁻²)	
			Crude		Crude		Crude		Crude		Crude	
			Toluene	oil	Toluene	oil	Toluene	oil	Toluene	oil	Toluene	oil
80/20	1	0.735	18.808	22.463	39.077	32.720	0.355	0.369	0.047	0.053	16.563	20.546
60/40	1	0.747	20.767	27.574	35.969	27.090	0.368	0.384	0.051	0.060	18.769	26.295
50/50	0.5	0.7	24.710	36.728	28.327	19.059	0.370	0.389	0.055	0.068	22.929	36.485
	1	0.73	30.684	49.827	23.790	14.650	0.386	0.408	0.063	0.080	29.717	52.149
	2	0.79	42.737	55.7601	18.485	14.167	0.405	0.452	0.075	0.094	43.843	61.643
	4	0.8	62.949	205.603	12.708	3.890	0.375	0.412	0.080	0.117	65.795	244.37
40/60	1	0.79	32.739	43.721	24.130	18.069	0.375	0.393	0.063	0.073	31.654	44.47
20/80	1	0.75	70.558	78.850	10.629	9.511	0.390	0.418	0.085	0.094	75.478	87.181

TABLE X
Network Parameters of Different Compositions of DCA/MMA Copolymers Crosslinked with Various Concentrations of TPT Crosslinker at 298 K

Xerogel composition	Crosslinker content	Density (ρ_p) kg/dm ³	$v_e \times 10^3$ (mol/dm ³)		M_c (g/mole)		χ		Φ_p		G_T (MN m ⁻²)	
			Crude		Crude		Crude		Crude		Crude	
			Toluene	oil	Toluene	oil	Toluene	oil	Toluene	oil	Toluene	oil
80/20	1	0.85	13.277	17.925	64.016	47.419	0.317	0.331	0.037	0.044	10.749	15.367
60/40	1	0.8	15.432	20.984	51.840	38.123	0.330	0.345	0.041	0.048	12.917	18.611
50/50	0.5	0.767	11.883	13.411	64.612	57.247	0.338	0.351	0.037	0.040	9.624	11.192
	1	0.78	15.775	23.010	49.444	33.897	0.352	0.369	0.044	0.054	13.512	21.123
	2	0.8	26.837	31.363	29.808	25.507	0.372	0.386	0.058	0.064	25.210	30.471
	4	0.83	40.105	53.849	20.695	15.413	0.379	0.397	0.068	0.08	39.895	56.283
40/60	1	0.78	16.516	19.462	47.224	40.077	0.376	0.390	0.048	0.053	14.570	17.830
20/80	1	0.75	26.819	33.753	27.964	22.219	0.384	0.400	0.060	0.068	25.472	33.530

ene and prepared DCA/CEMA networks and hence increased absorption capacity for them.

CONCLUSIONS

From previous results it can be concluded that:

- The higher SF % values for DCA/methacrylate crosslinked with TPT than those crosslinked with TPTm show that TPTm is more efficient than TPT as a crosslinker.
- SF % generally increases with increasing DCA percentage in all the copolymer composition.
- Oil absorbency is increased by increasing the DCA content.
- Oil absorbency for DCA/CEMA crosslinked with either TPT or TPT_m is higher in all percentages than that for DCA/MMA.
- More elastic networks are obtained by DCA/CEMA sorbers than DCA/MMA.

Sorbers as illustrated by network parameters.

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