Synthesis and evaluation of oil sorbent based on natural modified cellulose derivatives for treatment of oil spill

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ABSTRACT

Hydroxypropylcellulose acrylate (HPCA) macromonomer was prepared by esterification of hydroxypropylcellulose (HPC) with acryloyl chloride in homogenous solution of dimethyl formamaide (DMF). Then the produced HPCA macromonomer was copolymerized with ethylhexyl acrylate (EHA) using two types of crosslinkers and azobisisobutyronitrile(AIBN) as initiator. Several parameters were considered namely, monomers feed ratio, type and concentration of the applied crosslinkers. The synthesized macromonomer was characterized by fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^{1}HNMR) spectroscopic analyses. Also, the thermal properties of the crosslinked copolymers were investigated by using thermal gravimetric analysis (TGA). Furthermore, morphological properties of these crosslinked copolymers were studied through scan electron microscope (SEM) and their swelling efficiency was thoroughly investigated in heavy and light oil.

Introduction

Major oil spills attract the attention of the public and the media. In recent years, this attention has created a global awareness of the risks of oil spills and the damage they do to the environment. The movement of petroleum from the oil fields to the consumer involves as many as 10 to 15 transfers between many different modes of transportation including tankers, pipelines, railcars, and tank trucks. Accidents can happen during any of these transportation steps or storage times. The average cost of cleanup worldwide ranges from $20 to $200 per litter, depending on the type of oil and where it is spilled [1]. Crude oil spilt in the marine environment undergoes a wide variety of weathering processes, which include evaporation, dissolution, dispersion, photochemical oxidation, microbial degradation, adsorption onto suspended materials, agglomeration, etc. The methods commonly used to remove oil involve oil booms, dispersants, skimmers, sorbents etc. [2]. The use of sorbents is of great interest, as it allows the collection and complete removal of oil, by achieving a change from liquid to semi-solid phase there are three major classes of oil sorbents, namely, inorganic mineral products, organic synthetic products and organic natural products [3].

There are many natural products used for preparation of oil sorbers by different chemical modifications such as chitosan, rosin and cellulose. Cellulose is a nontoxic, renewable resource and one of the most abundant polymers on earth [4]. By chemical modification of this polymer, new characteristics can be introduced, e.g., improved solubility in various solvents. This opens up a broad range of applications in which modified cellulose can be used, e.g., in paint, food, and pharmaceutical industry [5,6]. To achieve the desired properties, the hydroxyl groups along the polymer chain are substituted with different groups, e.g., carboxymethyl or methyl, or with a mixture of different groups, e.g., hydroxypropyl and methyl groups. The

properties of the modified cellulose will thus not only depend on the chain length but also on the nature of the substituent, the degree of substitution (DS) and for some types of substituents, the length of the side chains. In addition, the distribution of the substituents along the backbone will influence the polymer properties [7, 8].

Among the cellulose derivatives, hydroxypropyl cellulose (HPC) is an alkyl-substituted hydrophilic cellulose derivative with advantages such as excellent film forming properties, degradability, biocompatibility etc [9, 10]. It also has a particular phase transition behavior in aqueous solution and some solvents [11-14]. Because of these unusual and desirable properties, and its prospects in industrial applications, HPC has been a focus of many researches [15- 17].

In this study, we used natural organic material to prepare modified natural oil sorbents that has the ability for biodegradation. This accomplished by use of HPC (cellulose derivatives) to prepare hydroxypropylcellulose acrylate (HPCA) macromonomer by esterification of HPC with acryloyl chloride in homogenous solution of DMF. Then the produced HPCA monomer was copolymerized with ethylhexyl crylate (EHA) in presence of two types of crosslinkers to produce oil gel. The prepared oil sorbents were characterized and evaluated in presence of light and heavy oil media. Furthermore, the chemical structure of the prepared sorbents was thoroughly investigated and correlated to their efficiency.

Method and Material:

Materials

Hydroxypropyl cellulose (HPC) was obtained from **Aqualon Co.** as industrial grade reagent with Mw 370,000. Other chemicals used in this study were purchased from **Aldrich chemical Co**. as analytical grade reagents and used as received. They include Acryloyl chloride, 2,2`azobisisobutyronitrile (AIBN), Ethylhexyl acrylate (EHA), Divinyl benzene (DVB),

Triethyl amine (TEA), Methylene bisacrylamide (MBA) Dimethylformamide (DMF) and Tetrahydrofuran (THF), Toluene. The crude oil was obtained from **PETRODARA OIL Co**.

Synthesis of hydroxypropyl cellulose acrylate (HPCA)

Hydroxypropyl cellulose acrylate (HPCA) was synthesized by the reaction of hydroxypropyl cellulose with acryloyl chloride in the presence of DMF. Hydroxypropyl cellulose (5.99 mmol based on hydroxypropylated anhydroglucose unit (HPAGU)) was added to 100 ml of DMF with vigorous stirring at room temperature. After complete dissolution of hydroxypropyl cellulose, the solution was transferred into a 500 ml four-necked flask fitted with a mechanical stirrer, thermometer, and Nitrogen inlet and dropping funnel. Then 36 mmol of TEA was added as an acid acceptor, the solution was cooled to zero temperature. After that 36 mmol acryloyl chloride was added dropwise in a period of about 60 min. The solution was stirred at 40 ^{o}C for 6 h. A yellowish precipitate of TEA hydrochloride was formed during the reaction. The reaction mixture was poured into a beaker containing 400 ml of THF. White hydroxypropyl cellulose acrylate coagulated. The product was filtered, washed with THF, and dried at 40 °C under vacuum.

Preparation of (HPCA-EHA) oil-absorbent:

Crosslinked copolymer of HPCA/ EHA was performed through coagulation followed by bulk polymerization. The HPCA monomer was dissolved in mixture solvent of methylene chloride and methanol (9:1 by volume) and mixed together with EHA in presence of 0.02 % (w/w) ABIN initiator. Then, different weight ratios of DVB or MBA crosslinker ranging from 2-10 % (w/w) were mixed and bubbled with nitrogen. The copolymerization reactions were performed in siliconized test tubes at 70 °C for 12 hrs. This procedure was repeated with different monomer feed ratios (mol % HPCA / mol% EHA) to prepare different compositions of crosslinked copolymers as listed in Table 1. The product was cut into thin discs for determining the soluble fraction (SF) and swelling parameters.

Characterization of the prepared copolymers

Spectroscopic analysis

Infrared spectra were performed in KBr disk with a Nicolet FTIR IS-10 spectrometer (Waltham, MA, USA). 1HNMR spectra were recorded on a Bruker EMX spectrometer (Billerica, MA, USA) with D2O as solvent.

Thermal Analysis (TGA)

Thermal properties of some samples of the prepared copolymers were determined using TGA: Q 600 SDT simultaneous DSC-TGA. Samples are heated from 25°C to 600 °C in N_2 flow (20 cm min $^{-1}$) at a heating rate 10 C/min.

Scan Electron Microscopy (SEM)

The morphology of the prepared crosslinked copolymers were characterized by a SEM, Jeol, Model JSM5300 at 15 Kev. Dried crosslinked polymers were cut to expose their inner structure, coated with a thin layer of palladium gold alloy.

Evaluation Of Crosslinked Polymers

Extraction of Soluble Fraction Materials (SF)

The polymer rods were post cured at 378K in an air oven for 24 hours to ensure complete polymerization. These rods were cut into thin discs and exhaustively dried in vacuum at 308K to a constant weight. The soluble fractions of these polymeric materials were determined via Soxhlet extraction technique. In this respect, the dried xerogel discs were transferred into an extraction thimble and were subjected to

Soxhlet extraction with chloroform. Normally three or four discs were used per soxhlet. A preliminary test was performed to establish the required time for complete extraction of the soluble fractions. Based on this test, 24 hr of extraction time was adopted for all samples. After extraction, the samples were dried in the atmospheric pressure for several hours and then dried to a constant weight in vacuum oven at 308K. The soluble fraction (SF) was expressed as the fractional loss in weight of xerogel [18]. SF values were calculated according to the following equation:

$$SF \% = ((W_0 - W)/ W_0) \times 100) \qquad (1)$$

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

The data of soluble fraction are given in Table 1.

Oil Absorption Test

Oil absorbency of synthesized crosslinked copolymers with either DVB or MBA were determined at., 298K to ASTM (F726-81) [19] : 0.1g polymer was put in a pure stainless steel mesh (4x4x2 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 sec, tapped with filter paper to remove excess oil from the bottom of the mesh, and then weighed. The oil absorbency (Q) equilibrium oil content (ETC and ECC) were calculated by following equations:

$$Q(g/g) = \frac{\text{Weight of absrobed oil in sample}}{\text{Weight of sample before oil absorbency}} \qquad (2)$$

$$ETC \% = \frac{\text{wt.of gel} - \text{wt.of xerogel}}{\text{wt.of gel}} \times 100 \qquad (3)$$

Swelling Kinetics of Oil Absorption

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 repeated measurements.

Swelling kinetics of the prepared crosslinked copolymers were determined according to Cho and Zhou [20] in which the swelling rate can be described by the following experimental equation:

$$\frac{dQ}{dT} = K (Q_{max} - Q) \qquad (4)$$

Where, Q_{max} and Q are the maximum and the characteristic oil absorbency respectively while K is the swelling kinetic constant. Integration from eq. (4) gives:

$$-\ln(Q_{max} - Q) = Kt + C \qquad (5)$$

Where, t is the characteristic swelling time and the integration constant.

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

$$\ln \frac{(Q_{max})}{(Q_{max} - Q)} = Kt \qquad (6)$$

The data obtained from these calculations are provided in Tables 2 and 3.

Also, the maximum oil absorbency was determined by allowing the tests to stand for 24 h. To study the kinetics of swelling, gel samples in triplicate, were immersed in toluene and crude oil. After equilibration-swollen gel samples were immersed in ethanol and then dried by using an air-oven at 318K for 12 h, for gels deswelling. The deswelling was then followed by weighing the gel at various times to constant weight. The reversibility of swelling and deswelling was determined using

the same samples for consecutive swelling and deswelling experiments [21].

Results and discussion:

Preparing the oil–absorbent:

Several researches dealing with preparation of super absorbents based on natural materials have been carried out [20-24]. Lei et al [21] prepared cyclodextrin-based oil-absorbents through the reaction cyclodextrin with acryloyl chloride then with butyl acrylate. In the present work, the basis of preparation of cellulose derivative oil sorbents is to substitute hydroxyl groups with some active groups such as C=O& C=C.

Firstly, some of the hydroxyl groups of HPC were substituted by reacting with acryloyl chloride to provide a multiacrylate-terminated hydroxypropyl cellulose acrylate (HPCA) as a macromonomer unit for the preparation of oil-absorbent. Then, HPCA was copolymerized with ethylhexyl acrylate (EHA) in the presence of DVB or MBA as crosslinking agent, and AIBN as a free radical initiator to obtain the designed poly (HPCA-co-EHA) oil-absorbent.

Synthesis and characterization of HPCA:

In this manuscript the HPCA was prepared by the acylation reaction of terminal hydroxyl group on the outside surface of hydroxypropyl cellulose (HPC) with acryloyl chloride to produced HPCA with terminal acrylate moiety.

The chemical structure was confirmed by IR spectra. Figure 1- a show FTIR of HPC before acylation and Figure 1- b show FTIR of HPCA after acylation. In Figure 1-b, the appearance of peak at 1728 cm^{-1} corresponding to C=O group, and peak at 1662 cm^{-1} attributed to C=C elucidate that acylation was successfully performed.

Moreover, from ^{1}HNMR spectra of HPC and HPCA as shown in figure 2 a, b. The appearance of signals at δ (4.2) and (4.3) may be due to the protons in CH$_2$ near the acrylate moiety. Peaks at δ between (5.6) and (6.5) are attributed to protons of acrylate double bond.

Preparation of crosslinked poly (HPCA-EHA) Oil-Absorbent:

Cross-linking is responsible for the formation of three dimensional network structures which is important for the preparation of organogels and hydrogels. In this respect, HPCA and EHA underwent crosslinking reaction at different molar feed ratios in presence of crosslinking agents and free radical initiator. It is also well known that elasticity and swelling properties are attributed to the presence of physical or chemical cross-links in polymer chains. The incorporation of the bulky hydroxypropyl cellulose acrylate molecules led to a great number of voids inside the network, which in turn is helpful to largely increase the oil absorbency.

Thermal characteristics of crosslinked HPCA-EHA copolymers

Thermal stability of the crosslinked copolymers was assessed by determination of decomposition temperatures using TGA. TGA is a technique to determine weight loss continuously while heating a sample [25-27]. The investigated samples were subjected to TGA before extraction of SF. As shown in Figure 3, there are two degradation steps for these copolymers; typically crosslinked polymers have only one degradation step.

The first lower degradation step may be due to the breaking of the unextracted soluble fraction (unreacted and short chain oligomers) present in the networks and the second step is due to degradation of the crosslinked copolymers. Accordingly, the determined weight loss values from 25 to 300 $^{\circ}$C can be

correlated with the SF results from Soxhlet extraction. Figure 3 shows good agreement between SF values and thermal decomposition at 300°C. Furthermore, the thermal stability of crosslinked networks increases with increasing EHA concentration, higher crosslinker contents and the presence of DVB/MBA crosslinker. This can be attributed to increase of crosslinking densities in the HPCA/EHA copolymers. It was also observed that the thermal stability of the copolymers crosslinked by using DVB is much greater than those crosslinked by using MBA. This may be explained on the basis of that benzene ring in DVB affords some rigidity to the copolymers in addition to the higher reactivity of DVB compared to MBA as obtained from the soluble fraction measurements Table 1. Our findings run parallel to Sannino et. al.'s findings [28].
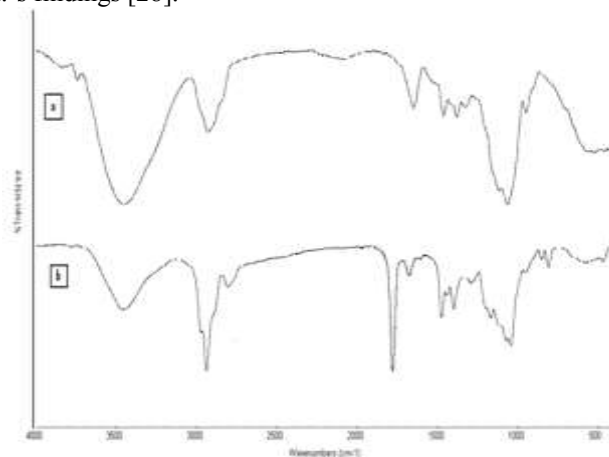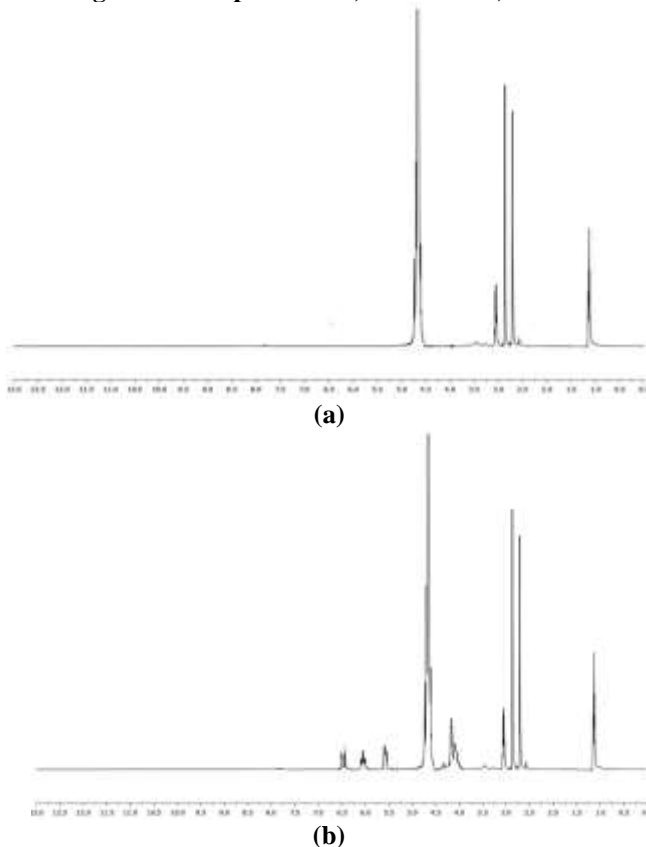

Figure 1: IR spectra of a) HPC and b) HPCA

(a)

(b)

Figure 2: ^{1}H NMR for a- HPC b-HPCA

Table (1) Constituents of the Prepared HPCA/ Alkyl Acrylate Crosslinked Copolymers and Soluble fraction values

Systematic name of the copolymer	Designation	Compositions (mole%)*		Crosslinker content(wt%)**		SF of crosslinked gel in chloroform (%)	
		HPCA	ODA	DVB	MBA	DVB	MBA
Hydroxypropyl cellulose acrylate-Ethylhexyl acrylate copolymers	HPCA / EHA	90	10	4	4	14.8	15.55
		75	25	4	4	12.85	14.73
		50	50	2	2	11.05	15.37
				4	4	9.61	13.36
				6	6	8.17	11.38
				10	10	6.25	8.69
		25	75	4	4	6.37	11.99
		10	90	4	4	4.42	11.17

*The weight of HPCA based on hydroxypropylated anhydroglucose unit
**The weight of Crosslinker based on the total weight of monomers

Table (2) Absorption Characteristics of the HPCA-EHA Copolymers Crosslinked With DVB Crosslinker at 298 K.

Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC%	ECC%	Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil			Toluene	crude oil	Toluene	crude oil	Toluene	crude oil
90/10	4	5.17	2.12	80.66	70.15	3.27	2.12	0.37	0.49	2.7	2.04
75/25	4	5.88	2.39	82.98	73.56	3.71	2.39	0.35	0.47	2.86	2.13
50/50	2	8.92	3.41	88.79	81.49	5.64	3.41	0.27	0.28	3.7	3.57
	4	9.46	3.18	89.43	80.12	5.98	3.18	0.24	0.29	4.17	3.45
	6	6.76	2.69	85.20	76.50	4.27	2.69	0.28	0.34	3.57	2.94
	10	5.31	2.12	81.16	70.14	3.35	2.12	0.31	0.39	3.22	2.56
25/75	4	12.62	6.02	94.08	89.50	7.98	6.02	0.23	0.27	4.35	3.70
10/90	4	20.75	8.26	95.18	92.35	13.11	8.26	0.21	0.25	4.76	4.00

Table (3) Absorption Characteristics of the HPCA-EHA Copolymers Crosslinked With MBA Crosslinker at 298 K.

| Xerogel composition	Crosslinker content	Q_{max} (g/g)		ETC%	ECC%	Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil			Toluene	crude oil	Toluene	crude oil	Toluene	crude oil
90/10	4	5.75	3.63	82.61	72.44	3.63	2.29	0.38	0.46	2.36	2.17
75/25	4	7.66	4.32	86.94	76.85	4.84	2.73	0.36	0.43	2.78	2.32
50/50	2	8.95	5.73	88.83	82.55	5.66	3.62	0.29	0.30	3.45	3.33
	4	10.47	5.53	90.45	81.92	6.62	3.50	0.27	0.32	3.70	3.12
	6	8.39	4.82	88.09	79.25	5.30	3.05	0.31	0.34	3.22	2.94
	10	6.76	3.88	85.21	74.23	4.27	2.45	0.32	0.37	3.12	2.70
25/75	4	19.66	12.44	94.91	91.96	12.43	7.86	0.25	0.25	4.00	4.00
10/90	4	25.54	16.68	96.08	94.00	16.14	10.54	0.23	0.22	4.35	4.54
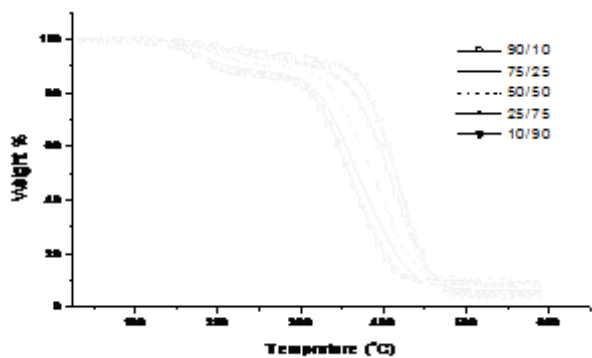
Figure 3: TGA thermogram of different molar ratios of HPCA/ODA crosslinked copolymers using 4 wt % of DVB crosslinker
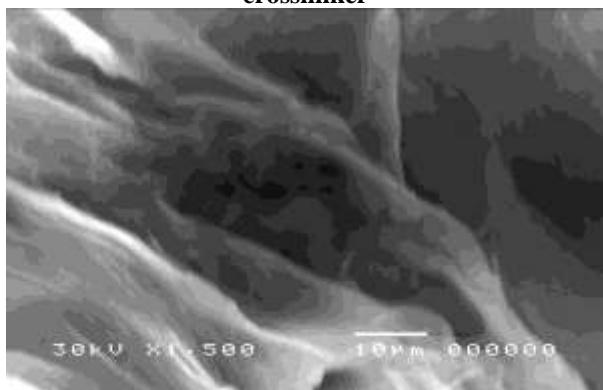
A
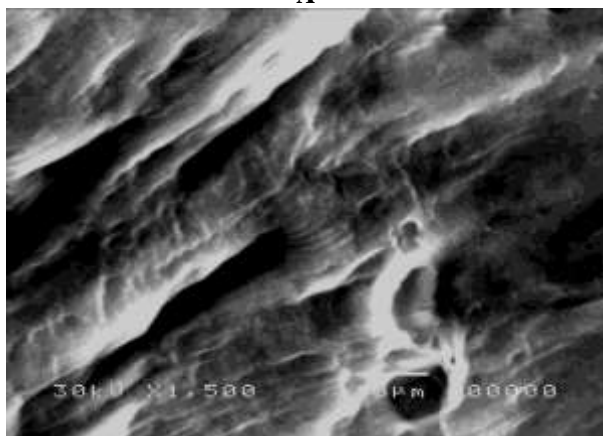
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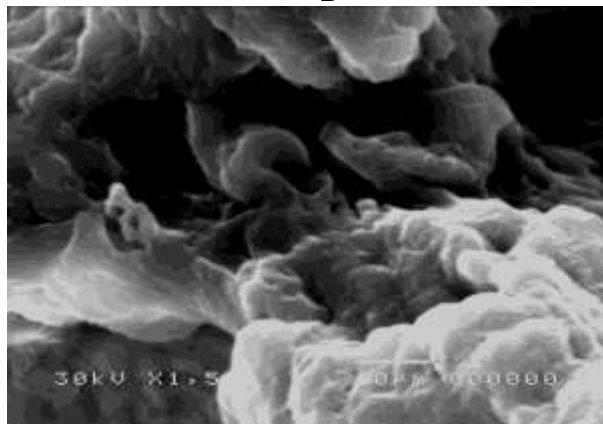
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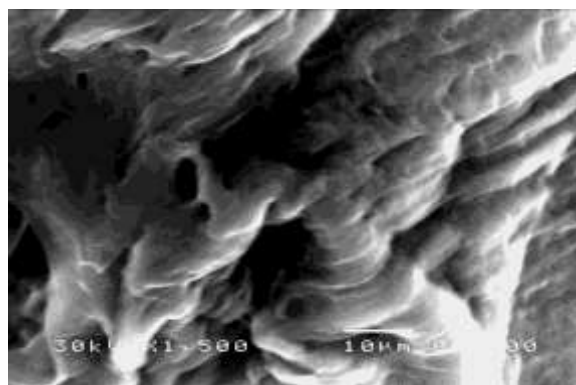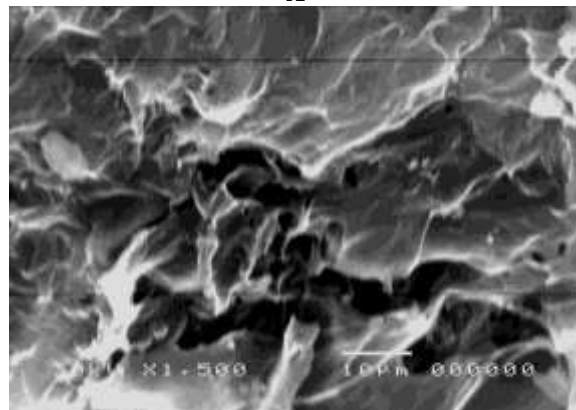**Figure 4: SEM micrographs of HPCA/EHA crosslinked copolymers by using 4 wt% of MBA a- HPCA/EHA 90/10, b-HPCA/EHA 50/50 and c- HPCA/EHA 10/90**

A

B

Figure 5: SEM micrographs of HPCA/EHA crosslinked copolymers 50/50 molar ratio, a- 2 wt% of MBA, b-HPCA/EHA, 50/50 10 wt% of MBA
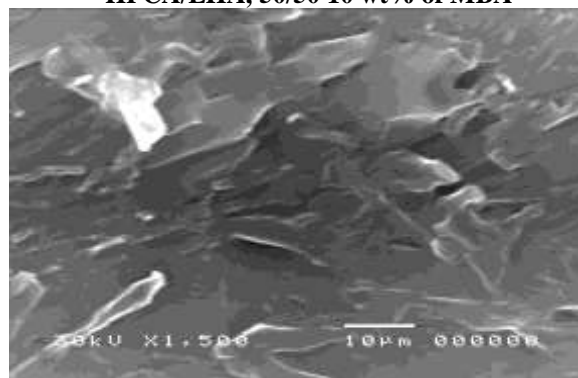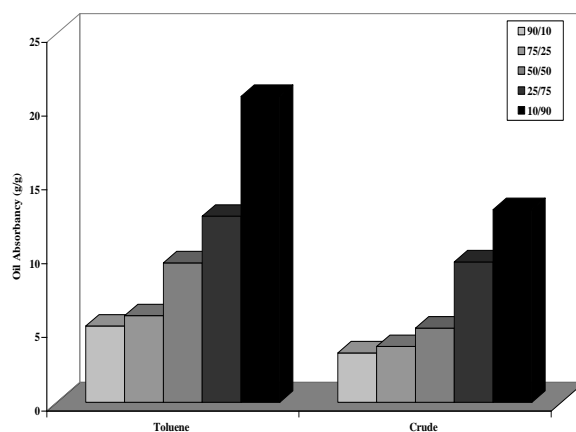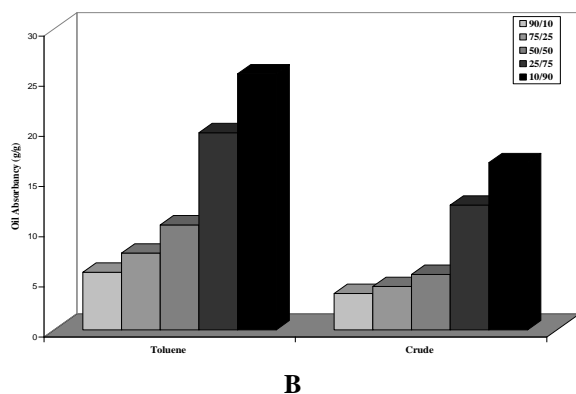

Figure 6: SEM micrographs of HPCA/EHA 50/50 crosslinked copolymers by using 2 wt% of DVB
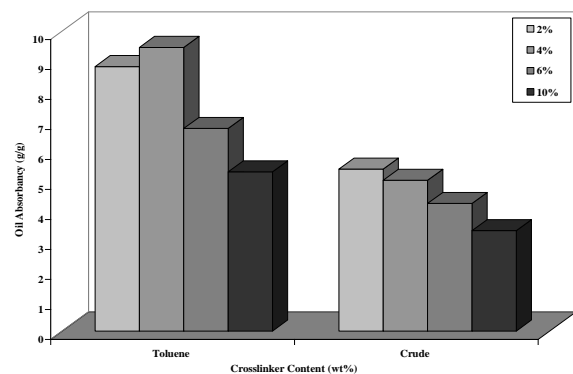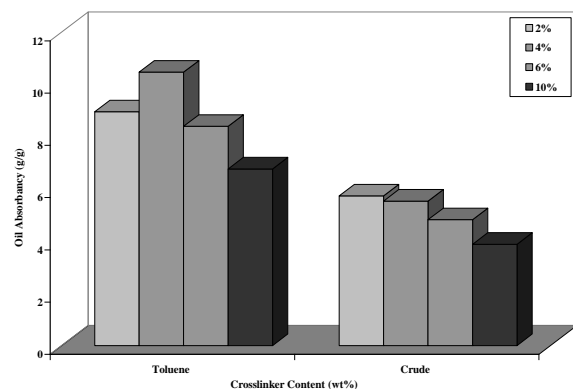

A

B

Figure 7: Effect of molar feed ratio of HPCA/EHA on oil absorbency at 298K, A- Using 4 wt% of DVB, B- Using 4 wt% of MBA.
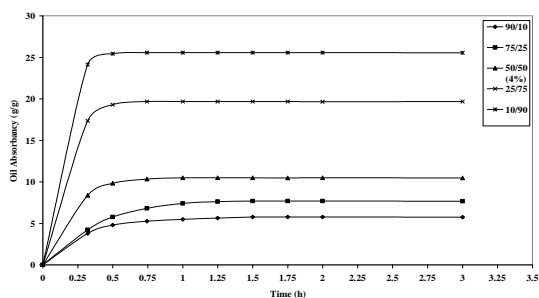

(B)

Figure 9: Oil absorbency (during 3 h) for HPCA-EHA copolymers with different mole ratios of HPCA to EHA using 4 wt% of MBA crosslinker at 298K a) in Toluene b) in 10% Crude oil.

A

B

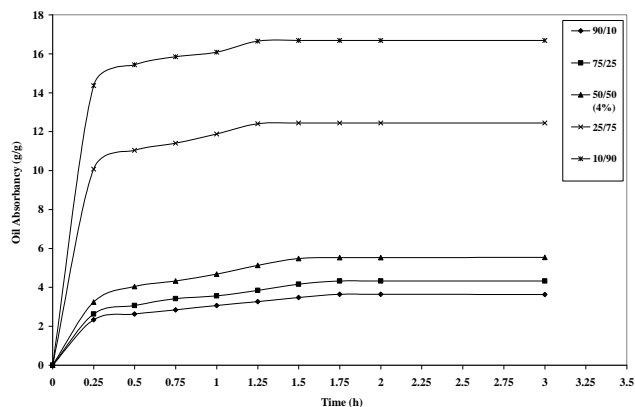**Figure 8: Effect of cross-linking agent content on oil absorbency of HPCA/EHA copolymers at 298K, A- Using DVB, B- Using MBA**
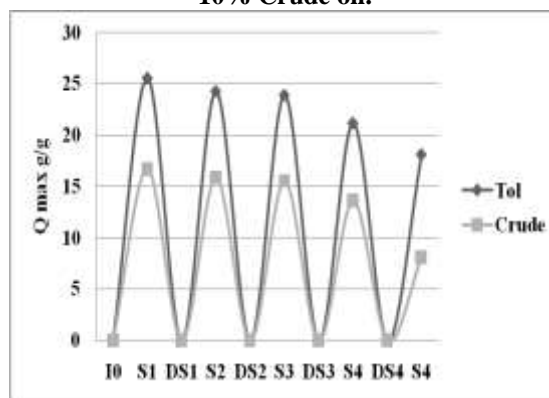

Fig. 10: Swelling Reversibility of HPCA/ODA 10/90 mol% crosslinked with 4 wt% of MBA in Toluene and Crude Oil: IO indicates initial condition, S1-4 = swelling cycle equilibrium condition and DS 1-4 = deswelling cycle equilibrium condition.

Morphology of crosslinked copolymers

　　　Morphology of the crosslinked HPCA/EHA copolymers can be studied by SEM; to that end micrographs of the crosslinked polymers are shown in Figure 4 a-c, Figure 5a, b and Figure6. First, Figure 4 a-c shows the morphology of several copolymer compositions (90/10, 50/50, and 10/90) prepared by bulk polymerization (with 4% MBA crosslinker). The micrograph of Figure 4(a) for HPCA/EHA 90/10 shows that surface texture of these crosslinked copolymers is smooth which means that they are homogeneous. The SEM micrograph of Figure 4(b) for HPCA/EHA 50/50 shows polymer morphology made up of disjointed cellular structures. It reveals very coarse irregularly shaped pores and finely dispersed second phase particles. Thus in Figure 4(c) of HPCA/EHA 10/90, we can see that the surface transferred from smooth to channel-like pores with increasing EHA content from 10 to 90 mol %. Our findings run parallel to those obtained by Atta and Arndt [29].

　　　Effect of crosslinker concentration on the network porosity is represented in Figure 5a and b. (SEM of HPCA/EHA, 50/50 2 and 10 wt% of MBA respectively). It can be seen that the heterogeneity in the networks depends on the crosslinker content; at 2 wt% of MBA we see large polymer domains with also large discontinuities between the domains. For the crosslinker contents of 10 wt %, the morphology changes drastically, aggregates of spherical domains appear. The

(A)

structure looks like cauliflowers, typical for a macroporous copolymer network. Atta et al [30] stated that the increase in the crosslinker concentration leads to microgel formation appears as microspheres.

SEM micrograph of HPCA/EHA crosslinked with 2 wt % of DVB (Figure 6) is different than that for sample crosslinked with 2 wt % of MBA (Figure 5a). More cavities are formed in case of MBA. Atta and his coworkers [31] found that the type of crosslinker greatly affect the morphology of the crosslinked network. The morphology can be correlated with SF values in Table 1. We recall higher crosslinking densities with the DVB crosslinker than MBA. Large cavities and convolutions are formed with increasing EHA content in the copolymers.

Oil Absoorption

According to the Flory swelling theory [32], 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 modulus. 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 [33]. SF data listed in Table 1 reveal that the increase in EHA molar ratio and the crosslinker concentration decreases the SF value for all the prepared oil sorbents. It was also found that SF values in case of using DVB are lower than those obtained in case of MBA. This may reflect the higher reactivity of DVB compared to MBA.

Kim and coworkers reported that petroleum absorptivity depends on bulkiness and length of alkyl substituents [34] and especially on porosity of the microstructure. In the present work, we designed and synthesized novel porous oil absorbent materials derived from hydroxypropyl cellulose and EHA as discussed above.

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. In terms of copolymer porosity, we have determined petroleum absorbencies of different compositions of HPCA/EHA crosslinked copolymers as a function of immersion time. Other variables were studied, namely, crosslinker type and concentration and the type of absorbed oil phase.

Effect of monomer feed ratio

In order to investigate the effect of monomer feed ratio two series of HPCA/EHA oil-absorbents with varied monomer feed ratios were prepared. It has been established that hydrophobicity and the effective volume of the cross-linking network are affected by monomer feed ratio [35], consequently, its oil absorption process and oil absorbency. The relevant oil absorption investigations are depicted in Figure 7. It can be seen that for the two types of oil tested, there was a maximum value for oil absorbency at monomer feed ratio 10/90 HPCA/EHA, mol/mol. In this copolymerization system, the hydrophobicity of EHA is much stronger than that of HPCA this is owing to the longer pendent alkyl chains in the former. Thus, an increase in the content of EHA will result in an increase in hydrophobicity and oil absorbency of the oil-absorbent. Also, it was observed

from the SEM micrograph Figure 4 (c) of HPCA/EHA 10/90 that the surface transferred from smooth to channel-like pores with increasing EHA this leads to more oil uptake

Effect of cross-linking agent content:

To investigate the effect of the cross-linking agent content on the oil absorbency, we prepared a series of HPCA/EHA (50/50) oil absorbents with varied DVB and MBA contents (from 2% to 10% based on the total mass of the two co-monomers), keeping all other conditions constant. Figure 8 illustrate the relationship between oil absorbency and crosslinker type and content. As shown in Figure 8 there was a maximum value in oil absorbency at 4 wt% in case of Toluene and 2 wt% in case of crude oil. This may be attributed to the effect of viscosity of oil and pore size of crosslinked oil sorbents. A lower concentration of cross-linking agent (DVB or MBA) (e.g. 2wt%) would lead to such an oil- absorbent in which the cross-linked network would be too loose. Accordingly, Lower oil absorbency was observed. When the amount of cross-linking agent (DVB or MBA) exceed 4wt%, the oil absorbency decreases to different extents in toluene and crude oil. It is well known that an excess of cross-linking agent will cause the formation of a too denser network of the copolymer and reduce drastically the chain length between cross-linking points, meanwhile causing an excessive decrease in the mobility of the polymeric chains (30, 35). This is disadvantageous for the oil to flow inside the network of the absorbent and accordingly the oil absorbency is low. The oil absorption efficiency in case of using DVB as crosslinker is lower than that of MBA. This finding runs parallel to the SF% results and reflects the higher reactivity of DVB compared to MBA.

Swelling kinetics of the synthesized crosslinked HPCA/ EHA copolymers

The sorption and diffusion of organic solvents through crosslinked polymer networks has been a subject of great interest [18, 20,28].

The rate of oil absorbent was illustrated in figure 9; the oil absorbency was increased rapidlly with increasing the EHA content and reached to equilibrium after 0.5 h in case of toluene, whereas in case of crude oil the rate of oil absorbent reach after 1.25 h and remained almost constant. Hence, it is concluded that oil absorption rate of the poly (HPCA/EHA) oil-absorbents is quite fast.

The sorption behavior gives an idea about the permeability, and diffusion coefficient of pentrant through polymers. They are used in various applications such as, gel permeation chromatography, ion-exchangers and controlled-release of drugs. As, such there is a growing interest in the study of the kinetics of gel swelling.

Swelling kinetic constant (k), listed in Tables 2 and 3, increases with increasing EHA mole ratio and also with decreasing crosslinker wt%. This result may be explained by the fact that the more crosslinker content, the stiffer the crosslinked polymer is, and the smaller cavities produce. Considering that the swelling kinetics may be dependent not only on the surfaces of the polymer but also on the number and volume of the pores in the polymer. The smaller cavities will provide larger absorption surfaces, which give higher swelling rate of the polymeric network (i.e.higher value of k). In other words, the polymer with higher swelling rate may have suitable structure for oil absorption [20].

The equilibrium toluene content (ETC) and equilibrium crude content (ECC), listed in Tables 2 and 3 increase with

increasing alkyl acrylates mol%. This high oil absorptivity of the polymer depends on the blockness of the alkyl constituent. The ability of the swelled gels to undergo several cycles of swelling and deswelling is shown in Figure 10 for crosslinked HPCA/EHA 10/90 mol% crosslinked with 4wt% MBA as representative sample in both toluene and crude oil. We can see that after the first cycle the gel did not achieve the original swollen state but in all the following cycles it swelled back to its previous swollen state. This indicates that small amount of soluble fractions still remains in the crosslinked gels which could have leached out upon deswelling, reducing the degree of successive swelling [36].

Conclusion:

Hydroxylpropyl cellulose acrylate (HPCA) macromonomer was prepared and copolymerized with ethylhexyl acrylate (EHA) in presence of two types of crosslinking agent to obtain (HPCA/EHA) oil-absorbent. The chemical structure of the prepared copolymers was confirmed by IR and ^{1}HNMR spectroscopy and there was a good accordance between the data obtained and the chemical structure of these copolymers. The morphology of the investigated crosslinked copolymers was studied by SEM. It was found that the increase in EHA content drastically changes the surface morphology from smooth to channel-like pores. By investigating oil absorption of the prepared oil sorbents, it was found that HPCA/HPCA 10/90 was the most efficient oil sorbent either in toluene or in 10% crude oil. The data also reveal that there was a maximum value in oil absorbency at 4 wt% in case of Toluene and 2 wt% in case of crude oil. The oil absorption efficiency in case of using DVB as crosslinker is lower than that of MBA. The reusability of the prepared oil sorbents was studied for HPCA/HPCA 10/90 mol% crosslinked with 4wt% MBA as representative sample in both toluene and crude oil. It was observed that the gel did not achieve the original swollen state after the first cycle but in all the next cycles it swelled back to its previous swollen state.

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