

Porous crosslinked copolymers of octadecyl acrylate with acrylic acid as sorbers for crude petroleum spills

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Abstract

Bulk and suspension polymerization were used to prepare octadecyl acrylate/acrylic acid (ODA/AA) copolymers. AA content ranged from 0 to 90 mol%. Divinyl benzene was used as a crosslinker at several concentrations (1, 4 and 10 wt%). Isopropyl alcohol or dioctyl phthalate and methyl benzoate were used as the reaction solvents in the presence of poly(vinyl alcohol) as a dispersing agent and 2,2-azobis isobutyronitrile as the initiator. The polymers so prepared were coated onto poly(ethylene terephthalate) nonwoven (NWPET) fibers. The effects of copolymerization, feed composition, crosslinker concentration and reaction medium or solvent on morphology including porosity and the dynamic mechanical and swelling properties of the crosslinked polymers were determined. Swelling tests were performed in toluene and in 10% crude petroleum diluted with toluene. Bulk polymerization does not result in the formation of a continuous liquid absorbing material while suspension polymerization enables sorbers to be obtained with desired properties. Coating ODA/AA copolymers onto NWPET increases liquid absorption.

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Keywords: petroleum sorption; crosslinked copolymers; poly(ethylene terephthalate); nonwoven fibers; octadecyl acrylate-co-acrylic acid; dynamic mechanical analysis

INTRODUCTION

There is no need to argue that petroleum spills are a leading cause of environmental pollution, resulting in both immediate and long-term damage to aquatic, coastal and land habitats, as well as to humans. Solid suspensions in water can be removed by processes such as flocculation¹ but there seems to be no substitute to taking petroleum out of water by gelling or absorption. We shall use here the words 'petroleum' and 'oil' interchangeably. Remediation of oil spills with either gelling agents or porous absorbents is quite difficult.^{2–12} The currently used methods have drawbacks: they are slow, the absorbing materials are bulky, the wastes produced are toxic and the remedies are costly. Thus, further work in this area is worthwhile. According to Flory's swelling theory,^{13–15} petroleum absorption is a process in which molecules penetrate into a three-dimensional polymer network continuously causing swelling until saturation is reached. The swelling process is affected by two factors: thermodynamic interactions between the liquid and the polymer and mechanical behavior which simply opposes polymer expansion.¹⁴ More specifically, the change of the Helmholtz function A^W on swelling of a polymer is¹⁴

$$A^W = A^M + A^Z \quad (1)$$

Here the superscript M denotes thermodynamic mixing of two components while the superscript Z represents the mechanical contribution. The mixed term A^{MZ} can be neglected without loss of accuracy. If the validity of Eqn (1) and of the Flory equation of state is assumed,^{16,17} in several natural rubber + liquid systems the

parameter X_{12} representing the polymer + solvent interactions is independent of composition.¹⁴ We shall discuss further parameters affecting swelling in a later paper.

The nature of swelling processes has been studied.^{18–23} Our objectives are largely practical, namely mitigating the drawbacks named above and achieving higher absorption capacities.

Oil sorbers consisting of hydrophobic three-dimensionally crosslinked polymers are able to absorb oil and swell. Crosslinked hydrophobic polymers are widely used as oil sorbents. Alkyl acrylate and aromatic polymers with nonpolar side chains have been attracting much attention in the preparation of crosslinked

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polymers for oil-swelling.^{2,24–26} Useful elements from our earlier work include copolymerization of acrylate monomers and subsequent crosslinking by electron-beam irradiation.⁷ Also one of us²⁴ used crosslinked cinnamoyloxyethyl methacrylate/isooctyl acrylate copolymers for oil absorbency applications. Crosslinked reactive macromonomers based on polyisobutylene and octadecyl acrylate (ODA) copolymers were used as crude oil sorbers.⁸ However, we need to keep in mind that chemical bonds providing crosslinking limit the network extension and thus make liquid penetration difficult. Physical entanglements – also resulting in network formation – might be better in this respect. It is well known that, in the radical copolymerization of ionogenic monomers such as acrylic acid (AA) and methacrylic acid, the reaction medium affects the copolymerization parameters and the homopolymerization rate. Previous work described how to produce elastic network hydrogels based on crosslinked ODA/AA copolymers prepared with *N,N*-methylene bisacrylamide (MBA) as a crosslinker and ethanol as a solvent.²⁷

In an earlier paper we developed polyurethane foams based in part on recycled poly(ethylene terephthalate) (PET) as oil sorbers.²⁸ In the present work we explore a different route. We study crosslinking copolymerization of ODA with AA and how it increases the oil absorbency of the prepared copolymers. We examine the effects of polymerization techniques of ODA monomers – such as bulk and solution crosslinking copolymerization – on the network structure. Our particular objective was the formation of networks with low forces restraining liquid absorption. We have further pursued the creation of petroleum sorbers based on PET fibers coated with ODA homopolymers and copolymers. PET fibers provide a suitable support for the ODA/AA gels, making them easier to work with as oil sorbers, while PET itself has low oil absorption capacity.

EXPERIMENTAL

Materials

ODA and 2,2-azobis isobutyronitrile (ABIN) were obtained from Aldrich Chemical Co. (Aldrich, Munich, Germany) and used without purification. AA, divinyl benzene (DVB), dioctyl phthalate (DOP), methyl benzoate (MB), poly(vinyl alcohol) (PVA) (number-average molecular weight $M_n \approx 2.5 \times 10^4 \text{ g mol}^{-1}$), toluene and isopropanol were obtained from Fluka. MBA was used as crosslinker and was purchased from Aldrich Chemical Co. Nonwoven PET (NWPET) fibers were purchased from Zhejiang Waysun Chemical Fiber Co. Ltd, China; the company produces these fibers from recycled PET bottles. The bottles have been cut into small pieces, cleaned in a hot water process to remove dirt, and then sorted and extruded to provide polyester fibers. Crude petroleum was obtained from Petrobel Egypt; its characteristics are provided in Table 1.

Synthesis of crosslinked copolymers and homopolymers

Suspension polymerization

Suspension copolymerization and crosslinking reactions of ODA with AA were completed with varied weight percentages of these two components. The monomers were mixed together in a 250 mL three-necked flask equipped with a thermometer, nitrogen gas and reflux condenser. To the monomers we mixed 0.02 wt% of ABIN initiator, 1.0 wt% PVA (170 mL for each 100 g of monomers) and several weight ratios of DVB crosslinker (1%, 4% and 10%). Two different reaction media were used, the first isopropanol

Table 1. Characteristics of the crude petroleum used

Test	Method	Value
Specific gravity at 60 °C	IP 160/87	0.875
API gravity	Calculated	21.7
Pour point (°C)	IP 15/67(86)	14.0
Kinematic viscosity (60 °F) (cSt)	IP 71	763
Wax content (wt%)	UOP 46/64	2.45
Asphaltene content (wt%)	IP 143/84	8.80

API, American Petroleum Institute.

and the second a mixture of DOP (18 mL) with MB (82 mL). The copolymerization reactions were performed at 60 °C for 3 h for monomer molar ratios (ODA/AA) of 90/10, 70/30, 50/50, 30/70 and 10/90. After the reaction was completed, the resulting ODA/AA precipitate was washed with methanol and dried in a vacuum oven at 40 °C until a constant weight was maintained.

The same procedure was used to prepare crosslinked ODA homopolymers in the presence of different weight percentages of DVB or MBA crosslinkers.

Bulk polymerization

For preparation of crosslinked ODA and AA without a solvent, different mole ratios of ODA and AA were mixed together with ABIN initiator (0.02 wt%) and different weight ratios of DVB crosslinker (1–10 wt%). The mole percentage of ODA in the copolymers ranged from 90% to 10% (as in the series prepared by suspension copolymerization). Copolymerization and crosslinking reactions were performed in siliconized test tubes at 60 °C for 3 h; the mixture was bubbled with nitrogen for 15 min before heating. The time of reaction was extended to ensure complete reaction of all monomers.

The same procedure was used to prepare crosslinked ODA homopolymers in the presence of different weight percentages of DVB or MBA crosslinkers.

Coating of ODA/AA onto NWPET fibers

To obtain PET fibers coated with the ODA/AA copolymers, the suspension polymerization was performed (according to the section above) in the presence of PET fibers, ODA, AA and crosslinker monomers. The weight ratios between PET fibers and monomers were between 1 and 3. The ODA/AA copolymers prepared by bulk polymerization (as above) were cast on the PET fibers before crosslinking. The coated rods – prepared by the two methods – were then cured at 105 °C for 24 h.

Characterization and physical properties of the prepared polymers

Fourier transform infrared (FTIR) spectra were recorded in KBr pellets using a Bruker FTIR model IF 566 spectrometer. An FEI Quanta environmental scanning electron microscope was used to evaluate the morphology of the ODA/AA copolymers.

Dynamic mechanical analysis (DMA) of the purified crosslinked ODA/AA copolymers was performed using a Perkin Elmer DMA 8000 in the compression configuration. Specimens were rectangular with nominal dimensions of 5 × 5 × 10 mm. Tests were conducted from –30 °C to 100 °C at a heating rate of 5 °C min⁻¹ and 1.0 Hz sinusoidal frequency.

The glass transition temperature T_g , melting temperature T_m and crystallization temperature T_c of the crosslinked ODA/AA copolymers were determined by DSC on a Perkin Elmer TGA 7. The samples were heated from 0 °C to 100 °C in a N₂ flow (20 cm min⁻¹) at a heating rate of 10 °C min⁻¹.

Characterization and chemical properties

Extraction of the soluble fraction (SF%)

The crosslinked ODA, ODA/AA and coated PET fibers were post cured at 105 °C in an air oven for 24 h to ensure complete polymerization. These crosslinked and coated PET fibers were thoroughly dried in vacuum at 30 °C to a constant weight. The soluble fractions were determined via the Soxhlet extraction technique. Dried ODA, ODA/AA and coated PET xerogels were transferred into an extraction thimble and were subjected to Soxhlet extraction with chloroform for 24 h. After extraction, the samples were dried in atmospheric pressure for several hours and then dried to a constant weight in a vacuum oven at 35 °C. The soluble fraction (SF), i.e. the fractional loss in weight of the xerogel, was calculated as

$$\text{SF\%} = [(w_1 - w_2) \times 100] / w_1 \quad (2)$$

where w_1 is the dry weight before extraction and w_2 is the dry weight of the sample after extraction.

Swelling analysis

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

$$\Phi_p = (W_1 - W_0) \rho_p / W_0 \rho_s \quad (3)$$

Here W_0 is the sample weight before swelling, W_1 is the sample weight after swelling, ρ_p is the density of the polymer sample and ρ_s is the density of the toluene solvent.

Oil absorption testing

Oil absorbency of the prepared ODA, ODA/AA and coated PET fibers was determined at 25 °C according to ASTM F726-81. Polymer (0.1 g) was placed in a pure stainless steel mesh (4 × 4 × 2 cm, pre-weighted) such that both were immersed in pure toluene or in crude oil diluted to 10% with toluene. The sample and the mesh were together picked up from the oil (or toluene), drained for 30 s, tapped with filter paper to remove excess oil from the bottom of the mesh, and then weighed on a balance. Oil sorption capacity Q in toluene (Q_T) and in crude oil (Q_{crude}) was calculated as

$$Q \text{ (gg)} = \frac{w_{\text{abs}}}{w_{\text{dry}}} \quad (4)$$

Here w_{abs} is the weight of oil (or toluene) that has been absorbed by the sample and w_{dry} is the weight of the sample before immersion in and absorption of oil (or toluene). Equilibrium toluene content (ETC) and crude oil content (ECC) were calculated as follows:

$$\text{ETC\% (or ECC\%)} = [(w_{\text{abs}} - w_{\text{dry}}) / w_{\text{abs}}] \times 100 \quad (5)$$

RESULTS AND DISCUSSION

Porous crosslinked ODA/AA copolymers, prepared by suspension polymerization in isopropanol or in a mixture of DOP with MB as solvent, were synthesized with DVB as the only crosslinker. DVB was the crosslinker used to prepare crosslinked ODA/AA copolymers by bulk polymerization as well. On the other hand, the crosslinked ODA homopolymers were synthesized with both DVB and MBA as crosslinkers, and with ABIN as chemical initiator. Based on the use of the two different crosslinkers (DVB and MBA), two series (suspension *versus* bulk polymerization) of crosslinked homopolymers were prepared from ODA.

Infrared spectroscopy

The IR spectrum of ODA/DVB was selected to represent the chemical structure of the prepared polymers and is presented in Fig. 1(a). All spectra show 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 ester group of ODA) and 1143 cm⁻¹ (assigned for stretching of the C–O of the ester group of ODA). The disappearance of vinyl group C=C stretching and bending vibrations at 3100 and 950 cm⁻¹, respectively, indicates complete polymerization and crosslinking of the ODA polymers. The FTIR spectrum of 90/10 (mol% ratio) ODA/AA shown in Fig. 1(b) is representative of the chemical structure of the prepared copolymers. All copolymer spectra show characteristic absorption bands at 2926 cm⁻¹ (assigned to stretching vibrations of the aliphatic C–H bonds), 1750 cm⁻¹ (assigned to stretching vibrations of the C=O ester group of ODA), 3450 cm⁻¹ (assigned to stretching vibrations of the OH groups of AA) and 1143 cm⁻¹ (assigned to stretching of the C–O of the ester groups of ODA). The disappearance of the vinyl group C=C stretching and bending vibrations at 3100 and 950 cm⁻¹, respectively, indicates complete copolymerization and crosslinking of the ODA/AA copolymers.

Soluble fractions of ODA/AA copolymers

We studied the degree of conversion and crosslinking copolymerization of ODA with AA or DVB as crosslinker. It is well known that different types of linear homopolymers and copolymers based on ODA or AA are formed during the crosslinking copolymerization reaction. The degree of conversion of ODA, AA and DVB to linear or crosslinked polymers depends on the reactivity ratios between monomers. Typically, after the reaction there remain some polymer chains not attached to the infinite network; these can be extracted from the gel fraction. The effect of these chains on behavior models is difficult to take into account; consequently they are usually neglected in theories. The chains do not contribute to the modulus but they can be solvated and therefore contribute to the swelling. Hence, it is desirable to eliminate or minimize the presence of these extractable molecules. The percentage of the extractable fraction (soluble fraction SF) depends on (a) the type and concentration of the monomers and (b) the type and concentration of the crosslinking agent. As noted above, the polymer rods of coated NWPET fibers were post cured to ensure complete polymerization. Afterwards, the soluble fractions were determined via the Soxhlet extraction technique using Eqn. (2). The total conversion of monomers to crosslinked polymers was estimated as

$$\text{total conversion (\%)} = (W_{\text{xl}} \times 100) / W_{\text{xt}} \quad (6)$$

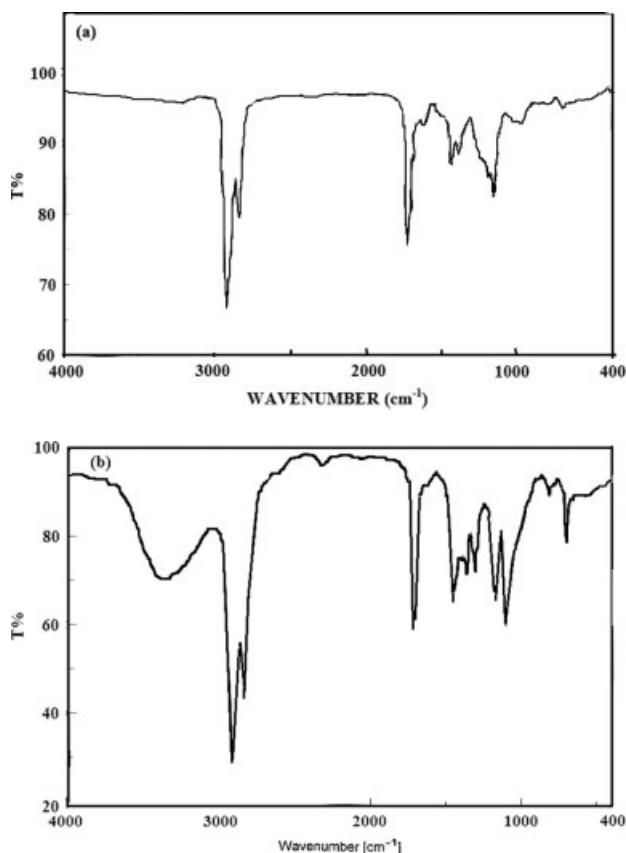


Figure 1. IR spectrum of (a) crosslinked ODA/DVB homopolymer (1 wt% DVB) and (b) ODA/AA/DVB 50/50/10 copolymer.

where W_{xl} and W_{rt} are the total weight of crosslinked polymers after post curing at 105 °C and the weight of reactants, respectively.

The values of SF% and total conversion of crosslinked ODA homopolymers and ODA/AA copolymers with and without NWPET are reported in Tables 2–5. We see that the total conversion increased while SF decreased with increasing concentrations of ODA and crosslinker. The SF values also decreased when the crosslinking polymerization was completed without solvent (i.e. in bulk). Moreover, SF was lower when using isopropanol rather than DOP + MB as solvent in the suspension technique.

These observations can be correlated to the difference in the reactivity ratios between ODA and AA with either DVB or MBA crosslinkers. The reactivity ratios between ODA (r_1) and AA (r_2) were previously determined²⁹ in ethanol as 3.0 and 0.5, respectively. We conclude from the SF% data listed in Tables 2 and 3 that the

crosslinking efficiency increases in the order ODA > ODA/AA > AA. Also, the data prove that isopropanol is a good solvent for crosslinking copolymerization of ODA/AA with DVB crosslinker. This may be due to the fact that each solvent has different interactions with crosslinker and other monomers, which in turn affects the reaction yield. With isopropanol as solvent, the total conversion increased with decreasing ODA content. The degree of crosslinking onto NWPET fibers was determined from weight loss measurements of NWPET following immersion in toluene for 24 h. The SF% results are listed in Tables 4 and 5. The degree of crosslinking increases with increasing DVB concentration.

Morphology of the ODA/AA copolymers

The morphology of the crosslinked ODA homopolymers and ODA/AA copolymers can be evaluated by SEM; micrographs of the crosslinked polymers are shown in Figs 2–4. First, Fig. 2 shows the morphology of several copolymer compositions (90/10, 50/50 and 10/90) prepared by bulk polymerization (with DVB crosslinker). The micrograph of Fig. 2(a) for ODA/AA/DVB 10/90/1 (crosslinked with 1 wt% DVB) shows a polymer morphology made up of disjointed cellular structures. It reveals very coarse irregularly shaped pores and finely dispersed second phase particles. This is typical of a closed cell porous polymeric material. The SEM micrograph of ODA/AA/DVB 90/10/1 (Fig. 2(b)) shows that the surface texture of the crosslinked copolymers is smooth which means that the polymer is homogeneous. The pore structure of the ODA/AA polymer depends on the concentration of AA and DVB crosslinker. Thus in Fig. 2(c) (of ODA/AA/DVB 50/50/10) we see that the surface changes from smooth to channel-like pores with increasing AA content from 10 to 50 mol%.

The micrographs of Fig. 3 show onset of the formation of a connected porous network. The disjointed cellular structure in Fig. 2(a) is replaced by the connected porous structure of Fig. 3(c). On polymerizing the ODA/AA precursor suspension polymerization in the presence of DOP and MB, the morphology of the polymer indicates an open cell porous structure, as seen in the micrographs of Figs 3(a) and 3(b). The dimensions of the open cell porous structure increase with increasing AA content of the precursor suspension crosslinking copolymerization, although the polymer morphology remains similar. The SEM micrograph shown in Fig. 3(c) for the crosslinked polymer synthesized from such polymerization containing 50 mol% AA indicates the pore sizes to be in the 2–4 μm range. In contrast, the pore sizes are 1–2 μm in Fig. 3(b) for polymer obtained from copolymerization with 10 mol% AA. The morphology of the polymer obtained by suspension crosslinking copolymerization containing isopropanol is similar to that of polymer from the DOP and MB system; see the open cell porous structure in Fig. 3(d). The surface morphology

Table 2. Soluble fraction and conversion in crosslinked ODA homopolymers							
Homopolymer/ crosslinker	Crosslinker (wt%)	Total conversion (%)			SF%		
		DOP + MB	Isopropanol	Bulk	DOP + MB	Isopropanol	Bulk
ODA/DVB	1	96	92	97	33	12	8
	4	97	94	98	26	9	6
	10	98	95	99	24	7	5
ODA/MBA	0.5	77	83	90	32	19	12
	1	85	89	93	24	10	6
	5	88	93	96	19	8	4

Table 3. Soluble fraction and total conversion of crosslinked ODA/AA (with DVB as crosslinker)

ODA/AA (mol%/mol%)	DVB crosslinker (wt%)	Total conversion (%)			SF%		
		DOP + MB	Isopropanol	Bulk	DOP + MB	Isopropanol	Bulk
90/10	1	90	98	99	19	12	10
70/30	1	80	95	98	25	20	12
50/50	1	97	92	95	28	24	14
	4	98	95	93	20	12	10
	10	99	99	91	12	8	5
30/70	1	98	95	94	30	26	15
10/90	1	99	94	93	34	30	16

Table 4. Soluble fraction and total conversion for crosslinked ODA homopolymers onto NWPET fibers

Homopolymers	Crosslinker (wt%)	SF%		
		DOP + MB	Isopropanol	Bulk
ODA/DVB	1	27	24	20
	4	19	18	16
	10	14	12	10
ODA/MBA	0.5	28	25	20
	1	20	20	15
	5	15	12	10

Table 5. Soluble fraction for crosslinked ODA/AA (with DVB as crosslinker) onto NWPET fibers

ODA/AA (mol%/mol%)	DVB crosslinker (wt%)	SF%		
		DOP + MB	Isopropanol	Bulk
90/10	1	24	22	20
70/30	1	25	23	22
50/50	1	30	26	25
	4	25	22	18
	10	20	18	12
30/70	1	32	29	27
10/90	1	33	30	29

of crosslinked ODA/AA based on suspension polymerization is irregular with a very rough, granular and porous appearance. In contrast, the morphology of the crosslinked ODA/AA copolymer in bulk polymerization lacked such porosity in the surface of the crosslinked polymers.

The SEM micrographs of the ODA/AA-coated PET fibers show a dramatic difference based on polymerization technique (suspension *versus* bulk). Compared with the PET coated with ODA/AA copolymer crosslinked in suspension polymerization (Fig. 4(a), (b)), there is no granular, porous appearance in the PET coated with ODA/AA copolymer crosslinked in bulk polymerization (Fig. 4(c), (d)). A polymeric material usable as a liquid (petroleum, toluene) sorber needs to have a continuous structure and therefore has to be crosslinked. However, high degrees of crosslinking result in short (low molecular weight) chains between crosslinks and therefore a high density of crosslinks per unit volume, and thus not much space for the liquid to get in. It is for this reason that bulk polymerization provides a polymer with crosslinking

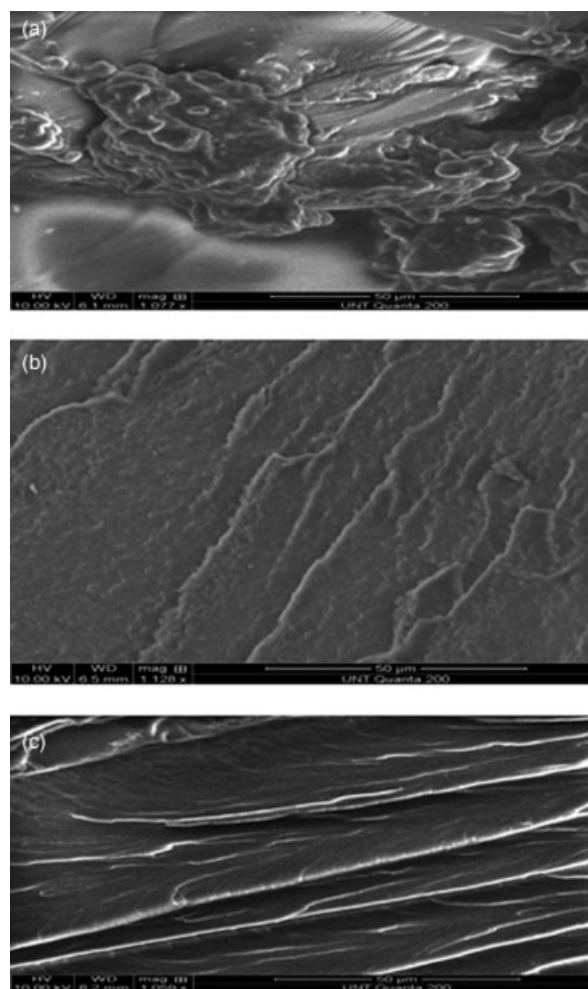


Figure 2. Environmental SEM micrographs of crosslinked ODA/AA/DVB 90/10/1 (a), 10/90/1 (b) and 50/50/10 (c) by bulk polymerization: (a) smooth surface texture; (b) disjointed cellular structures with coarse irregularly shaped pores and finely dispersed second phase particles; (c) channel-like pores.

density too high for efficient liquid sorbers. By contrast, suspension polymerization provides the capability to achieve crosslinking that is sufficient for sorber material continuity and at the same time not too high to lower the liquid absorption capacity.

The wet suspension polymerization technique also prevents collapse of the crosslinked ODA/AA/PET fiber network. Moist fibers allow for a more porous network and thus greater infiltration

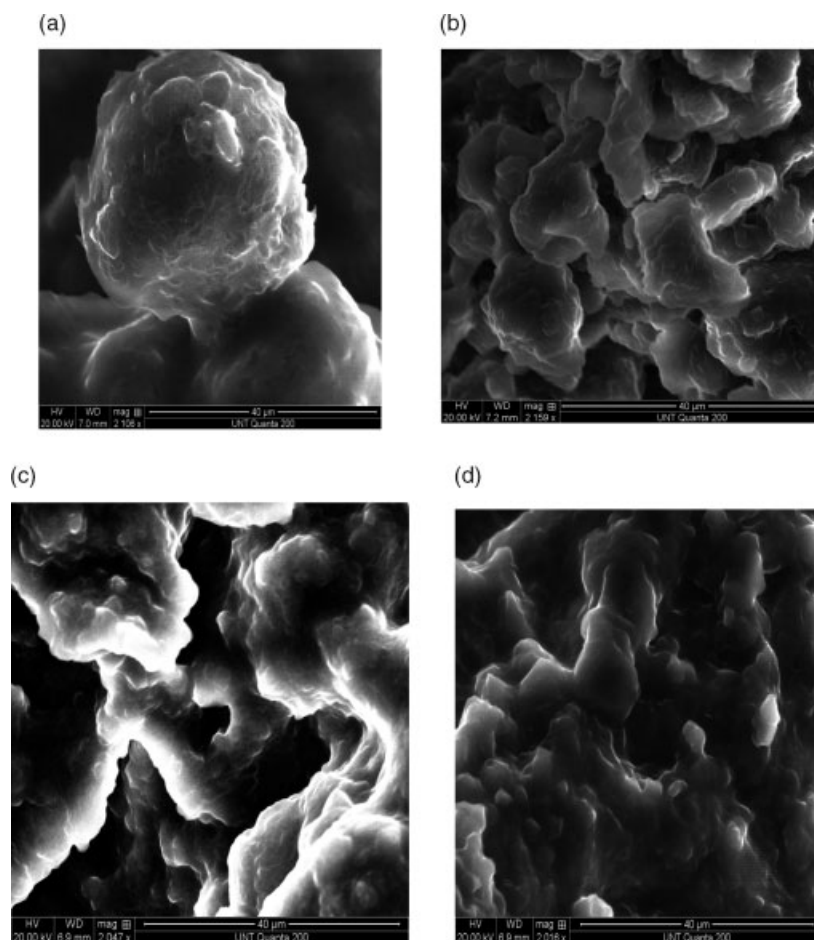


Figure 3. Environmental SEM micrographs of crosslinked ODA/AA/DVB 90/10/1 (a), 50/50/10 (b), 10/90/1 (c) synthesized with DOP + MB solvent and 90/10/1 (d) synthesized with isopropanol as solvent in suspension polymerization.

of adhesive monomers.²⁵ With the wet suspension technique the channels between the PET fibers are filled with solvent or monomer fluids. The only mechanism available for coating of PET fibers with ODA/AA is diffusion of the resin into whatever fluid is in the spaces of the substrate and along the PET fibers. Differences in quality of our coatings of ODA/AA systems can be attributed to factors such as dissimilar solvents and variations in the copolymer composition. These factors influence the ability of the ODA/AA to tolerate the solvent that is present within the suspension polymerization as a result of the wet bonding technique. As indicated, the hydrophobicity of isopropanol solvent is different from the hydrophobicity of DOP and MB solvents; isopropanol is relatively less hydrophobic than DOP + MB. Accordingly, isopropanol would resist diffusing into PET fibers. The ODA/AA may undergo phase separation as it interacts with wet PET fibers; such phase separation could compromise the structural integrity of the resultant coated PET fibers. Because isopropanol is present in both the crosslinked ODA/AA layer and the PET tubules, when hydrophobic ODA/AA monomers infiltrate the PET the material might undergo a microphase separation before it is light cured. As a consequence, the ODA/AA-rich phase may form microporous crosslinked ODA/AA gels within the interfibrillar spaces. By contrast, single-phase three-dimensional ODA/AA polymer networks could form porous ODA/AA. Consequently, the ODA/AA resin produced with suspension polymerization has phase separation and compromises the structural integrity

of the ODA/AA and leads to a very porous network. For this reason the wet suspension crosslinking polymerization route is recommended for preparation of ODA/AA porous polymers. Such porous systems contain more hydrophobic components (i.e. ODA). Although wet suspension may result in a better opportunity for resin infiltration, phase separation could compromise both the quality of the ODA/AA coating onto PET and durability.

Thermal and mechanical properties of ODA/AA copolymers

The elasticity and rigidity of the crosslinked ODA/AA networks were determined by measuring the mechanical and thermal changes of the crosslinked copolymer. Interestingly, the transition temperature at which the polymer is softened varies with the concentration of ODA units in the copolymer. This is seen in the DMA results; as an example in Fig. 5 we show the storage modulus E' versus temperature diagrams for some copolymers obtained by bulk polymerization. We recall that E' descent is one of the methods of locating the glass transition temperature T_g ,³⁰ while that temperature is actually representative of a region of temperatures.³¹

The drastic change in mechanical properties observed is reversible and cyclically reproducible with repeated temperature changes. This can be attributed to the order–disorder transition of the crystalline aggregates formed through side-by-side interactions of octadecyl groups, since the aggregates can reversibly ‘lock’ the original as well as the deformed shape on cooling.^{24,25}

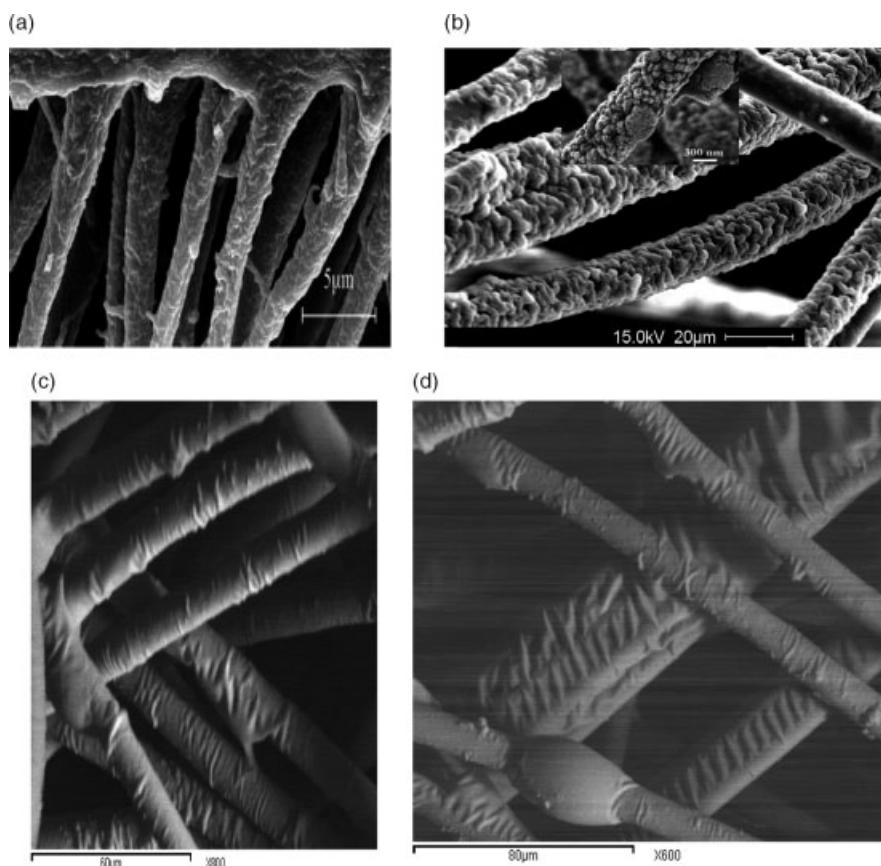


Figure 4. SEM micrographs of crosslinked ODA/AA/DVB on NWPET fibers: (a) 50/50/1 and (b) 50/50/10 using isopropanol, and (c) 50/50/1 and (d) 50/50/10 by bulk polymerization.

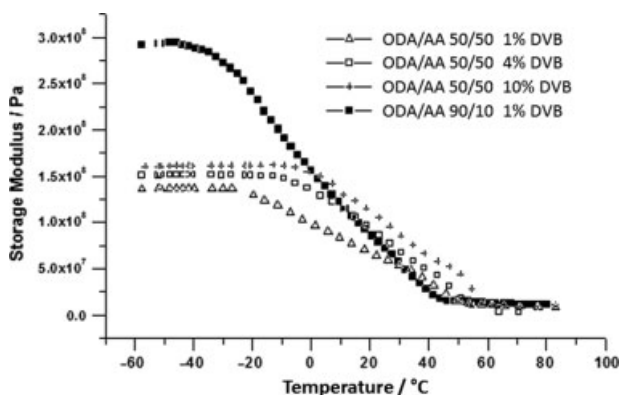


Figure 5. Storage modulus from DMA analysis for ODA/AA copolymers prepared by bulk polymerization with varying weight percentages of DVB crosslinker.

To confirm the crystallization process of the copolymer, DSC measurements were made to clarify the ordered structure of the ODA/AA copolymers by measuring the melting temperature T_m and cold crystallization temperature T_c . The results are listed in Table 6. The formation of the amorphous and semicrystalline or crystalline crosslinked ODA/AA is dependent on the ODA content, solvent polarity and polymerization technique. The appearance of an endothermic peak corresponds to the melting of side-chain crystallization in ODA homopolymers or in ODA/AA copolymers. Apparently an ordered ODA/AA copolymer structure is formed in the moderately swollen state if the hydrophobic alkyl groups

are long enough to align side by side. The relation between ODA content and T_g or T_m of the crosslinked ODA/AA/DVB obtained by suspension polymerization is presented in Fig. 6. The transition temperature changes from about 20 to 45 °C depending on the ODA/AA copolymer composition. These results are in contrast to earlier work on ODA/AA crosslinked with MBA crosslinker, in which gels have a melting temperature around 50 °C regardless of the ODA content.²⁴ The depression of the transition temperature at higher ODA might be associated with microphase separation occurring in the copolymers. This can be correlated to the difference in the reactivity ratios between ODA/AA towards MBA or DVB. Differences in the miscibility of ODA units with AA and DVB or MBA units in different solvents can also be a factor. In crosslinked ODA/AA/DVB in a mixed solvent of DOP and MB, ODA and AA units have fairly good miscibility with each other owing to their hydrophobic nature; consequently, small but stable aggregates are formed. By contrast, ODA units in ODA/AA when MBA is used are not miscible with MBA units due to the lower hydrophobicity of the latter, which brings about a loss in interfacial energy and larger aggregates are formed. Such crystallization–melting behavior was observed for other copolymer gels prepared from hexadecyl acrylate and AA, but no crystallized structure was observed in the copolymer gel of dodecyl acrylate and AA.²⁹ In the present work, DMA and DSC data indicate that the crosslinked ODA/AA based on DVB crosslinker and containing a content of ODA of more than 50 mol% forms elastic amorphous and semicrystalline polymer networks. The rigidity of these networks increases both with increasing AA and with increasing DVB content.

Table 6. DSC data for the crosslinked ODA/AA copolymers (with DVB as crosslinker)

ODA/AA (mol%/mol%)	DVB (wt%)	T_g (°C)			T_m (°C)			T_c (°C)		
		DOP + MB	Isopropanol	Bulk	DOP + MB	Isopropanol	Bulk	DOP + MB	Isopropanol	Bulk
90/10	1	—	29	39	35	35	—	26	21	—
70/30	1	—	28	22	30	32	—	24	22	—
50/50	1	17	19	20	31	33	—	26	28	—
	4	19	21	22	34	32	—	28	26	—
	10	21	22	23	44	43	—	25	26	—
30/70	1	—	—	—	36	35	39	30	32	33.8
10/90	1	—	—	—	42	44	45	34	35	37.3

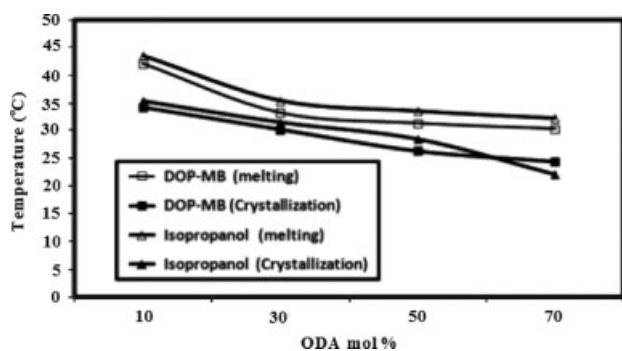


Figure 6. Dependences of melting temperature T_m and cold crystallization temperature T_c on composition for crosslinked ODA/AA with 1 wt% DVB material obtained by suspension polymerization in the solvents named in the key.

Oil absorptivity of treated NWPET with ODA/AA

The oil absorptivity of materials depends on the hydrophobicity of crosslinked polymers and on the porosity of the microstructure, which can be controlled by crosslinking. High porosity when present makes crosslinked polymers efficient sorbents for different odors and vapors as well as for removal of metal ions, dyes and various organic compounds from water. We have used petroleum diluted with toluene (10% petroleum). To validate performance for real applications in cleaning up oil spills, the oil absorption test has to be conducted using not only light or medium oil but also heavy oil, because crude oil has a high viscosity. Needless to say, the molecular mechanism of solvent transfer is dependent on the properties of the components. The large mass, chain structure and flexibility of macromolecules affect the nature of diffusion in polymer–solvent systems. At the same time, the materials used to absorb the oil do not have a sponge-like structure with open pores but only a network structure, formed by the crosslinking reaction. Therefore, heavy oil with high viscosity, such as Belayium crude oil, cannot easily diffuse from the surface of the samples into the internal space of the network. However, toluene is the solvent most frequently used to dissolve asphaltene in crude oil,^{32,33} while other factors such as the presence of dissolved gases affect the solubility of petroleum and of fractions made from it.^{34,35} Thus, we have used crude oil diluted with toluene so that the swelling behavior of the samples could be easily evaluated. The data (Q_T) for crosslinked ODA homopolymers and for ODA/AA copolymers, shown in Fig. 7, indicate that the toluene absorptivity increases with increasing immersion time and levels off after some 30–50 min, depending on the composition, for materials obtained by suspension polymerization. For materials obtained by

bulk polymerization the time to saturation is about 5 h and the amounts of liquid absorbed are much lower.

Data for oil absorption (Q_{crude}) by NWPET, uncoated and coated with ODA and ODA/AA, are illustrated in Fig. 8. As for toluene, there is much higher absorption by the copolymer obtained by suspension polymerization (Figs 8(a), 8(b)) than by the copolymer obtained by bulk polymerization (8(c)).

The increase of the swelling parameters with decreasing ODA concentration seen in Fig. 8 indicates the formation of dangling chains which increase the swelling and affect the modulus of the network as seen in the DMA data.^{3,4} We find that the oil absorptivity decreases slightly when using 10% crude oil instead of pure toluene. This may be explained through the swelling process of polymer networks which is primarily due to liquid penetration into the polymeric gel through capillary action and diffusion. Therefore, crude oil with a higher viscosity than toluene cannot as easily diffuse from the external surface of the sample into the internal space of the network.¹⁰ We also find that the absorption capacity of toluene and crude oil increases with increasing crosslinking degree onto NWPET. Zhou and Cho²⁶ and Zhou *et al.*³⁶ reported that the highest swelling uptake observed for 4-*tert*-butylstyrene-styrene butadiene rubber divinylbenzene was 57.8 g g⁻¹ polymer after being immersed in oil solution for 48 h. The oil absorptivity of 4-*tert*-butylstyrene-ethylene-propylene-diene-divinylbenzene (PBED) graft terpolymer showed maximum oil absorptivity (84.0 g g⁻¹) for the treated PBED.²⁴ In our previous work^{4,5,7} we achieved some good oil uptakes, ranging from 65 to 95 g oil g⁻¹, for crosslinked polymers based on alkyl acrylate homopolymers and copolymers by variation of the crosslinking techniques through thermal, photo or electron-beam irradiation initiation. In the present work, we succeeded in obtaining an oil sorption capacity of 100 g oil g⁻¹ of polymer in 60 min. This phenomenon may be explained by considering that oil absorption of composites is probably synergized by coating ODA/AA onto PET fibers as supporter. The formation of an elastic and porous network based on ODA/AA involving PET fibers gives a large specific surface area as well as interstitial spaces. This inference is supported by the SEM photographs in Figs 2–4.

The absorbed crude oil can be recovered from the modified NWPET by a simple squeezing operation or by deswelling in ethanol and so the sorbents can be recycled several times for oil spill cleanup, thus providing polymer regeneration. The efficiency of regeneration was calculated as regeneration efficiency = (total absorption capacity in the second run) × 100%/(total absorption capacity in the first run). Regeneration of the prepared grafted copolymers was calculated after five cycles; the results show that the efficiency decreased slightly in nearly all polymers in the second

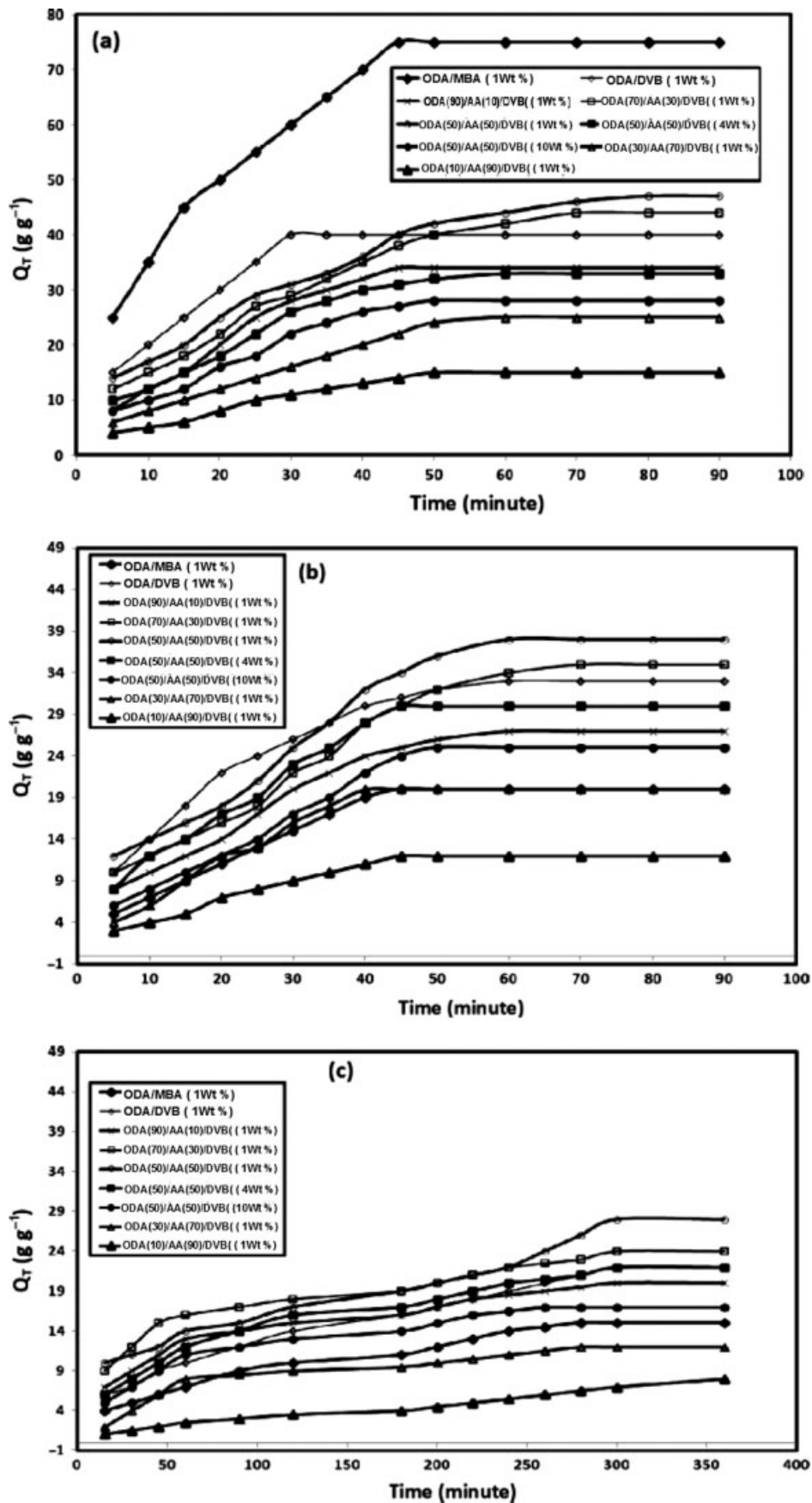


Figure 7. Toluene uptake of the crosslinked ODA/AA/DVB on NWPET fibers (a) in isopropanol, (b) in DOP + MB and (c) by bulk copolymerization.

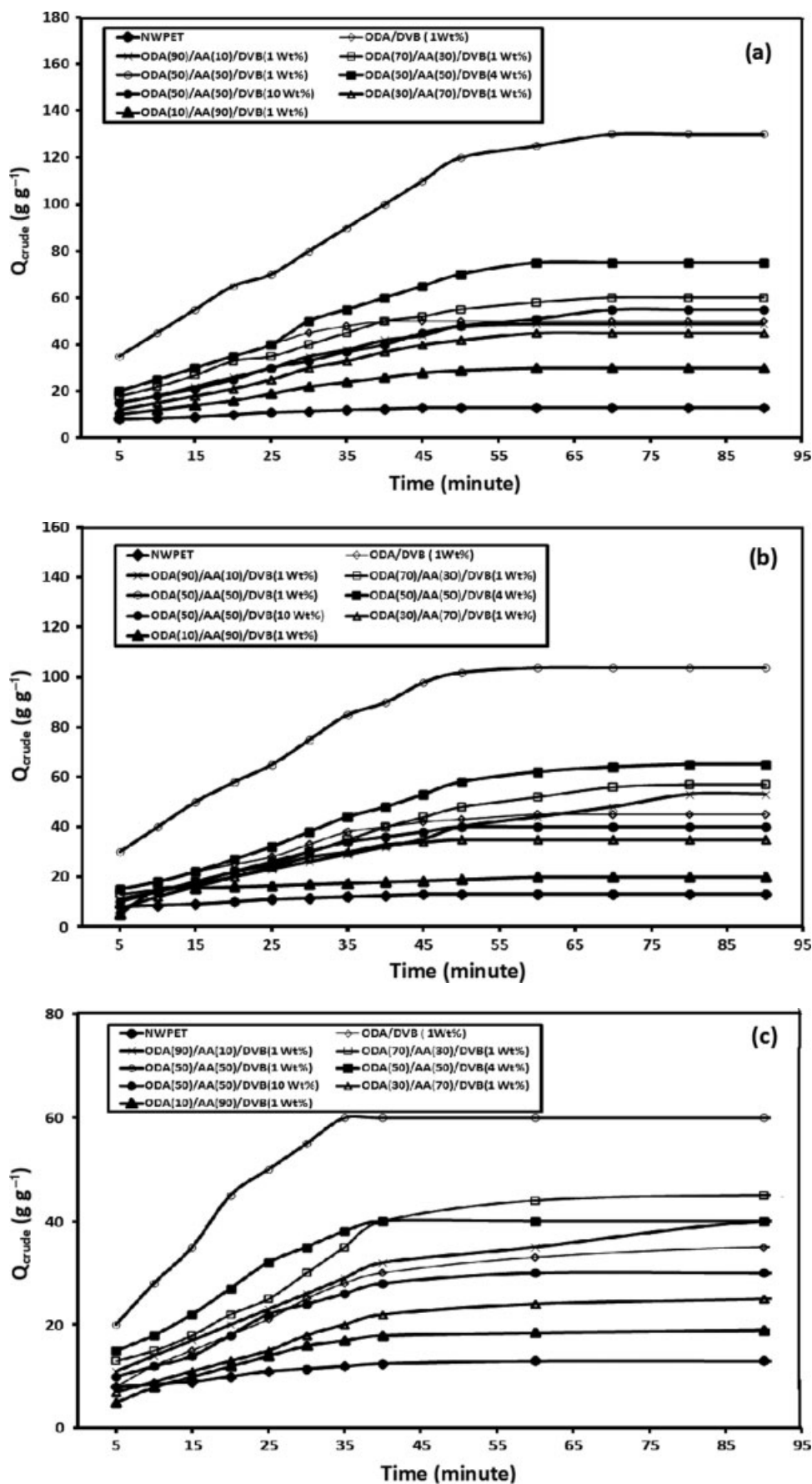


Figure 8. Oil uptake of the crosslinked ODA/AA/DVB on NWPET fibers (a) in isopropanol, (b) in DOP + MB and (c) from bulk copolymerization.

run – but providing a constant value after the second cycle. This reflects the stability of our grafted copolymers.

Other options for creating polymer-based petroleum sorbers could be pursued. For instance, sol–gel derived inorganic nanonetworks can be incorporated into polymers.³⁷ In dealing with multiphase materials it is important to keep in mind that their properties are strongly dependent on the interfaces.^{38–42}

A SURVEY OF RESULTS

The following conclusions can be drawn from the present results.

- The soluble fraction is lower for bulk polymerization or with isopropanol solvent. DOP + MB is the least desirable in the present scenario as it results in the highest SF% values. This holds for ODA homopolymers, ODA/AA copolymers and the ODA/AA-coated NWPET fibers.
- The soluble fraction decreases with increasing ODA content (Tables 3 and 5).
- Crosslinking efficiency is higher in bulk polymerization or with isopropanol, again rendering these methods preferable over the use of a DOP + MB solvent. However, given other drawbacks of bulk polymerization (such as poor morphology), suspension polymerization in isopropanol would stand as the most effective method. In other words, we need a relatively high degree of crosslinking but consistent with sufficiently large surfaces of the pores while the pores should be of comparable size.
- For the neat homopolymers and copolymers, crosslinking efficiency increases with increasing concentration of the crosslinker (whether DVB or MBA). There is not a clear link between ODA concentration and total conversion.
- Comparing crosslinkers, total conversion is generally higher with DVB rather than with MBA.

Therefore, suspension polymerization of ODA and AA in isopropanol with DVB crosslinker is proven to be an efficacious method of preparing oil sorbers on PET fiber supports. The bulk polymerization technique is not worthwhile owing to the lack of porosity necessary for good function as an oil sorber.

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