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Porous polymer oil sorbents based on PET fibers with crosslinked copolymer coatings†

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Oil sorbents—namely materials that can be used to extract oil after a spill—were fabricated from non-woven polyethylene terephthalate (NWPET) fibers modified by the adherence of crosslinked polymer coatings to the fiber surface. The NWPET fibers, which serve as a structural support for the applied functional coatings, were produced from recycled PET (polyethylene terephthalate) bottles. The oil absorbing coatings were comprised of crosslinked homopolymers and copolymers based on octadecyl acrylate (ODA), maleic anhydride (MA), and related esters of MA. The crosslinked polymer networks were synthesized by both suspension and bulk polymerization techniques using divinylbenzene (DVB) as the crosslinking agent. Efficacy of the coated NWPET fibers as oil sorbers was determined by oil absorption tests in toluene and in 10% crude oil in toluene. Rigidity, porosity and swelling of the crosslinked polymers were evaluated and correlated to the chemical structures, composition, and reaction media. Suspension polymerization yielded the desired morphology and function, providing higher porosity and in consequence a high absorption capacity.

1. Introduction

The recent Gulf of Mexico oil-spill reminds us again of the importance of oil spill cleanup and environmental remediation.[1] The typical methods of dealing with oil spills are mechanical extraction, in situ burning, and bioremediation.[2] One of the most economical and efficient methods for oil spill cleanup is mechanical extraction by sorbents.[3] Continuous sorbent belts constructed of polymers hold great promise since oil is removed from the water surface by the oleophilic material from which the belt is made. Oil sorbents are able to concentrate and transform liquid oil to the semi-solid or solid phase, which can then be removed from the spilled area in a convenient manner.[4] Such sorbents are typically made of polymers, while polymers also have other applications in the petroleum industry.[5–8] We have tested the capability to absorb petroleum as well as toluene; toluene has the advantage of being a good solvent for asphaltenes which are contained in crude oil.[9] These facts are the starting point for the present work, plus the finding of Kim and coworkers[10] that non-woven polyethylene terephthalate (NWPET) based sorbents might be useful for oil-spill recovery in marine environments, but only after modification with hydrophobic polymers. Furthermore, the sustainability of our approach is increased by our use of recycled PET.

Polymers based on crosslinked or grafted hydrophobic polymers like alkyl acrylates, rubber, and alkyl styrene have proved useful in the absorption of oil or oil-like solvents. Porous gels based on these materials have been intensively researched to evaluate the influence of the synthesis conditions on the structural characteristics and oil absorbency.[11–13] However, these gels alone lack the mechanical strength and structural integrity needed for the intended application. Similarly, emulsion templating offers an alternative route for preparation of functional porous polymers; however the materials produced by this method are not necessarily ideal for operation in the intended environmental conditions.[14] To overcome the disadvantageous mechanical properties of swollen polymeric gels, Ceylan and Okay designed tough macroporous gels based on butyl rubber.[15] We sought to achieve a similar effect by designing a composite material, thereby drawing on the strengths and minimizing the weaknesses of two materials to obtain the desired properties in the final product. Polyester terephthalate (PET) fibers offer suitable mechanical and thermal properties for application as oil sorbers, but their use is

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restricted by low hygroscopicity and undesirable oil swelling capacities. To modify properties of PET in these disadvantageous points, radiation-induced grafting of acrylic acid has been carried out with satisfactory results.[16] Modification of PET is not limited, though, to only radiation induced grafting. More generally, application of any type of monomer or polymer as a coating onto PET fibers depends on diffusion of the monomer or polymer solutions into the fibers.[16,17] Additionally, there are other challenges associated with modifying the surface of PET; these are well described by Chen and McCarthy.[18]

The oil sorption capacities of the sorbents typically used to coat NWPET are generally only ten grams of oil per gram of sorbent, while water is also absorbed. Given the extent of oil associated with spills and the importance of timeliness in cleaning up oil spills, it is clearly desirable to enhance the absorption capacity of the synthetic sorbents applied to NWPET substrates. Ono and coauthors report superabsorbent copolymers with not only improved mechanical properties and but also increased absorbency of non-polar compounds; however their materials did not absorb toluene to a significant degree.[19] Our aim was to design a novel oil sorbent at low cost, tailoring it to efficiently absorb oil in preference to water. We therefore selected NWPET fibers that were produced from recycled PET bottles as the substrate for our oil sorbers. These were coated with octadecyl acrylate maleic anhydride copolymers via suspension and bulk polymerization techniques. The sorption capacity and oil/water selectivity of the modified NWPET sorbents were evaluated through a variety of tests. Scanning electron microscopy was used to characterize the copolymer structures and help elucidate the oil sorption mechanisms.

2. Materials

Octadecyl acrylate (ODA), 2,2-azobis isobutyronitrile (ABIN), were obtained from Aldrich Chem. Co. (Germany) and used without purification. Maleic anhydride (MA), *n*-octanol, *n*-dodecyl alcohol (*i.e.* dodecanol), cyclohexane, polyvinyl alcohol (PVA) having average molecular weight 25000 g mol^{-1}, toluene, *p*-toluene sulfonic acid (pTSA), xylene, and divinylbenzene (DVB) were obtained from Fluka. White polyethylene terephthalate nonwoven fibers, produced from recycled PET bottles, were purchased from Zhejiang Waysun Chemical Fiber co., Ltd. (China). The NWPET is fabricated from PET that has been cut into small pieces, cleaned in a hot water process to remove dirt, then sorted and extruded to polyester fibers.

Table 1 Physicochemical properties of the 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

Petroleum crude oil was obtained from Petrobel Egypt, with the specifications listed in Table 1.

3. Experimental methods

3.1 Synthesis of maleic anhydride esters

Maleic anhydride was esterified using octanol (for synthesis of dioctyl maleate) or dodecanol (for synthesis of dilauryl maleate) in the presence of *p*-toluene sulphonic acid (1% per weight of reactants) and xylene as a solvent (comprising 60 wt% of the reactants. MA (1 mol)) and octanol or dodecanol (2 mol) were mixed together (constituting 40 wt%) in xylene using a three-necked flask fitted with condenser and Dean Sturk apparatus (to separate the water and excess of xylene) and refluxed at 140 °C for 5 hours and then at 170 °C for 30 minutes. The reaction products were evaporated to half and mixed with isopropanol followed by mixing with hot salty water (supersaturated with NaCl) to separate the aqueous and organic layers. The organic layer was evaporated using a vacuum rotary evaporator. The prepared dioctyl maleate (designated DOM) has the following properties: density (0.94 g cm^{-3}), boiling point at 10 mm Hg (235 °C), flash point (closed cup, 160 °C), refractive index (1.45) and freezing point (−40 °C). The prepared dilauryl maleate (designated DLM, synonym didodecyl maleate) has the following properties: density (0.921 g cm^{-3}), flash point (closed cup, 240 °C), and refractive index (1.46). Fig. 1 shows schematically the esterification reaction yielding DOM and DLM monomers. The esterification reactions were carried out in a nitrogen atmosphere to prevent oxidation of the double bonds and conversion to fumarate bonds. The isomerization of maleic
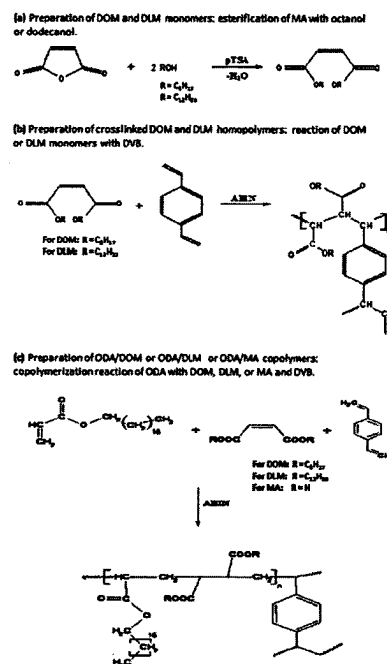

Fig. 1 Copolymerization reaction schemes. (a) Preparation of monomers, (b) preparation of homopolymers and (c) preparation of copolymers.

Table 2 Soluble fraction percentages for crosslinked ODA, DOM, and DLM homopolymers and for ODA/MA, ODA/DOM, and ODA/DLM copolymers as a function of DVB crosslinker concentration

Polymers	DVB/wt%	SF/%	
		Cyclohexane	Bulk
ODA	1	12[a]	8
	4	9[a]	6
DOM	1	16	14
	4	14	10
DLM	1	13	10
	4	11	8
ODA/MA	1	14	12
	4	11	8
ODA/DOM	1	21	19
	4	18	15
ODA/DLM	1	17	14
	4	14	11

[a] Polymerization completed in isopropanol rather than cyclohexane solvent.

anhydride to the fumarate was not obtained in the present reaction, while it has long been known that the isomerization of maleic anhydride to fumarate in polycondensation reactions depends on the temperature and the glycol chemical structures.[20] On the other hand, the isomerization to the fumarate can be carried out at high temperature in the presence of catalysts such as mineral acid or thiourea and under applied pressure, which further prevents the esterification reaction.[21]

3.2 Synthesis of crosslinked homopolymers and copolymers

Three series of crosslinked homopolymers and copolymers based on MA, ODA, DOM and DLM were prepared using DVB as crosslinker either in the presence of cyclohexane as solvent (suspension technique) or in absence of a solvent (bulk technique). Rod-shaped specimens of crosslinked homopolymers and copolymers were prepared.

The suspension homopolymerization and copolymerization of the monomers of MA, ODA, DOM and DLM were carried out in a 250 ml three-necked flask fitted with a thermometer, nitrogen gas, and reflux condenser. The monomers were mixed with 0.02 wt% of ABIN initiator, 1 wt% of PVA (170 ml for each 100 g of monomers), and different weight ratios of DVB crosslinker (1% or 4%) in isopropanol or cyclohexane solvents. Copolymerization reactions were all performed at a monomer mole ratio of 50/50; the different homopolymers and copolymers prepared are identified in the first column of Table 2. The polymerization reactions were performed at 60 °C for 3 hours. After the reaction was completed, the resulting precipitate was washed with methanol and dried in a vacuum oven at 40 °C until a constant weight was reached.

By the bulk technique, crosslinked homopolymers and copolymers were prepared in the same fashion as by suspension but without the PVA or solvent (cyclohexane or isopropanol). The amount of DVB crosslinker used varied between 1 and 10 wt%.

The synthesis reaction for DOM and DLM homopolymers is shown schematically in Fig. 1b, the copolymerization of DOM and DLM with ODA in Fig. 1c.

3.3 Coating of NWPET fibers

For the coating of crosslinked homopolymers and copolymers onto PET fibers, the NWPET fibers were added in a 3 : 1 weight ratio (fiber : monomers) to the reaction mixtures of the suspension technique as described in the previous sub-section b. The mixtures were bubbled with nitrogen. The copolymerization and crosslinking reactions were performed at 60 °C for 5 hours to ensure complete reaction of all monomers. The polymer-coated PET fiber was washed with methanol and dried at 40 °C until a constant weight was reached. The coated NWPET fibers were then post-cured at 105 °C for 24 hours.

Polymers prepared by bulk polymerization were cast on the PET fibers prior to thermal crosslinking. According to this method, the mixture was bubbled with nitrogen, then cast over rolled PET fibers. The weight ratio between PET fibers and monomers was 3 : 1, respectively. The copolymerization and crosslinking reactions were performed in siliconized test tubes at 60 °C for a total of 9 hours to ensure complete reaction of all monomers. The coated NWPET fibers were then post-cured at 105 °C for 24 hours.

3.4 Characterization of polymers

Infrared (IR) spectra were recorded in KBr pellets using a Bruker FT-IR model IF 566 spectrometer. Scanning electron microscopy (SEM) was used to study the morphology of the crosslinked polymers. Dynamic mechanical analysis (DMA) was carried out on the purified crosslinked copolymers (i.e. after extraction of soluble, uncrosslinked monomers and polymers as described in Section 3.2). The glass transition temperature T_g, melting temperature T_m, and crystallization temperature T_c of the crosslinked copolymers were determined by DMA as well as by differential scanning calorimetry (DSC). Electron microscopy, DMA and DSC methods are described in the ESI.†

3.5 Evaluation of absorption behavior

The Soxhlet extraction technique was used to determine the soluble fraction of the crosslinked polymer coatings. Dried xerogel discs of the polymer rods and coated fibers were transferred into an extraction thimble and extracted with chloroform for 24 h. After extraction, the samples were dried at atmospheric pressure for several hours and then dried to a constant weight in a vacuum oven at 35 °C. The soluble fraction (SF) was expressed as the fractional loss in weight of xerogel. SF values were calculated according to the following equation:

$$SF = ((w_1 - w_2) \times 100\%)/w_1 \tag{1}$$

where w_1 is the dry weight before extraction and w_2 is the dry weight of the sample after extraction. As discussed later, SF is indicative of the crosslinking efficiency of monomers, which is affected by reactivity ratios between monomers. Higher SF

values indicate low reactivity of homopolymers or copolymers with the chemical crosslinker DVB.

Data representing the swelling equilibrium reflect the nature of the polymer + solvent system. Practically, 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 swelling is the result of absorbed solvent, the polymer volume fraction Φ_p of the swollen polymers is:

$$\Phi_p = (\rho_p(W_1 - W_0))/W_0\rho_s \tag{2}$$

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

Oil absorbency of the homopolymers and copolymers crosslinked with DVB and prepared either in solution or by bulk polymerization were determined at 25 °C according to ASTM (F726-81): 0.1 g polymer (as coated onto NWPET) was put in a pure stainless steel mesh (4 × 4 × 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. Oil sorption capacity (Q) in both toluene (Q_T) and crude oil (Q_{crude}) was calculated as follows:

$$Q \ (g \ g^{-1}) = w_{abs}/w_{dry} \tag{3}$$

where 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 content (ECC) were thus calculated as:

$$ETC \ (or \ ECC) = [(w_{abs} - w_{dry})/w_{abs})] \times 100\%. \tag{4}$$

4. Results and discussion

4.1 Physicochemical characterization

It is well known that oil sorbents should exhibit hydrophobicity in order to swell in an oil medium. The primary aim of the work presented here was to synthesize new crosslinked polymers incorporating hydrophobic moieties such as alkyl or phenyl groups. MA (maleic anhydride) contains both hydrophilic and hydrophobic moieties. Consequently, it is important to convert it, by reaction of its anhydride group, into hydrophobic monomers. This was carried out by esterification reactions of MA with octanol or dodecanol (Fig. 1a) to add the alkyl moiety as a hydrophobic group. The prepared esters are not by themselves new materials, but the copolymerization of the esters to form crosslinked polymers that function as oil sorbers is indeed novel. For this purpose, it is necessary to use purified monomers, which was confirmed by measuring the physical properties (and comparing them to tabulated reference data) of the monomers to ensure that the copolymerization could be

completed without interference by impurities. FTIR and ^{1}HNMR were used to confirm the chemical structures of DOM, DLM, MA, and ODA, but for brevity only 3 spectra are shown in figures.

The IR spectrum in Fig. S1† of DLM monomer showed characteristic absorption bands at 3100 cm^{-1} (–CH stretching vibration of the C=C bond), 2859 cm^{-1} (stretching vibration of the aliphatic C–H bond), 1731 cm^{-1} (stretching vibration of C=O), 1460 cm^{-1} (bending vibration of CH$_2$), 1381 cm^{-1} (bending vibration of CH$_3$), 1164 cm^{-1} (stretching vibration of C–O and 950 cm^{-1} (bending vibration of C=C bond). An important feature of the prepared homopolymers and copolymers, based on ODA and MA, is their crosslinking. Crosslinking is responsible for formation of the three-dimensional network structure that is necessary for oil sorbers to swell rather than to dissolve. DVB (divinylbenzene) was used as a chemical crosslinker at 1% and 4% weight ratios. Recall the crosslinking reactions—of homopolymers and copolymers—are represented in Fig. S1b and c.† The IR spectrum of ODA homopolymer, Fig. S1b,† shows characteristic absorption bands at 2926 cm^{-1} (for stretching vibration of the aliphatic C–H bond), 1750 cm^{-1} (assigned for stretching vibration of the C=O ester group of ODA), 1143 cm^{-1} (assigned for stretching of C–O of ester group of ODA). The absence (compared to Fig. S1a†) of vinyl group C=C stretching and bending vibrations at 3100 and 950 cm^{-1}, respectively, suggests complete polymerization and crosslinking of ODA polymers; we recall that DVB concentrations were small. The same absorption bands were detected for all prepared copolymers, which indicated the crosslinking and copolymerization of ODA with DOM or DLM monomer. Similarly, the ^{1}HNMR spectrum (Fig. S2†) of DOM confirmed expectations. The absence of COOH peak at 10–14 ppm of MA indicated the formation of dialkyl maleate esters.

4.2 Structure and composition of crosslinked polymers and coated NWPET fibers

The preparation of composite materials is frequently used to increase strength of a material. Fibers, sponges and non-woven fabrics are sometimes used as reinforcements in composite materials. In the present work, non-woven PET fibers, derived from recycled PET bottles, were used as reinforcement and essentially a support structure for crosslinked ODA, DOM and DLM homopolymers and for crosslinked ODA/MA, ODA/DOM and ODA/DLM copolymers. As described earlier, the monomers were crosslinked onto NWPET fibers at 70 °C by radical bulk and solution suspension crosslinking copolymerization reactions.

A wide variety of vinyl crosslinking agents are used to form crosslinked polymer networks, and the available choices of a crosslinker for bulk and solution polymerization are numerous. Crosslinker concentration is usually about 0.05–1 wt%, and crosslinking can be used to produce superabsorbent polymers with high swelling capacity and low soluble polymer content.

However, many side reactions, such as intrachain cyclization, decrease the efficiency of the crosslinker and result in a later gel point in the polymerization than would be predicted by theory and in networks less crosslinked than would be

predicted from the number of potential crosslink sites. This deviation from theory can be significant at higher crosslinker concentrations, such as those used in styrene DVB copolymers, where intramolecular cyclization is believed to occur. Intramolecular cyclization increases with low monomer content and high crosslinker concentration. Because of the high monomer content and low crosslinker levels used in typical gel processes (such as what we have conducted), there is a reduced probability of this inefficient side reaction occurring, especially during the initial part of the polymerization process.

Furthermore, to understand the distribution of crosslinks in the network, reactivity of the various double bonds in the system should be assessed. This includes—in the present study—the reactions between double bonds of DOM, DLM, MA and ODA, the initial double bonds of the DVB crosslinker, and the various double bonds that are pendant from the polymer chain after incorporation of the crosslinker. Compared with ODA and MA, DOM and DLM monomers are expected to provide a certain level of hydrophobicity that improves oil affinity of the resultant polymer. As the reaction proceeds, the pace of the crosslinking reaction increases very rapidly at some point, and the reaction product begins to form an infinite molecular weight network—this is called the gel point. In the gel state, the chemical reaction can proceed and chains form the network by crosslinking, and the crosslink density or degree of crosslinking is a measure of the total links between chains in a given mass of substance. Typically, after the reaction there remain some polymer chains not attached to the infinite network; these can be extracted from the gel fraction. Thus, in a crosslinked system, there are soluble portions and insoluble portions: the former can be extracted with suitable solvents, whereas the latter cannot be extracted with any solvent owing to the crosslinking. This feature is quantified as the soluble fraction (SF) and contributes to the swelling behavior of the specimen.

Again, the swelling behavior of crosslinked polymer networks is critical to our aim of developing better oil sorbers. According to Flory's swelling theory,[22] swelling behavior is affected by rubber elasticity, affinity to solution and crosslinking density. Thus the soluble fraction and conversion of our polymer gels, prepared with a crosslinker concentration of 1 or 4 wt%, were determined. Note that SF measurements are indicative of the reactivity of the crosslinker towards the monomers. The insoluble material (w_2 in eqn (1)) is considered as the gel fraction, while the soluble materials are calculated as the soluble fraction (SF/%).

The soluble fraction data for crosslinked DOM, DLM, and ODA homopolymers (using the crosslinker DVB) and their copolymers were determined and calculated according to eqn (1); values for the polymers alone are listed in Table 2, for the polymers coated onto NWPET fibers in Table 3. Careful inspection of the data in Tables 2 and 3 shows that with and without the NWPET fibers the SF% was lowest at the high crosslinker concentration. For the plain (unsupported) polymers (Table 2), bulk preparation resulted in a smaller SF (*i.e.* greater extent of crosslinking) than solution preparation (in cyclohexane or isopropanol). However, that effect was not seen

Table 3 Soluble fraction percentages for crosslinked ODA, DOM, and DLM homopolymers and for ODA/MA, ODA/DOM, and ODA/DLM copolymers, all coated onto NWPET fibers, as a function of DVB crosslinker concentration

Polymers, as coatings on NWPET fibers	DVB/wt%	SF/%	
		Cyclohexane	Bulk
ODA	1	24[a]	20
	4	18[a]	16
DOM	1	25	33
	4	17	29
DLM	1	22	30
	4	13	25
ODA/MA	1	15	13
	4	12	10
ODA/DOM	1	35	40
	4	29	33
ODA/DLM	1	25	30
	4	18	22

[a] Polymerization completed in isopropanol rather than cyclohexane solvent.

for the polymers as coatings on NWPET fiber supports. This data and the physicochemical characterization show that it is possible to efficiently prepare crosslinked copolymers from octadecyl acrylate and maleic anhydride by both suspension and bulk polymerization techniques using DVB as the crosslinking agent. The crosslinking efficiency decreases in the order ODA > DLM > DOM > ODA/DLM > ODA/DOM > ODA/MA. Crosslinking is desirable to create a network structure suitable for oil absorption. However, too low or too high crosslinking efficiency limits the absorption. As a consequence of the former, the oil uptake of ODA/MA was quite low. Evaluation of the morphology of these specimens provides more insight.

4.3 Morphology of coated NWPET fibers

ESEM micrographs of the specimens are shown in Fig. 2. (Note that the images were taken of samples after extraction of the soluble fraction.) Crosslinked polymers on NWPET—by the bulk polymerization technique—are seen in Fig. 2b–d. They can be compared to the uncoated NWPET shown in Fig. 2a. The crosslinked polymers appear homogeneous on the surface texture. The surface changes from smooth to channel-like pores with increasing chain lengths of side groups, from MA to DOM to DLM. Fig. 2e–h shows homopolymers and copolymers on NWPET prepared by suspension technique.

On average, the size of NWPET fiber increased from *ca.* 12 μm for uncoated NWPET to *ca.* 20 μm for coated NWPET. Both synthesis methods utilized a similar weight of reactants. Fig. 2 shows that the coating layers obtained by the bulk polymerization technique are less porous than those obtained by suspension polymerization.

The variations in coating morphology and thickness suggest that different formation mechanisms for the skin layers of ODA, DOM, DLM, ODA/MA, ODA/DOM and ODA/DLM polymers onto NWPET fibers may be involved. On the basis of the above results, a fiber skin layer formation mechanism onto NWPET is
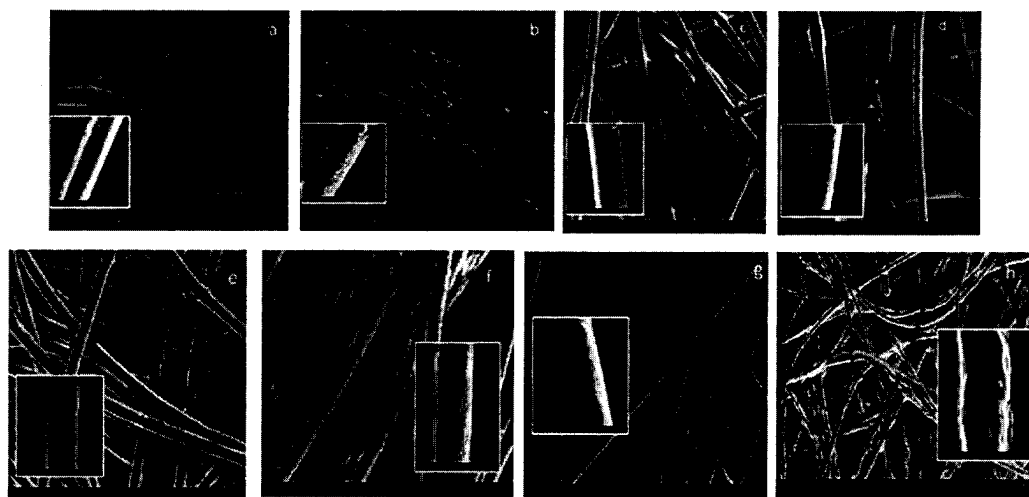
Fig. 2 ESEM micrographs. (a) Untreated NWPET fibers. Crosslinked copolymers on NWPET, prepared by *bulk technique*: (b) ODA/MA (4% DVB); (c) ODA/DOM (1% DVB); and (d) ODA/DLM (1% DVB). Crosslinked homopolymers and copolymers on NWPET, prepared by *suspension technique*: (e) DOM (4% DVB); (f) DLM (4% DVB); (g) DLM (1% DVB); and (h) ODA/DLM (1% DVB).

plausible. It is believed that most of the homopolymer and copolymer particles might have initiated and continued their growth in the solution phase, and only those particles (or the growing polymer chains) at or close to the liquid/solid interfaces had deposited onto the PET fibers *via* chemisorption and/or physical adsorption. The comparison of the results from the two coating systems also indicates that the bulk polymerization formed a dense mat inhibiting the diffusion of monomers around the PET fibers, making it difficult to create porous polymers. The wet suspension polymerization technique was developed to prevent the collapse of the crosslinked homopolymers and copolymers onto the NWPET fiber network. There are indications in the literature that a moist fiber substrate provides a more porous network support and thus greater infiltration of adhesive monomers and polymers.[14,23] When one uses the wet suspension technique, the channels between the NWPET fibers are filled with solvent or monomer fluids. The main mechanism available for coating of PET fibers with homopolymers and copolymers is thus diffusion of the resin into whatever fluid is in the spaces of the substrate as well as along the NWPET fibers. Our results confirm those in[14,23] showing, as already discussed above, higher porosity in materials obtained by suspension polymerization.

4.4 Thermal and mechanical properties

The elasticity and rigidity of the crosslinked polymer networks were determined by measuring the characteristic thermal changes of the polymers. Using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC), we identified the glass transition temperature T_g, which represents the temperature range at which amorphous polymers undergo a transition from a rubbery, viscous amorphous liquid to a brittle, glassy amorphous solid.[24] Both DMA and DSC techniques are well explained by Menard.[25] The T_g may be engineered by altering the degree of branching or crosslinking in the polymer

or by the addition of plasticizer.[26] The storage modulus E' (representing solid-like behavior) and tan delta, obtained by DMA for ODA/MA are shown in Fig. S3.† We see a single transition at 30 °C for ODA/MA (50/50 mol%) crosslinked with 1 wt% DVB. This while ODA/MA (50/50 mol%) crosslinked with 4 wt% DVB shows two transitions, namely at 10 °C and 42 °C. The lower and higher transition temperatures should, respectively, correspond to the T_g and the melting temperature T_m of soft segments. The high crystallinity of ODA/MA with 1 wt% DVB is reflected in a single transition corresponding to melting of soft segments. On the other hand, less perfect crystalline structures of ODA/MA with 4% DVB show both T_g for the amorphous domains and T_m for the crystalline domains. These
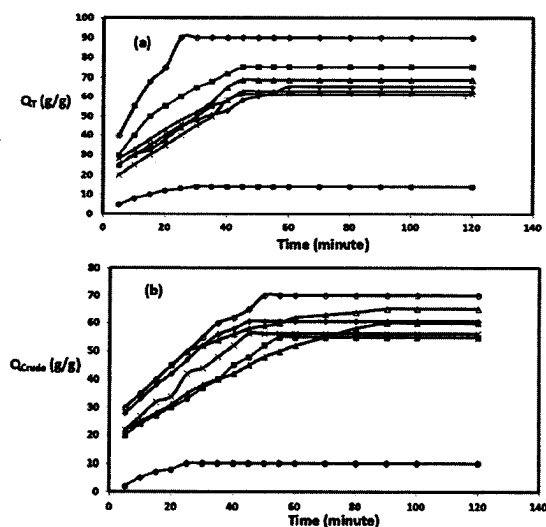

Fig. 3 Swelling uptake at 25 °C of NWPET fibers coated with crosslinked ODA/ MA, ODA/DOM and ODA/DLM copolymers using (a) suspension technique, and (b) bulk technique.

Fig. 4 Swelling uptake at 25 °C of NWPET fibers coated with crosslinked ODA/MA, ODA/DOM and ODA/DLM copolymers using (a) suspension technique, and (b) bulk technique.
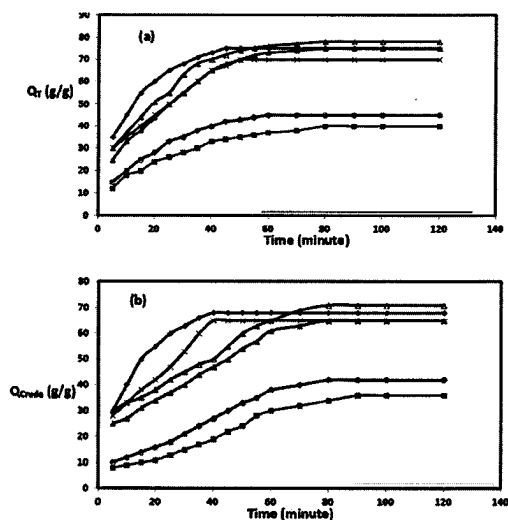
technique has some impact on the transition temperatures. Thus, glass transition temperatures of materials obtained by the bulk process are higher than those obtained by suspension polymerization. At a crosslink, adjacent polymer chains are pulled closer together, and the free volume is decreased, so raising T_g.[31,32] Apparently we have a higher crosslink density per unit volume in the copolymers created in the bulk.

Melting temperatures in Table S1† are also higher for products of bulk polymerization. Since the polymers are crosslinked, we are talking here only about melting of side chains. Overall the DSC data indicate that the crosslinked polymers based on the DVB crosslinker formed elastic amorphous and semicrystalline polymer networks. The apparent rigidity of the crosslinked networks generally increased with increasing DVB content, while less rigidity results in higher liquid uptakes.

4.5 Oil absorbency of coated NWPET

The crude oil used in this experiment (Table 1) was diluted (to 10% oil) with toluene. For real applications in cleaning up oil spills, the oil absorption test has to be operated using not only light or medium oil but also heavy oil, because crude oil has a high viscosity. 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, and as already noted, toluene is the most applicable solvent that is used to dissolve asphaltene of crude oil.[9] For these reasons, we have used crude oil diluted with toluene in this experiment so that the swelling behavior of the samples could be easily evaluated.

Swelling uptake by the homopolymer coatings on NWPET is shown in Fig. 3. Corresponding diagrams for the copolymers coated on NWPET are given in Fig. 4. Immersion times were from 0 to 120 minutes, and the oil and toluene absorbency increased with immersion time up to a maximum. In all cases a maximum absorbency was attained followed by a leveling off with no further absorption occurring with the increased immersion time.

Values of the swelling parameters such as Q_T, ETC, and Φ_p were calculated and are listed in Table 4. Based on their higher

large changes in mechanical properties observed are reversible and cyclically reproducible in 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; the aggregates can reversibly "lock" the original as well as deformed shape on cooling.[27,28]

Differential scanning calorimetry (DSC) provides additional information related to crystallization; both melting and crystallization temperatures (T_m and T_c) are observed. The transition temperatures are listed in Table S1.† The accuracy of ±0.1 °C comes from the equipment used and should not be taken literally. We do not include the DSC diagrams for brevity. Analysis of the glass transition behavior of crosslinked copolymers is typically more complicated than that of uncrosslinked copolymers.[29,30] Single glass transition temperatures are observed, indicating full miscibility. The polymerization

Table 4 Swelling parameters of crosslinked homopolymers and copolymers based on DVB crosslinker in toluene at 25 °C

Polymers	DVB wt%	ETC% Cyclohexane	ETC% Bulk	Q_T g g^{-1} Cyclohexane	Q_T g g^{-1} Bulk	Φ_p Cyclohexane	Φ_p Bulk
ODA	1	98.66^a	94.25	75.1^a	17.4	0.0075^a	0.0286
	4	98.34^a	93.01	60.1^a	14.3	0.011^a	0.0699
DOM	1	95.56	93.51	22.5	15.4	0.0350	0.0650
	4	94.62	92.42	18.6	13.2	0.0412	0.0758
DLM	1	96.17	95.53	26.1	22.4	0.0214	0.0451
	4	95.43	95.07	21.9	20.3	0.0297	0.0490
ODA/MA	1	94.22	93.55	17.3	15.5	0.0462	0.0657
	4	93.06	92.38	14.4	13.12	0.0582	0.0721
ODA/DOM	1	96.35	96.05	27.4	25.3	0.0182	0.0395
	4	95.82	95.48	23.9	22.1	0.0220	0.0452
ODA/DLM	1	97.01	96.91	34.5	32.3	0.0130	0.0310
	4	96.75	96.44	30.8	28.1	0.0156	0.0356

^{a} Polymerization completed in isopropanol rather than cyclohexane solvent.

equilibrium toluene contents, higher toluene sorption capacities, and lower polymer volume fractions, the materials prepared by solution polymerization (in cyclohexane or isopropanol) exhibit higher toluene uptake than their counterparts prepared by bulk polymerization. The low absorption capacity of the bulk polymerized specimens was attributed to their higher extent of crosslinking, a feature discussed earlier in relation to the soluble fraction data. While some crosslinking is needed, a very large extent of crosslinking limits the diffusion of solvent into the material and lowers its absorption capacity. Along with this, the higher porosity of specimens prepared in suspension contributes to their good swelling behavior.

We also see from these results that greater hydrophobicity of DLM and ODA/DLM increases absorption capacity. Additionally, Fig. 4 shows that of the copolymers, ODA/MA displayed the least absorption by far compared to ODA/DLM and ODA/DOM, while oil and toluene uptake of the latter two were similar to one another. These results agree with the findings of others who have looked at swelling in crosslinked copolymers systems containing maleic anhydride.[33]

5. Conclusions

Fig. 3 and 4 indicate also that the prepared polymers on NWPET fibers absorb a large quantity of toluene—from 35 to 90 g of toluene per g of polymer—in the time range from 30 to 90 minutes. Absorbency is slightly less for the 10% crude oil solution compared with pure toluene. Since the swelling process of polymer networks relies primarily on penetration into the polymeric gel through capillary action and diffusion, the crude oil with higher viscosity likely cannot diffuse as easily from the external surface of the sample into the internal space of the network.[34]

We also find that the absorption capacity of toluene and crude oil decreases with increasing the crosslinking degree onto NWPET. Zhou and Cho[35] and Zhou and Ha[36] reported the highest swelling uptake observed for 4-*tert*-butylstyrene-styrene butadiene rubber (SBR) divinylbenzene as 57.8 g g^{-1} polymer after being immersed in oil solution for 48 h. The oil absorbency of 4-*tert*-butylstyreneethylene–propylene–diene–divinylbenzene (PBED) graft terpolymer is the highest namely 84.0 g g^{-1} for the treated PBED.[32] In our previous works,[12,37-39] we achieved good oil uptakes, ranging from 65 up to 95 g oil per g, for crosslinked polymers based on crosslinking of alkyl acrylate homo- and copolymers by variation of the crosslinking techniques through thermal, photo and e-beam irradiation initiation techniques. In the present work we succeeded in obtaining oil sorption capacity of 90.2 g oil per g of polymer in 60 minutes. This phenomenon may be explained by considering that oil absorption by composites is probably synergized by the polymer coatings and the NWPET supporter. The formation of elastic and porous network based on ODA and MA apparently provides large specific surface areas as well as large interstitial spaces.

Furthermore, the absorbed crude oil can be recovered from the modified NWPET by a simple squeezing operation or by deswelling in ethanol. Thus, the sorbents can be recycled several times for oil spill cleanup. The efficiency of such regeneration

can be calculated as follows: regeneration efficiency = (total absorption capacity in the nth run) × 100%/(total absorption capacity in the first run). Regeneration of the prepared copolymers was calculated over 7 cycles; the data of regeneration show that the efficiency decreases slightly and in nearly all polymers reaches a constant value after the second cycle. The prepared polymers are glassy in the dry state and rubbery in the swollen state. The copolymers adhered onto PET fibers both before and after swelling as seen in SEM micrographs. This in conjunction with repeated swelling and deswelling without effect on the absorption rate suggests good stability of the formed copolymers.

Acknowledgements

References

1 J. L. Schnoor, The gulf oil spill, *Environ. Sci. Technol.*, 2010, **44**, 4833.

2 J. Whitfield, How to clean a beach, *Nature*, 2003, **422**, 464–466.

3 M. Radetic, V. Ilic, D. Radojevic, R. Miladinovic, D. Jocic and P. Jovancic, Efficiency of recycled wool-based nonwoven material for the removal of oils from water, *Chemosphere*, 2008, **70**, 525–530.

4 C. Teas, S. Kalligeros, F. Zanikos, S. Stournas, E. Lois and G. Anastopoulos, Investigation of the effectiveness of absorbent materials in oil spills clean up, *Desalination*, 2001, **140**, 259–264.

5 L. Vieira, M. Buchuid and E. F. Lucas, The influence of pressure and dissolved gases in petroleum on the efficiency, *Chem. Chem. Technol.*, 2008, **2**, 211.

6 I. da Silva, E. F. Lucas and F. de Franca, Study of Conditions for Polyacrylamide Use in Petroleum Reservoirs: Physical Flow Simulation in Porous Media, *Chem. Chem. Technol.*, 2010, **4**, 73–80.

7 M. de Melo and E. F. Lucas, Characterization and selection of polymers for future research on enhanced oil recovery, *Chem. Chem. Technol*, 2008, **2**, 295.

8 E. F. Lucas, C. R. E. Mansur, L. Spinelli and Y. G. C. Queirós, Polymer science applied to petroleum production, *Int. J. Pure Appl. Chem.*, 2009, **81**, 473.

9 A. Middea, M. B. de Mello Monte and E. F. Lucas, The influence of the solvent medium on the aggregation of asphaltene molecules and determination of their molar mass, *Chem. Chem. Technol.*, 2008, **2**, 91.

10 S.-H. Kim, I.-D. Chung, C.-S. Ha, K.-J. Kim and W.-J. Cho, Preparations and oil absorptivities of poly(stearyl methacrylate-co-cinnamoyloxyethyl methacrylate) and PET nonwoven fiber photocrosslinked with it, *J. Appl. Polym. Sci.*, 1999, **73**, 2349–2357.

11 A. M. Atta, R. A. M. El-Ghazawy, R. K. Farag and A.-A. A. Abdel-Azim, Crosslinked reactive macromonomers based on polyisobutylene and octadecyl acrylate copolymers as crude oil sorbers, *React. Funct. Polym.*, 2006, **66**, 931–943.

12 A.-A. A. Abdel-Azim, A. M. Abdul-Raheim, A. M. Atta, W. Brostow and T. Datashvili, Swelling and network parameters of crosslinked porous octadecyl acrylate copolymers as oil spill sorbers, *e-Polym.*, 2009, **134**, 1.

13 A. M. Atta and K. F. Arndt, Swelling and network parameters of high oil-absorptive network based on 1-octene and isodecyl acrylate copolymers, *J. Appl. Polym. Sci.*, 2005, **97**, 80–91.

14 S. D. Kimmins and N. R. Cameron, Functional Porous Polymers by Emulsion Templating: Recent Advances, *Adv. Funct. Mater.*, 2011, **21**, 211–225.

15 D. Ceylan and O. Okay, Macroporous Polyisobutylene Gels: A Novel Tough Organogel with Superfast Responsivity, *Macromolecules*, 2007, **40**, 8742–8749.

16 K. Kaji, Radiation-induced grafting of acrylic acid onto polyester fiber, *Ind. Eng. Chem. Prod. Res. Dev.*, 1985, **24**(1), 95–102.

17 B. Kim, V. Koncar, E. Devaux, C. Dufour and P. Viallier, Electrical and morphological properties of PP and PET conductive polymer fibers, *Synth. Met.*, 2004, **146**, 167–174.

18 W. Chen and T. J. McCarthy, Chemical Surface Modification of Poly(ethylene terephthalate), *Macromolecules*, 1998, **31**, 3648–3655.

19 T. Ono, T. Sugimoto, S. Shinkai and K. Sada, Molecular Design of Superabsorbent Polymers for Organic Solvents by Crosslinked Lipophilic Polyelectrolytes, *Adv. Funct. Mater.*, 2008, **18**, 3936–3940.

20 I. Vancsó Szmercsányi, L. K. Maros and A. A. Zahran, Investigations of the kinetics of maleate–fumarate isomerization during the polyesterification of maleic anhydride with different glycols, *J. Appl. Polym. Sci.*, 1966, **10**(4), 513–522.

21 S. Majumder and A. B. Pandit, Study of Catalytic Isomerisation of Malic Acid: Effect of Ultrasound, *Indian Chem. Eng.*, 1998, **40**(2), 187.

22 P. J. Flory, *Principles of Polymer Chemistry*, Cornell University, Ithaca, NY, 1953.

23 C.-C. Han, J.-T. Lee, R.-W. Yang and C.-H. Han, Formation Mechanism of Micrometer-Sized Carbon Tubes, *Chem. Mater.*, 2001, **13**, 2656–2665.

24 I. M. Kalogeras and H. E. Hagg Lobland, The nature of the glassy state: structure and transitions, *J. Mater. Educ.*, 2012, **34**, 69.

25 K. P. Menard, Thermal transitions and their measurement, in *Performance of Plastics*, ed. W. Brostow, Hanser, Munich, Cincinnati, 2000, ch. 8.

26 *Polymer Handbook*, ed. J. Brandrup, E. H. Immergut and E. A. Grulke, Wiley-Interscience, New York, 4th edn, 1999.

27 M. Atsushi, S. Junichi, Y. Hidekazu and O. Yoshihito, Order-Disorder Transition of a Hydrogel Containing an n-Alkyl Acrylate, *Macromolecules*, 1994, **27**, 7695.

28 U. Makoto, K. Miyuki and O. Yoshihito, Swelling Process and Order-Disorder Transition of Hydrogel Containing Hydrophobic Ionizable Groups, *Macromolecules*, 1995, **28**, 4583–4586.

29 J. Jang and B.-S. Kim, Studies of crosslinked styrene–alkyl acrylate copolymers for oil absorbency application. I. Synthesis and characterization, *J. Appl. Polym. Sci.*, 2000, **77**, 903–913.

30 M. Weber and R. Stadler, Hydrophilic-hydrophobic two-component polymer networks: 2. Synthesis and characterization of poly(ethylene oxide)-linked-polybutadiene, *Polymer*, 1988, **29**, 1071.

31 B. Hartmann, Acoustic Properties, in *Performance of Plastics*, ed. W. Brostow, Hanser, Munich, Cincinnati, 2000, ch. 9.

32 V. A. Bershtein and V. M. Egorov, *Differential Scanning Calorimetry of Polymers: Physics, Chemistry, Analysis, Technology*, Ellis Horwood, London, 1994.

33 Q. Luo, M. Liu, Y. Xu, M. Ionescu and Z. S. Petrović, Thermosetting Allyl Resins Derived from Soybean Oil, *Macromolecules*, 2011, **44**, 7149–7157.

34 J. Jang and B.-S. Kim, Studies of crosslinked styrene–alkyl acrylate copolymers for oil absorbency application. II. Effects of polymerization conditions on oil absorbency, *J. Appl. Polym. Sci.*, 2000, **77**, 914.

35 M. H. Zhou and W. J. Cho, Synthesis and properties of high oil-absorbent 4-tert-butylstyrene-EPDM-divinylbenzene graft terpolymer, *J. Appl. Polym. Sci.*, 2002, **85**, 2119.

36 M. H. Zhou, C. S. Ha, T. Hoang, I. G. Kim and W. J. Cho, Synthesis and properties of natural rubber modified with stearyl methacrylate and divinylbenzene by graft polymerization, *J. Appl. Polym. Sci.*, 2001, **79**, 2464.

37 A. M. Atta, S. H. El-Hamouly, A. M. Alsabagh and M. M. Gabr, Crosslinked poly(octadecene-alt-maleic anhydride) copolymers as crude oil sorbers, *J. Appl. Polym. Sci.*, 2007, **105**, 2113–2120.

38 A. M. Atta, S. H. El-Hamouly, A. M. Al Sabagh and M. M. Gabr, Crosslinking of reactive α-olefins and maleic anhydride copolymers as oil sorbers, *J. Appl. Polym. Sci.*, 2007, **104**, 871–881.

39 A. M. Atta, R. A. M. El-Ghazawy, R. K. Farag, A. F. El-Kafrawy and A.-A. A. Abdel-Azim, Crosslinked cinnamoyloxyethyl methacrylate and isooctyl acrylate copolymers as oil sorbers, *Polym. Int.*, 2005, **54**, 1088–1096.