

# Porous polyurethane foams based on recycled poly(ethylene terephthalate) for oil sorption

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## Abstract

In using recycled poly(ethylene terephthalate) (PET) as a petroleum sorbent we tried to achieve two important objectives simultaneously. PET waste was glycolized using trimethylolpropane (TMP) or pentaerythritol (PER) to produce suitable polyol oligomers for polyurethane (PU) foams. The glycolysis was carried out in the presence of manganese acetate as a catalyst under normal pressure in *m*-cresol at 220 °C. Producing polyols, PER degraded PET into lower molecular weights than TMP. So prepared oligomers were reacted with 2,4-toluene diisocyanate providing several types of PU foam. The effect of various variables (polyol reactivity, water content, type of catalyst, isocyanate amount and surfactant) on the foam structure and properties were analyzed. Porosity of the PU foams was examined using environmental scanning electron microscopy. Foams based on glycolized TMP contain small uniform cells whereas other foams form less uniform cells with varying sizes including closed cells. Dynamic mechanical analysis gives much lower storage moduli for TMP-based PUs than for those based on PER, an effect of dangling ethylene chains in the former case. The glass transition temperatures  $T_g$  are higher when PER rather than TMP is used. Our PU foams show good sorption properties and sufficient reusability.

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**Keywords:** petroleum absorption; polyurethane foams; polymer swelling; dynamic mechanical analysis

## INTRODUCTION

Despite efforts to create electric cars, cars running on gasoline are with us and will remain so in the foreseeable future. The current batteries with their weight and efficiency will not provide us with electric airplanes any time soon. While gasoline is obtained from petroleum, petroleum has another application of comparable or perhaps greater importance: as a raw material for synthesis of polymers. With a population of the globe that has exceeded 7 billion and keeps growing, the demand for petroleum will continue to increase – and along with it the danger of oil spills.<sup>1–3</sup>

We read about oil spills around Usinsk, Russia:<sup>3</sup> 'Oil spills in Russia are less dramatic than disasters in the Gulf of Mexico or the North Sea, more the result of a drip-drip of leaked crude than a sudden explosion. But they're more numerous than in any other oil-producing nation including insurgency-hit Nigeria, and combined they spill far more than anywhere else in the world, scientists say.' The Economic Development Ministry of Russia in a 2010 report estimated spills in that country as up to 20 million tons per year.<sup>3</sup> Clearly materials that can absorb spilled oil have a large potential worldwide. Pertinent in this context are reports on the interaction of liquid propane,<sup>4</sup> longer alkanes<sup>5–7</sup> and/or crude oil<sup>8</sup> with polymers.

Another environmental problem – in principle less toxic but much more prevalent – is waste of polymer-based materials after service. City dumps are growing in size but so is the waste accumulated in them. In contrast to metals that degrade fairly rapidly, polymer degradation is slow – hence recycling is important.<sup>9,10</sup> Among polymers manufactured in large quantities fairly prominent is poly(ethylene terephthalate) (PET).<sup>11</sup> Millions of

2 L soft drink bottles sold in the USA are made of PET, and of course not only with this specific size and not only bottles. The situation in Egypt is not much different, with the population of the city of Cairo not far from 10 million and the population of the country estimated at 79 million. One assumes that PET does not create a direct hazard to the environment but, due to its substantial fraction by volume in the waste stream and its high resistance to atmospheric and biological agents, it is seen as a noxious material.<sup>12</sup> Therefore, recycling of PET does not only provide a partial solution to the solid waste problem but also contributes to the conservation of raw petrochemical products and energy. Among the different recycling techniques, the only one acceptable according to the principles of sustainable development is chemical recycling, since it leads to the formation of the raw materials from which the polymer is made, as well as of other secondary value-added

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products.<sup>13</sup> A successful recycling program not only depends on post-consumer waste collection, but also on whether the products made out of collected, reclaimed and recycled material respond to consumer needs – in other words if recycled products are actually bought. Recently, a growing interest has been observed in the use of PET wastes for the production of specialized products such as unsaturated polyesters, epoxies, polyurethane foams and polymer concrete.<sup>9,10,12–22</sup>

In this situation we have decided to deal with the two problems outlined above together: to develop new petroleum spill sorbers from polymers including recycled PET. One candidate class of polymers is polyurethanes (PUs) which have a variety of chemical structures<sup>23–28</sup> – which provides us with maneuverability of properties. However, Sefton and Mann studied benzene absorption in PU foams.<sup>29</sup> They concluded that mass transfer was surprisingly slow, even when porosity is quite high. Diffusion in pores and matrix determines the rate of absorption in both open and closed cell foams, while bulk flow is less important. Thus, when going from PET to a petroleum-absorbing PU, we had to go through a different route. The results are reported below.

## EXPERIMENTAL

### Materials

The PET utilized was collected from beverage bottles, which were cut into pieces with approximately 5 mm<sup>2</sup> surface area. Each sample was then washed with acetone and dried at 100 °C for 8 h. Pentaerythritol (C(CH<sub>2</sub>OH)<sub>4</sub>, PEr), trimethylolpropane (CH<sub>3</sub>CH<sub>2</sub>C(CH<sub>2</sub>OH)<sub>3</sub>, Tmp), *m*-cresol, ethylene glycol (HO–CH<sub>2</sub>CH<sub>2</sub>–OH) and butylhydroxytin oxide (Bu(OH)SnO) were from Aldrich Chemical Co (Munich, Germany). A silicone surfactant polysiloxane–polyalkylene block copolymer (viscosity at 25 °C 1350 mPa s, density 1.02 g cm<sup>−3</sup>) was from Degussa. Stannous octoate (density 1.25 g cm<sup>−3</sup>, viscosity 270–430 mPa s, tin content 28.0%–29.3%) was also from Aldrich. Amine catalyst (33% triethylenediamine in dipropylene glycol) was from Degussa. 2,4-Tolylene diisocyanate (2,4-diisocyanatotoluene, TDI), dibutyl tin dilaurate, triethyl amine and toluene were from Aldrich. Manganese acetate, methylene chloride and poly(ethylene glycol) (PEG) with average molecular weight *ca* 600 were supplied by Adweic Chem. Co., Egypt. Methylene chloride used as a physical expansion agent was from Dow Chemical; demineralized water was used as a blowing agent.

Asphaltenic marine Belayium (Petrobel Co., Egypt) crude oil was used for oil sorption measurement; its characteristics are listed in Table 1.

Test	Method	Value
Specific gravity at 60 °F	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

### Techniques

#### Preparation of GPEr and GTMp

The reaction of PET with PEr or Tmp was discussed in a previous article.<sup>14</sup> Depolymerization of PET (1 mol) was performed with PEr (1.1 mol) using a conventional four-neck glass reactor, equipped with stirrer, thermometer, nitrogen inlet and reflux system, using *m*-cresol as a solvent (total weight concentration of the reactants in *m*-cresol was 85%). The reaction mixture was kept at 170–190 °C for 4 h and at 200–220 °C for 3 h. Then the reaction temperature was lowered to 100 °C for 1 h and finally the mixture was allowed to cool at room temperature. Purification was performed through extraction of depolymerized oligomers by hot water. After completion of the glycolysis, the product was cooled to room temperature, dissolved in a suitable quantity of methylene chloride and shaken vigorously with an equal volume of 5% aqueous sodium chloride solution to remove any unreacted PEr and residual catalyst. The organic layer was collected and washed several times with water. The glycolized PET products with PEr are designated GPEr-1, GPEr-2 and GPEr-3 for PEr/PET molar ratios 1.1, 2.0 and 3.0, respectively.

The same procedure of glycolysis and purification was repeated with different molar ratios of Tmp/PET and designated GTMp-1, GTMp-2 and GTMp-3 for Tmp/PET molar ratios 1.1, 2.0 and 3.0, respectively. The GPEr and GTMp oligomers were characterized by acid value and hydroxyl value determinations.

#### Preparation of PU foam

All oligomers were used as the polyol ingredients of foam formulation. They were mixed with PEG as a soft segment of the PU structure, TDI, dibutyl tin dilaurate and triethyl amine as catalysts, methylene chloride as a fire retardant and silicone surfactant as a cell stabilizer. The foams were produced in batches at room temperature according to the procedure outlined in Table 2. The route for making foams was as follows: (i) mechanical stirring of the GPEr or GTMp with water, silicone, catalyst and stannous octoate at 850 rpm for 1 min; (ii) addition of toluene diisocyanate and methylene chloride to the polyol mixture; (iii) stirring for 5 s and immediate casting into a 27 × 17.5 × 17.5 cm<sup>3</sup> mold in which the material expanded. The mixing had to cease before cream time (discussed below). Then the skin layer of each foam was removed and the foam was treated with chloroform for 24 h and with 5 wt% potassium hydroxide aqueous solution to remove unreacted material and to increase the oil uptake.

**Table 2.** Making PU based on a GTMp/TDI ratio of 1.1

Ingredient	Weight parts	Remarks
Glycolized PET	10	
Silicone oil	0.24	Cell-disrupting agent
Polyethylene glycol (molecular weight <i>ca</i> 600)	4	
Demineralized water	0.2	
PMEA, <i>N,N,N,N,N</i> ,9-pentane methyl ethylene triamine	0.3	Blowing catalyst
Dibutyl tin dilaurate	0.24	
DABCO-33LV, 33% triethylene diamine in dipropylene glycol	0.1	Gelation catalyst
PMDI, polymeric 4,4*-diphenylmethane diisocyanate	14	

### Characterization

The hydroxyl value of the oligomers was determined by a conventional acetic anhydride + pyridine method.<sup>20</sup>

The number-average molecular weights  $M_n$  of GPEr and GTMP oligomers were calculated according to end-group analysis by determination of the acid numbers ( $A$ ) and hydroxyl values ( $B$ ) (mg KOH (g sample)<sup>-1</sup>). With  $n$  as the number of hydroxyl groups per molecule, we have<sup>30</sup>

$$M_n = 56.1n \times 1000 / (A + B) \quad (1)$$

The molecular weight of the graft was measured by gel permeation chromatography (GPC) or SEC (Waters model 510) using tetrahydrofuran (HPLC grade) as eluent and Ultrastaygel 500, 1000, 10 000 and 100 000 Å as the columns. GPC measurements were completed using polystyrene molecular weight standards. Viscosity was determined using a rheo-test apparatus model LTV from Brookfield.

Dynamic mechanical analysis (DMA) of purified PU foam specimens with rectangular shape and dimensions of 5 × 5 × 10 mm was carried out using a Perkin Elmer model DMA 8000 from -30 °C to +100 °C at a heating rate of 5 °C min<sup>-1</sup>, 1.0 Hz sinusoidal frequency with the measuring system in the compression configuration.

The cell structure of our foams was observed by environmental scanning electron microscopy (ESEM) (GSM-5900L, Electronic Corp., Japan).

### Oil absorption measurements

The soluble fraction (SF) was determined after soaking PU foam in chloroform for 24 h followed by rinsing in 5 wt% aqueous KOH solution for 24 h. SF was calculated as

$$SF/\% = (w_1 - w_2) / w_1 \quad (2)$$

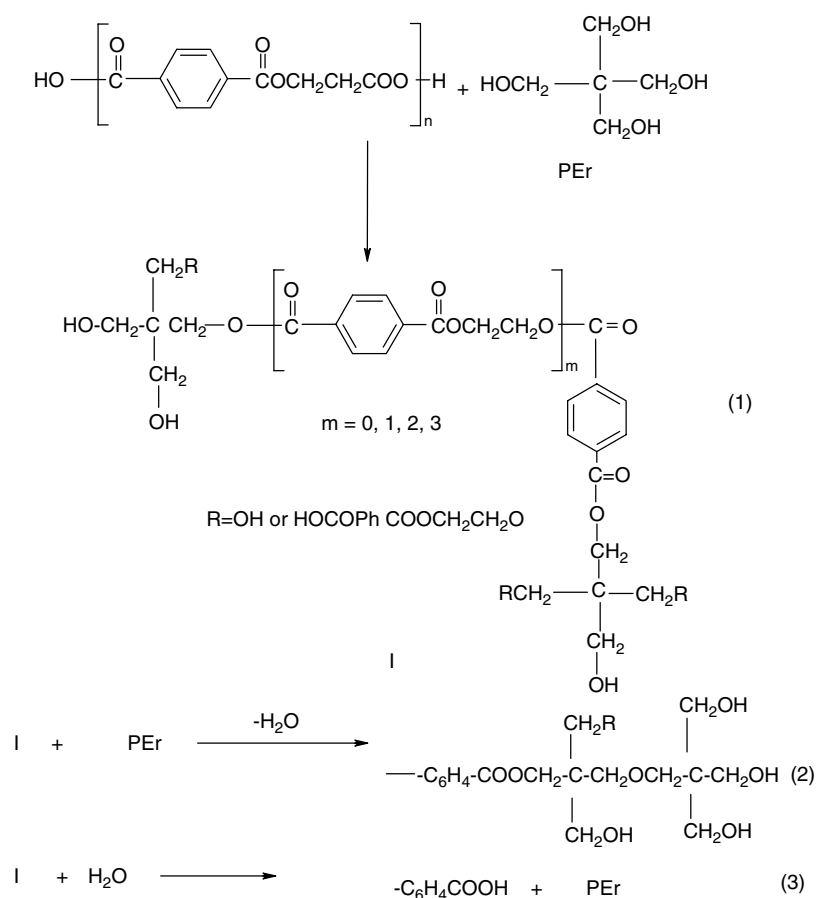
where  $w_1$  is the dry weight before and  $w_2$  the dry weight after extraction.

The volume fraction  $\phi$  of the polymer in the swollen sample was calculated as

$$\phi = (w_2 / \rho_2) / [(W - w_2) \rho + (w_2 / \rho_2)] \quad (3)$$

Here  $W$ ,  $\rho_2$  and  $\rho$  are the weight of swelled foam with toluene, the density of toluene at 25 °C and the foam density, respectively.

The fluid and oil used for the oil absorption experiment were toluene and marine Belayium crude oil. PU foam samples of 1 cm diameter and 5 cm length were cut using a sharp-edged steel die. Each sample was weighed before being immersed in oil or toluene at 25 °C. For the first 30 min the samples were removed from the test bottle every 5 min and reweighed quickly. After that, removal intervals were 30 min. Also, the procedure was continued for 10 days and samples were reweighed every day until each PU foam sample reached a constant weight. Oil sorption capacities  $Q$



**Scheme 1.** PET depolymerization with PEr.

**Table 3.** Physical characteristics of prepared GPEr and GTMp oligomers

Sample	Free glycol (wt%) <sup>a</sup>	End group analysis		GPC data			Yield (%)	Viscosity (cP) at 25 °C
		Hydroxyl value (mg KOH g <sup>-1</sup> )	<i>M<sub>n</sub></i> (g mol <sup>-1</sup> )	<i>M<sub>n</sub></i> (g mol <sup>-1</sup> )	<i>M<sub>w</sub></i> (g mol <sup>-1</sup> )	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i>		
GPEr-1	63	299	1125	1350	1463	1.33	65	ca 9500
GPEr-2	77	379	888	920	1115	1.36	70	ca 8500
GPEr-3	83	392	858	830	1100	1.39	75	ca 8400
GTMp-1	76	405	554	620	738	1.19	60	ca 7000
GTMp-2	79	412	544	600	684	1.17	65	ca 6590
GTMp-3	89	481	466	500	627	1.18	70	ca 6400

<sup>a</sup> Unreacted glycol.

in both toluene  $Q_T$  and crude oil  $Q_{\text{crude}}$  were calculated as follows:

$$Q(\text{g g}^{-1}) = (\text{weight of absorbed oil})/(\text{dry foam weight}) \quad (4)$$

The equilibrium toluene content (ETC) was calculated as

$$\text{ETC}/\% = [(\text{weight of gel} - \text{weight of xerogel})/(\text{weight of gel})] \times 100 \quad (5)$$

Crude oil content ECC was calculated analogously. This provides gross oil uptake since it includes any oil diffused into the solid polymer matrix as well as oil taken up into the pores. Clearly ECC is the key parameter representing the efficiency of a particular foam for oil spill recovery applications.

## SYNTHESIS RESULTS

Appropriate conditions for the preparation of oligoester polyols by glycolysis of PET using PEr and TMp were investigated earlier.<sup>20</sup> Depolymerization of recycled PET was carried out in a nitrogen atmosphere and in the presence of 0.5 wt% manganese acetate as the transesterification catalyst, with reaction times 3–8 h. The glycolysis consists of transesterification of PET and degradation of its polymer chain, resulting in a decrease of PET molecular weight. The glycolysis of PET with PEr and TMp was carried out at a reaction temperature not higher than 220 °C. Under these conditions there is formation of alicyclic derivatives between hydroxyl groups of poly-hydroxy glycolized PET. We have used *m*-cresol to provide good miscibility of the reactants, especially at high TMp or PEr and PET contents. Alcoholysis of PET with PEr and TMp proceeded according to Scheme 1. The alcoholysis consists of the transesterification of PET without degradation of its polymer chains, resulting in a decrease of its molecular weight. Using glycols in the depolymerization of PET, the oligoesters obtained have two, three or four hydroxyl end-groups, i.e. oligoester polyols are formed. The products of PET degradation using TMp or PEr are dark and viscous liquids with different hydroxyl numbers. The transesterification with PEr or TMp is represented in reaction (1). Structure I is proposed for identification of the oligoester polyols so obtained. According to structure I, if one replaces *m* with 0, 1, 2 and 3 the following molecular weights are obtained: 402, 610, 818 and 1026 g mol<sup>-1</sup>, respectively. The number-average molecular weights *M<sub>n</sub>* of all oligomers were determined and are listed in Table 3. The final *M<sub>n</sub>* values of the isolated oligomers decrease slightly upon increasing the PET: alcohol ratio from 1:1 to 1:2. This can be attributed to increase of depolymerization

reactions with increasing glycol ratio.<sup>14</sup> It is well known that the use of a large excess of glycol in degrading PET leads to formation of secondary OH groups in the oligoesters resulting from the reaction. The hydroxyl numbers after removing the free glycol indicate that the extent of depolymerization was significant; the resulting oligomers are mostly terminated with hydroxyl groups. In this respect, some etherification side reactions, water, TMp or PEr formation might occur, resulting in glycols or carboxylic acid end-groups, respectively. Another important side reaction is hydrolysis by water formed or present as impurity as represented in the reaction in Scheme 1. Such carboxylic acid end-groups usually are later esterified with excess glycol. As for the type of alcohol used, PEr is more effective in degrading PET than TMp – as reflected in the final molecular weights. This may be due to more inclusion of PEr than TMp into the PET backbone.<sup>14</sup>

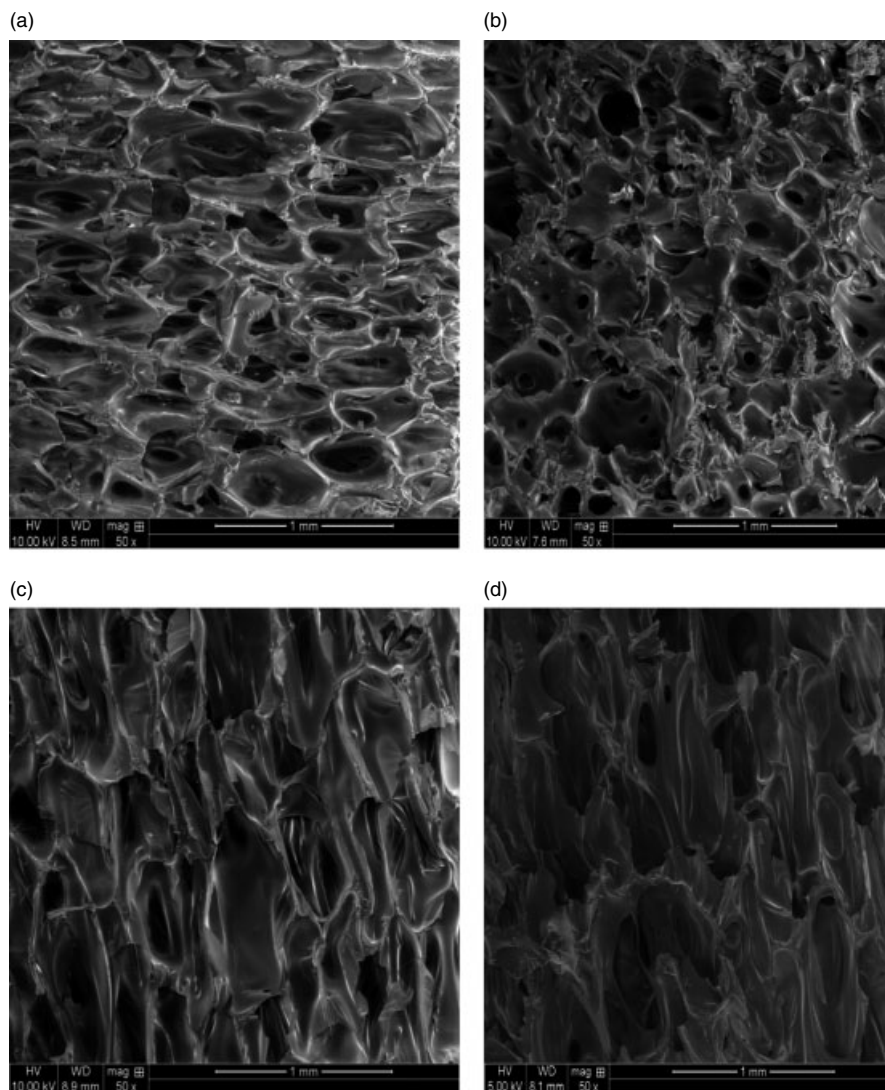
In an earlier paper<sup>14</sup> <sup>1</sup>H NMR spectra were used to determine the percentage of TMp or PEr used in the glycolysis of PET waste. Two peaks with the same proton number were used to compare the integration values. Thus, the integrations of CH<sub>2</sub> protons attached to OH groups of TMp and PEr were compared with integrations of CH<sub>2</sub> protons of PET. Comparison of the peak integration of GTMp-2 at  $\sigma = 3.4$  ppm (assigned to three methylene protons attached to OH groups of the TMp moiety) with that at  $\sigma = 4.4$  cm<sup>-1</sup> (assigned to one methylene group of the ethylene glycol moiety of PET) provides the TMp:PET ratio ca 1.5:1. The mole ratio of reactants TMp:PET which was 3:1 became 0.5:1 in oligomers. Thus approximately 12.5 mol% of TMp has reacted with PET. This result agrees with the data listed in Table 3, namely the expected value from weight loss after purification of 11 mol%. On the other hand, peak integration for PEr at  $\sigma = 4.4$  ppm (assigned to one methylene proton of ethylene glycol of PET) is 15.96 whereas that at  $\sigma = 4.18$  ppm (assigned to four methylene groups of the ethyl moiety of PEr) is 7.76; thus, their ratio is approximately 0.5:1. PEr is found mainly at chain ends and approximately 12.5 mol% (0.5 × 100/4, where 4 and 0.5 are mol% of PEr in the reactant and product, respectively) of PEr was reacted with PET at a molar ratio of PEr:PET = 3:1. We have 17 mol% unreacted PEr.

An inspection of the molecular weight data of glycolized oligomers in Table 3 indicates that the *M<sub>n</sub>* values determined by GPC are higher than those obtained from end-group analysis. Apparently there are more hydroxyl groups per molecule attached in glycolized products. The expected number of OH groups per molecule of GPEr and GTMp are 6 and 4, respectively. Accordingly, our oligomers with high numbers of OH groups per molecule and with branching are suitable polyols for obtaining PU systems that can cure quickly and are expected to form strong rigid foams.



**Table 4.** Curing conditions of PU foam based on TMp and PEr oligomers

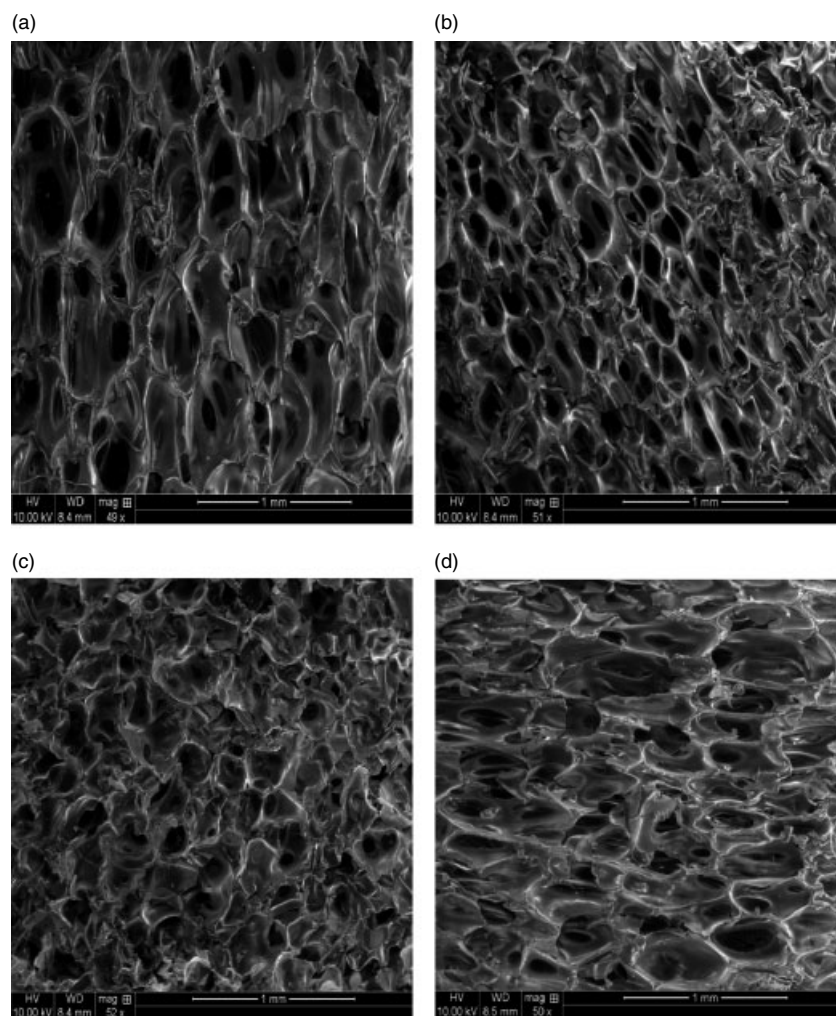
Properties	PU-GTMp-1 GTMp/TDI (wt ratio)			PU-GTMp-2 GTMp/TDI (wt ratio)			PU-GTMp-3 GTMp/TDI (wt ratio)			PU-GPEr-2 GPEr/TDI (wt ratio)			PU-GPEr-3 GPEr/TDI (wt ratio)		
	1.1	1.2	1.3	1.1	1.2	1.3	1.1	1.2	1.3	1.1	1.2	1.3	1.1	1.2	1.3
Mix time (s)	8	10	15	10	15	20	15	20	25	5	8	10	3	5	7
Cream time (s)	12	16	20	15	20	22	20	25	30	8	10	13	5	7	10
Gel time (s)	35	50	55	40	50	53	45	60	65	20	22	25	13	15	17
Rise time (s)	50	60	65	55	75	80	60	80	85	40	43	45	35	38	42
Free rise density (kg m <sup>-3</sup> )	75	70	90	70	65	88	65	61	78	90	85	105	110	100	135


**Figure 1.** ESEM micrographs of (a) PU-GPEr-2 (1.1), (b) PU-GPEr-2 (1.2), (c) PU-GPEr-3 (1.2) and (d) PU-GPEr-3 (1.3).

## POLYURETHANE FOAMS BASED ON GPEr AND GTMp OLIGOMERS

As already noted, we have used both GPEr and GTMp oligomers as polyols to react with TDI to produce PU foams. The effect of the GPEr and GTMp oligomer mass ratio on the foam structure was evaluated. We have prepared materials with a mass ratio between polyol oligomers (GTMp-1, GTMp-2, GTMp-3, GPEr-2 or

GPEr-3) and TDI of 1.1, 1.2 and 1.3. The GPEr-1 oligomer was not used in making PU foams because of its relatively high viscosity. The structures of PU foams are highly dependent on the relative rates of the two reactions involved in the use of isocyanate in the cellular foaming process (reaction (2)). If the first reaction is faster, the polymer may cure before the foam is fully expanded by the slower CO<sub>2</sub> reaction and the final foam will have a higher density



**Figure 2.** ESEM micrographs of (a) PU-GTMp-3 (1.1), (b) PU-GTMp-3 (1.2), (c) PU-GTMp-3 (1.3) and (d) PU-GTMp-1 (1.2).

with smaller cells. If reaction (2) is faster, the foaming process occurs fast, before the polymer solidifies via the slower reaction (1). In the latter case, the cured foam will have a lower density with an irregular cell structure. The water is the reactive blowing agent and it is added for the production of  $\text{CO}_2$  during the foam formation resulting in a lower final density. It has been reported that an increase in the water content produces an expansion of the foam volume, resulting in thinner foam cell walls and changing the density of the foam and the morphology.<sup>31</sup> Apparently the cell structure becomes more uniform with lower water content. Therefore, demineralized water (2 wt%) was used to prepare PU foams based on glycolized PET oligomers similar to before.<sup>20</sup> Now, however, a surfactant was added to help the foam-forming process via stabilization of the growing cells. Campanella and coworkers reported that a surfactant helps by controlling the size of the foam cell by stabilizing the gas bubbles formed during nucleation.<sup>32</sup> While making a flexible foam, the surfactant allows control of the degree of cell opening and the subsequent collapse of the foam.

The curing conditions for making PU foams based on GTMp and GPEr oligomers are listed in Table 4. The cream time occurs when the mixture changes from a clear dark-colored liquid to an opaque light-colored liquid; that time represents the onset of the rise of the foam. Gel time is quite important in systems including PU base and isocyanate hardener for the simple reason that after that time the

system fluidity is lost. Gelation can be separated from vitrification if DMA is applied together with thermally modulated differential scanning calorimetry.<sup>33</sup> In our systems the gel time varies with variation in the amount of GPEr or GTMp oligomers and the NCO:OH ratio. We have found that the gel time decreases with increasing content of GPEr or GTMp. Apparently higher cohesive forces reduce the gel time whilst also increasing the molecular weight. Further, smaller amounts of the TDI hardener increase the gel time. Rise times of PU foams with the procedure shown in Table 2 range from 35 to 85 s. The rise time is the time required for a foam to reach its maximum height since mixing polyol and TDI components. The core density was found to be between 61 to 135  $\text{kg m}^{-3}$ . We were able to create PUs without problems of shrinkage. We have found that the GTMp route provides higher expansion than GPEr – with obvious consequences for the petroleum absorption by our foams.

## FOAM MORPHOLOGY

We now discuss the effects of different parameters on the foam structure, including the relative reactivity of the GPEr- and GTMp-based polyol and isocyanate, the ratio of GPEr and GTMp polyol, and the amount of water, catalyst and surfactant added to the mixture.

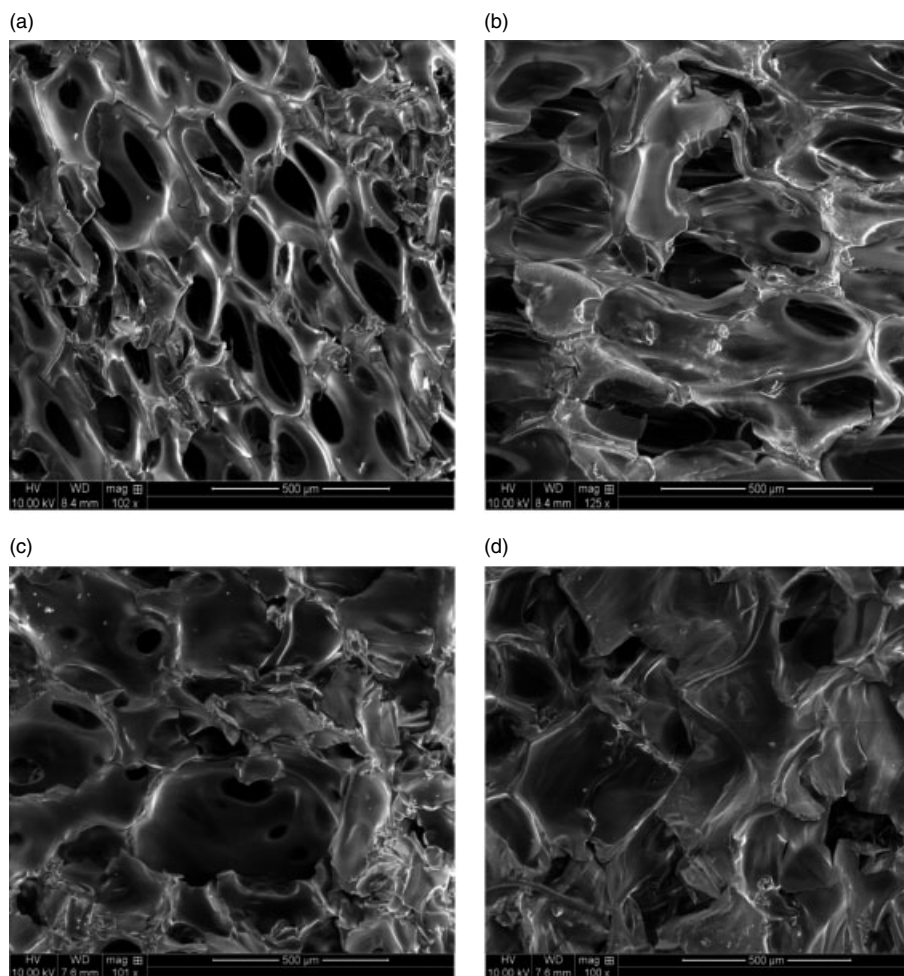


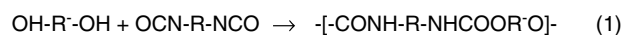
Figure 3. ESEM micrographs of (a) PU-GTMp-3 (1.2), (b) PU-GTMp-3 (1.3), (c) PU-GTMp-2 (1.2) and (d) PU-GTMp-2 (1.3).

Table 5. SF and DMA results															
Properties	PU-GTMp-1 GTMp/TDI (wt ratio)			PU-GTMp-2 GTMp/TDI (wt ratio)			PU-GTMp-3 GTMp/TDI (wt ratio)			PU-GPEr-2 GPEr/TDI (wt ratio)			PU-GPEr-3 GPEr/TDI (wt ratio)		
	1.1	1.2	1.3	1.1	1.2	1.3	1.1	1.2	1.3	1.1	1.2	1.3	1.1	1.2	1.3
SF (%)	4.4	6.2	7.5	5.4	7.3	10.6	3.4	6.8	8.6	2.1	3.5	5.7	1.8	2.5	4.9
Glass transition temperature $T_g$ (°C)	81.1	75.4	78.1	66.2	62.4	64.3	59.2	50.3	55.2	74.1	70.3	72.3	82.3	78.3	81.4
Peak of $\tan \delta$	0.74	0.78	0.76	0.91	0.96	0.98	1.05	1.32	1.22	0.62	0.68	0.65	0.59	0.65	0.61
$\tan \delta$ at 25 °C	0.148	0.26	0.15	0.26	0.27	0.28	0.35	0.44	0.41	0.25	0.30	0.27	0.22	0.28	0.24
$E'$ (MPa)	0.21	0.58	0.44	1.53	1.56	1.6	0.36	0.39	0.38	9.7	11.2	9.9	11.6	14.6	12.3
$E''$ (MPa)	0.03	0.15	0.07	0.39	0.42	0.44	0.13	0.17	0.16	2.5	3.36	2.67	2.65	4.08	2.95

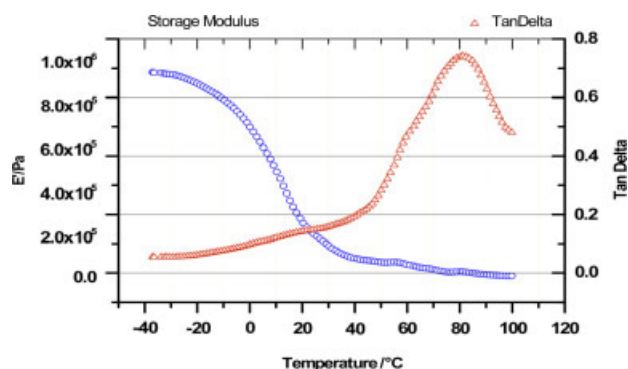
We have first made PU foams from GPEr and GTMp without any catalyst. In this case the cure rate (reaction (1)) was much slower than the gas formation rate (reaction (2)). The foam completely collapsed before curing, and the resulting density was the highest obtained in this study. When 1 wt% of 33% triethylene diamine in dipropylene glycol (DMBA) catalyst was added (Table 2), reaction (2) still dominated the kinetics and the foam was well expanded; the cured foam had a relatively low density. The foam morphology was studied by considering the different types of GPEr and GTMp oligomers. Figures 1–3 show

ESEM micrographs of the cellular structures in the cores of the PU foams. A higher concentration of OH groups causes stronger reactivity with the isocyanate. We provide the amount of hydroxyl groups present in the polyols in Table 3. As seen in Figs 1–3, cells with more structural homogeneity are obtained with the polyols that contain TMp OH groups. The data in Tables 3 and 4 provide the following sequence of the reactivity of our polyols: GTMp-3 > GTMp-2 > GTMp-1. For GPEr-PU, Fig. 1 shows largely nonuniform cells. When GPEr/TDI increases, we get more closed cells; apparently the reactivity of GPEr polyols toward TDI is higher





**Scheme 2.** Reaction between polyol or water and diisocyanate.



**Figure 4.** Storage modulus  $E'$  and  $\tan \delta$  of PU-GTMp-1 foam cured at a GTMp-1/TDI ratio of 1.1.

than that of GTMp oligomers. This can be attributed to higher numbers of OH groups per molecule for GPEr than for GTMp oligomers.

As shown in Table 4, the density decreases as the GTMp/TDI ratio increases from 1.1 to 1.2 and then increases. We shall discuss these facts in relation to the DMA results in the next section.

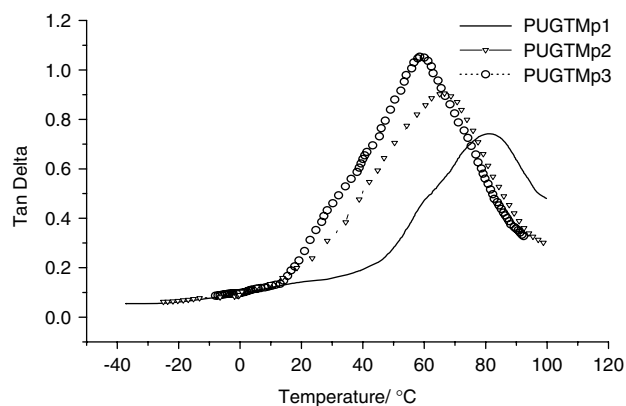
## SOLUBLE FRACTION AND DMA RESULTS

Before measuring the mechanical and swelling oil uptake parameters, the cured foams were subjected to extraction to remove the soluble fraction (unreacted GPEr or GTMp oligomers). The soluble fraction was determined as described in the section on oil absorption measurements above and calculated from Eqn (5). The results are listed in Table 5. We find that the SF values increase with decreasing TDI amount (from left to right in the table for each of the five materials). What happens is that, with decreasing OH functionality, the SF percentage increases since fewer crosslinks are formed, a finding already reported by Montevario *et al.*<sup>34</sup>

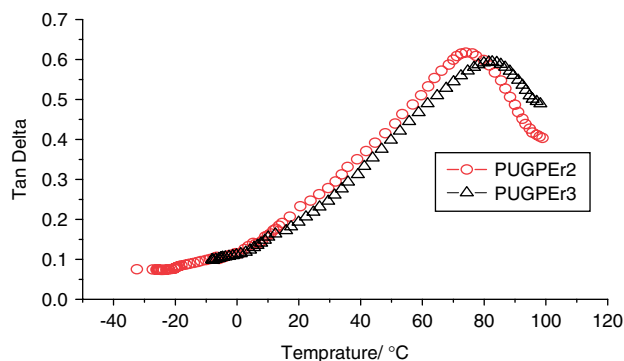
Long ago Bastide *et al.*<sup>35</sup> reported that the presence of dangling or pendant chains in the polymeric network affects the compression moduli. Namely, and as in fact expected, the moduli decrease drastically when the proportion of pendant chains increases. Dangling chains as well as pendant chains result in spatial inhomogeneities which affect the rigidity of the network.

We now discuss the results of the DMA reported in Table 5 (selected diagrams in Figs 4–6) taking into account the morphology results from the previous section. DMA has been well described by several authors.<sup>36–39</sup> Application of a sinusoidal load (see the section on characterization) provides values of the storage modulus  $E'$  (elastic or solid-like behavior), loss modulus  $E''$  (loss or liquid-like behavior) and their ratio  $\tan \delta = E''/E'$ . DMA also allows determination of the glass transition temperature  $T_g$  by several procedures – as discussed in some detail by Menard.<sup>39</sup> We stress that  $T_g$  constitutes a representation of a temperature region by a single value.<sup>40,41</sup>

The presence of the dangling chains in the chemical structures of PU foams based on TMp oligomers results in much lower storage modulus  $E'$  values than for the foams based on PER oligomers. TMp



**Figure 5.**  $\tan \delta$  versus temperature for PU-GTMp foams cured at a GTMp/TDI ratio of 1.1.



**Figure 6.**  $\tan \delta$  versus temperature for PU-GPEr foams cured at a GPEr/TDI ratio of 1.1.

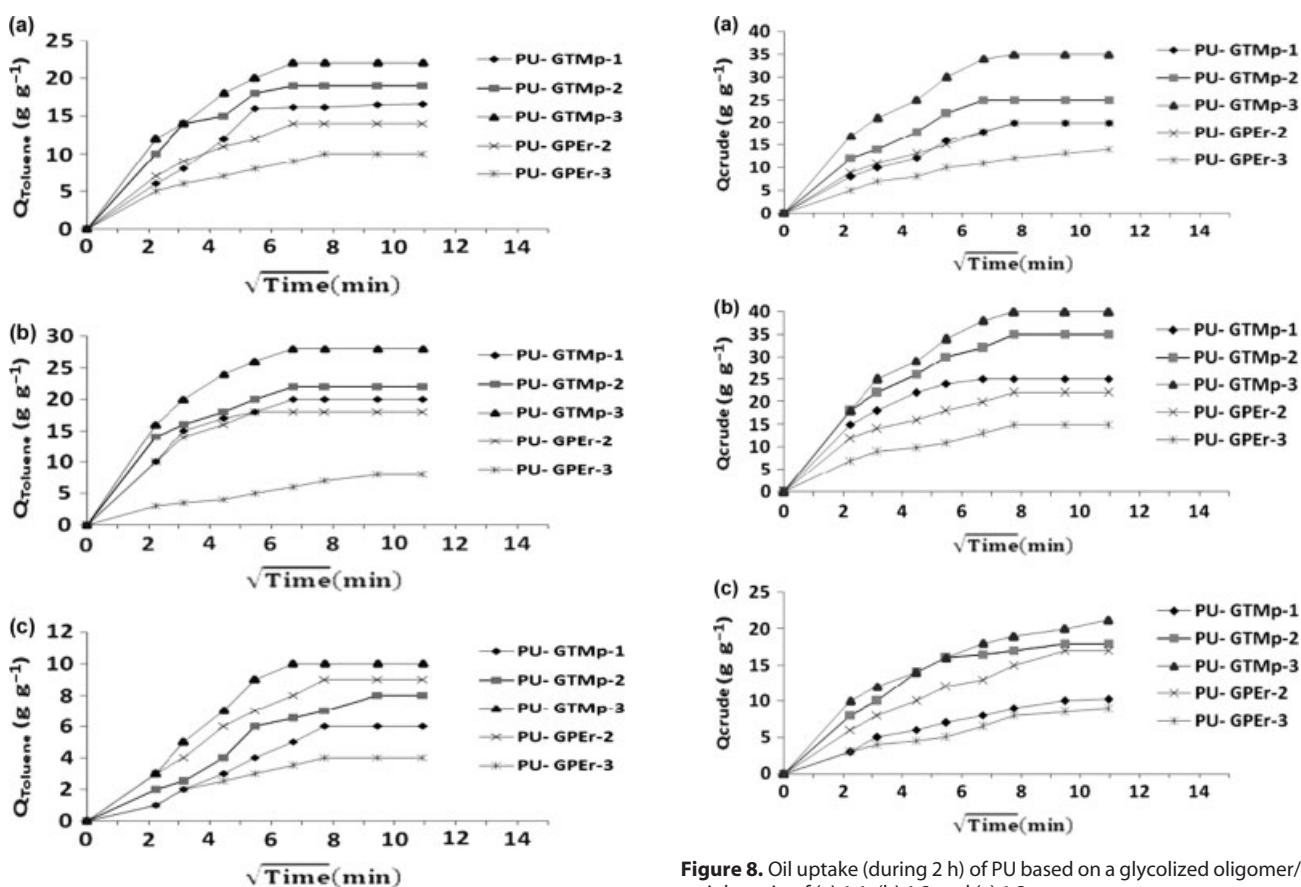
oligomers contain so-called dangling (here ethylene) groups – also called spacers – which decrease the effects of the rigidity of phenyl groups and also of rigid double bonded  $\text{N}=\text{C}=\text{O}$  groups in TDI molecules. The dangling groups counteract the steric hindrance of phthalate groups of glycolized oligomers located near the polymer backbone. Qualitatively, one talks about increased flexibility of the material caused by the dangling groups (also called dangling chains). DiMarzio<sup>42</sup> pointed out that flexibility in polymers manifests itself not only in the main chains but also in side chains. We note, however, that there is still no generally accepted quantitative definition of flexibility of solids. Our systems are complicated because of the presence of the pores, the dangling chains just mentioned and also crosslinking – all factors which affect the properties including the glass transition.<sup>43</sup> A plausible explanation for the large drop in  $E'$  is in terms of the dangling chains acquiring more mobility.

When we look at the glass transition temperatures  $T_g$  determined from  $\tan \delta$  peaks in DMA, we find an interesting result. We have five groups of materials; within each group the ratio of either TMp or PER to TDI takes values of 1.1, 1.2 and 1.3. Within each group the  $T_g$  for the 1.2 ratio is the lowest. This result deserves an explanation. Return now to reactions (1) and (2) in Scheme 2. At a ratio of 1.1, we have the lowest concentration of the hydroxyl groups in polyols. As already noted, reaction (2) is faster than reaction (1). Large amounts of  $\text{CO}_2$  are formed; the gas easily escapes from the PU being formed, leaving large pores behind. Materials with such pores provide little resistance to compression: hence the  $E'$  values are here the lowest in each series of three while  $E''$



**Table 6.** Swelling parameters of PU foams based on GTMp and GPEr oligomers at 25 °C

Properties	PU-GTMp-1 GTMp/TDI (wt ratio)			PU-GTMp-2 GTMp/TDI (wt ratio)			PU-GTMp-3 GTMp/TDI (wt ratio)			PU-GPEr-2 GPEr/TDI (wt ratio)			PU-GPEr-3 GPEr/TDI (wt ratio)		
	1.1	1.2	1.3	1.1	1.2	1.3	1.1	1.2	1.3	1.1	1.2	1.3	1.1	1.2	1.3
Volume fraction of the polymer in toluene ( $\phi_T$ )	0.43	0.39	0.64	0.40	0.37	0.60	0.37	0.35	0.56	0.42	0.37	0.50	0.46	0.52	0.68
Volume fraction of the polymer in crude oil ( $\phi_C$ )	0.38	0.34	0.76	0.34	0.28	0.66	0.28	0.27	0.61	0.33	0.32	0.58	0.36	0.38	0.76
$Q_T$ ( $\text{g g}^{-1}$ )	16	20	6	19	22	8	22	28	10	14	18	9	10	8	4
$Q_{\text{crude}}$ ( $\text{g g}^{-1}$ )	20	25	4	25	35	6	35	40	8	20	22	7	15	15	3
ETC (%)	93.7	95.0	83.3	94.7	95.4	87.5	95.4	96.4	90	92.8	94.4	88.8	90	87.5	75.0
ECC (%)	95.0	96.0	75.0	96.0	97.1	83.3	97.1	97.5	87.5	95.0	95.5	85.7	93.3	93.3	66.6



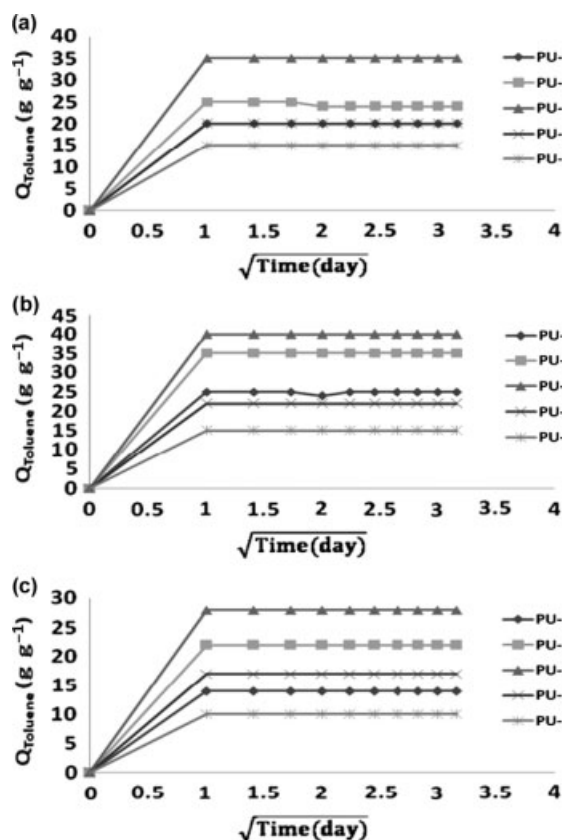
**Figure 7.** Toluene uptake (during 2 h) of PU based on a glycolized oligomer/TDI weight ratio of (a) 1.1, (b) 1.2 and (c) 1.3.

are also low. Jackovich and her colleagues reported low values of the quasi-static compressive modulus  $E_c$  corresponding to low values of density in PU foams.<sup>28</sup> An assumption of proportionality between  $E_c$  as reported by Jackovich *et al.*<sup>28</sup> and  $E'$  determined by us using DMA in compression is at least a plausible one; it provides support for our hypothesis.

When we move to a ratio of 1.2, more polyol allows formation of a stronger material, and  $E'$  values in each series of three go up;  $E''$  values go up too since the resistance to flow also increases.

**Figure 8.** Oil uptake (during 2 h) of PU based on a glycolized oligomer/TDI weight ratio of (a) 1.1, (b) 1.2 and (c) 1.3.

However, the resistance to flow has increased faster; therefore,  $\tan \delta$  goes up and is the highest in the series of three. When we move to the highest value of the ratio equal to 1.3, we have less  $\text{CO}_2$  formation than before; the polyol in reaction (1) takes away some of the TDI for the formation of PU. Insufficient carbon dioxide results in less formation of pores; some of the pores now are closed ones. The SEM results in Figs 1–3 agree with this. So do the values of density in the last line of Table 4. Given fewer pores, the loss modulus  $E''$  goes down;  $\tan \delta$  goes down as well. Return now to the middle composition characterized by the ratio 1.2 in each series of three. In this case we have the highest amounts of



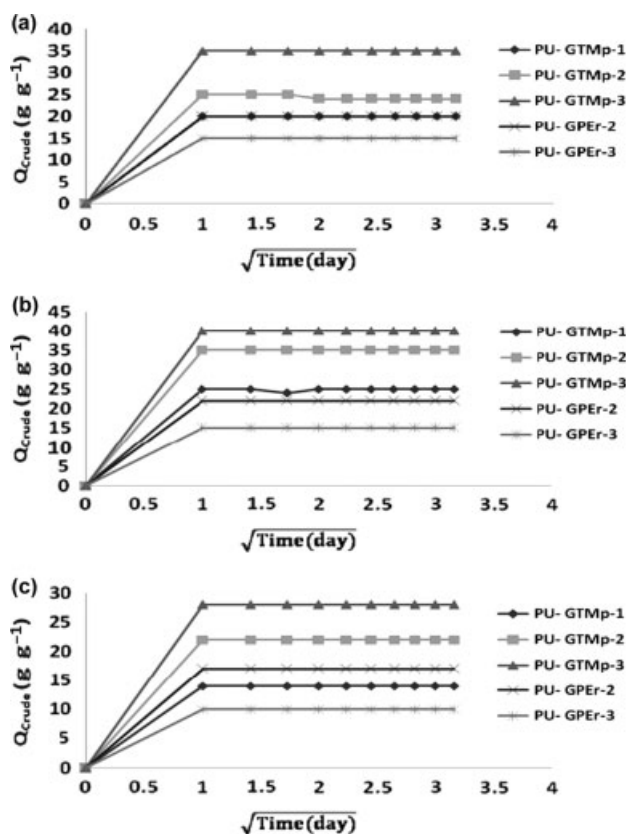
**Figure 9.** Toluene uptake (during 10 days) of PU based on a glycolized oligomer/TDI weight ratio of (a) 1.1, (b) 1.2 and (c) 1.3.

open pores and hence the lowest densities – and correspondingly the lowest  $T_g$ .

## PETROLEUM ABSORPTION

The swelling parameters, such as toluene swelling uptake ( $Q_T$ ), crude oil swelling uptake ( $Q_{crude}$ ), equilibrium crude oil and toluene contents (ETC and ECC) and the volume fractions  $\phi_T$  and  $\phi_C$  of the polymer in the swollen sample in toluene and crude oil were determined at 25 °C, as described in the section on oil absorption measurements, and are listed in Table 6. Toluene is one of the liquids recommended by the ASTM F726-81 standard. The dependence of  $Q_T$  or  $Q_{crude}$  on the square root of the swelling time (2 h or 10 days) is represented in Figs 7–10. The reason for using the square root of time is the law formulated by Adolf Fick in 1855 according to which the rate of diffusion is a function of  $t^{1/2}$ . In general, the swelling processes we study depend not only on diffusion – see more below. The oil sorption ( $g\ g^{-1}$ ) of PU foams is mostly higher for oil than for toluene.

We believe the primary mechanism is pore filling rather than diffusion into the polymers since the diameter of each foam sample remains approximately constant during exposure to oil. Looking again at our five sets of three materials, we find that for each the middle member of the set with a ratio of polyol to TDI equal to 1.2 has the highest absorption of either toluene or petroleum. Our hypothesis is as follows. The amount of liquid absorbed is proportional to the surface area of the pores per unit volume of the pore-containing polymer. With a polyol/TDI ratio of 1.1 we have large pores – so that the relative surface area of the pores per



**Figure 10.** Crude oil uptake (during 10 days) of PU based on a glycolized oligomer/TDI weight ratio of (a) 1.1, (b) 1.2 and (c) 1.3.

unit volume is not very high. With that ratio equal to 1.3 we have the lowest relative surface area in each group of three – a result of less  $CO_2$  available, as discussed already in the previous section. The middle value of the ratio equal to 1.2 results in the highest absorption of petroleum and, with one exception, also of toluene. A simple relation is seen between density listed in the last line of Table 4 and liquid absorption results in Table 6: a density increase is accompanied by a liquid absorption decrease. We know that at a more fundamental level the absorption of liquids takes place on the porous polymer surface.

We were not certain whether after longer times further liquid absorption still takes place. Therefore, we have performed experiments lasting 120 min as well as 10 days. The latter – seen in Figs 9 and 10 – show that in toluene measurable swelling can occur on the ninth day. For petroleum all significant swelling occurs on the first day.

We measured reusability of the prepared PU foams after pressing them to exude oil. Initially some 2% remains absorbed. However, in the following absorption–desorption cycles that 2% retained remains practically constant for more than five absorption cycles. Thus, our foams can be used for petroleum spill cleanup. As for biodegradability, the presence of dangling chains is expected to facilitate it. We are planning future work involving crosslinking hydrophobic monomers to produce coated PUs that are even more compatible with petroleum or toluene.

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## REFERENCES

- Available: <http://www.gadling.com/2010/11/29/bowermasters-adventures-measuring-the-extent-of-oil-spillage> [25 August 2012].
- Available: [http://news.yahoo.com/s/ap/us\\_sci\\_oil\\_spill\\_lingers](http://news.yahoo.com/s/ap/us_sci_oil_spill_lingers) [25 August 2012].
- Available: <http://finance.yahoo.com/news/ap-enterprise-russia-oil-spills-050153139.html> [25 August 2012].
- Hedenqvist M, Johnsson G, Tränkner T and Gedde UW, *Polym Eng Sci* **36**:271–282 (1996).
- Hedenqvist MS and Gedde UW, *Polymer* **40**:2381–2393 (1999).
- Neway B, Hedenqvist MS and Gedde UW, *Polymer* **44**:4003 (2003).
- Ritums JE, Neway B, Doghieri F, Bergman G, Gedde UW and Hedenqvist MS, *J Polym Sci Phys* **45**:723–734 (2007).
- Ritums JE, Mattozzi A, Gedde UW, Hedenqvist MS, Bergman G and Palmlöf M, *J Polym Sci Phys* **44**:641–648 (2006).
- Paukszta D and Garbarczyk J, *J Mater Ed* **21**:277 (1999).
- Kozłowski M, *Polimery* **48**:606–609 (2003).
- Mano JF, *J Mater Ed* **25**:151 (2003).
- Scheirs J, *Polymer Recycling*. John Wiley & Sons, Chichester (1998).
- Achiias DS and Karayannidis GP, In: *Proceedings of the International Conference 'Protection and Restoration of the Environment VI', Skiathos, 1–5 July 2002*, pp. 925–936.
- Abdel Azim AA, Atta AM and El-Ghazawy RA, *Cellular Polym* **125**:35 (2006).
- Abdel-Azim AA and Atta AM, *Polymer J* **29**:21 (1998).
- La Mantia FP and Vinci M, *Polym Degrad Stab* **45**:121–125 (1994).
- Atta AM, Elnagdy SI, Abdel-Raouf ME, Elsaheed SM and Abdel-Azim AA, *J Polym Res* **12**:373 (2005).
- Atta AM, Abdel-Raouf ME, Elsaheed SM and Abdel-Azim AA, *Prog Org Coat* **55**:50 (2006).
- Fraisse F, Verney V, Commereuc S and Obadal M, *Polym Degrad Stab* **90**:250–255 (2005).
- Atta AM, Abdel-Raouf ME, Elsaheed SM and Abdel-Azim AA, *J Appl Polym Sci* **103**:3175 (2007).
- Awaja F and Pavel D, *Eur Polym J* **41**:1453–1477 (2005).
- Atta AM, El-Kafrawy AF, Aly MH and Abdel-Azim AA, *Prog Org Coat* **58**:13 (2007).
- Foks J and Janik H, *Polym Eng Sci* **29**:113–119 (1989).
- Wirpsza Z and Kemp TJ (eds), *Polyurethanes: Chemistry, Technology and Applications*. Ellis Horwood, New York (1993).
- Brostow W (ed.), *Performance of Plastics*. Hanser, Munich (2000).
- Rutkowska M, Krasowska K, Heimowska A, Steinka I and Janik J, *Polym Degrad Stab* **76**:233–239 (2002).
- Janik J, Palys B and Petrovic ZS, *Macromol Rapid Comm* **24**:265–268 (2003).
- Jackovich D, O'Toole B, Cameron Hawkins M and Sapochak L, *J Cell Plastics* **41**:153 (2005).
- Sefton MV and Mann JL, *J Appl Polym Sci* **25**:829 (1980).
- Sorenson WR, Sweeny T and Campbell WW, *Preparative Methods of Polymer Chemistry*, 3rd edn, p. 358. Wiley-Interscience, New York (2001).
- Lin Y, Hsieh F and Huff HE, *J Appl Polym Sci* **65**:695 (1997).
- Campanella A, Bonnaillie LM and Wool RP, *J Appl Polym Sci* **112**:2567 (2009).
- Bilyeu B, Brostow W and Menard KP, *Polym Compos* **23**:1111 (2002).
- Montevario AE, da Silva EO, Costa APO, Samios D, Gerbase AE and Petzhold CL, *J Am Oil Chem Soc* **82**:395 (2005).
- Bastide J, Picot C and Candau S, *J Polym Sci Phys* **17**:1441 (1979).
- Menard KP, Thermal transitions and their measurement, in *Performance of Plastics*, ed. by Brostow W. Hanser, Munich (2000).
- Lucas EF, Soares BG and Monteiro E, *Caracterização de polimeros*. e-Papers, Rio de Janeiro (2001).
- Gedde UW, *Polymer Physics*. Springer, Dordrecht, Boston (2001).
- Menard KP, *Dynamic Mechanical Analysis*, 2nd edn. CRC Press, Boca Raton, FL (2008).
- Brostow W, Chiu R, Kalogeras IM and Vassilikou-Dova A, *Mater Lett* **62**:3152 (2008).
- Brostow W, Deshpande S, Pietkiewicz D and Wisner SR, *e-Polymers* (2009). no. (109).
- DiMarzio EA, *Polymer* **31**:2294 (1990).
- Mitra S, Chattopadhyay S and Bhowmick AK, *Nanoscale Res Lett* **4**:420 (2009).