

Effect of Foam Density, Oil Viscosity, and Temperature on Oil Sorption Behavior of Polyurethane

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ABSTRACT: This paper examines the effect of foam density, oil viscosity, and temperature on the oil sorption behavior of polyurethane foams. Four polyurethane foams with different densities and two oil types with different viscosities were investigated. The amount of oil uptake was measured gravimetrically. Oil transport through the foams was analyzed by nondestructive X-ray microtomography. Oil sorption capacity increased significantly with the decrease in foam density, due to the increase in the number of

open cells. The oil sorption capacity depended only slightly on sorption temperature and oil viscosity. X-ray visualization allowed pore filling behavior to be observed directly, and further scope to extend the technique is revealed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 360–367, 2006

Key words: polyurethanes; foams; diffusion; oil spill cleanup; X-ray microtomography

INTRODUCTION

One of the consequences of economies based on oil refining is the potential for oil spills during transport. Such disasters are highly visible and extensively reported.

Four basic methods are used for oil spill cleanup and collection: chemical dispersants, biodegradation, *in situ* burning, and use of sorbents. Each method has its own advantages and disadvantages. Even though no oil spill technique is completely effective, the use of sorbents is considered the most ideal solution because it can remove oil from the sea. Sorbents can be divided into three basic types: natural inorganic, natural organic, and synthetic. Choi and Moreau investigated the oil sorption capacities of various natural and man-made sorbents.¹ The advantages of natural inorganic sorbents such as clay, perlite, and glass wool are that they are inexpensive and available in large quantities. Natural organic sorbents consist of hay, feather, straw, peat moss, and other carbon-based products. The disadvantage of natural sorbents is that they are dusty, difficult to use under windy conditions, and hazardous if inhaled. In addition, some natural organic sorbents sorb not only oil but also water, causing the sorbents to sink. Synthetic organic sorbents are polymeric foams such as polyurethane, polypropylene,

polyethylene, and crosslinked polymers including rubber.

While the ingestion of fluids into cellular materials including polymeric foams appears to be of considerable practical importance, this area has been rather sparsely documented. For example, Sefton and Mann studied benzene absorption in polyurethane foams.² 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. They stated that they were unclear about the reason for this.

A recent study of oil cleanup techniques focused on the use of microbe-containing materials.³ In this work the inherent oil-absorbing performance of various polyurethane foams was measured. Isocyanate/polyol ratios were optimized at 2 : 10 for maximum Arabian light crude oil absorption and various surface area/weight ratios were also examined. Maximum oil absorbance was around 7–9 g oil/g polyurethane foam, which appears rather low compared with other data, including our own as outlined below.

Commercial interest in liquid absorbent materials, ranging from nonwoven fabrics to diapers, is strong, and patents are often extended to foams. The U.S. patent by Kalentun et al. is an example,⁴ although specific citation of crude oil recovery is not made in most patents.

Dissolving a polymer can be a slow process and it occurs in two stages.⁵ First, solvent molecules diffuse slowly into the polymer to produce a swollen gel. The second stage may occur if polymer–solvent interac-

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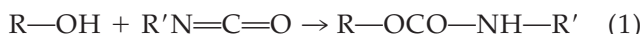
tions can overcome polymer–polymer interactions, when the gel will disintegrate into a true solution. For oil spill cleanup, it is necessary for the oil to diffuse rapidly and substantially into the polymer, but the second stage of dissolution must be avoided. Therefore, a highly porous and oil-swellable polymer with a low but finite level of effective crosslinking is sought.

In this research, polyurethane foams are examined with respect to oil sorption capacity and behavior. Polyurethanes are materials that can be processed with low energy consumption and relatively low capital investment for machinery. The cost of polyurethane foams on a weight basis is rather high, but on a volume basis the cost can be low, as foams with low bulk density can be easily made. Many monographs have been published relating to polyurethane.^{6–8}

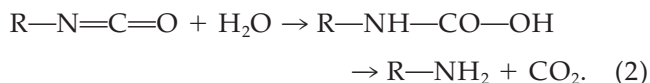
Di- or polyfunctional hydroxyl (polyol) or amino-group-containing compounds react with di- or polyisocyanates to form polyurethanes.⁶ The polyol can be polyether or polyester based. Polyisocyanates can be aromatic, or aliphatic. Polyurethanes, therefore, are versatile and have wide applications, because a wide range of end-product chemical and physical forms can be produced.

Polyurethane foams are blown with carbon dioxide, which is generated by the reaction of water with isocyanate groups. The amount of water present controls the density and the hardness of the foam. There are two main reactions involved in polyurethane foam formation:⁸

reaction of isocyanate with hydroxyl to form urethane



reaction of isocyanate with water to form carbon dioxide, a blowing agent



The ability of polyurethanes, including elastomers and foams, to imbibe organic solvents and oils has been investigated by several workers. However, the primary focus has been upon the interaction between the polyurethane and low-molecular-weight solvents.⁹ Oil sorption capacity has been investigated with only a single polyurethane foam and a single oil sample at one temperature.¹⁰

The aim of this research is to examine the effect of polyurethane foam density, type of oil, and temperature on oil sorption capacity. Therefore, four different polyurethanes with varying foam densities were used. Sorption experiments were conducted with two different types of oil, light sweet crude oil and process naphthenic oil, at 15 and 35 °C (approximating the

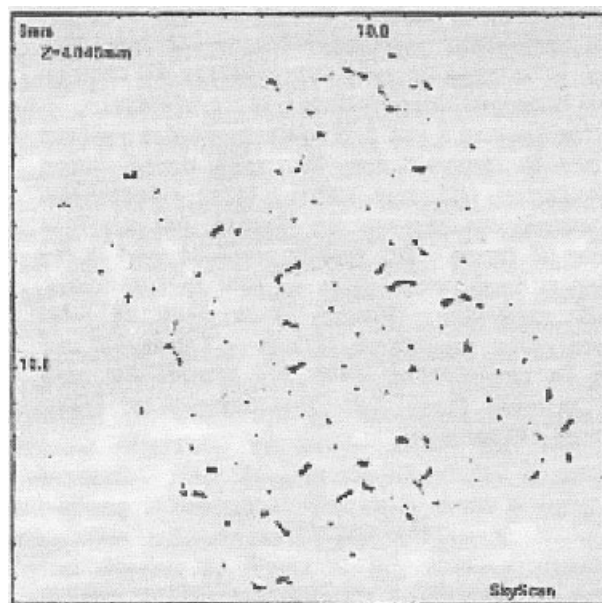


Figure 1 A cross section of a foam sample obtained via X-ray microtomography.¹¹

average temperature of seawater in winter and summer).

The sorption capacity can be measured by the weight uptake method, which is simple and low-cost. Thermogravimetric analysis (TGA) is a potential method, but oil quantification is difficult for low-pore-density polyurethanes due to the extremely high weight uptake of oil, making calculation of percentage uptake based on absolute polymer mass measurement from the TGA output error-prone.

The sorption behavior can be visualized by X-ray microtomography, developed, for example, by SkyScan. This rather new technique is potentially better than conventional methods for producing three-dimensional visualization. In addition, it is a nondestructive technique and requires little sample preparation. The method entails the restoration of a finely collimated X-ray beam layer by layer through an uncoated specimen in air. The X-ray density encountered at any moment is recorded to form a series of cross-sectional images, which when combined lead to a 3D profile. Typically, each section is confined to 1024 × 1024 pixels and with a sample dimension of around 5 × 5 mm, the effective resolution is about 10 μm for a given region of interest. The algorithms of the method, however, still need further development because some struts and windows in the foam are missed.¹¹ In addition, the magnification is fairly low, although this is expected to be improved in a new model, the SkyScan 2011 NanoTomograph.TM

Polyurethane foams have been previously imaged via X-ray CT, with a cross section shown in Figure 1.¹¹ The technique has also been used to investigate the

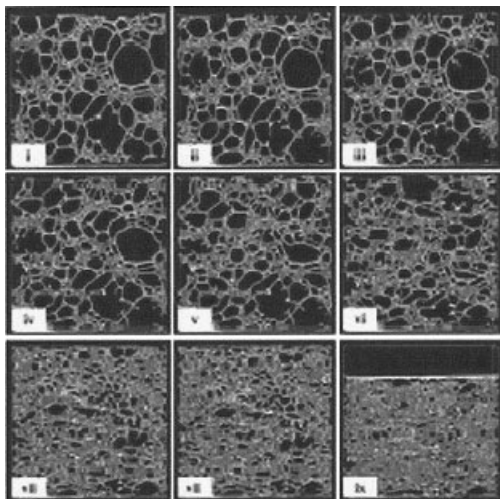


Figure 2 X-ray tomographic images of the deformed polyurethane foam as a function of compressive strain.¹²

deformation of an open-cell flexible PU foam due to compression, as shown in Figure 2.¹² These two articles provide recent evidence of the usefulness of X-ray microtomography for characterizing polyurethane foam. However, the method has not, to our knowledge, been applied to oil or other liquids in polymer foams. Indeed, X-ray microtomography is still emerging as a technique, and so very little other published work in this area exists for polymers.

EXPERIMENTAL

Materials

Raw materials of polyurethane were obtained from ERA Polymers, based in Botany, NSW, Australia. Raw materials consisted of a "P" component containing polyisocyanate and a "R" component containing polyol, catalysts, surfactants, additives, and distilled water and were mixed at UNSW according to the recommended procedure below.

The polyol (R component) is weighed accurately in a dry and clean container; isocyanate (P component) is then weighed into the same container, where the reaction begins immediately. The mixing must cease before cream time (see the listed cream time in Table I). The polyurethane foam samples from ERA Polymers used in this research were GP6, GP2, and Greenlink Erapak with mixing procedures recommended by ERA in Table I. Greenlink Erapak (9 kg/m³) is the lowest density polyurethane foam available from ERA. The low-density foam Erapak is hand mixed, whereas the other two general purpose (GP) foams were mixed using a drill mixer.

In addition, a large sample of commercial polyurethane packaging foam called Instapak, which was measured to have a mean bulk density of 6 kg/m³,

was used. This density is even lower than the lowest density polyurethane foam commercially available from ERA.

Oil samples

Two different types of oil were used: light sweet paraffin oil, supplied by BHP Billiton, and naphthenic oil (222B), supplied by Nynas. The viscosity data for the light sweet paraffin oil is 1.612 cST at 40°C and the density is 0.7920 g/mL at 15°C. The viscosity of the naphthenic oil is given as 100 cST at 40°C and density is 0.893 g/mL at 15°C. The light hydrocarbon fraction was removed by placing the oil in an exhaust fume hood until the oil sample weight remained constant.

Sorption experiment

Polyurethane foam samples of 1 cm diameter and 5 cm length were cut using a sharp-edge steel die. Each sample was weighed to ± 0.05 mg before being immersed in oil at 15 and 35°C. For the first 5 min, the samples were removed from the test bottle every minute and reweighed quickly. After that, removal intervals were 5 min. The procedure was continued until each polyurethane foam sample reached a constant weight. Oil sorption was calculated by the equation

Oil sorption (g/g)

$$= \frac{\text{weight of oil uptake(g)}}{\text{polyurethane foam weight(g)}}$$

This is gross oil uptake, as it includes any oil diffused into the solid polymer matrix as well as oil taken up into the pores. This parameter is a relevant indicator of the practical efficiency of a particular foam for oil spill recovery applications.

X-ray microtomography analysis

Images were acquired using a SkyScan 1072 desktop instrument operated at 42 kV and 56 μ A. The X-ray

TABLE I
Mixing Procedures of GP6, GP2, and Greenlink Erapak Recommended by ERA

	GP6	GP2	Greenlink Erapak
Mix ratio by weight (polyol : iso)	100 : 100	100 : 100	100 : 120
Mix time (s)	20	20	8
Cream time (s)	60	38	10
Gel time (s)	240	175	40
Tack free time	420	235	55
Free rise density (kg/m ³)	96	32	9

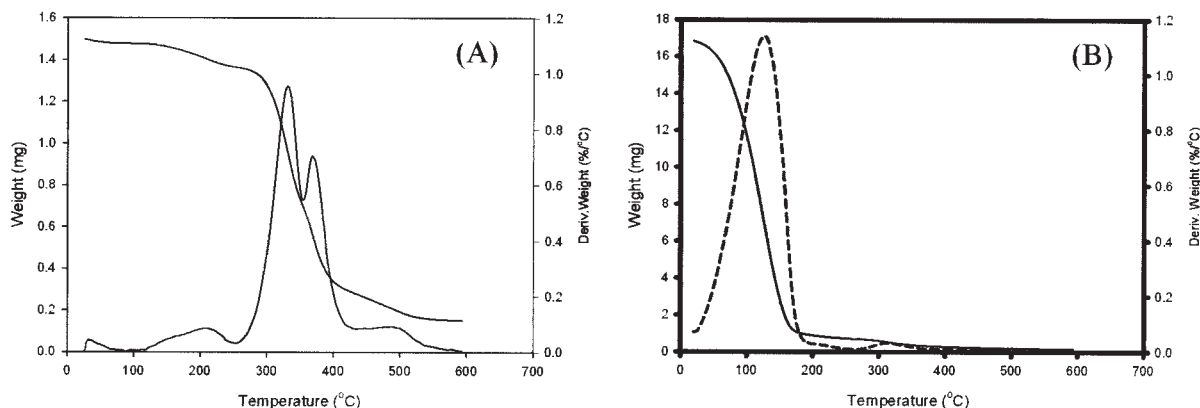


Figure 3 Thermogravimetry analysis results. (A) Greenlink Erapak; (B) light sweet paraffinic crude oil sorbed Greenlink Erapak.

shadow images were acquired by a sensitive X-ray camera and the sample was rotated through 180° with a rotation step size of 0.9° during image acquisition. Images were recorded for each rotation step of the sample. The volume image was reconstructed from a dataset of 200 images using cone-beam reconstruction. A maximum magnification of 120 times can be used, but 70 times was appropriate here and results in a resolution of $8 \mu\text{m}$.

RESULTS AND DISCUSSION

Figure 3 shows the TGA results for Greenlink Erapak before [Fig. 3(A)] and after [Fig. 3(B)] light sweet paraffin crude oil sorption at 35°C . Due to the high weight of oil taken up, polymer mass is low in Figure 3(B). For example, 20 mg of swollen polyurethane foam will

only have 0.5 mg of remaining polymer, making gravimetric quantification difficult. For this reason, a gross gravimetric weight uptake method was used.

Weight uptake curves of selected polyurethane foams in light sweet paraffin at 15°C and in naphthenic oil at 35°C are shown in Figures 4 and 5. Oil sorption (g/g) increases rapidly in the first 5 min and then remains constant. For Greenlink Erapak and Instapak, which have very low densities (9 and 6 kg/m^3 , respectively), oil uptake is very substantial. However, the oil sorption capacity of GP2 and GP6, with densities of 32 and 96 kg/m^3 , respectively, increases much less. The lightest PU foam (6 kg/m^3) increases in weight by almost 100 times, whereas the densest PU foam (95 kg/m^3) sorbed only about 4 g of oil per gram of polyurethane foam. This is estimated to be due to the increase in the number of open cells when the

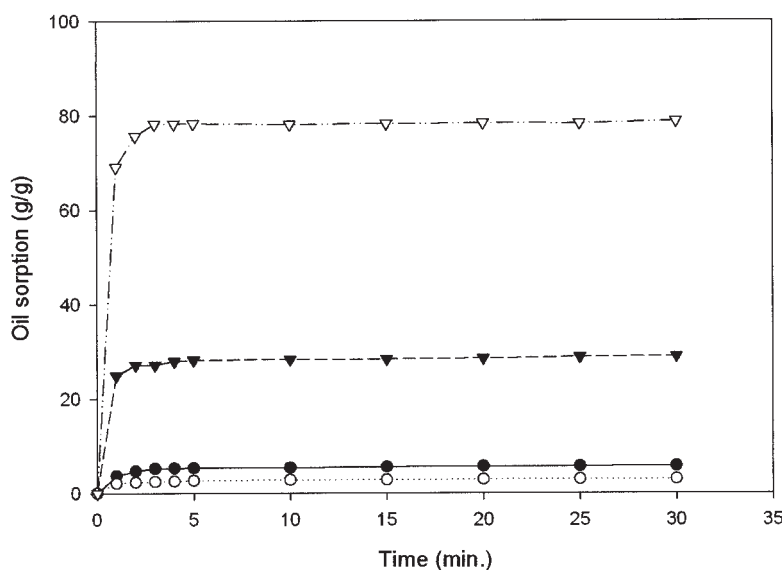


Figure 4 Weight uptake of GP6, GP2, Greenlink Erapak, and Instapak in light sweet paraffinic oil at 15°C . (○) GP6; (●) GP2; (▼) Greenlink Erapak; (△) Instapak.

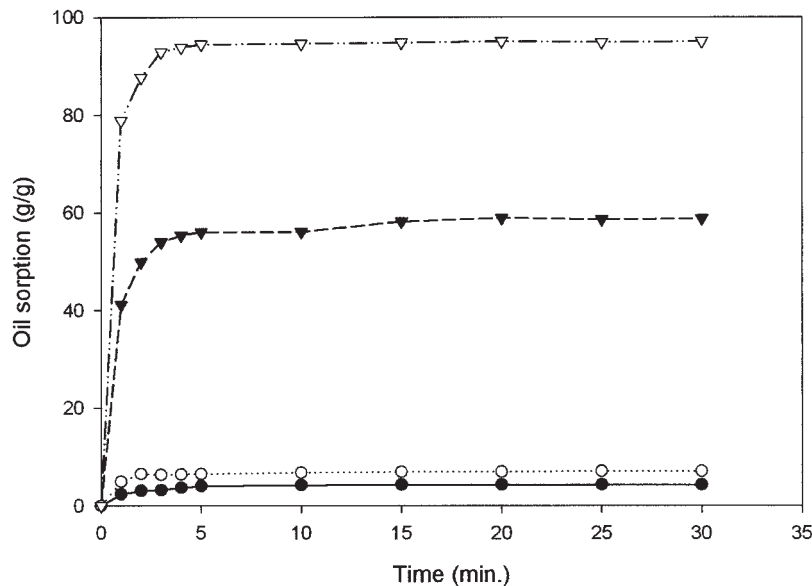


Figure 5 Weight uptake of GP6, GP2, Greenlink Erapak, and Instapak in naphthenic oil at 35 °C. (○) GP2; (●) GP6; (▼) Greenlink Erapak; (Δ) Instapak.

density of polyurethane foam is lowered. This estimate coincides with the explanation in Ref. 8. As the cell size increases, the thickness of the cell wall decreases. For the behavior of the polyurethane foams in light sweet paraffin oil at 35°C and in naphthenic oil at 15°C, the sorption curves are not shown, but the density foam dependence is essentially identical to the above trend.

The effect of sorption temperature and density of oil on the oil sorption (g/g) of GP2 and Instapak can be seen from the data shown in Figures 6 and 7. Oil

sorption depends only slightly on temperature and oil viscosity. The foams tend to sorb slightly more oil when the temperature increases from 15 to 35 °C, due both to increased polyurethane foam segmental motion (of low significance, as diffusion into the matrix is inherently low) and to lower oil viscosity. This allows increased pore filling.

The oil sorption (g/g) of polyurethane foam at a given temperature is always higher for naphthenic oil than for light sweet paraffin oil. We believe the primary mechanism is pore filling rather than diffusion

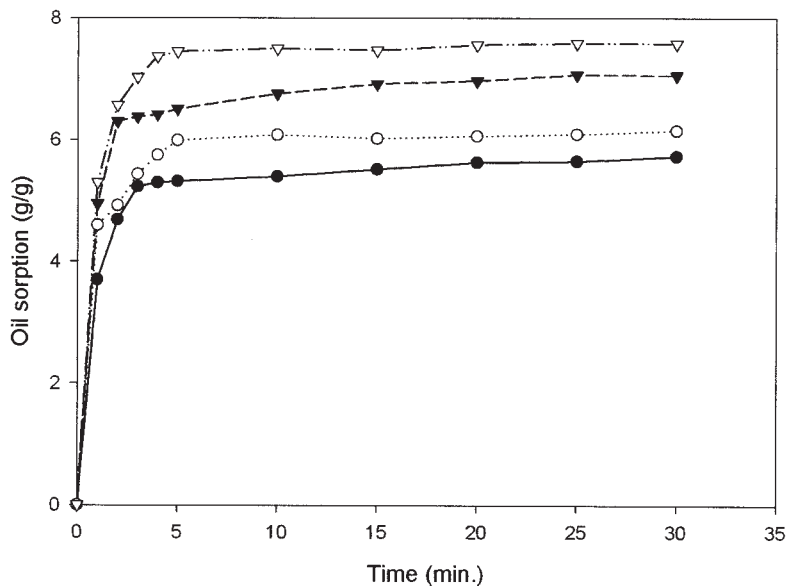


Figure 6 Weight uptake of GP2 (●) in light sweet paraffinic oil at 15°C; (○) in light sweet paraffinic oil at 35°C; (▼) in naphthenic oil at 15°C; (Δ) in naphthenic oil at 15°C.

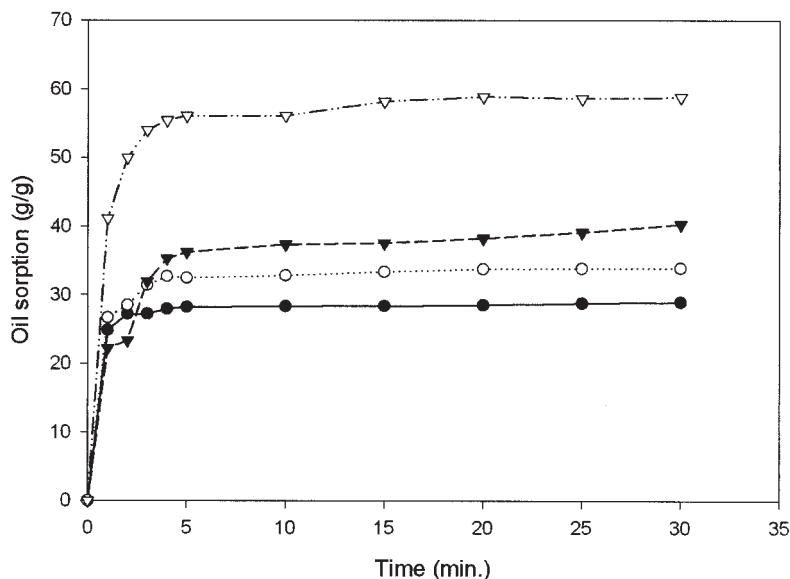


Figure 7 Weight uptake of Greenlink Erapak (●) in light sweet paraffinic oil at 15°C; (○) in light sweet paraffinic oil at 35°C; (▼) in naphthenic oil at 15°C; (△) in naphthenic oil at 35°C.

into the polymers, as the diameter of each foam sample remains constant during exposure to oil. The somewhat higher weight gain for naphthenic oil can largely be attributed to its higher density (0.9 compared with 0.8 g/cm³ at 15°C). Although the sorption curves are not presented, the dependence of oil sorption of polyurethane foams GP6 and Greenlink Erapak on temperature and density of oil is similar to that of GP2 and Instapak.

We measured oil imbibed foam weight. Initially, about 20% weight is lost but then weight remains

nearly constant, as shown in Figure 8. This shows that adequate entrapment has occurred to make the foam useful for oil spill cleanup.

The internal microstructure of polyurethane foams was observed using a desktop SkyScan 1072, an X-ray microtomography system. The reconstructed data for this analysis was a set of sequential 2D cross sections of the foam. These sequential images then were combined into a single 3D volume. Figures 9 and 10 show the reconstruction results on the internal microstructure of GP2 and Greenlink Erapak. Figures 9(A) and

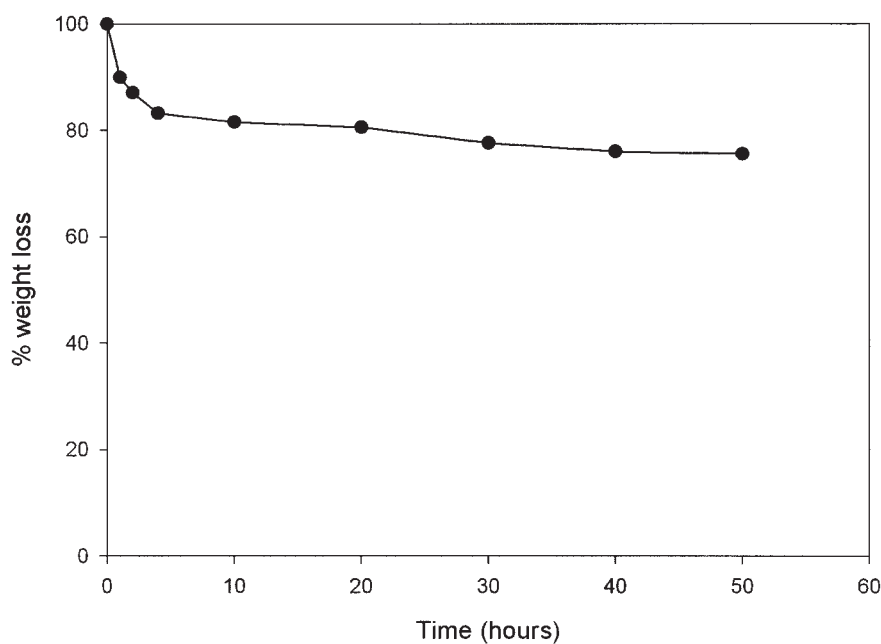


Figure 8 Weight loss of light sweet paraffinic oil imbibed Erapak.

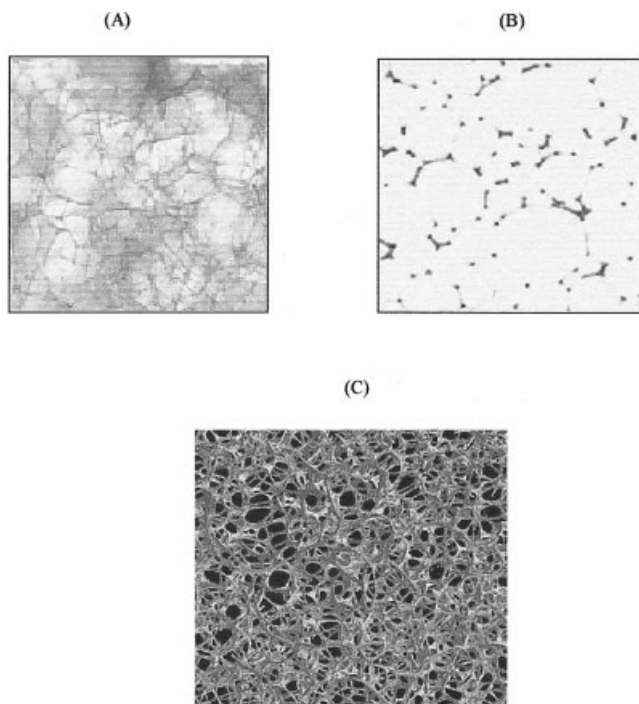


Figure 9 Microtomography reconstruction of GP2. (A) Transmission X-ray image; (B) one of the reconstructed cross sections; (C) 3D rendering of the results of reconstruction.

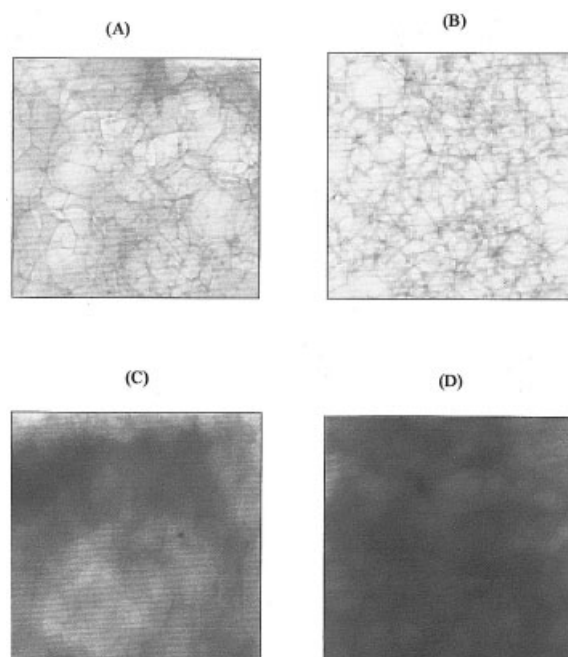


Figure 11 Shadow images of light sweet paraffinic crude oil sorbed polyurethane foams. (A) GP2; (B) GP6; (C) Greenlink Erapak; (D) Instapak.

10(A) show the shadow images through the samples. Figures 9(B) and 10(B) show one of the reconstructed cross sections. 3D renderings of the results of reconstruction are shown in Figures 9(C) and 10(C), and these clearly reflect the differences in pore density.

Figure 11 shows the shadow images of four investigated polyurethane foams after oil sorption. However, it is difficult to observe how oil diffuses from these shadow images. Reconstructed cross sections shown in Figure 12 provide much more useful information, and we now can conclude that as polyurethane foam decreases, oil diffusion into the polymer becomes easier. The darker voxels (the 3D analog of pixel) represent polymer structure in untreated polyurethane foam or polymer with oil in oil-sorbed polyurethane foam, while the lighter voxels represent void space. There are many gray levels in the volume, but a binary or black-and-white volume is required for object analysis. In this case the black pixels represent the polyurethane or polyurethane structure and sorbed oil, while the white pixels represent the empty part. Volumetric analysis thus requires taking intermediate gray levels to be classified as black or white.

CONCLUSIONS

In this research, the effect of foam density, temperature, and oil viscosity on oil sorption capacity of polyurethane was investigated. Oil sorption (g/g) increases significantly with decrease in foam density. The ultralight Instapak is capable of increasing nearly

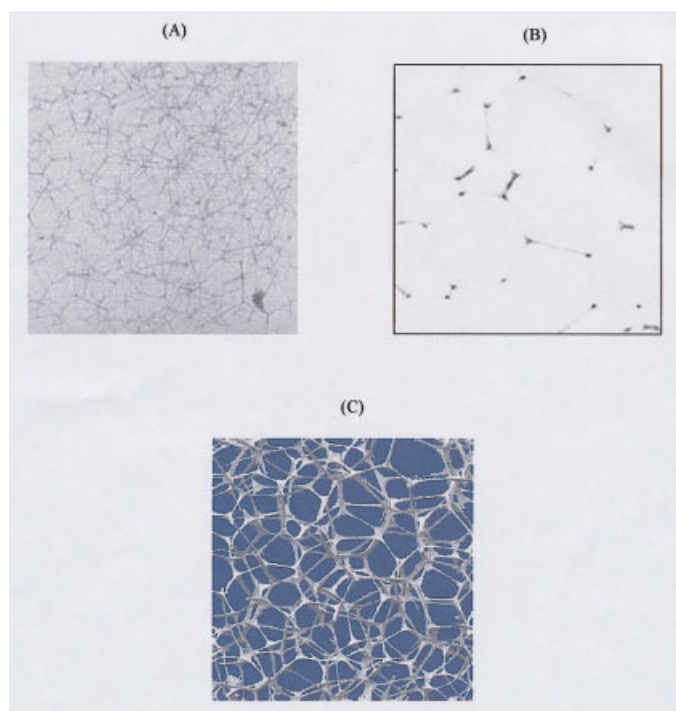


Figure 10 Microtomography reconstruction of Greenlink Erapak. (A) Transmission X-ray image; (B) one of the reconstructed cross sections; (C) 3D rendering of the results of reconstruction.

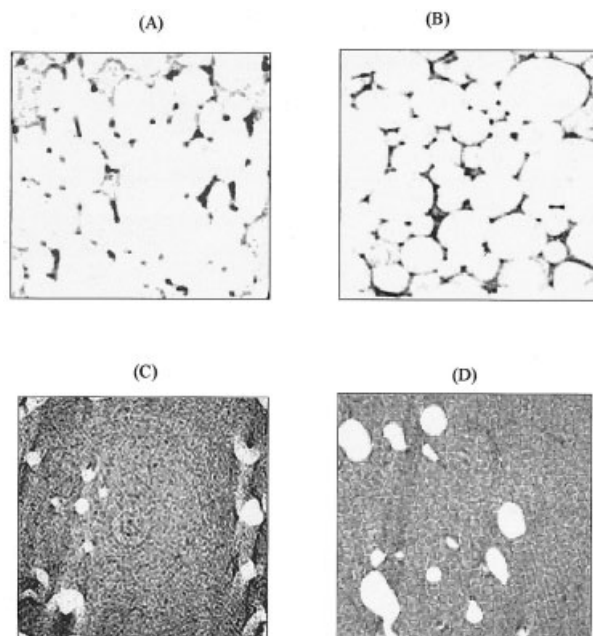


Figure 12 Cross sections of light sweet paraffinic crude oil sorbed polyurethane foams. (A) GP2; (B) GP6; (C) Greenlink Erapak; (D) Instapak.

100 times its own weight with oil, making this type of foam a potential candidate for oil spill cleanup applications. With variations in temperature and oil viscosity, oil sorption only changes slightly, making the method versatile for varying conditions of oil spill types and ambient temperatures.

X-ray microtomography was used to characterize the 3D structure of PU foam before and after oil immersion. This nondestructive reconstruction allows direct observation of oil transport through polyurethane foam.

The oil sorption proficiency of a sorbent was found to depend mainly on foam density. Polyurethane

foams not only can be “tailormade” with defined polymer foam density but also can vary in chemical composition. Future work using other raw materials will be to synthesize polyurethanes that are even more compatible with oil. We also plan direct observation of the sorption behavior using environmental scanning electron microscopy (ESEM), which is suitable at the submicrometer level, compared with the 8- μm resolution used in our X-ray CT work. ESEM also allows dynamic experiments to be undertaken due to the acceptance of volatile components in the ESEM stage, although the potential for oil contamination in the system has so far discouraged extensive studies of oil-containing polymers.

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References

1. Choi, H.; Moreau, J. P. *Microsc Res Tech* 1993, 25, 447.
2. Sefton, M. V.; Mann, J. L. *J Appl Polym Sci* 1980, 25, 829.
3. Oh, Y.-S.; Maeng, J.; Kim, S.-J. *Appl Microbiol Biotechnol* 2000, 54, 418.
4. Kalentun, P.; Buschka, A.; Schmid, A.; Stronmbom, E. SCA Hygiene Products AB, Foam Materials. US Pat. 6, 040, 494.
5. Billmeyer, F. W. *Textbook of Polymer Science*, 3rd ed.; Wiley: New York, 1984.
6. Oertel, G. *Polyurethane Handbook*; Hanser: New York, 1985.
7. Woods, G. *Flexible Polyurethane Foams*; Applied Science Publishers: London, 1982.
8. Klemperer, D.; Frisch, K. C. *Handbook of Polymeric Foam and Foam Technology*; Hanser: New York, 1991.
9. Khinnavar, R. S.; Aminabhavi, T. M. *J Appl Polym Sci* 1991, 42, 2321.
10. Shimizu, T.; Koshiro, S.; Tada, K. *J Appl Polym Sci* 1997, 65, 179.
11. Montminy, M. D.; Tannenbaum, A. R.; Macosko, C. W. *J Cell Plast* 2001, 37, 501.
12. Elliott, J. A.; Windle, A. H.; Hobdell, J. R.; EEckhaut, G.; Oldman, R. J.; Ludwig, W.; Boller, E.; Cloetens, P.; Baruchel, J. *J Mater Sci* 2002, 37, 1547.