

Effect of Cell Structure on Oil Absorption of Highly Oil Absorptive Polyurethane Foam for On-Site Use

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ABSTRACT: This article reports the effect of cell structure on oil absorption of highly oil-absorptive polyurethane foam (ON-PUR), which is suitable for on-site foaming. We have developed ON-PUR as an oil absorbing polyurethane foam using a very reactive recipe. ON-PUR was synthesized by mixing polyol, water, additives, and polymeric diphenylmethane diisocyanate (P-MDI) using a high-pressure foaming machine. Density, airflow, oil absorption of this foam, and cell structure by microscopy were measured. From these results, it was found that the airflow of this foam increased by crushing, and the oil absorption of this foam increased sharply in a narrow airflow range (from 0.1 to 0.8 scfm). This increase is estimated to be due to the decrease of closed cell structures by crushing treatment. Furthermore, we constituted on-site foaming system in bench scale, which was expected to be applicable to on-site preparation of ON-PUR. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 179–186, 1997

Key words: cell structure; oil absorption; oil-absorptive polyurethane foam; on-site foaming; air flow

INTRODUCTION

Recently, the ocean pollution by a vast outflow of oil has been noted as a big environmental problem for the earth.¹ Representative treatments of the spilt oil include usages of oil dispersant, oil gelling agent, and oil absorbent.² Brief descriptions of these treatments for oil are given. Oil dispersants are to emulsify the spilt oil, and the resulting emulsions are to be digested by some microbes in ocean; thus, the marine environment is purified in a long time. Oil gelling agents are to coagulate oil by spreading the agents over the oil, enabling the spilt oil to solidify; and the solid is recovered with, for example, a net. Oil absorbents are solid reagents to absorb the oil. As oil absorbents, a polypropylene mat and a polyurethane foam sheet have been proposed.³

Each treatment has, of course, advantages and

disadvantages; but one of the most serious ones is difficulty in recovering vast outflowed oil in the ocean. Based on this consideration, we have been developing an oil-recovering system using highly oil-absorptive polyurethane foam, which is expected to be applicable to on-site foaming, that is, preparing the foam at the site where a large amount of oil spills. In nature, polyurethane foams have a serious disadvantage, which is much bulkiness. Consequently, it is difficult to use them for the recovery of a large amount of outflowed oil. It is not practical at all to transport polyurethane foams to the site corresponding to the amount of the vast outflowed oil to be recovered. To resolve this disadvantage, on-site foaming is expected to be a most effective solution. In other words, two of the polyurethane liquid components are transported to the site of spilt oil, and polyurethane foams are produced there by mixing the two components.

Oil absorption behavior of polyurethane foams has been reported: the effect of airflow on oil ab-

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Table I The Recipe of ON-PUR

Component	Ingredient	Parts	Composition	Remarks
R	Polymer polyol	100	Styrene-modified polymer	OH value = 28.0 mg KOH/g
R	Flame retardant	10	Phosphoric ester	—
R	Surfactant A	2	Modified silicone oil	—
R	Surfactant B	0.35	Modified silicone oil	Cell-disrupting agent
R	Distilled water	9	—	—
R	Catalyst A	3	PMEA	Blowing catalyst
R	Catalyst B	1	DABCO-33LV	Gelation catalyst
P	Isocyanate	1.04 ^a	P-MDI	NCO (wt %) = 31.0

PMEA, *N,N,N',N',N''*-pentane methyl ethylene triamine; DABCO-33LV, 33% triethylene diamine in dipropylene glycol; P-MDI, polymeric 4,4'-diphenylmethane diisocyanate.

^a NCO index is 1.04 [see eq. (1)].

sorption for some polyurethane foams with normal reactivity has been investigated, and it has been pointed out that oil absorption increases with the increase of airflow.⁴ It is very probable that airflow has a great influence on oil absorption of polyurethane foams. As to the recipe of polyurethane foams for the increased airflow, it is reported that the type and concentration of surfactant and catalyst, and a few other factors, have great influence on the airflow of polyurethane foam.⁵⁻⁸ However, since a highly reactive recipe of polyurethane foam is required for on-site foaming, it is necessary to elucidate the conditions in order to achieve both high reactivity and high oil absorption of the polyurethane foam.

This study investigates the effect of cell structure on oil absorption of the polyurethane foam (ON-PUR), the recipe and the reaction conditions of which are applicable to on-site foaming. The polyurethane foam developed in this study is a promising material to treat a large amount of spilled oil for the protection of marine environments. Furthermore, we constitute the system to produce ON-PUR in succession in a bench scale level and estimate the oil absorption of ON-PUR produced by this system. The system is expected to be applicable to on-site preparation of ON-PUR.

EXPERIMENTAL

Materials

The recipe for the preparation of ON-PUR is shown in Table I. The recipe consists of R component containing polyol, catalyst, surfactant, distilled water, and additives, and P component con-

taining polymeric isocyanate (P-MDI). R component was mixed well just before use. For the forming, chlorofluorocarbons or dichloromethane have been used, but they are known to be very harmful for the atmospheric environment on the earth. In this study, they were not used, and only distilled water was employed as a blowing agent.

Preparation of ON-PUR

The polyurethane foaming reaction occurs between R and P components.⁹ In this study, as the recipe of ON-PUR was highly reactive, R and P components were mixed with a high-pressure foaming machine. The weight of polymeric isocyanate per 100 g of polyol is determined according to the following NCO index, defined by eq. (1).

$$\begin{aligned} \text{NCO index} &= \text{polymeric isocyanate (meq/g)} \\ &\times \text{the weight of isocyanate (g)/} \\ &[\text{polyol (meq)} + \text{distilled water (meq)}] \quad (1) \end{aligned}$$

The temperature of the R component was kept at $50 \pm 3^\circ\text{C}$, and the temperature of the P component was kept at $30 \pm 3^\circ\text{C}$ in a tank. The injection pressures of R and P components were adjusted to 120 kg/cm^2 . The skin layer of the prepared ON-PUR was removed, and the ON-PUR was cut to a prescribed size by a foam cutter. Conventional polyester foam (ES-PUR; density = 28.0 kg/m^3 ; Inoac Co.) and conventional high resilience foam (HR-PUR; density = 38.0 kg/m^3 ; Toyo Tire & Rubber Co.) were selected to compare the properties with ON-PUR. To study the effect of airflow, ON-PUR and HR-PUR were treated with crush-

ing, that is, mechanical treatment to increase airflow; while ES-PUR was treated with 5 wt % potassium hydroxide solution to increase the airflow ON-PUR, ES-PUR had airflow below 0.1 (scfm), and HR-PUR had 1.97 (scfm) without any treatment. Here, the airflow value stands for the volume of air passing through each specimen in a minute; thus, the unit is represented by scfm, whose dimension is ft^3/min .

Oil Absorption Measurements

The oil used for the oil absorption experiment was EL-X-1 (Nippon Petroleum Co., $97.56 \text{ mm}^2/\text{s}$, at 20°C , whose viscosity was almost similar to that of B heavy oil at 20°C). Specimens of a diameter of 45 mm and a thickness of 10 mm was used in oil absorption experiments. After each specimen was immersed in the oil for a prescribed time, the weight of absorbed oil was measured. Oil absorption was calculated by eqs. (2) and (3), as follows:

$$\begin{aligned} \text{Oil absorption (g/g)} \\ &= \text{a weight of absorbed oil (g)} \\ &\quad / \text{foam weight (g)} \quad (2) \end{aligned}$$

$$\begin{aligned} \text{Oil absorption (g/cm}^3\text{)} \\ &= \text{a weight of absorbed oil (g)} \\ &\quad / \text{foam volume (cm}^3\text{)} \quad (3) \end{aligned}$$

Airflow Measurements

The airflow of each specimen was measured according to ASTM D3574 by an airflow meter (Model 82-FPI foam porosity instrument, Fluid Data Inc.). The size of the specimen was of $2 \times 2 \times 1$ in.

Cell Structure Observation

The cell structure of each foam with or without treatment was observed by a video microscope (Model VH-6100, Keyence Co.).

RESULTS AND DISCUSSION

Features of ON-PUR Preparation

Rise time of ON-PUR with the recipe shown in Table I was about 3 s. Here, rise time stands for the time required for a foam to reach its maximum height since mixing R and P components. The core

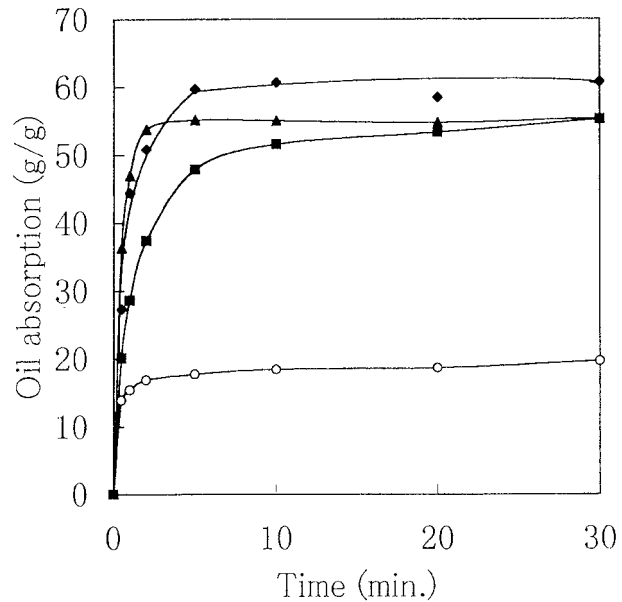


Figure 1 Behavior of oil absorption of ON-PUR at various airflows: (O) below 0.1, (■) at 0.34, (◆) at 0.79, and (▲) at 1.16 scfm.

density was found to be 17.5 kg/m^3 . ON-PUR was able to be produced without any problems, such as shrinkage, scorching, collapse, etc., in the producing process. It was confirmed that the recipe of ON-PUR afforded a much more reactive system and ON-PUR showed higher blowing expansion ability than HR-PUR and ES-PUR. It is expected that the high reactive recipe of ON-PUR leads to higher productivity of ON-PUR on-site, and higher expansion of ON-PUR gives rise to much larger oil absorbing polyurethane foams.

Effect of Cell Structure on Oil Absorption of ON-PUR

Figure 1 shows the behavior of oil absorption against time of ON-PUR at various airflows. Oil absorption (g/g) increased with time and attained an equilibrium state at which the oil absorption (g/g) remained almost constant. However, oil absorption (g/g) below 0.1 scfm (with no treatment) hardly increased with time. Oil absorption (g/g) and the rate of it increased with the increase of airflow, except in the case in which airflow of ON-PUR was 1.16 scfm. For comparison, the behaviors of oil absorption against time of HR-PUR and ES-PUR at various airflows are shown in Figures 2 and 3, respectively. The behavior of HR-PUR and ES-PUR was similar to that of ON-PUR. For example, oil absorption (g/g) increased with time,

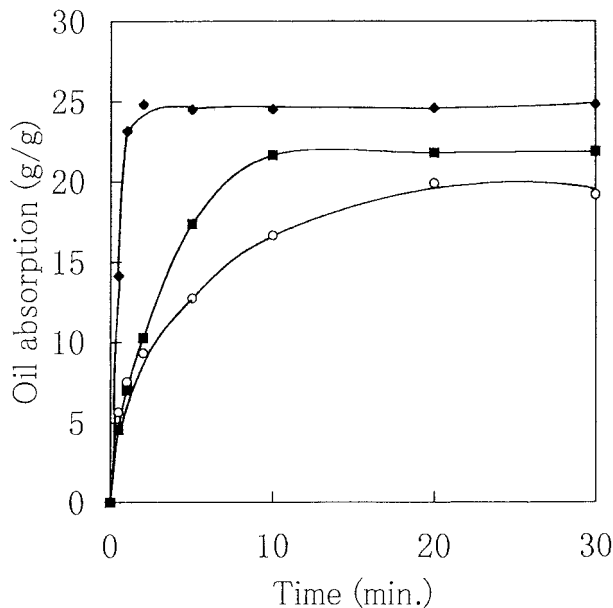


Figure 2 Behavior of oil absorption of HR-PUR at various airflows: (O) at 1.97, (■) at 3.33, and (◆) at 4.74 scfm.

and the rate of it increased with the increase of airflow. But, as airflow of HR-PUR was 1.97 (scfm) without any treatment, oil absorption (g/g) of it increased gradually with time and attained an equilibrium state.

The relation between oil absorption (g/g) at 5

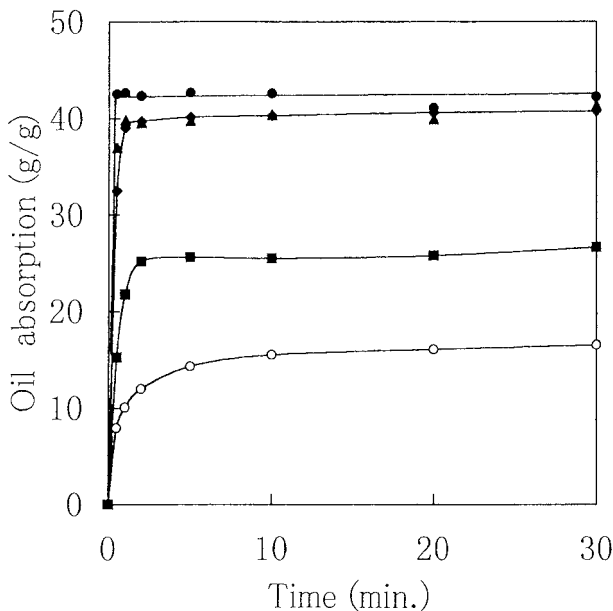


Figure 3 Behavior of oil absorption of ES-PUR at various airflows: (O) below 0.1, (■) at 0.35, (◆) at 2.75, (▲) at 5.58, and (●) at 7.10 scfm.

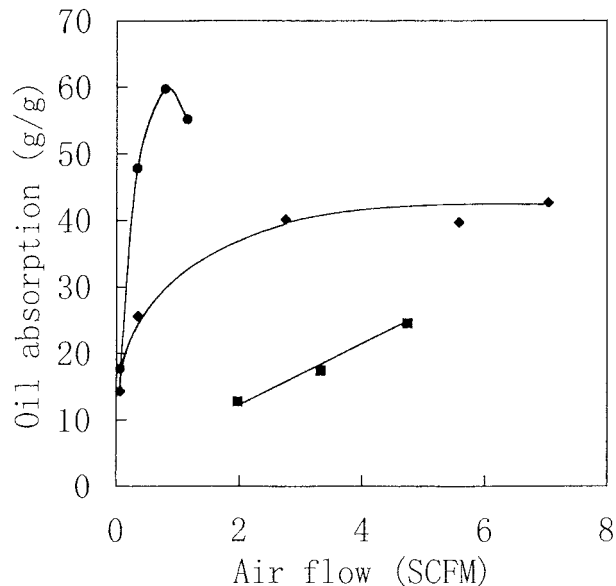
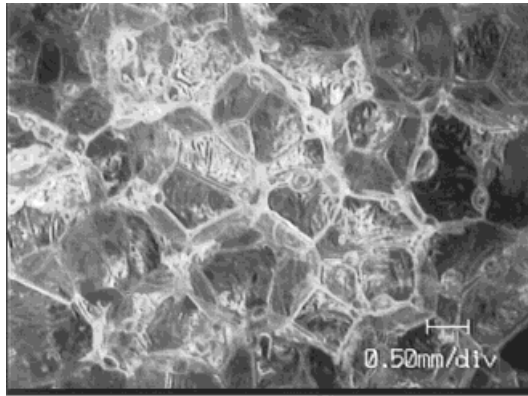


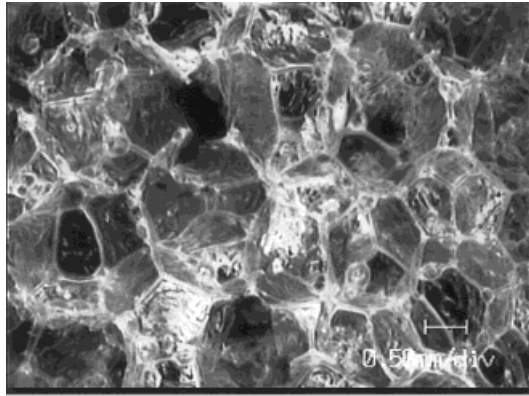
Figure 4 Relation between oil absorption (g/g) at 5 min (soaking in the test oil for 5 min) and airflow of each specimen: (●) ON-PUR, (◆) ES-PUR, and (■) HR-PUR.

min (soaking in the test oil for 5 min) and airflow of each specimen is shown in Figure 4. ON-PUR showed a higher oil absorption (g/g) than the others. This result is estimated to be due to the lower density of ON-PUR than those of the others. Furthermore, the effect of airflow for oil absorption (g/g) at 5 min (soaking in the test oil for 5 min) was different among their foams. Especially, oil absorption (g/g) of ON-PUR increased with the increase of airflow in a narrow range (from 0.1 to 0.8 scfm).

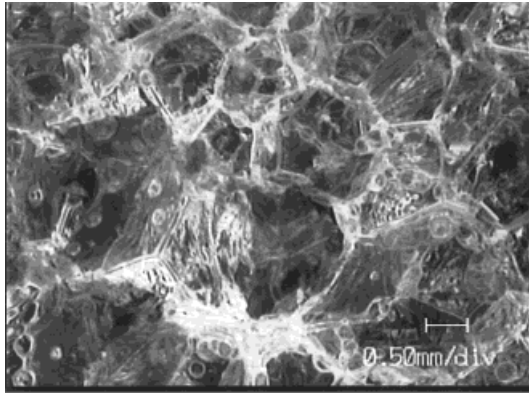
To study the relation between oil absorption and cell structure more, cell structures of ON-PUR, HR-PUR, and ES-PUR were observed with a video microscope. Figure 5(a-c) shows the photographs of ON-PUR at 0.06, 0.79, and 1.16 scfm airflow, respectively. Figure 6(a-c) shows the photographs of HR-PUR at 1.97, 3.33, and 4.74 scfm airflow, respectively; and Figure 7(a-c) shows the photographs of ES-PUR at 0.06, 2.75, and 7.1 scfm airflow, respectively. ON-PUR had a closed cell structure before the crushing. The partial rupture of cell structure of ON-PUR with crushing treatment was observed as shown in Figure 5, while HR-PUR had some open cell structures in addition to the closed cell structures before the treatment. Cell structures of HR-PUR were not varied with the increase of crushing treatment, as shown in Figure 6. ES-PUR, as it was, consisted of closed cell structures; but closed



(a)



(b)



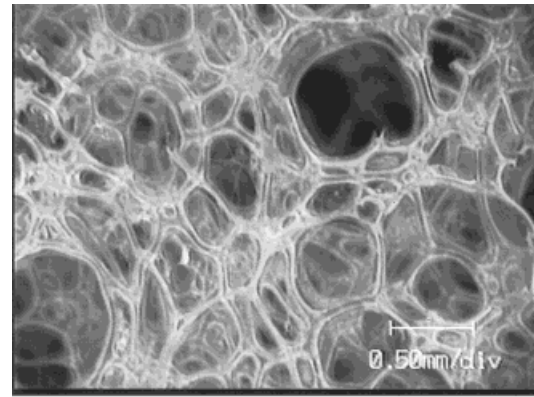
(c)

Figure 5 Photographs of ON-PUR at (a) 0.06, (b) 0.79, and (c) 1.16 scfm airflow, respectively.

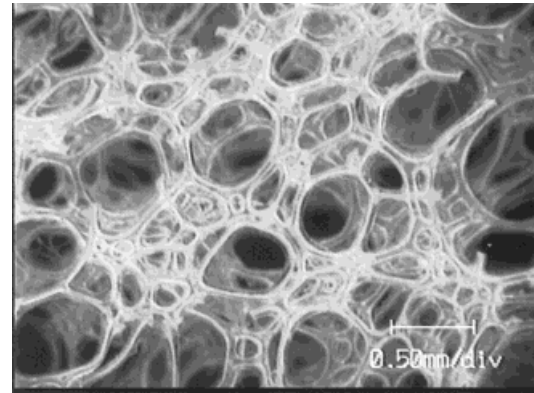
cell structures of ES-PUR were changed to open cell structures gradually with increasing alkali treatment (soaking in potassium hydroxide solution).

When the airflow of ON-PUR was below 0.1

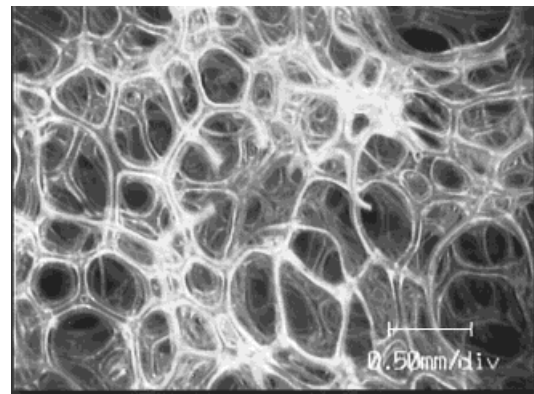
scfm (with no treatment), oil absorption (g/g) hardly increased with time. This is estimated to be due to the nonavailability of the space for absorbing oil because the closed cell structure was predominant. Oil absorption (g/g) of ON-PUR in-



(a)



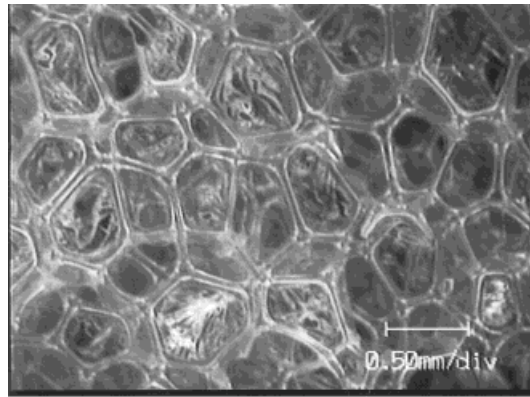
(b)



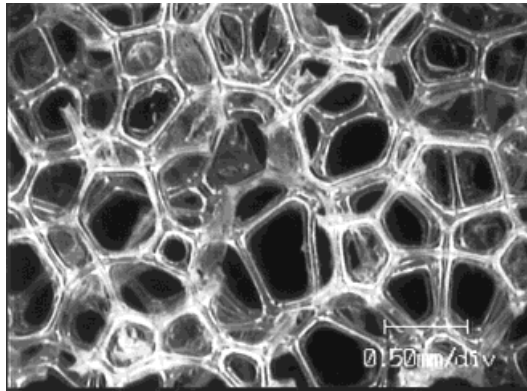
(c)

Figure 6 Photographs of HR-PUR at (a) 1.97, (b) 3.33, and (c) 4.74 scfm airflow, respectively.

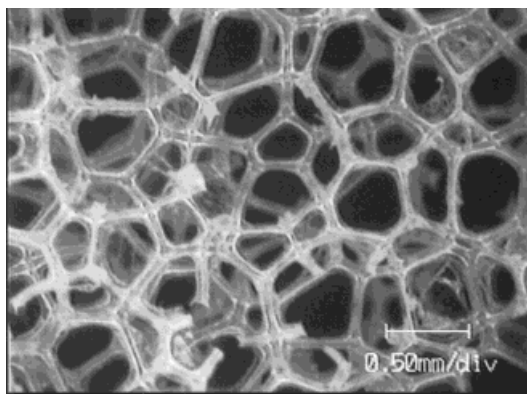
creased sharply, with airflow increased in a narrow range (from 0.1 to 0.8 scfm). This increase of airflow in the narrow range was supposed to be due to a partial breaking of cell membranes of ON-PUR with the crushing treatment. On the



(a)



(b)



(c)

Figure 7 Photographs of ES-PUR at (a) 0.06, (b) 2.75, and (c) 7.1 scfm airflow, respectively.

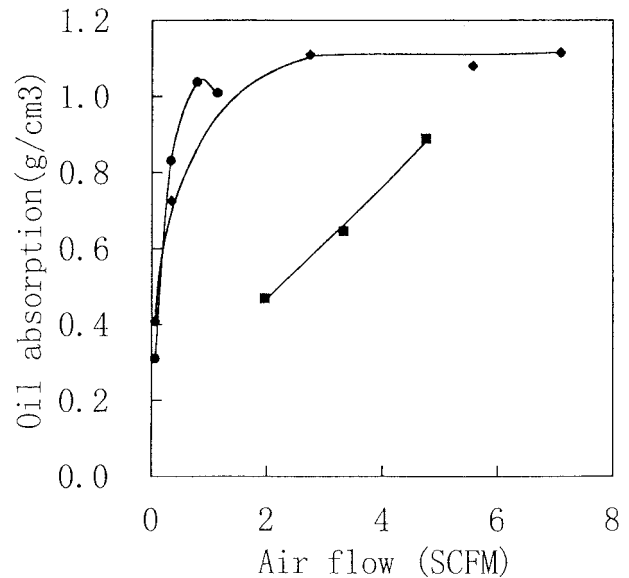


Figure 8 Relation between oil absorption (g/cm^3) at 5 min (soaking in the test oil for 5 min) and airflow of each specimen: (●) ON-PUR, (◆) ES-PUR, and (■) HR-PUR.

contrary, dissolution of cell membranes of ES-PUR with increasing alkali treatment was estimated to increase the airflow in a wide range (from 0.1 to 7.1 scfm) and, hence, the increase of oil absorption. Cell membranes of HR-PUR was very resilient so that it was difficult to break cell membranes of HR-PUR with the crushing treatment.

In addition, the effect of the foam's density for oil absorption was studied. Figure 8 shows the relation between oil absorption (g/cm^3) and air flow at 5 min (soaked in the test oil for 5 min). Compared to Figure 4, the behavior of oil absorption per foam volume against airflow was similar to that of oil absorption per foam weight. However, oil absorption (g/cm^3) of ES-PUR was almost the same as that of ON-PUR. This result suggests that the availability of the space in ES-PUR for absorbing oil is almost similar to that of ON-PUR. Thus, it is obvious that oil absorption (g/cm^3) was independent of density of foam.

Development of On-Site Foaming System

It is apparent that the recipe of ON-PUR is a very highly reactive one, and ON-PUR is highly oil-absorptive with crushing treatment. Thus, it is expected to be a promising material to treat a

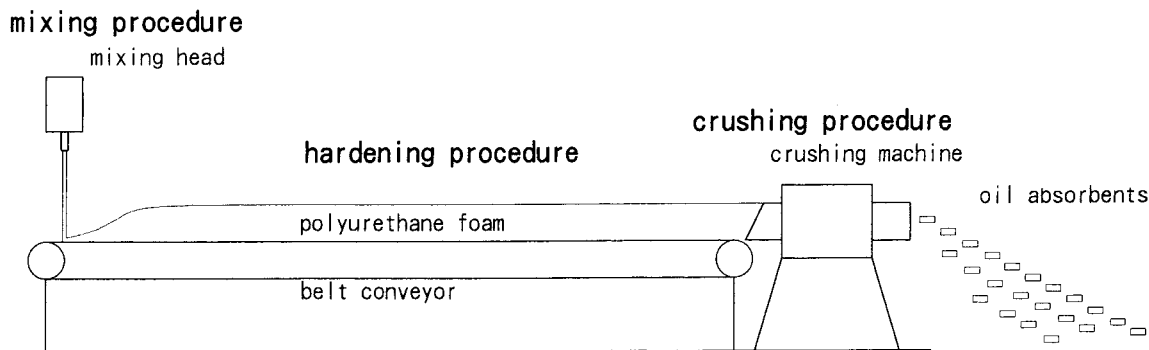


Figure 9 Concept of apparatus for producing ON-PUR *in situ*.

large amount of spilt oil for the environmental protection with on-site foaming.

We constituted on-site foaming system in bench scale, which was expected to be applicable to practical on-site foaming. Figure 9 shows the concept of apparatus for producing ON-PUR *in situ*, and Table II shows the conditions for the on-site forming system.

This system consisted of mixing, hardening, and crushing procedures. In the mixing procedure, the polyurethane reactants were flowed from a mixing head of a high-pressure foaming machine. In the hardening procedure, the reactants foamed and hardened on the conveyer, which was made of fluorocarbon polymers. At the final stage of the crushing procedure, the hardened polyurethane foam was crushed and cut in a certain size by the crushing machine (Model UG-102; IEC Co.). Mixing and hardening procedures and hardening and crushing procedures were connected so that it was possible to produce ON-PUR in succession from

mixing two of polyurethane liquid components to crushing and cutting of the resulted polyurethane foam. The features of ON-PUR in this system is shown in Table III.

Oil absorption (g/g) of the present ON-PUR in this system was 40.8 g/g. This oil absorption (g/g) was lower than that of ON-PUR in the previously mentioned specimen, and its size was as follows: diameter, 45 mm; thickness, 10 mm; density, 17.5 kg/m³. This decrease was supposed to be due to a skin layer of the ON-PUR by this system, which was not oil-absorptive, and the density of it was much higher than the core density. However, it is confirmed that the ON-PUR by this system still kept a high oil absorption (g/g) and is able to be produced without any troubles in bench scale at the site. Furthermore, it is expected that the development of this on-site foaming system in bench scale to a practical level will make a great contribution for the recovery of vast outflowed oil in marine environments.

Table II Conditions for On-Site Forming System

Procedure	Apparatus	Condition, Model, Maker, etc.
Mixing	Foaming machine	MEG-HK-135
	Mixing head	MX-12
	Injection pressure	120 kg/cm ²
	Liquid temperature (<i>P</i>)	30 ± 3°C
	Liquid temperature (<i>R</i>)	50 ± 3°C
	Flow rate	3.1 kg/min
Hardening	Belt conveyer	Belt: SL-8F(GR)TS (Bando Chem. Co.)
	Conveyor length	5.8 m
	Conveyor speed	8.5 m/min
Crushing	Crushing machine	UG-102 (IEC Co.)
	Crusher speed	8.5 m/min

Table III ON-PUR in an On-Site Forming System

Feature	Result
Rise time (s)	About 3
Appearance	Crushed foam, including skin layer
Foam size (mm)	About 24 × 24 × 100
Density (kg/cm ³)	25.0 (including skin layer)
Oil absorption (g/g)	40.8

CONCLUSION

ON-PUR was developed for absorbing polyurethane foam with very reactive recipe, and the effect of cell structure on oil absorption of ON-PUR was investigated. The results were summarized as follows. Oil absorption (g/g) of HR-PUR and ES-PUR increased with the increasing airflow by removing their cell membranes, but oil absorption (g/g) of ON-PUR sharply increased with the increasing airflow in a narrow range (from 0.1 to 0.8 scfm). This increase is estimated to be due to the decrease of closed cell structure by crushing treatment. Furthermore, an on-site foaming sys-

tem was constructed in a bench scale, which enabled us to produce ON-PUR in succession from on-site foaming to crushing and cutting; and it was confirmed that the oil absorption (g/g) of the ON-PUR by this system was more than 40 g/g by 5 min of immersion in oil.

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