12-Hydroxystearic acid의 리튬 염을 셀 개방제로 사용한 개방 셀 구조의 경질우레탄 폼

안원술†⑩ · 이준만*

계명대학교 화학공학과, *영남이공대학교 화장품화공계열
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Open-Cell Rigid Polyurethane Foam Using Lithium Salt of 12-Hydroxystearic acid as a Cell Opening Agent

WonSool Ahn†⑩ and Joon-Man Lee*

Department of Chemical Engineering, Keimyung University, Daegu 42601, Korea
Division of Cosmetics Chemistry, Yeungnam Univeresity College, Daegu 42415, Korea
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초록: 일반적인 독립 셀 구조의 경질 폴리우레탄 폼을 제조하기 위한 조성비에 12-hydroxystearic acid의 리튬 염 (Li-12HSA)을 셀 개방제로 사용하여 개방 셀 구조를 가지는 경질 폴리우레탄 폼을 제조하기 위한 연구를 진행하였다. Li-12HSA는 일반적인 폴리우레탄 폼 조성에 사용되는 실리콘 계면활성제를 기유로 사용하여 합성되었고 기유내에 나노스케일로 잘 분산되도록 하였다. 실험의 결과로서 약 1.0 phr의 Li-12HSA가 사용된 샘플 폼에서 거의 100%의 셀 개방률을 나타내어 Li-12HSA가 적절한 셀 개방제로 사용될 수 있음을 보여주었다. 이는 폼 생성 과정 중에서 폴리우레탄의 주사슬에 Li-12HSA가 곁사슬로 형성되어 셀 개방에 크게 영향을 미치기 때문인 것으로 생각되었다. 또한 생성된 개방 셀 구조의 경질 우레탄 폼은 독립셀 구조의 폴리우레탄 폼의 기계적 특성을 크게 저해하지 않으면서도 바람직한 셀 크기, 벌크 밀도, 및 열전도도 특성을 가지는 것으로 나타났다.

Abstract: Cell opening characteristics of a polyurethane foam (PUF) with conventional formulation for a closed-cell rigid PUF was studied using lithium salt of 12-hydroxystearic acid (Li-12HSA) as a cell-opening agent. The cell-opening agent, Li-12HSA, was properly prepared in the surfactant silicone oil, in which it existed as uniformly distributed in nanoscale. Cell opening content of nearly 100% could be obtained for the sample with *ca.* 1.0 phr of Li-12HSA. As the results, it showed that a fully open-cell rigid PUF could be obtained by introducing Li-12HSA as a new reactive cell opener, having a functional group which is able to form a bulky flexible side-chain on PU main chains. Furthermore, the formed open cell rigid PUF showed desirable cell size, bulk density, and thermal conductivity without severe loss of mechanical properties compared to those of the closed-cell PUF which was made without Li-12HSA.

Keywords: open-cell, rigid polyurethane foam, lithium 12-hydroxystearic acid, cell opening agent.

Introduction

Polyurethane foams (PUFs) are prepared by the condensation polymerization of component A and B, in which component A is mainly composed of a polyol, a catalyst, a foam stabilizer, and a blowing agent and component B is mainly a polymeric isocyanate. The components are mixed together so that reaction is carried out with foaming process. PUF is generally classified into three groups according to foam types, which are flexible, semi-flexible, and rigid. Among them, closed-cell rigid PUF is widely used as the thermal insulating material in refrigerators, buildings, storage tanks, and pipings etc. because of its low thermal conductivity and good processibility.[1-4]

Meanwhile, development of more energy efficient materials having better thermal insulation properties becomes an essential task due to the recent trends of global warming or drastic decrease of natural resources.[5,6]

Since thermal conductivity of closed-cell rigid PUF is greatly dependent on the blowing gas such as chlorofluoro-carbons (CFCs) or cyclopentane (CP), it is impossible to make a closed-cell rigid PUF of which thermal conductivity is smaller than that of the blowing gas.[7,8]

Vacuum insulation panel (VIP) is, therefore, recently getting attention as one of the alternative solutions to this problem, which is composed of a core material, getter, and an airtight metal-laminated plastic film packaging.[9-12]

Open-cell rigid PUF as the core material of VIP has many advantages compared to the inorganic core materials such as glass fibers or perlite in viewpoints of workability, density, and cost.[13-15]

There are two critical problems to be solved for utilizing the open-cell rigid PUF as the VIP core material. One of them is that PUF should have very small-size cells to retain the low thermal conductivity for the long service time, because the thermal conductivity of PUF is proportionally dependent on the cell size.[16,17] The other more important one is that it should have no closed cells. If the foam has even a small amount of closed cells, the blowing gas in those cells seeped out grad-ually into the VIP as time passes so that the pressure inside VIP rises, reducing greatly in the thermal insulating perfor-mance of the VIP.[16-18]

Cell opening during foaming process of PUF is carried out through the complex mechanisms.[19-24] Among the various cell opening mechanisms proposed by many researchers, cell-opening by urea precipitation is one of the generally approved mechanism, which is originally proposed by Rossmy and coworkers.[22] They proposed that the cell opening always occurs after urea precipitation regardless of the formulation used, as is consistent with the classical particle defoaming mechanism. Neff also proposed that the precipitated urea would trigger the cell-opening process due to the rapid increase in the foam matrix viscosity, since the particles act as physical cross-links which make the system unstable by hin-dering of the surfactant diffusion.[20]

Various liquid or solid types of cell opening agent are con-ventionally used for cell opening in the rigid PUF during foaming process.[25] Typical examples of liquid type are polydimethylsiloxanes or the derivatives of high molecular weight poly(oxyalkylene).[26] However, the main disadvantage with use of such a liquid type cell opener is that the cell open-ning tends to occur early in the foaming reaction, thus, making a coarse cell structured PUF and consequently unattractive thermal insulation properties. On the other hand, solid types such as divalent metal salts of fatty acids, typically calcium stearate, or polymeric solid powders can be also used as cell openers.[13,14] Another adverse effects, however, may be caused in this case such as the mechanical wear due to the use of solid inorganic powders or non-uniform dispersion.

In the present study, therefore, we tried to find a new method to overcome the above mentioned problems by using the lith-ium salt of 12-hydroxystearic acid (Li-12HSA) as a reactive cell opening agent. A grease, in which Li-12HSA is finely dis-persed in a silicone base oil, was prepared by the reaction of LiOH with 12HSA through the conventional method of grease fabrication.[27] Because –OH functional group of Li-12HSA can react with isocyanate to make a bulky and rod-like side chain during PUF formation, it was expected that they can play an efficient role on the cell opening process. The focus of the work, therefore, was on the cell opening effect of Li-12HSA during the PUF foaming process using a conventionally opti-mized formulation for a closed-cell rigid PUF. Open-cell con-tent, cell morphology, thermal conductivity, and mechanical properties of resulted samples were also measured.

Experimental

Materials. The polyol used for rigid PUF was a polyether-based polyol (KP-999C, KPX Chemical Co., Korea), having a hydroxyl value of 410 mgKOH/g. The isocyanate used was a modified-polymeric MDI (diphenyl methane 4,4'-diisocyanate, Kumho-Mitsui Chemical Co., Korea), having NCO value of 31.0%. Other components were catalysts (triethylene diamine, Tin-derivatives), modified-silicone surfactants. Distilled water were used as chemical blowing agents. Li-12HSA was prop-erly prepared as below and used as a reactive cell opening agent. For the sysnthesis of Li-12HSA, lithium hydrate (LiOH·H$_2$O) of purity 99.995% and 12-hydroxystearic acid (12HSA) of purity >80% were used as purchased from Merck and Tokyo Chemical Industry Co., respectively. Typical formu-lation for the rigid PUF used in the present study is represented in Table 1.

Preparation of Li-12HSA. Li-12HSA used as cell opener in the present study was prepared by the neutralization reaction of lithium hydrate (LiOH·H$_2$O) with 12HSA in the presence of silicone base oil which was just the same as the silicone sur-factant in Table 1. A grease, in which Li-12HSA was uni-formly dispersed in the base silicone oil, was prepared through the following procedures:

1) 700 g of the silicone oil surfactant and 177.9 g of 12HSA

Table 1. Typical Formulation for a Rigid PUF

Component	Description	Chemicals	Composition [phr]*
Component A	Polyol	PEG derivatives	100.0
	Catalyst	Amine/Sn	1.45
	Blowing agent	Distilled Water	2.0
	Surfactant	Modified silicone oil	3.0
	Cell-opener	Li-12HSA	0 - 1.5
Component B	Isocyanate	Modified MDI	146.4

*Parts per hundred polyol by weight.

(0.59 mol) were poured together into 3 L-glass container and raised temperature up to 100 °C during mixing with 1900~3600 rpm.

2) 22.1 g of LiOH·H$_2$O (0.53 mol) was dissolved in approximately 100 mL of distilled water at 70 °C and the solution was gradually added in the above 12-HSA container for about 30 min, by which the acid-base neutralization reaction of LiOH·H$_2$O with 12HSA is carried out to form Li-12HSA.

3) After reaction was finished, remaining water in the product was removed completely by heating the container gradually up to 200 °C with slow mixing for about 1 h, and cooled down again slowly to room temperature.

4) High viscosity grease-type mixture of Li-12HSA/silicone oil surfactant, in which solid content of Li-12HSA was 30% by weight, was finally prepared with post-treatment by roll-mill and filtration.

Preparation of Open-cell Rigid PUF. Each of 1, 2, 3, 4, and 5 phr of the mixture of Li-12HSA/silicone oil surfactant was blended with the component A in Table 1. Total composition of surfactant in the blend was balanced to 3 phr by addition of surfactant separately. Stoichiometric amount of component A and B as given in Table 1 was mixed together with drastic stirring at 5000 rpm for 6 sec and poured immediately into the open-mold of 200 mm×200 mm×200 mm dimensions. After free-rising foaming process is completed, the sample was post-cured for 24 h at room temperature.
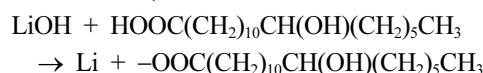
Characterization. Synthesis of Li-12HSA was confirmed using FTIR (Jasco FTIR-620). Open-cell content of the sample foam was measured by an air flow pycnometer (Tokyo Science, Air Comparison Pycnometer 1000) using the sample of 20 mm×20 mm×20 mm dimension. Cell morphology was examined using scanning electron microscopy (SEM, Tescan Vega II LSH SS-V). The bulk density of the sample was directly calculated from the known dimension and weight.

Thermal conductivity of the foam was measured by a thermal conductivity analyzer (Laser Comp, HC-074) using the sample of 200 mm×200 mm×200 mm dimension. Measurements was carried out by setting constant temperatures of 10 and 38 °C on the upper- and below-plates, respectively. Compressive stress-strain measurement was performed using universal stress-strain tester (KST-S, Kyoung Sung Tester Co., Korea) with compressive mode. Samples cut with 20 mm×20 mm×20 mm were measured with compressive strain rate of 2.0 mm/min at room temperature.
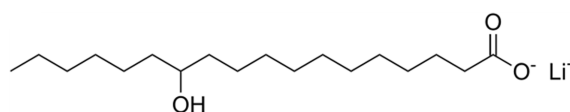
Results and Discussion

Synthesis of Li-12HSA. There is well-known by many researchers that, when Li-12HSA is properly synthesized as grease type by the neutralization reaction of LiOH with 12HSA in the base oil, it exists as a fine dispersion of crystallized lithium soap in the oil, usually in the form of long, twisted and well-entangled fibers.[28-31] More recently Sanchez and co-workers showed this fine dispersion state through atomic force microscopy (AFM).[31] Chemical structure of Li-12HSA is shown in Figure 1.

Since the neutralization reaction between LiOH and 12HSA occurs as follows;

$$\text{LiOH} + \text{HOOC(CH}_2)_{10}\text{CH(OH)(CH}_2)_5\text{CH}_3$$
$$\rightarrow \text{Li} + {}^-\text{OOC(CH}_2)_{10}\text{CH(OH)(CH}_2)_5\text{CH}_3$$

characteristic peaks due to the asymmetric carboxylate stretching associated with Li$^+$, $^-$OOC- group appear at around 1560 and 1580 cm^{-1} in the FTIR spectrum.[27,32] Since, considering the low purity of 12HSA, its molar amount was somewhat over-calculated, an excess LiOH peaks are found in the spectrum and is considered as the result from the incorrect molar ratio of LiOH·H$_2$O/12HSA, showing a slight molar lack of 12HSA. When referring more published reports,[33,34] therefore, it is considered that Li-12HSA in the present work was also properly synthesized as explicitly shown in FTIR spectrum of Figure 2.

Open-cell Content and Bulk Density. Change of open-cell content measured by an air flow pycnometer is shown in Figure 3 as a function of Li-12HSA concentration.
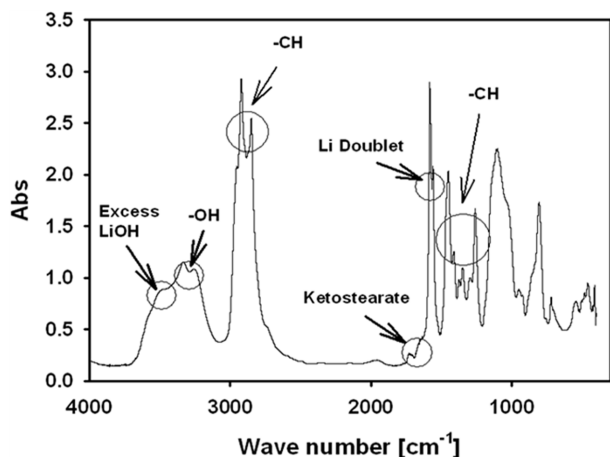

Figure 1. Chemical structure of Li-12HSA.

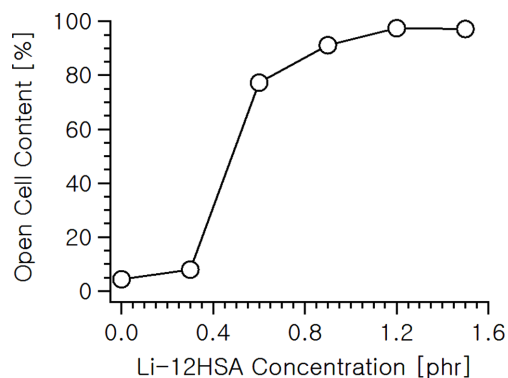**Figure 2.** FTIR spectrum of Li-12HSA dispersed in silicone surfactant oil.

Figure 3. Open-cell content as a function of Li-12HSA concentration.

Figure 4. Bulk density of the samples as a function of Li-12HSA concentration.

Figure 5. Thermal conductivity of the samples as a function of Li-12HSA concentration.

As is shown evidently, while the open-cell content of the sample without Li-12HSA is below 5.0%, it increases drastically in the Li-12HSA concentration range of 0.3~0.6 phr and reach to nearly 100% at about 1 phr. This remarkable cell-opening characteristics of Li-12HSA was considered as the results that –OH functional group in the Li-12HSA molecule could react with isocyanate during the foaming process to form a bulky, flexible side chains of the Li-12HSA salt on the PU main chains, which is able to play a more effective role on the cell-opening. As is mentioned in the introduction part, cell-opening in a PUF foaming process is triggered always by the precipitated urea particles which may act as the physical crosslinks, making the system unstable by hindering of the surfactant diffusion.[20] When considering this cell-opening mechanism, it may be concluded that molecularly dispersed Li-12HSA, which is dangling as the chemically bonded side-chains along the PU molecules, may be more effective to make the system unstable, which resulted in cell-opening.
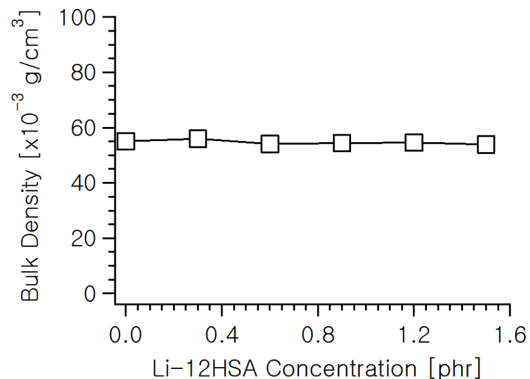
On the contrary, the bulk density of the samples was nearly constant as 54.0×10^{-3} g/cm^3 regardless of Li-12HSA concentration as shown in Figure 4.

Thermal Conductivity. Thermal conductivity of the samples is given in Figure 5, showing nearly constant about 31.0 mW/m·°K. As mentioned above, thermal conductivity of the rigid PUF is greatly dependent on the blowing gas.

Because the samples in the present work were prepared by using distilled water as blowing agent, CO_2 gas formed by the reaction with isocyanate with H_2O in the foaming process is initially filled in the foam, which is gradually replaced with air in the case of open-cell PUF. When considering the thermal conductivities of CO_2 and air are 16.8 and 26.2 mW/m·°K at 27 °C, respectively, almost same values with slight increase in thermal conductivity for the samples can be easily understood.

Cell Morphology. Figure 6 shows the SEM micrographs of the rigid PUF perpendicular to the foam rise direction with Li-12HSA of 0.9 phr.
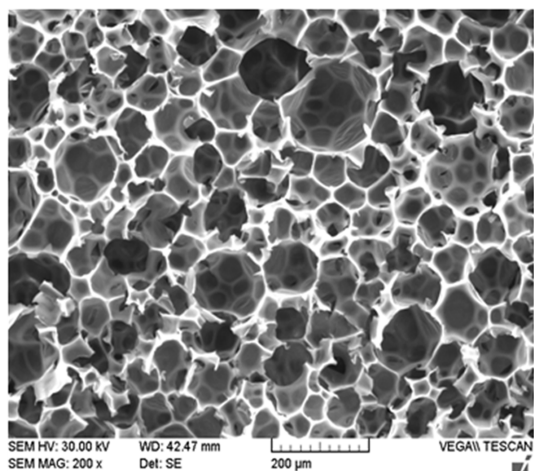
Figure 6. SEM micrograph of the rigid PUF prepared with Li-12HSA of 0.9 phr.
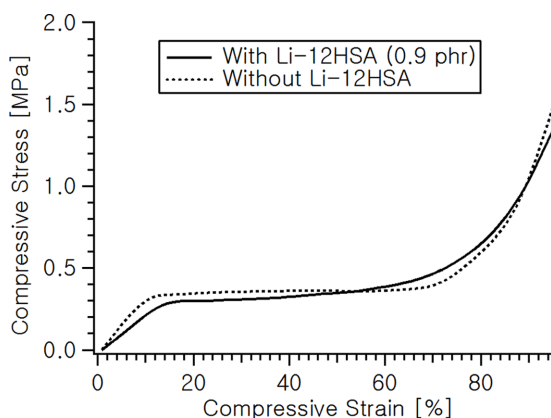

Figure 7. Compressive strengths of the rigid PUF samples with and without Li-12HSA.

As clearly shown in the figure, most of the cell windows of the sample are observed to exist as nearly all broken and connected state. Cells which are partially open and connected with pinholes can be also observed. This fact is consistent with data for the measurement of open-cell content of the samples as already shown in Figure 3. On the other hand, cell size distribution is observed to be somewhat non-uniform, which is considered as the result from the disturbance of the reacting system due to the formulation change by Li-12HSA.

Mechanical Property. Mechanical properties of rigid PUF samples prepared with and without Li-12HSA is compared by the compressive strength as shown in Figure 7.

Though somewhat decrease of yield strength might be observed at sample prepared with Li-12HSA, significant differences in the compressive strength could not be found

between two samples exhibiting yield strength of *ca.* 0.32±0.02 MPa at about 14±2% of compressive strain. This fact may also be understood from SEM images in Figure 6. As shown in the figure, though the open-cell structure and comparatively broader cell size distribution may tend to weaken the compressive strength compared to that of closed-cell structure of the rigid PUF, cell struts of the both foams are present at the networked-state regardless of the cell structures, exhibiting similar extent of compressive strength. From the results of these facts, therefore, it is considered that a 100% open-celled rigid PUF may be prepared using only a small amount of Li-12HSA without significant damage of mechanical properties.

Conclusions

Cell-opening characteristics of a Li-12HSA as a reactive cell-opening agent with a conventional formulation for the closed-cell rigid PUF was investigated.

Li-12HSA was used as a new reactive cell-opening agent for a PUF foaming process and was confirmed to work properly, showing drastic changes of cell-opening content at concentration range of 0.3~0.6 phr and reach to nearly 100% at about 1 phr, which was also confirmed with SEM micrographs. It was considered from the results that molecularly dispersed Li-12HSA, which is dangling as the chemically bonded side-chains along the PU molecules, may be more effective to make the system unstable, which resulted in cell-opening.

On the other hand, while open-cell content increases drastically with Li-12HSA, other properties such as the bulk density and thermal conductivity of the samples were observed to be nearly not changed regardless of Li-12HSA concentration. And mechanical properties like compressive strength also showed little significant changes.

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