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푸리에 적외선 분광법을 이용한 폴리우레탄 폼 황변 정량화 평가

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Quantitative Evaluation of the Yellowing Polyurethane Foam by Fourier-Transform Infrared (FTIR) Spectroscopy

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초록: 다양한 재료에서 원하지 않는 변색은 중요한 문제로, 종종 그들의 고유한 특성을 손상시킨다. 특히 폴리머복합재는 빛 노출, 열적 조건 및 산화와 같은 환경적 요인에 매우 민감하여 변색을 초래할 수 있다. 본 연구에서는 자동차 산업에서 음향 흡수를 위해 중요한 재료인 폴리우레탄 폼(polyurethane foam, PUF)의 변색 정도를 정량적 으로 평가하는 것을 목표로 한다. 푸리에 적외선 분광법(Fourier transform infrared spectroscopy, FTIR) 스펙트럼을 각 샘플에 대해 얻어, 변색이 더 심한 PUF 샘플과 덜 변색된 PUF 샘플 사이에서 중요한 스펙트럼 차이를 확인한다. 특히, 비대칭 CH_2 결합(2900 cm^{-1})과 대칭 CH_2 결합(2850 cm^{-1})의 강도 비율 I(비대칭 CH_2 at 2900 cm^{-1})/I(대 칭 CH_2 at 2850 cm^{-1})를 조사하여 각 PUF 샘플의 변색 정도를 정량적으로 구분하여 한다. I(비대칭 CH_2 at 2900 cm^{-1}) / I(대칭 CH_2 at 2850 cm^{-1}) 값이 높을수록 PUF의 변색 정도가 더 크다는 것을 의미한다. 이는 염색단으로 작용하는 비대칭 CH_2 결합 때문이다. 이러한 구조적 비대칭성은 빛을 강하게 흡수하는 조건을 만들고, 결과적으로 황 변이나 다른 염색단 거동과 같은 visible dislocation을 초래한다. 우리는 C-O-C의 황변 및 적색 시프트 간의 반 상관관계가 PUF의 많은 변형을 초래한다는 사실을 알아내었다. I(비대칭 CH_2 at 2900 cm^{-1}) / I(대칭 CH_2 at 2850 cm^{-1})의 값이 높고, C-O-C 피크 위치의 적색편이 변화하는 실험적 반비례 현상은 변색 정도를 더 명확히 입증할 수 있다. 본 연구는 시각적 검사만으로는 명확하지 않은 폴리우레탄의 원래 변형(예: 변색, 황변)에 대한 통찰을 제공할 수 있는 길을 열어줄 수 있다.

Abstract: Unwanted discoloration in various materials is a significant issue, often compromising their unique properties. Polymer composites, in particular, are highly susceptible to environmental factors such as light exposure, thermal conditions, and oxidation, which can lead to discoloration. In this study, we aim to quantitatively assess the degree of yellowing in polyurethane foam (PUF), a crucial material for sound absorption in the automotive industry. Fourier-transform infrared spectroscopy (FTIR) spectra are obtained for each sample, revealing significant spectral differences between more yellowed and less yellowed PUF samples. Specifically, the intensity ratio I(asymmetric CH_2 at 2900 cm^{-1}) / I(symmetric CH_2 at 2850 cm^{-1}) is investigated to quantitatively differentiate the degree of yellowing in each PUF sample. A higher I(asymmetric CH_2 at 2900 cm^{-1}) / I(symmetric CH_2 at 2850 cm^{-1}) value indicates a greater degree of yellowing in PUF. This can be attributed to the asymmetric CH_2 bonds in PUF, which act as chromophores. Their structural asymmetry creates conditions that favor strong absorption of light, resulting in visible discoloration, such as yellowing or other chromophoric behaviors. Also, we found that the anti-correlation between yellowing and red-shifting of C-O-C leads to more deformation of PUF. This experimental anti-correlation phenomenon between higher I(asymmetric CH_2 at 2900 cm^{-1}) / I(symmetric CH_2 at 2850 cm^{-1}) and red-shift of C-O-C peak position change can substantiate the degree of yellowing more evidently. This work may pave the way for providing insights into the original polyurethane deformation (*e.g.*, discoloring, yellowing), which may not be apparent through visual inspection alone.

Keywords: polyurethane foam, yellowing, Fourier-transform infrared spectroscopy, chromophore.

Introduction

Polyurethane plays a pivotal role in various industries as a versatile material capable of adjusting flexibility and strength

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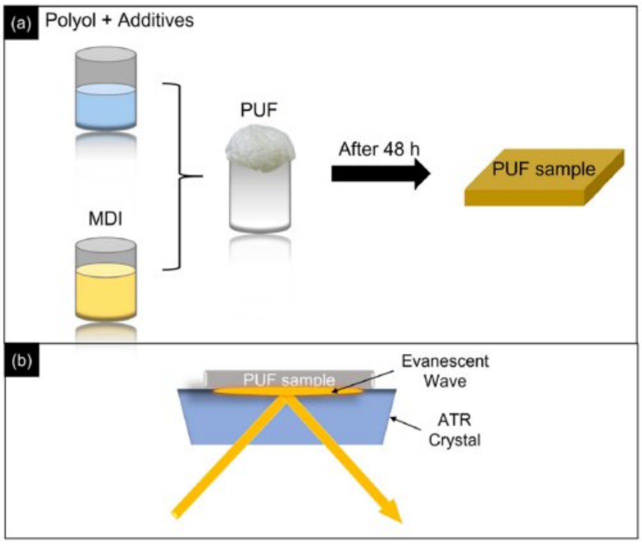
to suit diverse applications. It is widely utilized in manufacturing mechanical parts and structures due to its exceptional strength and durability.[1,2] In the furniture industry, polyurethane is employed for crafting foam pads, sheets, and cushions and serves as a material for footwear in the fashion sector. Additionally, it serves as an adhesive to fortify architectural structures with robust bonding materials.[3,4] Specifically, polyurethane foam (PUF), produced through a chemical reaction between isocyanate and polyol, is instrumental in fabricating automotive seats, steering wheels, interior components, and more. Its attributes include durability, lightweight properties, and excellent sound absorption capabilities.[5-7] One critical element for improving sound absorption performance involves actively controlling the open cell size of PUF in a hierarchical manner.[8-10] Adjusting the mixing ratio between isocyanate and polyol or incorporating additives such as catalysts or surfactants into the polyol has been encouraged to enhance PUF's sound absorption performance in automobiles. Yuan and colleagues investigated the incorporation of Al_2O_3 nanoparticles.[11] They found that filling PUF with Al_2O_3 nanoparticles effectively enhances sound absorption performance in the low-frequency range by creating larger single cavity holes. Research by Shafig and co-workers explored the acoustic behavior of wood fibers.[12] They demonstrated that increasing the thickness with higher filler loading (~20%) improves the sound absorption coefficient (α), attributed to forming a structure with relatively smaller pore sizes (open cells) in PUF. Lee and colleagues investigated the tuning effect of sound absorption frequency by adjusting the open cell size in PUF through graphene oxide (GO) impregnation.[13] They highlighted that sound-absorbing properties can be significantly enhanced by GO impregnation. Specifically, the properties can be tailored to maximize absorption within specific frequency ranges by varying the density of GO impregnation, utilizing its ability to navigate tortuous paths and longer passages even at the same thickness. Apart from achieving hierarchical open cell formation, another critical challenge in enhancing sound absorption performance is addressing discoloration events, such as yellowing in polyurethane foam (PUF).[14-16] Yellowing signifies chemical changes or degradation in the material, potentially altering its physical properties, including porosity, density, and elasticity, all of which can impact sound absorption characteristics. Yellowing in PUF is primarily attributed to exposure to light (including UV), heat, and oxidation processes. It often results from the breakdown of chemical bonds within the foam's structure, leading to the formation of chromophores (molecules responsible for color) due to surrounding light irradiation.[17,18] Various methods have been proposed for quantitatively assessing the degree of yellowing in PUF. Thermal analysis techniques such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) can evaluate the thermal stability and decomposition behavior of PUF.[19,20] However, these methods do not directly provide information on yellowing associated with chemical structural changes. Colorimetry is another method suggested for estimating the degree of yellowing in PUF. However, it requires a reference sample to obtain quantitative information, which can introduce uncertainties and potential errors. Spectroscopic analysis using UV-Visible spectroscopy is also a viable approach for quantitatively evaluating the degree of yellowing in PUF. Yellowing involves the formation of chromophores that absorb light at specific wavelengths. UV-Visible spectroscopy can quantify these absorption changes, offering a measure of yellowing intensity. Nevertheless, quantifying yellowing based solely on single absorption peak intensity in UV-Visible spectroscopy may introduce systematic errors due to variations in sample thickness, position, and weight, potentially hindering exact quantitative comparisons.

Here, we aim to develop a new and straightforward characterization method to quantify the degree of yellowing using Fourier-transform infrared spectroscopy (FTIR). FTIR spectra are capable of detecting functional groups associated with oxidation or degradation products that contribute to yellowing.



Scheme 1. (a) shows the schematic image for producing PUF from mixing between polyol+additives and methylene diphenyl diisocyanate (MDI); (b) after 48 h curing time, the PUF samples are loaded onto the ATR crystal to obtain FTIR spectrum.

Changes in peak intensities or shifts in absorption bands can indicate the extent of yellowing. Specifically, we utilize the intensity ratio I (asymmetric CH_2 at 2900 cm^{-1}) / I(symmetric CH_2 at 2850 cm^{-1}) to quantitatively and simply assess the degree of yellowing in PUF. This ratio serves as a representative measure because changes in the intensity of these bands reflect alterations in the polymer structure due to aging, degradation, or exposure to environmental factors. This structural change can lead to the formation of chromophores and subsequent emission of yellow color. Normalizing intensity between these two bands minimizes systematic errors, enhancing the reliability of the method.

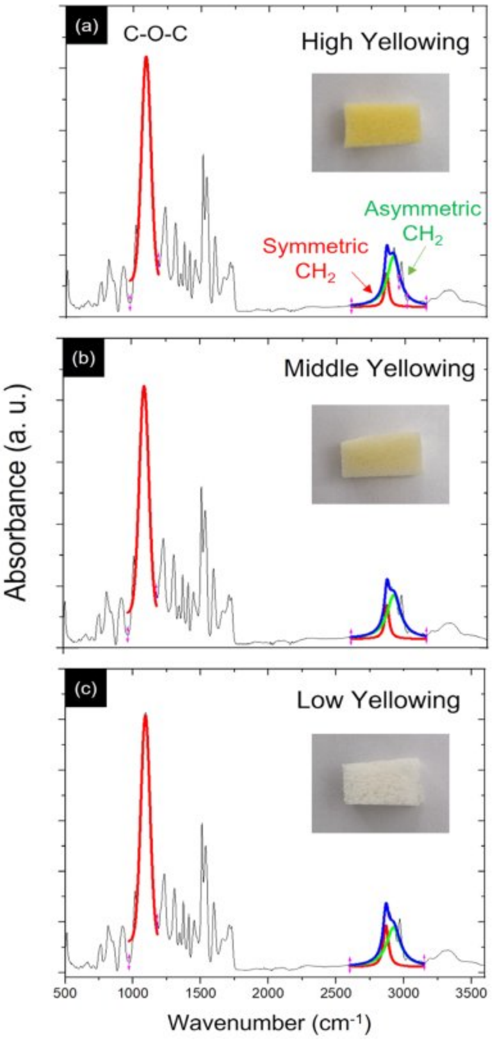


Figure 1. (a, b, c) show the FTIR spectra obtained from the high yellowing (HY), middle yellowing (MY), and low yellowing (LY) PUF samples, respectively. The PUF samples corresponding to each spectrum are displayed in the respective insets. The peaks at ~1090 cm^{-1} in each spectrum is fitted as a single peak, while the symmetric and asymmetric CH2 bonds are deconvoluted into red and green curves.

Experimental

Polyol and methylene diphenyl diisocyanate (MDI) were purchased from BASF Korea. Various additives, including catalysts, surfactants, and chain extenders, were incorporated into the polyol. The liquid polyol and MDI were mixed at a specific ratio and then poured simultaneously into an open paper mold to produce free-rise polyurethane foam (PUF). Subsequently, the PUF was allowed to cure at room temperature for 48 hours. Samples were then cut into specific sizes for Attenuated Total Reflection (ATR) type FTIR experiments, as shown in Scheme 1. ATR-FTIR, which is a very convenient system for obtaining not only liquid- but solid type samples such as film and foam, is employed for obtaining IR spectrum from PUF samples. The spectral resolution is 2 cm^{-1} and the FTIR spectra are obtained by 4 times accumulation.

Results and Discussion

Figure 1 shows the representative FTIR spectra obtained from the High Yellowing (HY), Middle Yellowing (MY), and Lower Yellowing (LY) of the PUF samples. The inset images display the samples used to obtain the corresponding FTIR spectra. The PUF samples used in this work are prepared by varying the illumination time: approximately 10 days for the high yellowing (HY) samples, 4 days for the middle yellowing (MY) samples, and a few hours for the low yellowing (LY) samples. First of all, during the formation of polyurethane, isocyanates (–NCO groups, ~2270 cm^{-1}) react with alcohols (–OH groups) to form urethane linkages (–NH–COO–). This reaction consumes the isocyanate groups. When the NCO peak disappears or decreases significantly in the FTIR spectrum, it usually means that the isocyanate groups have been used up in the reaction, indicating the formation of polyurethane linkages. Thus, a reduction or disappearance of the NCO peak can be associated with a higher degree of polyurethane linkage formation in this work. Previously, Tarkiewicz and colleagues reported on yellowing issues of PUF due to varying storage temperatures over 10 weeks.[16] They demonstrated that differential scanning calorimetry (DSC) indicated an average increase in the glass transition temperature (T_g) by 15% and 80% for samples heated at 40 ℃ and 80 ℃, respectively. However, their work did not include qualitative or quantitative characterization of yellowing. Singh and colleagues explored the relationship between photo-oxidation and PUF yellowing.[21] They suggested that the transformation of MDI with π-electrons played a cru-

Table 1. Quantitative Value of the Degree of Yellowing

Degree of PUF yellowing	I (asymmetric CH_2) / I (symmetric CH_2)	Max peak position of C-O-C
Higher yellowing (HY)	4.85 ± 0.20	1090.3 ± 0.306
Middle yellowing (MY)	4.01 ± 0.05	1091.2 ± 1.506
Lower yellowing (LY)	2.50 ± 0.10	1093.2 ± 0.288

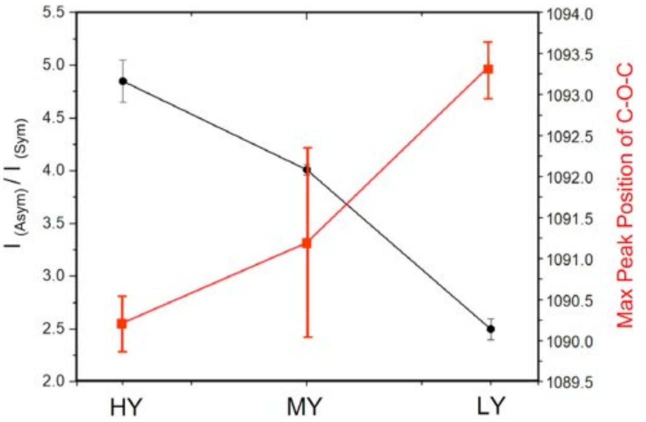


Figure 2. Anti-correlation between I(asymmetric CH_2 at 2900 cm^{-1}) / I(symmetric CH_2) and the maximum peak position of C-O-C peak is exhibited.

cial role in yellowing under visible light irradiation. While their research was valuable in uncovering the chemical reaction mechanisms behind PUF yellowing, appropriate characterization methods were not specified. Building on these previous studies,[16,21] we propose a straightforward method for characterizing PUF yellowing using FTIR. Initially, the region from 2800 to 2950 cm^{-1} in Figure 1 is selected to analyze the intensity ratio between asymmetric CH_2 and symmetric CH_2, which are deconvoluted as green and red curves, respectively. The C-O-C peak (at 1090 cm^{-1}, skeletal bond of polyurethane) is also fitted as a single peak to determine its maximum position, while the symmetric and asymmetric CH_2 bonds are deconvoluted into red and green curves. Specifically, we can use the ratio of intensities between the asymmetric CH_2 band at 2900 cm^{-1} and the symmetric CH_2 band at 2850 cm^{-1} to quantitatively assess the degree of yellowing in PUF, defined as, I (asymmetric CH_2 at 2900 cm^{-1}, green curve) / I (symmetric CH_2 at 2850 cm^{-1}, ref curve). Indeed, chemical degradation involves changes in the molecular structure of PUF, where the CH_2 stretching bands in FTIR spectra are particularly sensitive to alterations in the polymer's chemical environment and structure. The asymmetric CH_2 band (around 2900 cm^{-1}) and the symmetric CH_2 band (around 2850 cm^{-1}) are especially informative in this regard. The variations in these bands can indicate structural changes due to oxidation.

The ratio I(asymmetric CH_2 at 2900 cm^{-1}) / I(symmetric CH_2 at 2850 cm^{-1}) serves as a quantitative metric of yellowing, which inversely correlates with changes in the maximum peak position of the C-O-C stretching vibration band (The maximum position value of each C-O-C band is obtained by single gaussian peak fitting). The C-O-C stretching vibration band is a skeletal feature of polyurethane, a class of polymers formed by the reaction of diisocyanates with polyols, resulting in a urethane linkage (-NHCOO-) in their backbone structure. The C-O-C bonds primarily originate from the polyol component during polyurethane synthesis.[18,22] In cases of yellowing, an increase in the ratio of I (asymmetric CH_2 at 2900 cm^{-1}) / I (symmetric CH_2 at 2850 cm^{-1}) is often observed due to the formation of conjugated double bonds or other unsaturated groups that absorb more strongly in the region of the asymmetric CH_2 band. Table 1 summarizes the values of I (asymmetric CH_2 at 2900 cm^{-1}) / I(symmetric CH_2 at 2850 cm^{-1}) and the corresponding maximum peak positions of the C-O-C peaks. The range of change in the I(asymmetric CH_2 at 2900 cm^{-1}) / I (symmetric CH_2 at 2850 cm^{-1}) ratio is wider than that of the maximum peak position of C-O-C. Nevertheless, a clear anti-correlation between them can be observed. In other words, a higher value of the I (asymmetric CH_2 at 2900 cm^{-1}) / I (symmetric CH_2 at 2850 cm^{-1}) can be indicative of the formation of chromophores in PUF. During oxidative degradation of PUF, such as exposure to oxygen or UV light, chemical changes occur in the polymer structure. This can lead to the formation of conjugated double bonds or other unsaturated groups, which are often associated with chromophores.[15,20]

Such changes are consistent with the red-shift of the C-O-C peak position; higher yellowing indicating higher chemical degradation and a greater probability of chromophore formation may exhibit weaker bond strength in the skeletal back-bone C-O-C band of PUF, as shown in Figure 2. The exact position of this peak can be influenced by the chemical environment and structural changes within the PUF, causing a shift towards lower wavenumbers (red-shift) in the FTIR spectrum.

Conclusions

In this study, we propose a method to quantitatively assess the degree of yellowing in polyurethane foam (PUF). Fourier-Transform Infrared Spectroscopy (FTIR) spectra were obtained for each PUF sample, revealing significant spectral differences between more and less yellowed samples. Specifically, we investigated the intensity ratio of the I (asymmetric CH_2 at 2900 cm^{-1}) / I (symmetric CH_2 at 2850 cm^{-1}) to differentiate the degree of yellowing in PUF samples. A higher value of the I (asymmetric CH_2 at 2900 cm^{-1}) / I (symmetric CH_2 at 2850 cm^{-1}) indicates a greater degree of yellowing in PUF. Furthermore, we observe a direct experimental anti-correlation between higher the I (asymmetric CH_2 at 2900 cm^{-1}) / I (symmetric CH_2 at 2850 cm^{-1}) and a red-shift in the C-O-C peak position, which provides further substantiation of the degree of yellowing.

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Conflict of Interest: The authors declare that there is no conflict of interest.

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