Komatsu Technical Report

Technical Paper

The Degradation Mechanism of High-Strength Polyurethane Elastomers in the Presence of Water

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This paper focuses on the deterioration of ester polyurethanes used in hydraulic components, and reports on the quantitative evaluation of the deterioration state and changes in chemical structure. Polyurethane is often used in construction machinery and is characterized by high mechanical strength and durability in harsh operating environments. However, the thermal effects of sliding and operation in aqueous environments can decrease the mechanical properties of polyurethane, resulting in defects. In order to understand the causes of these defects and take appropriate corrective measures, it is important to accurately evaluate the deterioration state of polyurethane. It is also necessary to know the deterioration mechanism in order to verify whether changes in the deterioration state are correctly detected. In this study, ester polyurethanes used in hydraulic components were experimentally deteriorated, and the degree of deterioration was evaluated by Fourier Transform-Infrared Spectroscopy (FT/IR), and changes in chemical structure were analyzed by Liquid Chromatography-Mass Spectrometry (LC-MS). In this way, new knowledge was obtained about the deterioration state under actual operating conditions.

Key Words: *Polyurethane, Hydrolytic deterioration, Infrared spectrometry, FT/IR, Liquid chromatography mass spectrometer, LC-MS*

1. Introduction

Steel is the primary material used in construction machinery, while many resin materials are also used due to their demanding characteristics. In particular, sealing materials for sliding parts must be both flexible and mechanically strong to prevent oil from leaking and dust and muddy water from entering from the outside. They must also resist oil, water, and heat generated by sliding. For this reason, high-strength polyurethane, which combines mechanical strength and environmental resistance, was selected as one of the materials for the seals.

However, because polyurethane is a resin, decreasing properties due to deterioration is inevitable. In particular, we consider chemical changes to be the main cause of the decrease in mechanical properties. To clarify the causes of decreasing properties in actual use and to take appropriate countermeasures, it is important to quantitatively understand the property changes over time under the environment in which the material is used and to understand what external factors in the environment are involved in the chemical changes that affect the properties of the material.

As shown in **Fig. 1**, polyurethanes (mainly elastomers) are composed of isocyanates, polyols, and chain extenders, and their mechanical and deterioration properties vary depending on each component’s type and molecular weight. Among these, polyol components are classified into ether, ester, carbonate, and lactone systems according to their bonding. The main properties of each polyol are that ether-based polyols have high hydrolysis resistance but average mechanical properties, while ester-based polyols (including lactone-based polyols) have low hydrolysis resistance but high mechanical properties. Also, polycarbonates have high hydrolysis resistance and mechanical strength but are challenging to process. In this way, each polyol product has its own characteristics [1]. In this study, we used polyurethane, which is in use, and conducted experiments to determine its resistance to water and temperature. Lactone-based polyurethanes, in which polycaprolactone diol with ester bonds is the polyol, were used and immersed in warm water. The chemical changes over time were measured using FT/IR.

The measurement results of these samples showed that the characteristic absorption of ester bonds caused by hydrolytic deterioration decreased over time, but the characteristic absorption of urethane bonds, which was expected not to undergo any change, increased [2]. Although deterioration may cause the bonds to break and new bonds to form, and their characteristic absorption may increase in strength over time, the reason for the increase in absorbance of the characteristic absorption of the urethane bonds in this experiment is unknown.

In this report, using polyurethane, whose structure was clarified using the polyol component identification method reported previously [3], we performed LC-MS analysis of the components dissolved in hot water and bulk residue in the soaking water. We clarified the hydrolysis mechanism of caprolactone-based polyurethane from the degradation reaction products and estimated the mechanism by which the characteristic absorption of urethane bonds increased.

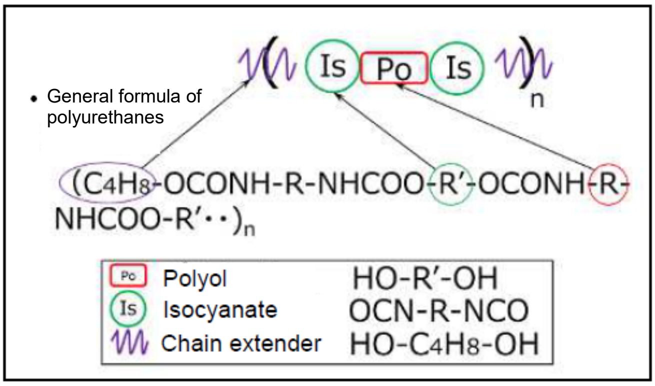


Fig. 1 General structure of polyurethanes

2. Analysis and experiments

2.1 Samples for analysis

The caprolactone-based polyurethane we used was composed of polycaprolactone diol (PCLD) as the polyol, tolidine diisocyanate (TODI) as the isocyanate, and 1,4-butanediol (BD) as chain extender. Furthermore, the binding substance of polycaprolactone diol was identified as diethylene glycol using a selective degradation method of urethane bonds by pyridine. The structure of the polyurethane used in this test is shown in **Fig. 2** [4].

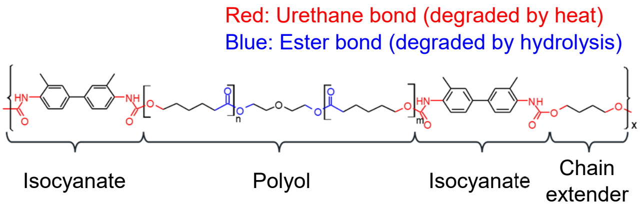


Fig. 2 Structural formula of polyurethane

2.2 Sample preparation

Weighed polyurethane was placed in a polypropylene bottle filled with a fixed volume of ultrapure water and immersed in water at an arbitrary temperature for a fixed period. The removed polyurethane and the immersion solvent were used as the hydrolytic deterioration test product and the hydrolytic deterioration test solvent, respectively, as analysis samples.

2.3 FT/IR measurement

To evaluate the degree of deterioration by IR absorbance, thin-film samples (target film thickness: 5 μm) were cut from the hydrolytic deterioration test products for each temperature-time level using a Leica-made microtome.

FT/IR microscopic IR measurements were performed using an infrared spectrometer (FT/IR-6600) and a microscope unit (IRT-5200) manufactured by JASCO Co. The average absorbance measured at eight locations within the thin film sample was used.

The absorption wavelength peak of the carbonyl group derived from the urethane bond (1,697 $\mathrm{cm^{-1}}$) and the peak of the carbonyl group derived from the ester bond in polycaprolactone (1,743 $\mathrm{cm^{-1}}$) were used as characteristic absorption wavelengths for evaluation. The FT/IR spectrum of polyurethane obtained in this experiment is shown in **Fig. 3** [5].

2.4 LC-MS measurement and structural analysis

The hydrolytic deterioration test solvent was used for analysis directly, and the hydrolytic deterioration test product was dissolved in dimethyl sulfoxide (DMSO) for analysis. For the LC-MS analyzer, UPLC-QTofMS (LC: ACQUITY UPLC H-Class PLUS, MS: XevoG2-XS QTof) manufactured by Waters was used. For the column, ACQUITY BEHC18 (50 mm long, 2.1 mm i.d., 1.7 μm in particle size) manufactured by Waters was used. The gradient conditions of the mobile phase are shown in **Table 1**. Accurate mass measurements of the components eluted in the hydrolytic deterioration test solvent and the components of the hydrolytic deterioration test product were performed by MS, and their structural analyses were performed by MS/MS using the collision method. The collision voltage was set at 30 eV.

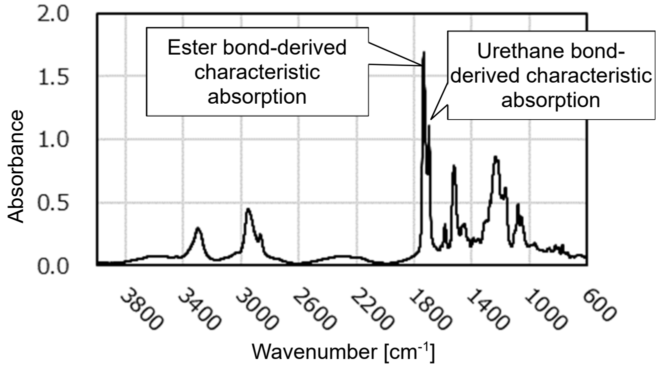


Fig. 3 IR spectra of ester-based polyurethanes

Table 1 Gradient conditions

Time [min]		0	3	6	15
Gradient mixing ratio [%]	10 mM ammonium formate solution	95	95	30	30
	Acetonitrile	5	5	70	70

3. Results and discussion

3.1 FT/IR analysis results of hydrolytic deterioration test products

Figure 4 and **5** show the variation of the IR peak intensity of the ester bond-derived carbonyl group and the IR peak intensity of the urethane bond-derived carbonyl group over elapsed time versus the immersion temperature level. The IR peak intensity derived from ester bonding was hardly observed at the 70°C and 80°C temperature levels and decreased with time above 90°C. At 98°C, the decrease in IR peak intensity over time became more pronounced. On the other hand, the IR peak intensity derived from urethane bonding also showed little change at the 70°C and 80°C temperature levels but increased with time at 90°C and above.

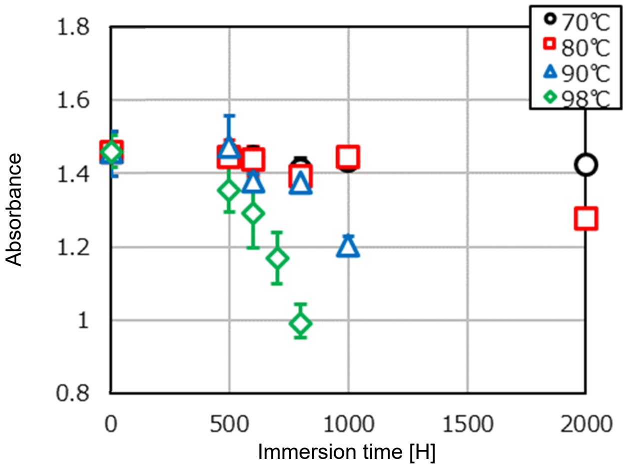


Fig. 4 Ester bonding results over time

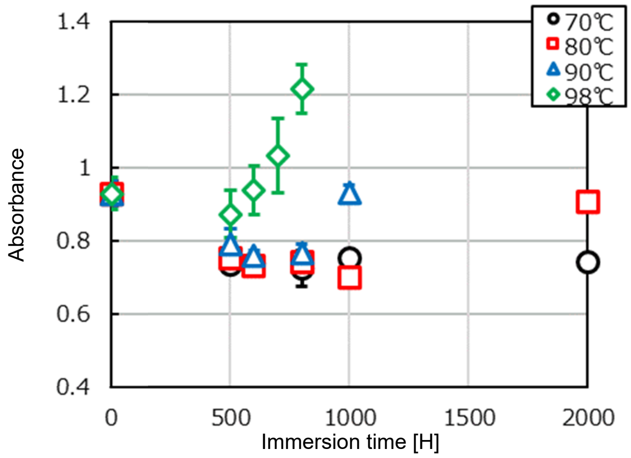


Fig. 5 Urethane bonding results over time

The polyol component of polyurethane used in this experiment is a polymer of caprolactone polymerized by ester bonds. Ester bonds are generally considered to undergo hydrolysis in the presence of water. The decrease in the ester bond-derived IR peak is thought to be simply due to hydrolysis of the polyol component. In contrast, the increase in IR peak intensity of the carbonyl group derived from the urethane bond was considered from the principle of FT/IR. FT/IR is an analytical instrument that transmits infrared light through a material and records the absorbance specific to the bond at the frequency as an absorption spectrum. The absorbance follows Lambert-Beer's law, which is determined by the concentration of the bond and the optical path length in the material. In this experiment, the specimens were cut with a constant thickness using a microtome, and the optical path length was constant. Therefore, the increase in absorbance was assumed to be caused by an increase in the concentration of urethane bonds in the material. When a change in concentration occurs in a sample, factors include the incorporation of substances from outside into the sample, swelling, or shrinkage that changes the sample size. Assuming that a substance has been taken in from the outside, permeation of a material with urethane bonds is necessary, but since the solvent is water, the urethane bonds are not expected to increase even if the material permeates. Therefore, the concentration change was considered to be caused by size change (shrinkage). Density measurements were conducted using the underwater gravimetric method for confirmation. The results of the density measurement are shown in **Fig. 6**. The density increased with time, confirming shrinkage. Shrinkage was estimated to be caused by the degradation of the polycaprolactone component by hydrolysis, resulting in a low molecular weight, the elution of the low molecular weight component into the solvent, and the resulting volume reduction.

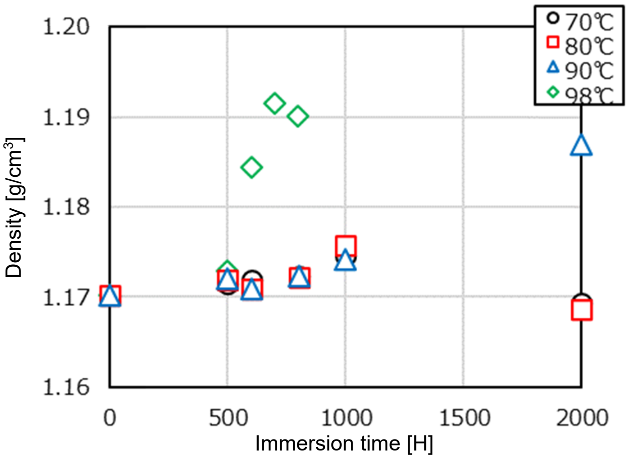


Fig. 6 Density measurement results

3.2 Analysis of degraded components by LC-MS

The shrinkage observed in the polyurethane immersion test in water is thought to be due to hydrolysis of the polyurethane. This suggests that the degraded low-molecular-weight polyol leaches out of the polyurethane, the urethane bonds do not undergo degradation, and the components with urethane bonds remain inside. Component analysis of the hydrolytic deterioration test solvent and the hydrolytic deterioration test product by LC-MS was performed, and the validity of the IR results and the degradation mechanism were examined.

3.2.1 Analysis results of hydrolytic deterioration test solvents

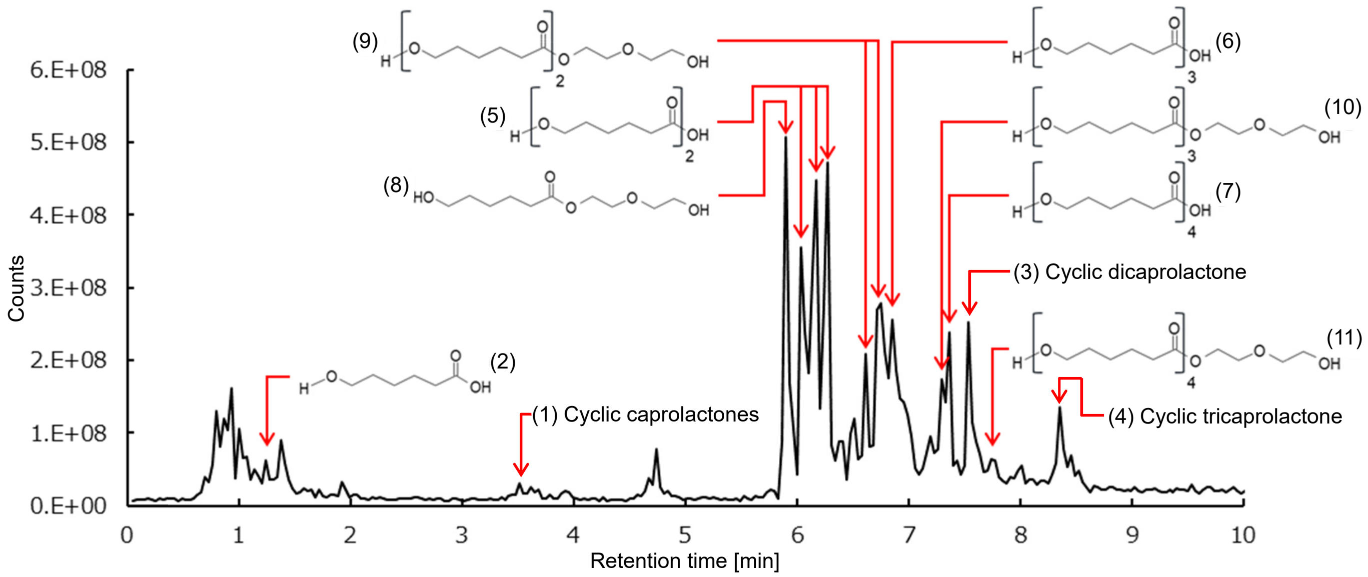
We analyzed the eluted components in the hydrolytic deterioration test solvent and discussed the degradation mechanism of polyurethane when it undergoes hydrolysis.

The LC-MS analysis results for the test solvent are shown in **Fig. 7 (a)**. The horizontal axis indicates retention time, and the vertical axis indicates detection intensity. The identification results of the compounds corresponding to the obtained peaks are shown in the figure. A test solvent in which commercially available polycaprolactone diol was hydrolytically deteriorated was used as a reference for the identification of polyurethane degradation products. **Figure 7 (b)** shows the results of the LC-MS analysis of the reference and the estimated structures of the compounds formed by hydrolytic deterioration. Considering that the degradation of polyurethane occurred at the ester bond position, we compared the exact mass calculated from the structure of the estimated degradation products with the exact mass of each peak obtained by LC-MS analysis to identify degradation products. The compounds detected were (1) ε-caprolactone (*m/z* 114.14), a raw material for polyol, and (2) 1-hydroxyhexanoic acid (*m/z* 132.16), in which ε-caprolactone has opened the ring and the end is stabilized by water. As polymers, (3) cyclic dimer (*m/z* 228.28) and (4) cyclic trimer (*m/z* 342.43) of ε-caprolactone; (5) linear dimer (*m/z* 246.30), (6) linear trimer (*m/z* 360.44), and (7) linear tetramer (*m/z* 474.58) polymerized as hydroxyhexanoic acid by ring-opening; (8) reaction product of hydroxyhexanoic acid and diethylene glycol (*m/z* 220.26), (9) dimer of hydroxyhexanoic acid and diethylene glycol (*m/z* 334.40), (10) compound of trimer and diethylene glycol (*m/z* 448.55), and (11) compound of tetramer and diethylene glycol (*m/z* 562.96) were detected. No urethane bond-containing or urethane bond-degrading compounds were identified.

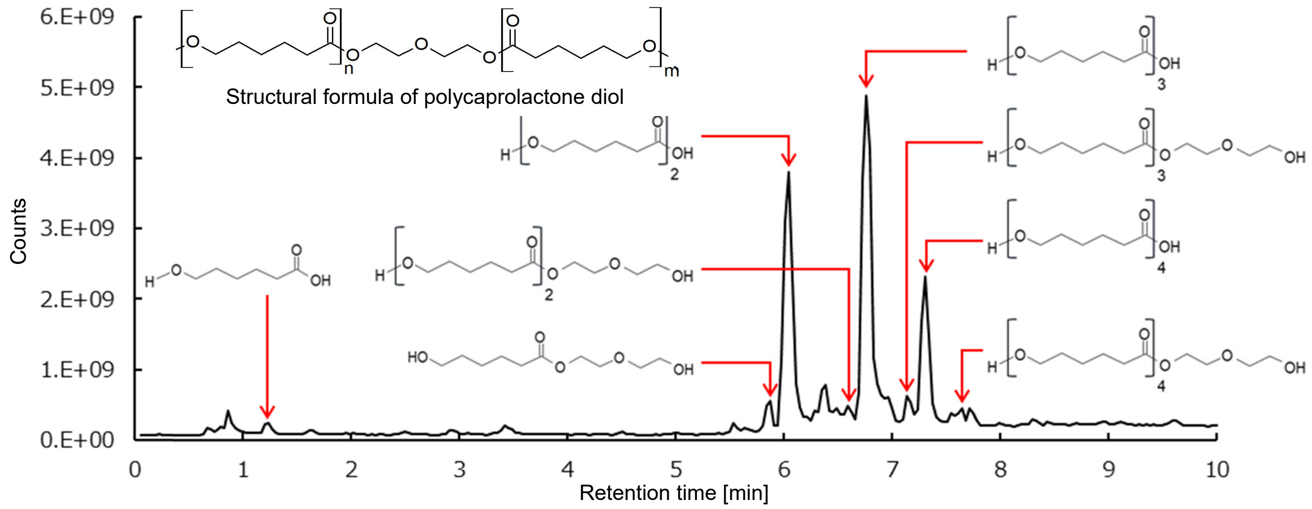
The compounds that hydrolyzed the polyurethane and leached into the soaking water were polymers of polyol degradation products with a degree of polymerization of 4 or less. It is considered that those of a smaller degree of polymerization dissolved out due to the solubility in water. Shrinkage is thought to have been caused by the elution of polyol degradation products.

3.2.2 Analysis results of hydrolytic deterioration test products

Since isocyanate-derived compounds with urethane bonds were not identified in the test solvent, we assumed that they remained in the hydrolytic deterioration test product and analyzed the hydrolytic deterioration test product. The compound with the smallest unit containing isocyanate and having urethane bonds was estimated from the structural formula of polyurethane, and this compound was selected as the target compound for analysis. The structural formula is shown in **Fig. 8**. The compounds identified in the test solvent were polyol degradation products, and no compounds containing urethane bonds or urethane bond degradation compounds were identified. Therefore, if the smallest unit of the target compound is identified in the hydrolytic deterioration test products, urethane bond degradation does not occur, and it can be assumed that the main cause of deterioration is the degradation of the ester bond of the polyol. Residual components were identified from the component analysis of the hydrolytic deterioration test products.



(a) Chromatogram of hydrolysis solvent



(b) Chromatogram of reference (PCLD soaking water)

Fig. 7 Chromatogram (a) Hydrolysis solvent (b) Reference (PCLD immersion water)

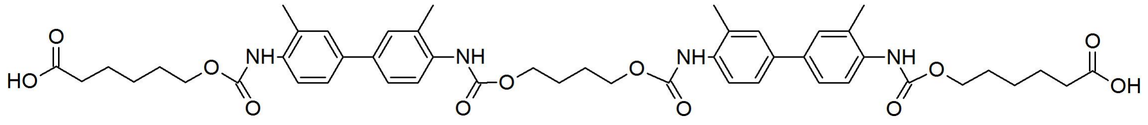


Fig. 8 Minimum molecular structure of the estimated residual component (*m/z* 883.4)

LC-MS analysis was performed on the hydrolytic deterioration test product, and a mass chromatogram expressed as the mass number (*m/z* 883.4) of the target compound with a urethane bond is shown in **Fig. 9**. A peak with the same molecular weight as the target compound was identified at a retention time of 7.79 min.

Fragment analysis using the collision method was performed to verify whether the compound in this peak has the structure shown in **Fig. 8**. **Figure 10** shows the results. The analysis identified six product ions corresponding to the substructures for the precursor ions.

(1) Proton adduct of hexanoic acid (*m/z* 133.1)
(2) Proton adduct of the tolidine skeleton cleaved at the nitrogen and carbon positions of the urethane bond (*m/z* 239.2)
(3) Proton adduct of the tolidine skeleton cleaved on the alcohol-adduct side of the urethane bond (*m/z* 283.1)
(4) Proton adduct of a compound with one diol bonded to a tolidine skeleton (*m/z* 356.2)
(5) Proton adduct of a compound with one hexanoic acid bonded to a tolidine skeleton (*m/z* 415.2)
(6) Proton adduct of a compound with diol and hexanoic acid attached to both ends of a tolidine skeleton (*m/z* 471.2)

These product ions have the masses of the substructures of the skeleton of the compound in **Fig. 8**, and the assumed minimum unit structure is considered correct.

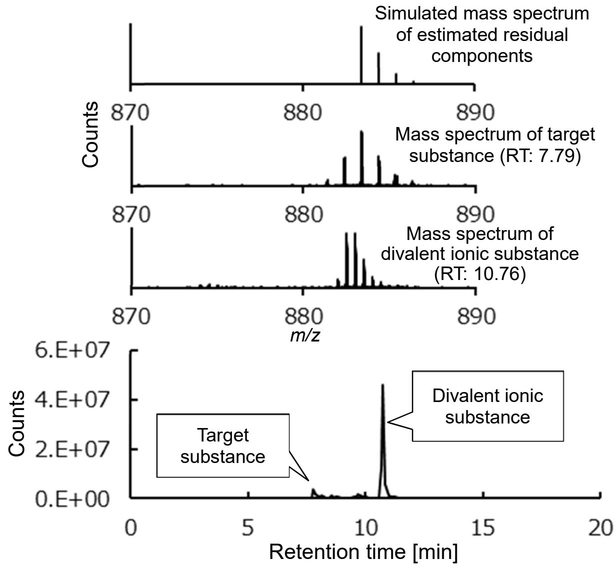


Fig. 9 MIC (*m/z* 883.4) analysis results

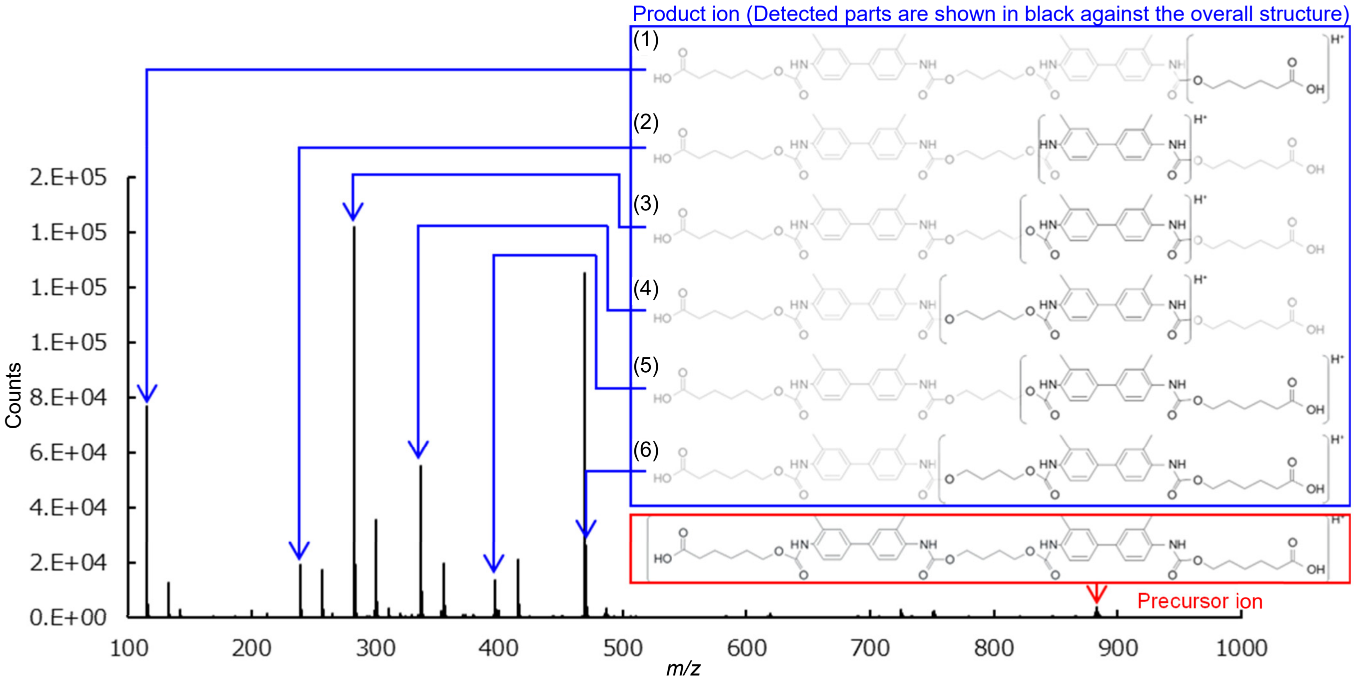
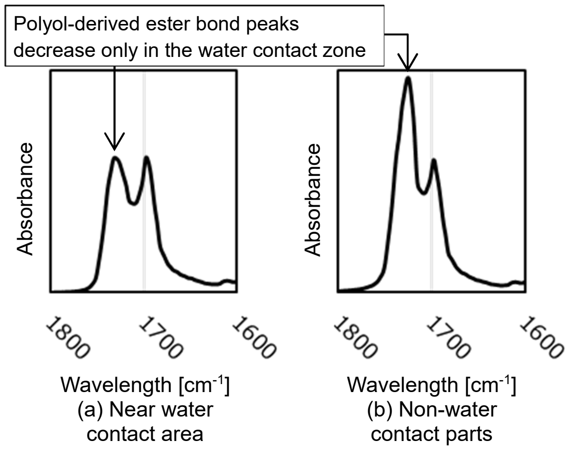


Fig. 10 Structural analysis results

3.3 Observation

The analysis results of the hydrolysis solution and the hydrolytic deterioration test product show that hydrolysis of the ester bonds of polyols in polyurethane occurs in aqueous environments, and degraded products with small molecular weights are eluted. In contrast, urethane bonds do not degrade, and compounds with large molecular weights of polyol degradation products and compounds with urethane bonds are expected to remain in the hydrolytic deterioration test product. Although the characteristic absorption of ester bonds is reduced by the elution of polyol degradation products, it is considered that the apparent thickening of urethane bonds is reflected in the measurement results when the shrinking polyurethane is measured by IR at a constant thickness.

Figure 11 shows the results of infrared spectroscopic analysis of the parts of the hydrolytic deterioration test product in contact with water and the parts not in contact with water for the water immersion test piece. The extent of water's influence is limited; only surfaces in contact with water are presumed to undergo hydrolysis. This result suggests that the increase in density is less than the increase in urethane bonds.



(a) Near water contact area

(b) Non-water contact parts

Fig. 11 Results of infrared spectroscopy analysis

4. Conclusion

Hydrolytic deterioration of ester-based polyurethanes is caused by the degradation of ester bonds in the polyol, and temperature is an accelerating factor. In addition, urethane bonds are not subject to degradation.

The increase in the IR peak intensity of the urethane bond-derived IR peak over time was caused by the apparent thickening of the urethane bonds when measured at a constant film thickness due to the shrinkage of the polyurethane itself caused by the elution of degradation components from the hydrolytic deterioration of the urethane. Since the increase in the IR peak intensity of urethane bonds correlates with the shrinkage of polyurethane, the increase in the IR peak intensity of urethane bonds could be used to make corrections and more accurately measure the amount of deterioration.

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[A comment from the authors]

Because construction machinery operates in a severe environment, the resin materials used in its components can deteriorate in a short time. Therefore, one of the countermeasures is selecting a high-durability resin. However, resin selection and evaluation cannot be performed without clearly understanding the deterioration mechanism that caused the problem. We would like to contribute to solving quality problems by improving the evaluation technology of material properties through developing our own analytical technology that clarifies degradation mechanisms for projects such as deterioration determination and life prediction.