Technical paper

Structural Analysis of High-Strength Urethane Resin Used in Construction Machinery by Py-GC/MS and NMR

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There are a wide variety of resins used in construction machinery, and they are also used in important components. In the application, durability under severe use environment such as resistance to heat and water and high mechanical strength is required. Methods such as pyrolysis gas chromatography-mass spectrometry and infrared spectroscopy are mainly used in the analysis of resins, and the resin is analyzed by comparing these analytical data with a reference chart. However, the high-strength urethane resin used at the site where the application of the elastomer is required is composed of a combination of three components. In addition, since one of the components, alcohol, is a polymer, it is substantially equivalent to analyzing two mixed polymers. Therefore, it is difficult to adapt the analysis using the existing resin reference. In this paper, the analysis method of urethane resin was examined, and its structural analysis is reported.

***Key Words**: Urethane resin, polyol, Py-GC/MS, NMR*

1. Introduction

Steel is the main material used in construction machinery, but on the other hand, various resin materials are also used due to their physical properties and characteristics. In particular, the resin used for the sliding part is required to maintain mechanical strength and also to be resistant to sliding heat under the influence of oil and moisture in the environment. Therefore, high-strength urethane resin is often used for the sliding material.

One of the causes of the decrease in the mechanical properties of urethane resin is deterioration due to heat or water, which is a chemical change. In order to clarify the cause of the deterioration of characteristics and take appropriate countermeasures, it is important to know the cause of the deterioration of the urethane resin. For that purpose, it is necessary to quantitatively understand the change in chemical structure due to deterioration.

A urethane resin is generally composed of isocyanate, a chain extender and a polyol, as shown in **Fig. 1**. The mechanical strength and the deterioration characteristics differ depending on the type of each component, and especially the polyol affects the deterioration characteristics. Polyols are classified into various types, such as ether, ester, carbonate, and lactone. The main characteristics differ depending on the types. The ether type has high hydrolysis resistance but ordinary mechanical strength, whereas the ester type has low hydrolysis resistance but high mechanical strength. The carbonate type has high hydrolysis resistance and high mechanical strength, but are difficult to manufacture [1]. In other words, in order to judge the characteristics of urethane resin, it is necessary to identify which kind of polyol it is. However, urethane resins have similar components and have many types, making it difficult to identify the components. In particular, there have been many reports on the analysis of polyols, but no uniform analysis or analysis method has been found [2] [3]. In this study, a new method for identifying polyols was devised and its structure was identified by pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) and nuclear magnetic resonance (NMR) using a model material of high-strength urethane resin [5]. This paper introduces the detailed concept of the polyol identification.

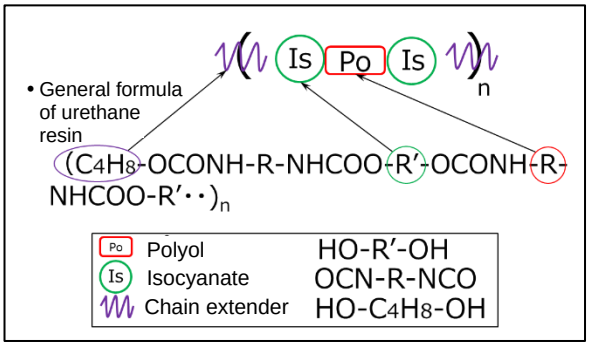


Fig. 1 General structure of urethane resin

2. Analysis

In the analysis, the Py-GC/MS system was used for the overall structural analysis, and the NMR system was used for the local structural analysis. In Py-GC/MS, the analyte was instantaneously pyrolyzed in an inert gas, and the resin was identified from the decomposed components. Since the resin undergoes thermal decomposition at a certain temperature and maintains a certain structure in an inert gas, the type of the constituent components and the bonding form were specified from the obtained pyrolysis product. In NMR analysis, when the atomic nucleus was placed in a constant magnetic field and irradiated with radio waves (60 MHz to 1 GHz), different resonances occur for each difference in coupling. From this resonance frequency, the bonding state of atoms was analyzed to estimate the molecular structure.

2.1 Py-GC/MS analysis

Approximately 0.1 mg of the specimen cut with a scalpel was collected in an analytical pan and pyrolyzed at 550ºC for analysis. The mass spectra obtained by the GC/MS_EI method (EI: electron ionization) were used to identify compounds by similarity search (matching search) using a library.

Compounds that could not be identified by the similarity search were identified by GC/MS_CI method (CI: chemical ionization) based on the molecular weight and fragment pattern analysis.

2.2 NMR analysis

After adding 0.0542 g of the specimen to 650 μL of DMSO-D6 and then swelling at 120ºC, ^{1}H-NMR and ^{13}C-NMR measurements were performed. The cumulated number was 64 for ^{1}H-NMR and 10240 for ^{13}C-NMR. The local structure was analyzed from the obtained results.

3. Results and discussion

Using Py-GC/MS_EI method, the constituent isocyanate and chain extender were identified by similarity search, which is a general method used to identify organic compounds. However, since the polyol could not be identified by similarity search, the structure was identified by using both Py-GC/MS_CI method and NMR.

3.1 Analysis of isocyanate and chain extender

The chromatogram observed by Py-GC/MS_EI method is shown in **Fig. 2** (hereinafter, the chromatogram obtained by pyrolysis GC is referred to as pyrogram). The peak obtained at a retention time (RT) of 6.5 minutes was identified as 1,4-butanediol (1,4-BD) by a similarity search and identified as a chain extender. Similarly, the peak at RT 16.7 minutes was 4,4’-diphenylmethane diisocyanate (hereinafter, 4,4’-MDI) and identified as isocyanate.

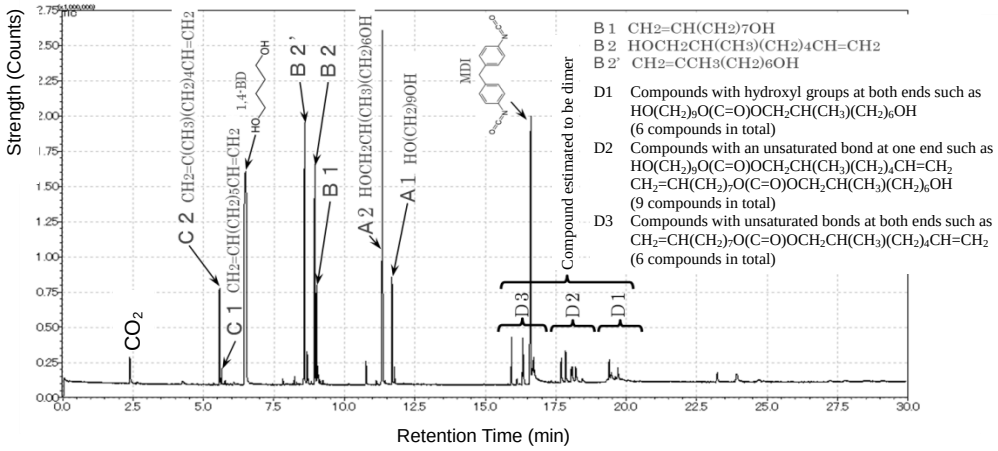


Fig. 2 Pyrogram of urethane resin by Py-GC/MS_EI analysis [5]

3.2 Analysis of polyol monomer

A similarity search was performed using the pyrogram of the Py-GC/MS_EI method. The compounds obtained from the search results had a low matching degree and could not identified the monomer; however, the search results indicated that peaks A1 and A2 were alcohol compounds. The molecular weight was measured by the Py-GC/MS_CI method, and the result was 160.

The compounds of peaks A1 and A2 shown in **Fig. 2** were assumed to be diols having a molecular weight of 160, and GC/MS_EI analysis was performed using available standard diols having a molecular weight of 160. As a result of examining the RT, peak A1 was identified as 1,9-nonandiol (hereinafter, referred to as 1,9-ND). In general, RT of GC is faster for isomers with a branched structure than for linear structures, and for compounds without a polar group (e.g. alcohols). Based on this, peak A2 was presumed to be a branched isomer of peak A1.

Fig. 3 shows the ^{1}H-NMR results of the urethane resin. Assignment of proton (^{1}H) to each monomer of the urethane resin indicated that peak A2 had a branch at the 2-position and a methyl group. Based on this result, peak A2 was identified as 2-methyl-1,8-octanediol (2-MOD), which is a diol having 8 straight carbon atoms. Assignments were also made for 1,9-ND, MDI, and BD, confirming that there was no difference from the identification results of Py-GC/MS.

The validity of this identification of the diol was verified as follows. When a polyol composed of two diols, 1,9-ND and 2-MOD, is thermally decomposed, the oxygen-binding part with a weak binding force is cut off. If the bond is broken between hydrogen and oxygen, it is considered that hydrogen is replenished and stabilized, and 1,9-ND and 2-MOD are generated. In addition, when the bond is broken between carbon and oxygen, it is considered that an unsaturated bond is formed on the carbon side and a stable compound is formed. **Fig. 4** shows the results of the molecular weight measurement of 2-MOD-derived pyrolysis products by CI method. The molecular weight of the peak A2 compound changes from peak A2 to peak B2 and B2' to peak C2, and its mass difference is 18. Based on this, it is presumed that peaks B2 and B2' and peak C2 were cut at a position between carbon and oxygen, and oxygen was eliminated as water (H_2O, *m/z* 18).

Fig. 5 summarizes the results of the monomer analysis. In the case of 1,9-ND (molecular weight 160), mono-ol having 9 carbon atoms (C_9) with unsaturated bond at one end (molecular weight 142) or C_9 diolefin having unsaturated bonds at both ends (molecular weight 124) is generated. In the case of 2-MOD (molecular weight 160), two mono-oles of 2-methyl branched isomer (molecular weight 142) and C_8 diolefin of 2-methyl branched isomer having unsaturated bonds at both terminals (molecular weight 124) are generated. As shown in **Fig. 5**, the 1,9-ND of peak A1 changes to peak B1 (molecular weight 142) and peak C1 (molecular weight 124). In contrast, the 2-MOD of peak A2 changes to peak B2, peak B2' (molecular weight 142), and peak C2 (molecular weight 124). Furthermore, the peak intensity ratios of peak B1 to peak B2 and peak B2', and peak C1 to peak C2 are by the peak intensity ratios of peaks A1 and peak A2 are almost the same; therefore, the identification result of the monomer is considered valid.

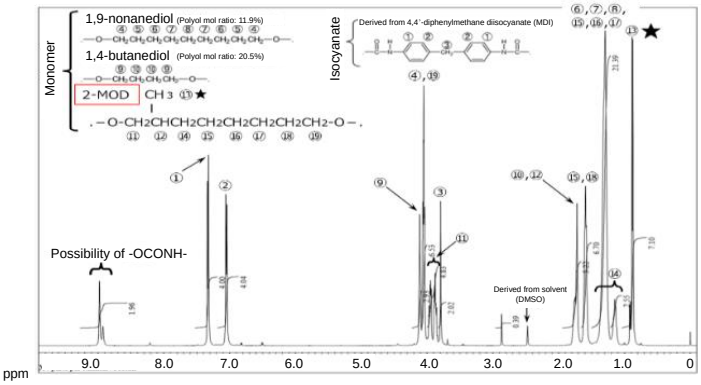


Fig. 3 ^{1}H-NMR analysis results of urethane resin

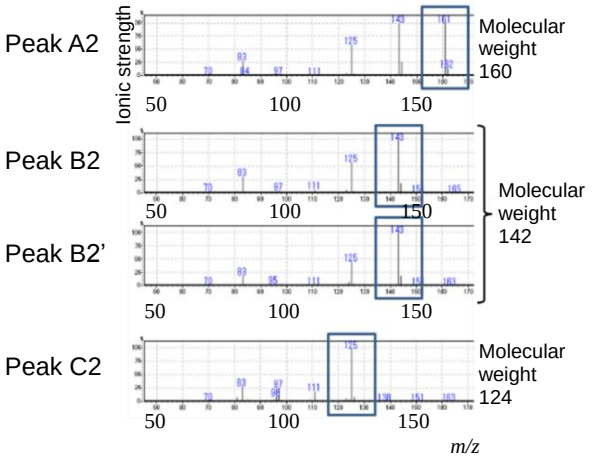


Fig. 4 Measurement of molecular weight of thermal decomposition products derived from 2-MOD by CI method

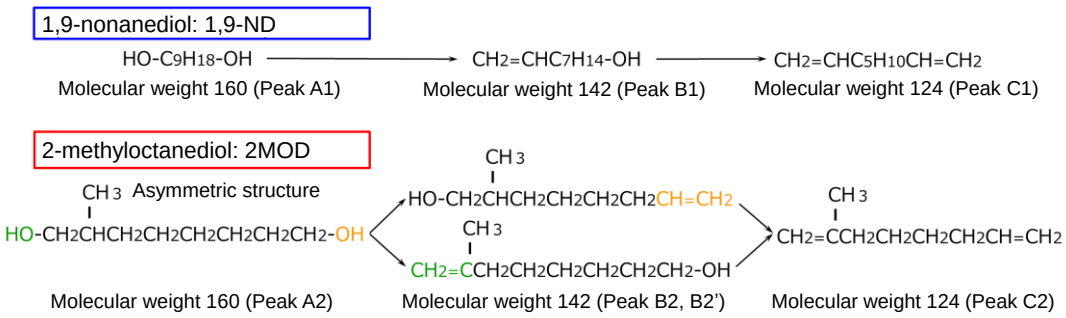


Fig. 5 Changes in terminals due to thermal decomposition of 1,9-ND and 2-MOD (structure transition of monomer)

3.3 Structure identification of polyol

The dimer, which is the minimum unit of the components of the polyol, was analyzed, and the bonding form of the monomer was analyzed. The compound peak detected at 2.4 minutes in the pyrogram of the Py-GC/MS_EI method was identified as carbon dioxide (CO_2) with a molecular weight of 44 (see **Fig. 2**). CO_2 is characteristically detected when a compound having a carbonate bond (–O–C(=O)–O–) is thermally decomposed [4]. This suggests that the polyol has a structure of –O–C(=O)–O– in the molecule, and the dimer was assumed to be carbonate diol.

In the pyrogram shown in **Fig. 6**, the group D was divided into three blocks from RT 16 minutes to 20 minutes, and the D1 group (6 peaks), the D2 group (9 peaks) and the D3 group (6 peaks) in order of longer RT, respectively, were confirmed. Peak assignment in each group was determined by molecular weight measured by Py-GC/MS_CI method and fragment pattern analysis of MS (see **Table 1**). Peak D1 was a compound having a molecular weight of 346 and a hydroxyl group at both ends, which was presumed to be a dimer of diol. Peak D2 group has a molecular weight of 328 and was 18 less than Peak D1 group. This was thought to be due to the elimination of one molecule of water (H_2O, *m/z* 18), and was presumed to be a compound having a terminal unsaturated bond and a hydroxyl group. The molecular weight of the peak D3 group having the earliest RT was 310, which was a molecular weight in which water was further eliminated from the peak D2 group and both terminals became unsaturated bonds. Therefore, this result was consistent with the relationship between the RT and structure.

In order to verify the results of the dimer analysis, all the isomers of the dimer when the two identified monomers had a carbonic bond were estimated. There are three possible combinations: 1,9-ND combination, 1,9-ND and 2-MOD combination, and 2-MOD combination. In addition, because 2-MOD has a side chain, the structure of the compound changes depending on the direction of the bond. For this reason, the structure of dimer diol has one kind of combination of 1,9-ND, two kinds of combination of 1,9-ND and 2-MOD, and three kinds of combination of 2-MOD. A total of six types of compounds are obtained. This corresponded to 6 peaks in group D1. Also, as in the verification of the validity of the diol, when a break occurs between oxygen and carbon, an unsaturated bond is formed and it is stabilized. The combination of 1,9-ND is one, the combination of 1,9-ND and 2-MOD is four, and the combination of 2-MOD is four, giving a total of nine compounds. These compounds corresponded to 9 peaks in group D2. Similarly, there are six types of compounds having unsaturated bonds at both ends, which correspond to six peaks in group D3 (see **Table 2**). These 21 compounds were all assigned to peaks D1 to D3, and the polyol could be identified as a polyol having a carbonate bond.

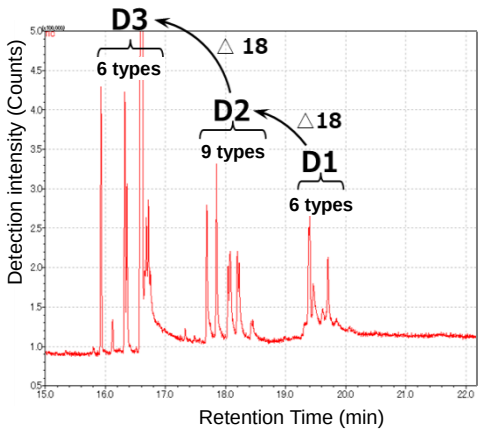
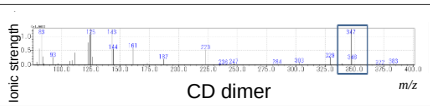
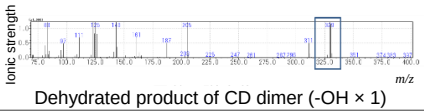
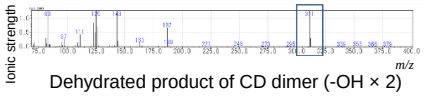


Fig. 6 Partial enlargement of **Fig. 2** (Group D)

Table 1 Representative CI mass spectrum of group D

Peak group	Mass spectrum	Molecular weight
D1	 CD dimer	346
D2	 Dehydrated product of CD dimer (-OH × 1)	328
D3	 Dehydrated product of CD dimer (-OH × 2)	310

CD (carbonate diol)

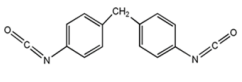
Table 2 Analysis results of dimer in group D

Polymer		Original structure of Alcohol	→ Thermal decomposition: Molecular weight is 18 Phenomena	→ Thermal decomposition: Molecular weight is 18 Phenomena
		Molecular weight 346 (D1)	**Molecular weight 328 (D2)**	**Molecular weight 310 (D3)**
Dimer	①	N-ol – O C=O O – N-ol (Molecular weight 44)	N-ene – O C=O O – N-ol	N-ene – O C=O O – N-ene
	②	N-ol – O C=O O – 2MO-ol	N-ol – O C=O O – 2MO-ene N-ene – O C=O O – 2MO-ol	N-ene – O C=O O – 2MO-ol
	③	N-ol – O C=O O – 7MO-ol	N-ol – O C=O O – 7MO-ene N-ene – O C=O O – 7MO-ol	N-ene – O C=O O – 7MO-ene
	④	2MO-ol – O C=O O – 2MO-ol	2MO-ene – O C=O O – 2MO-ol	2MO-ene – O C=O O – 2MO-ene
	⑤	2MO-ol – O C=O O – 7MO-ol	2MO-ol – O C=O O – 7MO-ene 2MO-ene – O C=O O – 7MO-ol	2MO-ene – O C=O O – 7MO-ene
	⑥	7MO-ol – O C=O O – 7MO-ol	7MO-ene – O C=O O – 7MO-ol	7MO-ene – O C=O O – 7MO-ene
		D1 (6 types)	**D2 (9 types)**	**D3 (6 types)**

List of abbreviations used in **Table 2**

N-ol : HOC_9H_{18}-	2MO-ol : $-OCH_2CH(CH_3)(CH_2)_6OH$	7MO-ol : $-O(CH_2)_6CH(CH_3)CH_2OH$
N-ene : $CH_2=CH(CH_2)_7$-	2MO-ene : $-OCH_2CH(CH_3)(CH_2)_4CH=CH_2$	7MO-ene : $-O(CH_2)_6C(CH_3)=CH_2$

Table 3 Results of component analysis of urethane [5]

Structural component	Diol	Isocyanate	Chain extender
Substance name Structural formula	①1,9-nonandiol $HOCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$ ②2-methyl-1,8-octanediol $HOCH_2CH(CH_3)CH_2CH_2CH_2CH_2CH_2CH_2OH$	MDI 	1,4-butanediol $HOCH_2CH_2CH_2CH_2OH$

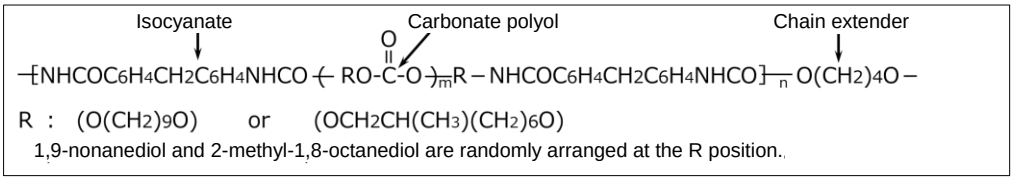


Fig. 7 Identified structural formula of urethane resin

4. Conclusion

In this study, by combining the similarity search of the Py-GC/MS_EI method, which is the conventional method, with the structural analysis method of polyol, which is one of the components of urethane resin newly devised, we determined that the high-strength urethane resin is a carbonate diol obtained by randomly polymerizing isocyanate with MDI, chain extender with 1,4-BD, polyol with 1,9-ND and 2-MOD (**Table 3** and **Fig. 7**).

In addition, it is possible to estimate the structure of this analysis method with high-strength urethane resin used for other sliding materials, and the usefulness of this analysis was also confirmed.

Generally, degradation analysis of resins requires quantitative measurement of changes in molecular structure using methods such as infrared spectroscopy. In the case of urethane resin, heat and water are the main decomposing factors. However, the position of the structure subject to decomposition differs depending on each factor. Therefore, it is possible to estimate in advance whether degradation will occur due to thermal decomposition or hydrolysis by grasping the structure. In the future, we will apply the results of this study to the life estimation of urethane material parts.

Acknowledgments

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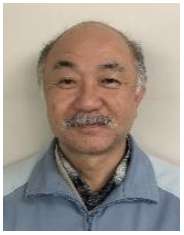

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[A comment from the authors]

Since the resins used in construction machineries that operate in harsh environments deteriorate in a short time, a highly durable resins will be used. Although it is necessary to quantitatively evaluate the degree of deterioration in order to judge deterioration and predict the life, it is difficult to analyze a highly durable resin because the deterioration rate is small. For such difficult projects, we would like to evaluate the characteristics of materials by devising new analytical techniques and contribute to quality improvement.