TG–FTIR studies on biodegradable polyurethanes containing mono- and disaccharide components[1]

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Abstract

TG–FTIR measurements of polyurethanes derived from mono- and disaccharides and their raw materials were carried out in order to investigate the thermal decomposition mechanism. It was found that polyurethanes decomposed in two steps; the first step of decomposition was observed at about 300 to 450°C and the second at about 450 t0 to 700°C. The first step was attributed to the breakage of pyranose rings, aromatic rings and/or alkylene chains and the second step to the production of CO_2, and H_2O.

Keywords: Biodegradable polyurethanes; Thermal decomposition; TG-FTIR

1. Introduction

We have reported that polyurethanes (PUs) derived from various plant components are biodegradable. The Degradation rate of the PUs in soil ranges between those of Japanese cedar and beech [1]. It was considered that the glucopyranose ring and the phenolic groups comprising the PUs are preferentially broken in the soil. At the same time, our recent research using model compounds indicated that, as well as the natural components, the urethane linkage is also broken by microorganisms in soil [1, 2].

Physical properties of the PUs derived from various plant components can be controlled by preparative conditions such as content of natural component, and

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crosslinking density. Among various physical properties, the thermal properties of PUs have been intensively studied [3–6]. Current results suggest that the glass transition temperature increases with increasing plant components and that the decomposition temperature decreases with increasing plant components. In order to use the PUs as an environmentally friendly material, it is necessary to confirm the degraded compounds by thermal decomposition.

Simultaneous measurements of thermal analysis, such as gas chromatography–mass spectrometry (GC–MS), thermogravimetry–mass spectrometry (TG–MS), and thermogravimetry–Fourier transform infrared spectroscopy (TG–FTIR), have been developed in the past decade [7]. In this study, TG–FTIR of PUs derived from mono- and disaccharides was investigated in order to establish the decomposition mechanism.

2. Experimental

2.1. Samples

PUs were prepared by polymerizing saccharides, such as glucose (Glc), fructose (Fru) and sucrose (Suc), with poly(ethylene glycol) (PEG) and diphenylmethane diisocyanate (MDI) using 1,4-diazabicyclo(2,2,2)octane as catalyst at room temperature. PU sheets were obtained by curing the prepolymers at 120°C. Polyols were prepared by mixing PEG having molecular weights of 200 and 400 in the mixture ratio 80% and 20%, and various saccharides of Glc, Fru and Suc. The saccharide contents in the polyol were 2,4,6,8 and 10%. The weight ratio of polyol: MDI was 1:1. PU sheets were homogeneous and transparent, although they were light brown and darkened with increasing saccharide content in the polyol. The precise experimental method has been reported previously [8–10]. The PU of the PEG–MDI system was also prepared in order to compare its properties with those of PUs containing saccharides i.e. Glc–PEG–MDI, Fru–PEG–MDI and Suc–PEG–MDI.

2.2. Measurement

TG–DTA–FTIR measurements of the samples were simultaneously carried out with a gas transfer system between TG–DTA (Seiko Instruments Inc., TG/DTA220, SSC5200) and FTIR (Japan Spectroscopic Co. Ltd., FT/IR700). The heating rate was $20°C$ min^{-1} in the temperature range from 40°C to 800°C. The flow rate of carrier gas was 100 ml min^{-1} and sample weight was about 7 to 10 mg. TG–DTA measurement in this study was carried out in air in order to simulate the actual treatment of waste plastics by a refuse burner. The gas transfer system was maintained at 270°C. The resolving power of FTIR was 8 cm^{-1}, the number of integrations was ten and the data incorporation time was 30 s. The precise mechanism and the measuring method used for TG–DTA–FTIR has been reported by Kinoshita et al. [11].

Decomposition temperatures were evaluated from TG curves as previously reported [12].

3. Results and discussion

Fig. 1 shows TG curves of the raw materials used to prepare the PU samples, that is, PEG, MDI, Glc, Fru and Suc. Two-step decompositions at about 200 ~ 280°C and 280 ~ 330°C for PEG, and at about 200 ~ 300°C and 300 ~ 700°C for MDI were observed in TG curves. Three-step decompositions at about 200 ~ 250°C, 250 ~ 350°C and 350 ~ 650°C were observed for Glc, Fru and Suc. Three-step changes were clearly confirmed in TG derivative curves (DTG), although they are not shown in the figure. The weight losses of the first, second and third steps were about 10%, 70% and 20%, respectively. Decomposition temperatures of the first step decomposition (T_{d_1}) of PEG, MDI, Glc, Fru and Suc were 195, 200.1, 199.6, 196.3 and 215.7°C, respectively. The above results suggest that the aromatic group (MDI) is more stable than linear chain molecules (PEG).

Fig. 2 shows TG curves of PUs containing various amounts of Glc. TG curves of PUs containing Fru and Suc showed similar patterns to those of Glc. All TG curves show the two step decompositions at about 250 ~ 450°C and 450 ~ 700°C. The marked difference between TG curves of raw materials and PUs is that the first step of decomposition (200 ~ 250°C) of the raw materials was not observed for the PUs, and T_{d}s of PUs were higher than those of the raw materials. The T_{d} of the PEG–MDI system without any saccharides was 314°C and T_{d}s of Glc–PEG–MDI, Fru–PEG–MDI and Suc–PEG–MDI systems decreased with increasing saccharide content in the polyol. It is considered that the T_{d} of PUs containing large amount of Glc finally approached the T_{d} of Glc.

Fig. 3 shows FTIR spectra of gases evolved from PUs of Glc–PEG–MDI (a), Fru–PEG–MDI (b) and Suc–PEG–MDI (c) systems at various temperatures. Five FTIR spectra were selected at the following temperatures from the TG curves: near T_{d_1} (200 ~ 320°C), the temperatures at two of the main decomposition points
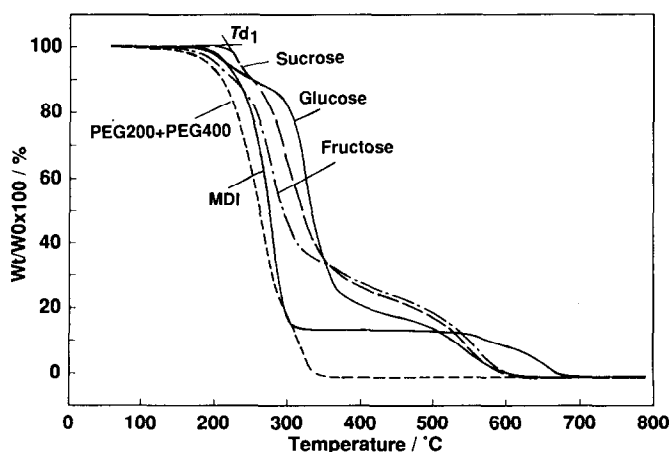

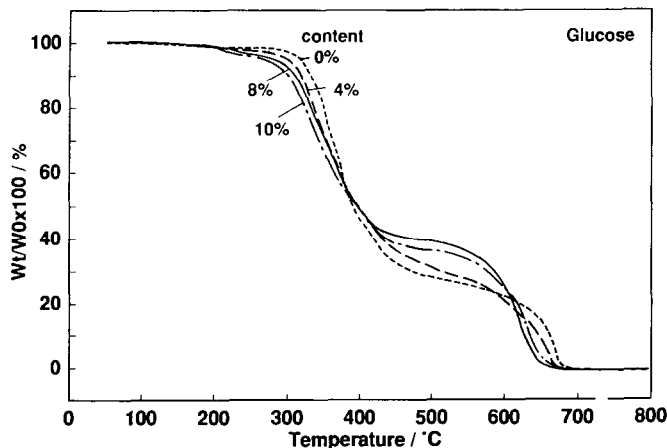Fig. 1. TG curves of the raw materials PEG, MDI, Glc, Fru and Suc used for preparation of PUs.

Fig. 2. TG curves of PUs. containing various amounts of Glc.

(240 ~ 350°C, and 280 ~ 380°C), a second step decomposition temperature (310 ~ 550°C) and a temperature near the end point of decomposition (530 ~ 660°C). FTIR absorption bands were observed at 670, 1160, 1510, 1740, 2350, 2900 and 3740 cm^{-1} due to gases evolved from the PUs. These absorption bands were assigned to carbon dioxide (670 cm^{-1}), ether (1160 cm^{-1}), aromatic ring vibration (1510 cm^{-1}), ester and/or aldehyde $C = O$ stretching (1740 cm^{-1}), CO_2, $-NCO$ and/or NO_x (2350 cm^{-1}), C–H stretching (2900 cm^{-1}) and –OH stretching (3740 cm^{-1}), respectively. The absorption bands of evolved gases for PUs containing various amounts of mono- and disaccharides are almost similar to those of PUs containing 8% saccharides as shown in this figure.

Fig. 4, (a) to (e), shows three-dimensional diagrams (intensity, wave number, and TG temperature) of FTIR spectra of evolved gases from the systems PEG (a), MDI (b), PEG–MDI (c) and Glc–PEG–MDI (d) and (e). The highest intensity of FTIR spectra of all samples were observed at about 2350 cm^{-1}, which was mainly assigned to absorption of CO_2. The highest intensity of absorption bands of 2350 cm^{-1} for PEG was observed at about 280°C, while that for MDI was observed at about 600°C. Considering both TG curves and FTIR spectra of PEG and MDI, the main chain of PEG was broken at a temperature higher than 280°C and CO_2 gas was mainly evolved as a result of the decomposition, whereas in the case of MDI, first step decomposition up to about 340°C occurred by production of a free aromatic ring, because 1510 cm^{-1} absorption of C=C in the benzene ring was observed near 340°C. CO_2 gas from decomposition of aromatic rings evolved at a temperature higher than 600°C because the highest temperature of 2350 cm^{-1} peak was observed near 600°C.

FTIR spectra of evolved gases from PU (Glc–PEG–MDI system) containing small amounts (2%) of Glc were similar to those from PEG–MDI systems without Glc. While in the case of PU containing 10% Glc, FTIR spectra of 670, 2350 and 3740 cm^{-1}
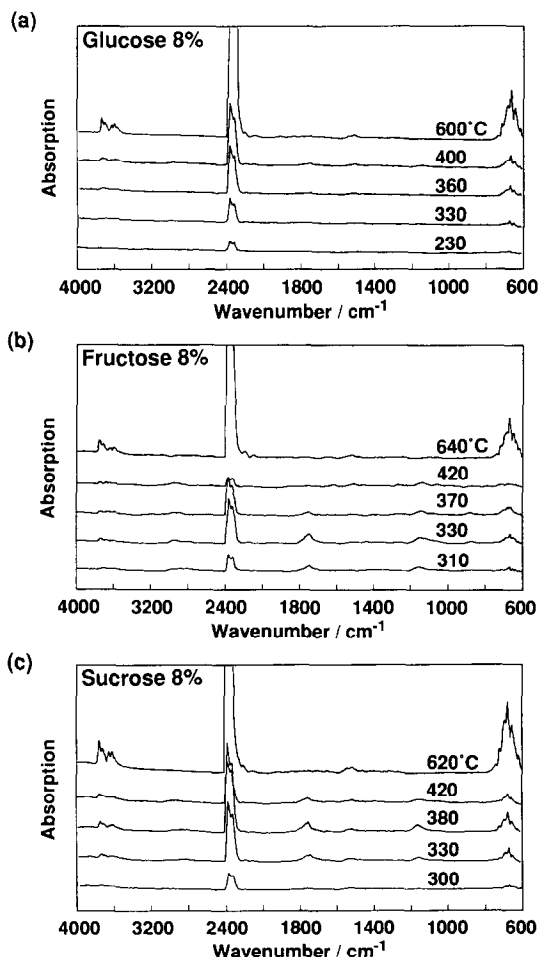
Fig. 3. FTIR spectra of gases evolved at various temperatures from PUs prepared from the systems Glc–PEG–MDI (a), Fru–PEG–MDI (b) and Suc–PEG–MDI (c).

were observed but other spectra became less prominent compared with those of the PEG–MDI system. Peaks observed at about $300 \sim 450°C$ in Fig. 4(e) (PU sample) were attributed to the breakage of pyranose rings, aromatic rings and/or linear alkylene chains, and peaks observed at $450 \sim 700°C$ were attributed to the production of low molecular mass materials such as CO_2 and H_2O. It is seen from the figures that the CO_2 absorption band at 2350 cm^{-1} changed with increasing temperature and two main peaks at about $400°C$ and $600°C$ were observed. This means that decomposition of PUs occurs mainly in two steps, the gases in the first step are evolved as a result of decomposition of the PU linkage and those at the second step arise from decomposition of low molecular mass chains.
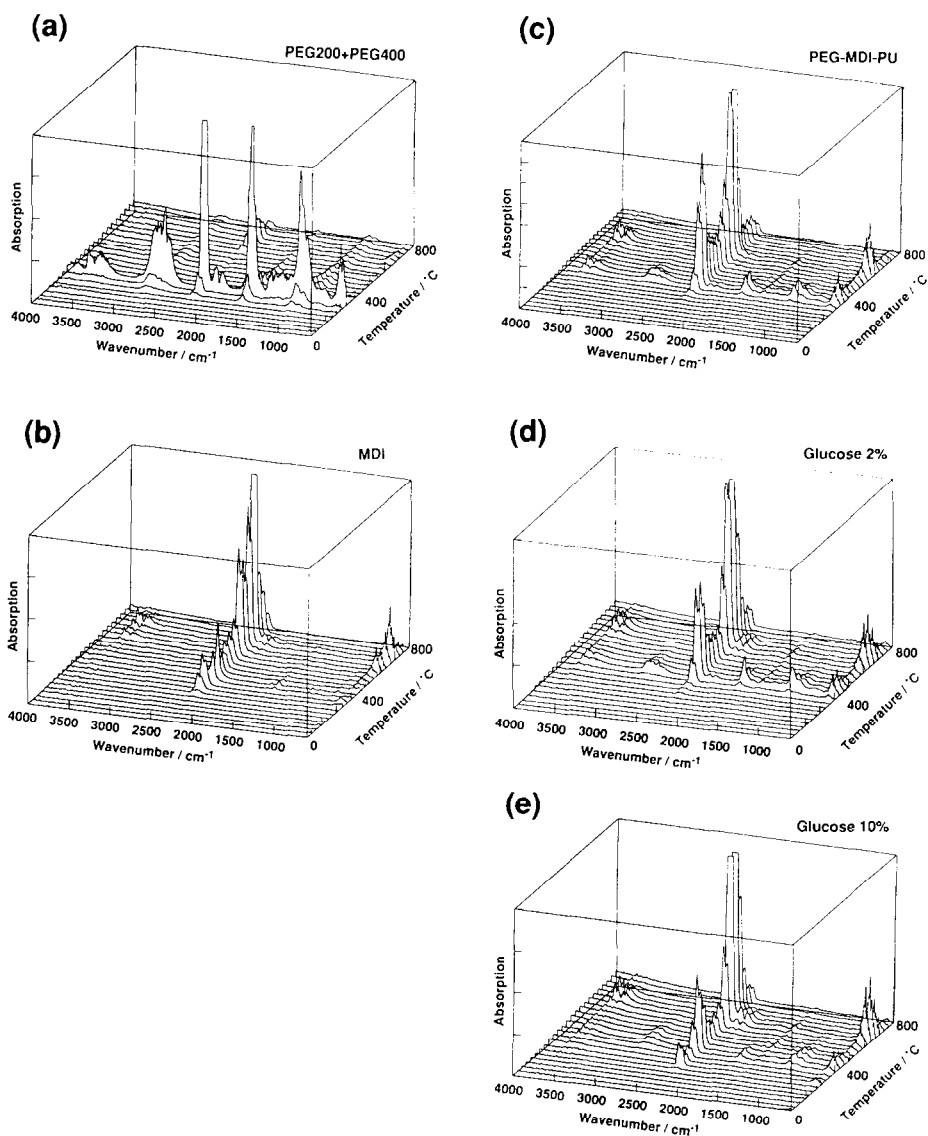
(a)

(c)

(b)

(d)

(e)

Fig. 4. Three-dimensional diagrams (intensity, wave number, and TG temperature) of FTIR spectra of gases evolved from PEG (a), MDI (b), PEG–MDI (c) and Glc–PEG–MDI systems (d) and (e).

Fig. 5 shows the relationship between TG temperature and FTIR absorption intensities of evolved gases from the raw materials PEG, MDI and Glc, and PU of the Glc-PEG-MDI system having 8% Glc content. The decomposition gases of PEG and Glc were mainly evolved in two steps at 280°C and 600°C, and at 380°C and 550°C, respectively. In the case of PEG, all absorption bands of evolved gases at 670, 1160, 1740, 2350, 2900 and 3740 cm^{-1} were observed at 290°C, and three peaks of 670, 2350
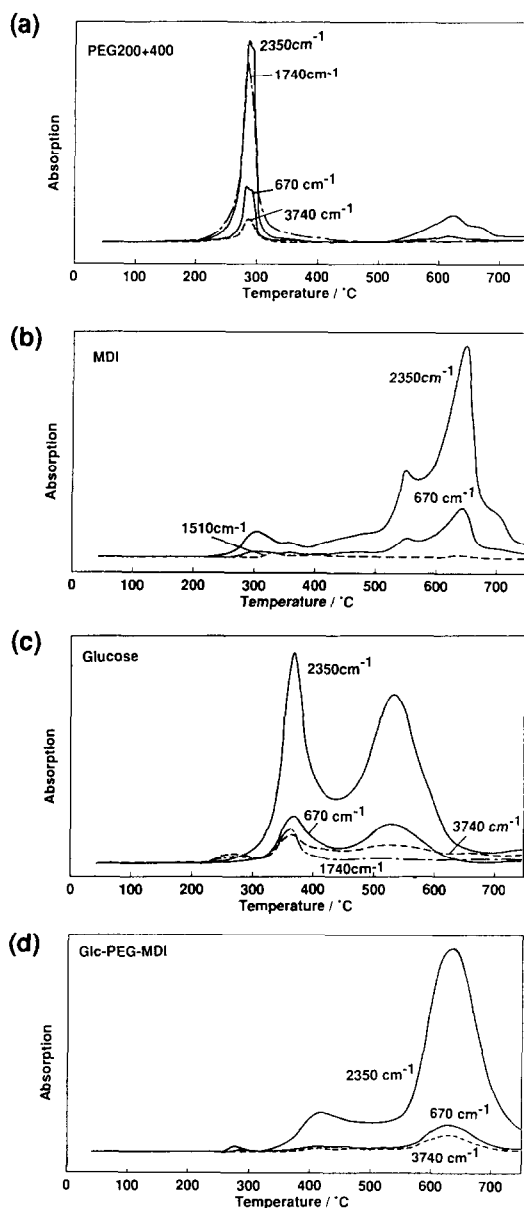
Fig. 5. The relationship between TG temperature and FTIR absorption intensities at 670, 2350 and 3740 cm min^{-1} of gases evolved from Glc–PEG–MDI system having 8% Glc content.

and 3740 cm^{-1} were observed at 630°C. In the case of Glc (Fig. (5c)), the absorption peaks of 670, 1510, 1740, 2350 and 3740 cm^{-1} were observed at 380°C and the peaks of 670, 2350 and 3740 cm^{-1} were observed at 540°C. FTIR absorption bands of MDI (Fig. (5b)) were complex in nature; peaks at 670 and 2350 cm^{-1} for CO_2 absorption

Table 1
The FTIR intensities of all the absorption bands observed in evolved gases from raw materials and PUs[a]

sample	$670\,cm^{-1}$	$1160\,cm^{-1}$	$1510\,cm^{-1}$	$1740\,cm^{-1}$	$2350\,cm^{-1}$	$2900\,cm^{-1}$	$3740\,cm^{-1}$
PEG 200 + PEG 400	M	S	–	VS	VS	M	W
MDI	M	–	W		VS	–	W
PEG–MDI	M	W	VW	W	VS	W	W
Glucose	M	–	VW	W	VS	–	W
Glc(8%)–PEG–MDI	M	–	VW	VW	VS	–	W
Fructose	M	–	VW	W	VS	VW	W
Fru(8%)–PEG–MDI	M	W	–	W	VS	VW	W
Sucrose	M	–	VW	W	VS	VW	W
Suc(8%)–PEG–MDI	M	W	VW	W	VS	–	W

[a] VS = very strong, S = strong, M = medium, W = weak, VW = very weak.

bands were observed at 300°C, 550°C and 640°C. A weak peak at $1510\,cm^{-1}$ for the aromatic C=C absorption band was observed at 330°C. In the case of PU of Glc–PEG–MDI system (Fig. (5d)), the absorption band at $2350\,cm^{-1}$ showed three major peaks at about 280, 410 and 630°C. The absorption band at $670\,cm^{-1}$ showed a peak at 630°C and weak peaks at 410 and 280°C. This means that CO_2 gas was mainly evolved at 410 and 630°C which corresponded to the temperatures of the first and second step decompositions in TG curves. An absorption band at $3740\,cm^{-1}$, which was assigned to H_2O, also showed two peaks at about 630 and 410°C. The other PU samples containing various amounts of Glc, Fru and Suc showed curves similar to those in Fig. 5(d).

Table 1 shows all the absorption bands observed in evolved gases from raw materials and PUs. Three absorption bands of 670, 2350 and $3740\,cm^{-1}$, assigned to CO_2 and H_2O were common to all samples. In the case of MDI, it is considered that NO_x gases and –NCO were evolved by decomposition. In this study, however, these gases could not be detected. FTIR spectra of these absorption bands might have overlapped with the CO_2 absorption band at $2350\,cm^{-1}$. The other characteristic absorption bands were $1510\,cm^{-1}$ of aromatic ring vibration for MDI and $1160\,cm^{-1}$ of ether or alcohol for PEG.

From the above results it is suggested that the first step of decomposition of polyurethanes, observed at about 300 to 450°C, could be attributed to the breakage of pyranose rings, aromatic rings and/or alkylene chains, and that the second step of the decomposition at about 450 to 700°C could be attributed to the production of CO_2 and H_2O.

Acknowledgments

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