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TG-FTIR STUDIES ON LIGNIN-BASED POLYCAPROLACTONES

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Abstract

Thermal degradation behaviour of alcoholysis lignin-based polycaprolactones (ALPCL's) with various molar ratios of ε-caprolactone monomer to each hydroxyl group of lignin (CL/OH ratios) was studied by TG-FTIR. The temperature was varied from 20 to 800°C. Thermal degradation temperatures (T_d's) of alcoholysis lignin (AL) and ALPCL's were determined using TG curves. T_d increased with increasing CL/OH ratio, suggesting that AL becomes thermally stable after the derivatization with PCL chains. Mass residue (*MR*) at 500°C was also determined using TG curves. *MR* values decreased with increasing CL/OH ratios. The evolved gases formed by thermal degradation of ALPCL's at various temperatures were simultaneously analyzed by FTIR. The main peaks observed for the samples are as follows: wavenumber (assignment): 1160 cm^{-1} (νC–O–), 1260 cm^{-1} (–C(=O)–O–C–), 1517 and 1617 cm^{-1} (νC=C), 1770 cm^{-1} (νC=O), 2345 cm^{-1} (νCO$_2$), 2945 cm^{-1} (νC–H) and 3700 cm^{-1} (νOH). It was found that the peak intensities for C=O, CH, C–O–C, OH peaks, which were observed for evolved gases at 430°C, increased with increasing CL/OH ratios, suggesting that the evolved gases at 430°C are mainly formed by thermal degradation of PCL chains in ALPCL's.

Keywords: alcoholysis, lignin-based polycaprolactones, TG-FTIR, thermal degradation

Introduction

Lignin is one of the main components of plant materials and it is a highly branched polymer consisting of phenyl propane units. However, lignin can not be used as a polymer material, since it does not have sufficient viscoelasticity for processing [1]. Therefore, many attempts have been made to utilize it as raw materials for the preparation of various three dimensional polymers such as polyurethanes, epoxy resins and phenol resins. In the above polymer systems, lignin can be directly introduced into the polymer chains. We have studied biodegradable polyurethanes with excellent physical properties [2–5]. Lignin can also be derivatized, and then the derivatives are introduced into the polymer chains. Hofmann and Glasser studied hydroxypropylated

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lignin derivatives as raw materials for polyurethanes and epoxy resins [6]. It is known that lactones can be polymerized by active hydrogens in hydroxyl groups and amino groups with and without catalysts [7]. Aliphatic polyesters have received particular attention due to their biodegradability. Therefore, we have recently synthesized lignin-based polycaprolactones by the polymerization of ε-caprolactone which is initiated by hydroxyl groups of lignin. Studies on the phase transition of the above lignin-based polycaprolactones and their polyurethane derivatives have been reported [8]. In the present study, thermal degradation of alcoholysis lignin-based polycaprolactones (ALPCL's) is investigated by thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR).

It is known that the initial stage in thermal degradation of lignin is concerned with hydroxyl groups of lignin [9, 10]. We have already reported that the starting temperature of thermal degradation (T_d) and also activation energy of thermal degradation in the initial stage becomes higher after methylation and acetylation of hydroxyl groups of dioxane lignin [11]. We have also reported the thermal degradation behaviour of polyurethane derivatives of lignin analyzed by TG-FTIR [12]. Concerning the thermal degradation of polycaprolactones, Persenaire *et al.* recently reported the mechanism and kinetics of thermal degradation of α-hydroxyl, ω-isopropylester PCL samples with various molecular masses studied by TG-FTIR-mass spectroscopy (MS), ^{1}H nuclear magnetic resonance spectroscopy and gel permeation chromatography [13]. Thermal degradation usually proceeds in a complicated manner when the sample consists of multiple components. Therefore, thermal degradation behaviour of graft copolymers i. e. lignin-based PCL's (ALPCL's) is investigated by TG-FTIR in the present study.

Experimental

Samples

An alcoholysis lignin sample was kindly supplied by Repap Co., U. S. A. and it was dried in vacuo at 70°C. Lignin-based PCL's were synthesized by the polymerization of ε-caprolactone (ε-CL) which was initiated by AL. The amount of ε-CL was varied from 2 to 25 moles per OH group of lignin (CL/OH ratio, mol mol^{-1}). The polymerizations were carried out for 12 h at 150°C with the presence of a small amount of dibutyltin dilaurate (DBTDL). The contents of AL and PCL in ALPCL's with various CL/OH ratios are shown in Table 1.

Measurements

Thermogravimetry (TG)-Fourier transform IR (FTIR) measurements were carried out using a Seiko TG 220 – Jasco FTIR 420 system at a heating rate of 20°C min^{-1} and at a nitrogen flow rate of 200 mL min^{-1}. The interface between the TG and FTIR was produced by Seiko Instruments Co. Ltd. The temperature was varied from 20 to 800°C, and TG and derivative TG curves (DTG) were recorded. The evolved gases during thermal degradation were simultaneously analyzed by FTIR. In order to obtain one spectrum, the data of ten scans with a scan interval of 1 s were accumulated. Each spectrum was recorded every 30 s. The resolution of the spectra was 1 cm^{-1}.

Table 1 Contents of AL and PCL in ALPCL's with various CL/OH ratios

CL/OH ratio/ mol mol^{-1}	AL moiety content/ mass%	PCL moiety content/ mass%
0	100	0
2	38.5	61.5
4	23.9	76.1
5	20.1	79.9
10	11.1	88.9
15	7.7	92.3
20	5.9	94.1
25	4.8	95.2

Results and discussion

Figure 1 shows TG and derivative TG (DTG) curves of AL and ALPCL's with various CL/OH ratios. Thermal degradation temperatures (T_d's) were determined from TG curves by a method reported by Nakamura *et al.*, as shown in Fig. 1 [14]. It is clearly seen from DTG curves in Fig. 1, that samples start to decompose at around 200°C. It is also seen from the DTG curves that samples with low values of CL/OH ratios (CL/OH ratio=0, 2 and 4) decompose in multiple steps in the temperature range lower than DTG peak temperatures. However, DTG curves are smooth at the temperature range lower than the DTG peak temperature for ALPCL with CL/OH ratio 25. Therefore, it can be said that thermal degradation of ALPCL's with lower values of CL/OH ratios is strongly affected by thermal degradation of lignin in ALPCL's.

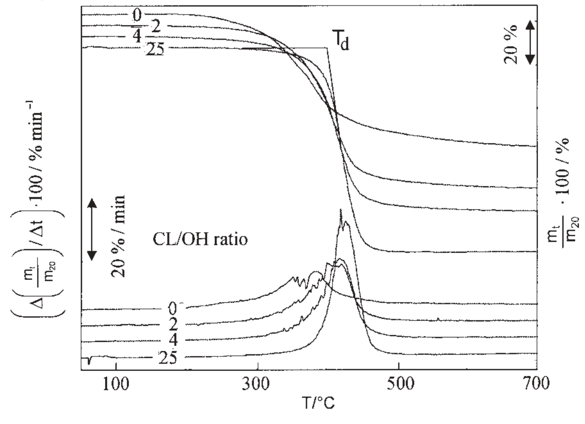

Fig. 1 TG and derivative TG (DTG) curves of AL and ALPCL's with various CL/OH ratios measured at 20°C min^{-1} in nitrogen

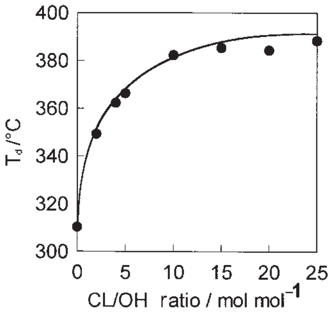

Fig. 2 Relationship between CL/OH ratio and T_d for AL and ALPCL's with various CL/OH ratios

Figure 2 shows the relationship between T_d and CL/OH ratio for AL and ALPCL's. T_d initially increases and then approaches a constant value with increasing CL/OH ratio. We have reported that lignin becomes thermally stable when hydroxyl groups of lignin are methylated and acetylated [11]. Accordingly, the increase in T_d values of ALPCL's, i. e., the increase in short-term thermal stability, seems reasonable when we consider that hydroxyl groups are changed into ester groups after PCL derivatisation.

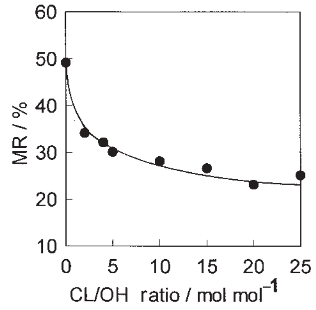

Fig. 3 Relationship between CL/OH ratio and mass residue at 500°C (*MR*) for AL and ALPCL's with various CL/OH ratios

Figure 3 shows the relationship between mass residue at 500°C (*MR*, $m_{500}/m_{20}100/\%$) and CL/OH ratio. *MR* values decrease with the increase in CL/OH ratio. It is known that lignin molecules readily react into a condensed structure and form a charcoal-like substance when they are heated to high temperatures in nitrogen [15]. Accordingly, the decrease in *MR* indicates that the residual substance is mainly formed from lignin molecules.

Figure 4 shows stacked TG-FTIR spectra of gases evolved at various temperatures. The main peaks observed for the samples are as follows: wavenumber (assignment): 1160 cm^{-1} (νC–O–), 1260 cm^{-1} (–C(=O)–O–C–), 1517 and 1617 cm^{-1} (νC=C), 1770 cm^{-1} (νC=O), 2345 cm^{-1} (νCO_2), 2945 cm^{-1} (νC–H) and 3700 cm^{-1} (νOH). Figure 5 shows FTIR spectra at 430°C of AL and ALPCL's with CL/OH ratios 4 and 25. The assignments for the peaks are also indicated in the figure. It is seen that the intensities of absorption peaks change according to CL/OH ratio values of the samples.

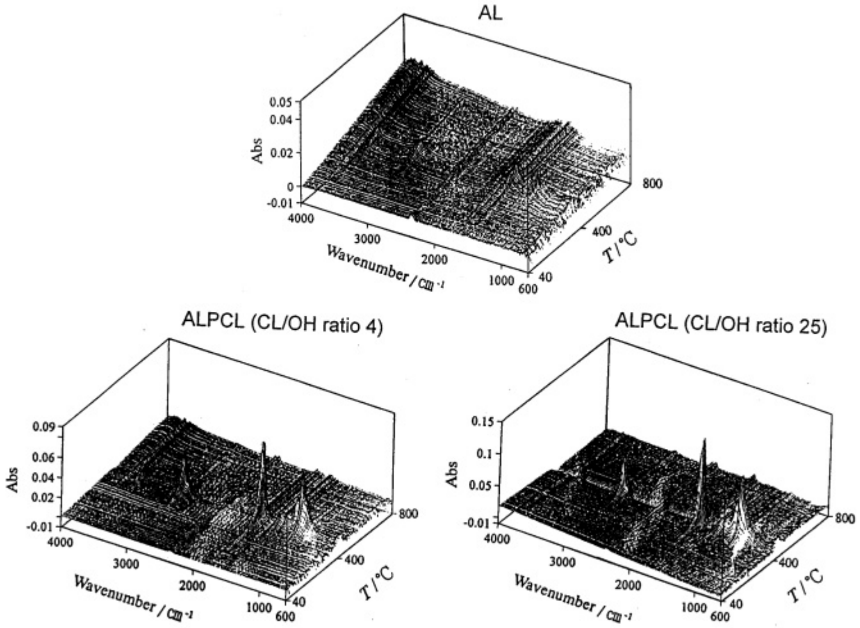

Fig. 4 Stacked FTIR spectra of evolved gases during thermal degradation of AL, ALPCL with CL/OH ratio 4 and ALPCL with CL/OH ratio 25

Figure 6 shows the changes of CH, C–O–C and C=O peak intensities of ALPCL's with various CL/OH ratios with temperature. The peak intensities of the above peaks increase with increasing CL/OH ratios and also the maximum temperatures shift when CL/OH ratios increase. This result indicates that the evolved gases at 430°C are mainly produced by thermal degradation of PCL chains in ALPCL's.

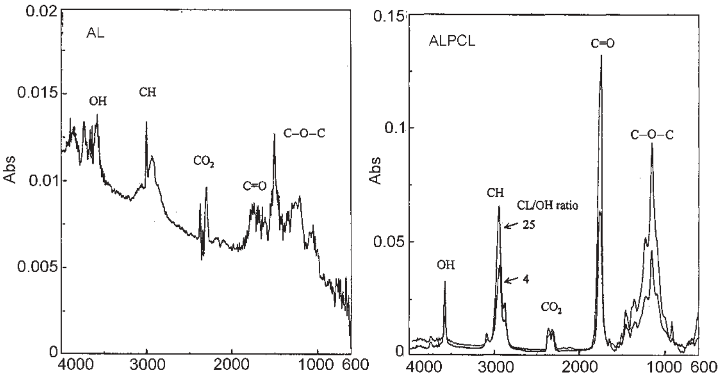

Fig. 5 FTIR spectra of evolved gases at 430°C for AL, ALPCL's with CL/OH ratio 4 and 25. The assignments for absorption peaks are indicated in the figure

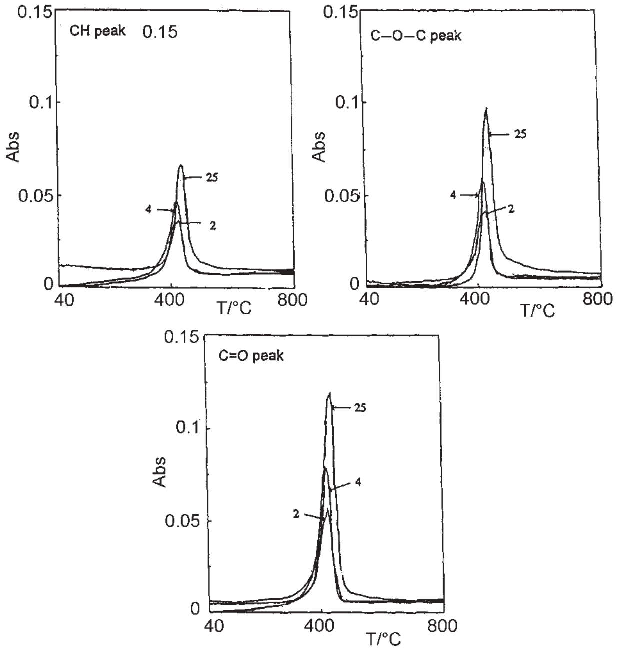

Fig. 6 Changes of peak intensities of ALPCL’s having various CL/OH ratios with temperatures for CH, C–O–C and C=O peaks

Figure 7 shows the changes of C–O–C, C=O, CH, CO_2 and OH peak intensities with CH/OH ratios in ALPCL’s at 380, 400, 420, 430 and 440°C. The peak intensities of CO_2 and OH peaks at 380°C decrease with increasing CL/OH ratios, suggesting that the evolved gases are mainly formed by the degradation of lignin in ALPCL’s. The C–O–C, C=O and CH peaks show a maximum at around CL/OH ratio 4. The tendency observed at 380°C becomes clearer at 400 and 420°C, as shown in Fig. 7. This indicates that gases with C=O and CH groups are formed by the interacted reactions during the thermal degradation of both lignin and PCL chains when CL/OH ratios are smaller than 4, and the effect of the above interacted reactions becomes less apparent when CL/OH ratios are larger than 5. At 430 and 440°C, the intensities of the C–O–C, C=O, CH and OH peaks increase with increasing CL/OH ratios. This indicates that the evolved gases with the above groups are formed by the thermal degradation of PCL chains.

Conclusions

Thermal degradation behaviour of ALPCL’s with various CL/OH ratios was studied by TG-FTIR. T_d’s of AL and ALPCL’s were determined using TG curves. T_d increased with increasing CL/OH ratio, suggesting that AL becomes thermally stable after the derivatization with PCL chains. Mass residue (*MR*) at 500°C was also determined using TG curves. *MR* values decreased with increasing CL/OH ratios. The

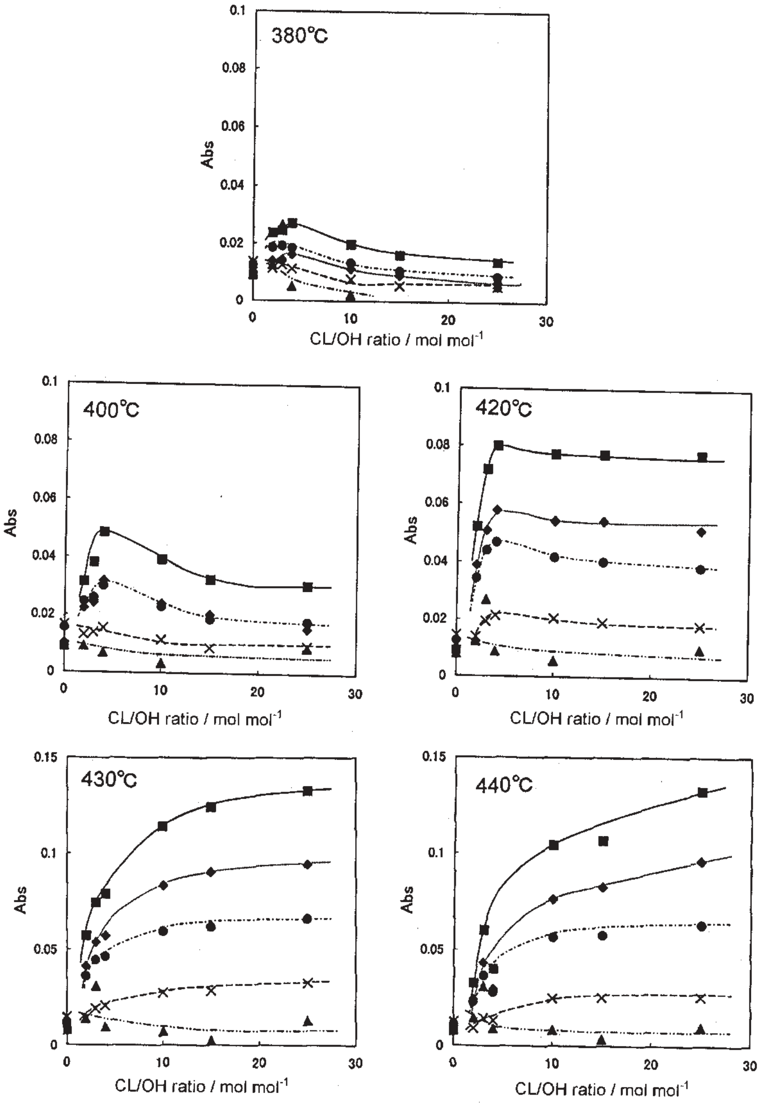

Fig. 7 Change of ◆ – C–O–C; ■ – C=O; ● – CH; × OH and ▲ – CO_2 peak intensities with CL/OH ratios in ALPCL's at 380, 400, 420, 430 and 440°C. The temperatures are shown in the figures

evolved gases formed by thermal degradation of ALPCL's at various temperatures were simultaneously analyzed by FTIR. It was found that the effect of lignin on evolved gases during thermal degradation was clear when degradation temperatures and also CL/OH ratios were low. It was also found that evolved gases were mainly formed by thermal degradation of PCL chains in PCL's when degradation temperatures were high (ca 430°C).

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