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Bio-based polyurethane composite foams with inorganic fillers studied by thermogravimetry

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Abstract

Bio-based polyurethane (PU) composite foams filled with various inorganic fillers, such as barium sulfate ($BaSO_4$), calcium carbonate ($CaCO_3$) and talc were prepared using polyols, such as diethylene glycol, triethylene glycol and polyethylene glycol (molecular weight ca. 200) containing molasses and lignin. Reactive hydroxyl groups in plant components and above polyols were used as reaction sites. Morphological observation of fracture surface of composites was carried out by scanning electron microscopy. Thermal properties of bio-based PU composites were examined by thermogravimetry. It was found that the above composites decompose in two stages reflecting decomposition of organic components. Decomposition temperature increased with increasing filler content, when plant components were homogenously mixed with inorganic fillers. Activation energy calculated by Ozawa–Wall–Flynn method was ca. 150 kJ mol^{-1}. The durability of composites was predicted using kinetic data. Calculated values indicate that composites with fillers are more durable than that of those without fillers at a moderate temperature region.

Keywords: Lignin; Molasses; Polyurethane foam; Composites; Inorganic fillers

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1. Introduction

Bio-based polymer composites have been in demand on the housing and construction market in recent years, from the view points since they are environmentally compatible and energy conserve [1]. In our previous studies, we reported the preparation of physical properties of bio-based polyurethanes [2–5] and geocomposites [6] derived from lignin and molasses. Biomass, particularly that obtained from industrial residues, such as lignin and molasses are easy to process and that market price is competitive in comparison with that of ordinary polymers derived from petroleum. Physical properties of the above geocomposites which include sand in polyurethane (PU) network structures derived from lignin or molasses showed excellent properties for practical application.

In this study, biomass-based polyurethane foams filled with various kinds of inorganic compounds were prepared using polyols containing lignin or molasses. Both plant components contain highly reactive hydroxyl groups, which can be used as reaction sites. In order to obtain stable structures and reliable properties for practical application, particularly when using the above biocomposites as construction materials, it is important to investigate the thermal properties, especially thermal stability. Among various thermoanalytical methods, in this study, thermogravimetry (TG) is extensively used. Thermal decomposition and decomposition kinetics are investigated by TG.

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2. Experimental

2.1. Sample preparation

Kraft lignin (KL) was obtained from West Vaco Co. Ltd. Molasses (glucose 8.5%, sucrose 32.5%, fructose 9.2%) was obtained from Tropical Technology Centre. Diethylene glycol (DEG), triethylene glycol (TEG) and poly(ethylene glycol) having molecular weight of M_n 200 (PEG200) were commercially obtained from Daiichi Kogyo Seiyaku Co. Ltd. Polyphenyl polymethylene polydiisocyanate (MDI) was commercially obtained from BASF Inoac Co. Ltd.

Lignin in powder form was dissolved in DEG. TEG or PEG at 65–75 °C. KL was dissolved in DEG, TEC and PEG and KL-DEG, KL-TEG and KL-PEG systems (KL polyol, KLP) with concentration 33% were prepared. Molasses in liquid form was dissolved in DEG. TEG or PEG at 25 °C. Molasses–DEG, molasses–TEG and molasses–PEG systems (ML polyol, MLP) with concentration 33% were prepared.

As shown in the preparation scheme in Fig. 1, each of the above polyol system was mixed with barium sulfate ($BaSO_4$), calcium carbonate ($CaCO_3$) or talc powder with various ratios. DEG, TEG or PEG was added in order to control viscosity of the system. Total content of lignin and molasses in mixed polyols was maintained at 33% through this experiment. The amount of inorganic materials in polyols was varied, at 40, 80, 120, 160, 200 and 240%, respectively. Silicone surfactant and di-*n*-butyltin dilaurate (DBTDL) as a catalyst, were added and a small amount of water was used as a foaming agent. This pre-mixture was reacted with MDI at 25 °C. NCO/OH ratio of the above systems was 1.2.

Inorganic materials content in polyols was calculated using the following equation:

$$\text{inorganic material content/\% in polyol} = \left(\frac{W_{\text{inorganic material}}}{W_{\text{KL or ML}} + W_{\text{DEG,TEG, or PEG}}}\right) \times 100 \qquad (1)$$

where $W_{\text{KL or ML}}$ is the mass of KL or molasses, $W_{\text{inorganic materials}}$ the mass of $BaSO_4$, $CaCO_3$ or talc and $W_{\text{DEG, TEG or PEG}}$ the mass of DEG, TEG or PEG.

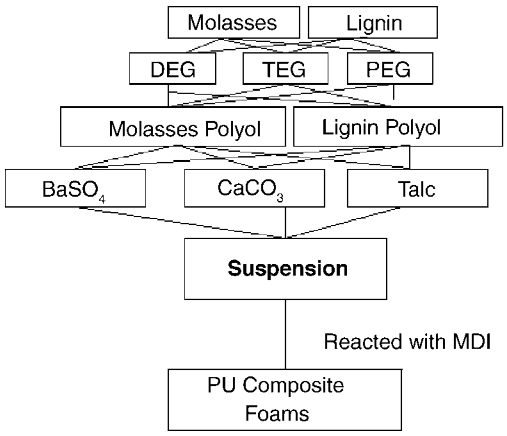


Fig. 1. Preparation scheme of biocomposite foams: DEG, diethylene glycol; TEG, triethylene glycol; PEG, polyethylene glycol.

Table 1
Biocomposites filled with inorganic materials used in this study

Fillers	Polyol					
	KL[a]			ML[b]		
	DEG[c]	TEG[d]	PEG[e]	DEG	TEG	PEG
$BaSO_4$	–	KLT/Ba	KLP/Ba	MLD/Ba	MLT/Ba	MLP/Ba
$CaCO_3$	–	KLT/Ca	KLP/Ca	MLD/Ca	MLT/Ca	MLP/Ca
Talc	KLD/Ta	KLT/Ta	KLP/Ta	MLD/Ta	MLT/Ta	MLP/Ta

[a] Kraft lignin.
[b] Molasses.
[c] Diethylene glycol.
[d] Triethylene glycol.
[e] Polyethylene glycol.

Table 1 shows combination of biomaterials, inorganic materials, kind of ethylene glycol and their abbreviations. The mount of inorganic materials is shown numerals after each abbreviated letters, for example, KLT/Ba$_{160}$ indicates that the PU composite prepared using kraft lignin polyol and triethylene glycol filled with 160% $BaSO_4$. PU samples prepared by the same conditions without fillers were used as reference materials.

2.2. Apparent density

Sample piece, 40 (width, mm) × 40 (length, mm) × 30 (thickness, mm), were prepared. The size of samples was measured using a caliper and sample mass was measured using a balance. Apparent density (ρ_a) of three pieces for each sample was measured and the mean value was calculated.

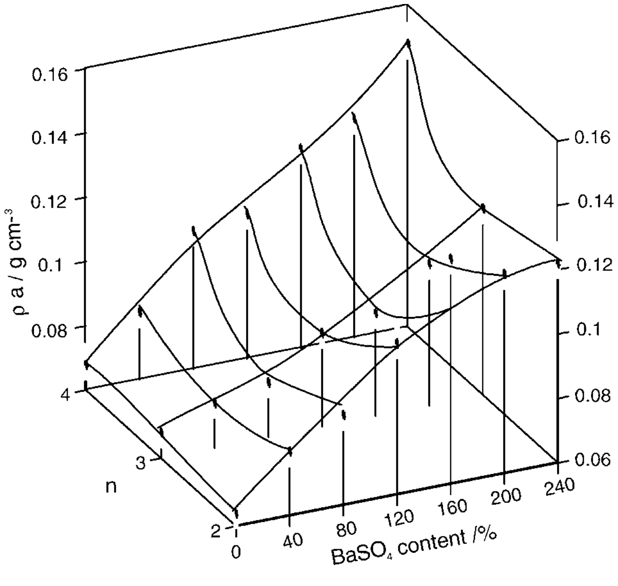
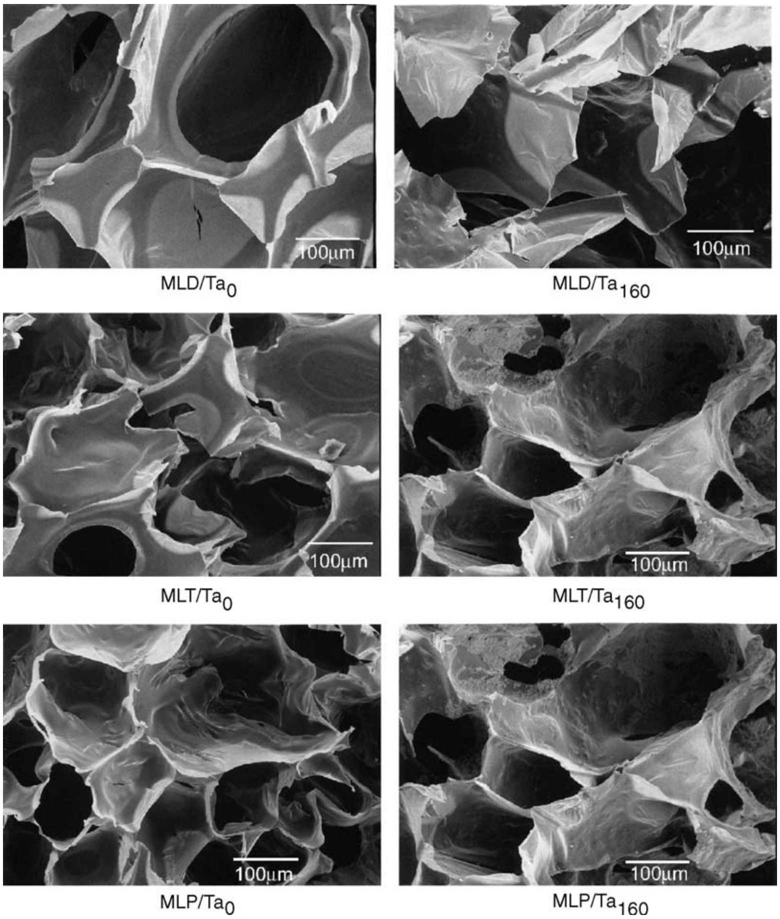


Fig. 2. Three-dimensional diagram of apparent density, $BaSO_4$ content and number of repeating units of ethylene glycol (*n*) of composites prepared using molasses polyol.



MLD/Ta_0 MLD/Ta_{160}
MLT/Ta_0 MLT/Ta_{160}
MLP/Ta_0 MLP/Ta_{160}

Fig. 3. Scanning electron micrographs of bio-based composite foams containing talc. Scale bar indicates 100 µm. Abbreviation of samples: see Table 1.

2.3. *Scanning electron microscopy*

A JEOL scanning electron microscope JSM-35CF was used. Fracture surface of the sample was coated with Au in vacuo.

2.4. *Infrared spectrometry*

A Perkin-Elmer Spectrum One Fourier infrared spectrometer equipped with a universal ATR unit was used for infrared spectrometry.

2.5. *Thermogravimetry*

A Seiko Instruments thermogravimeter-differential thermal analyzer, TG-DTA 220 was used. Sample mass was ca. 7 mg, heating rate was 20 °C min^{-1}, N_2 flow rate was100 ml min^{-1}. Temperature was changed from 25 to 600 °C. In order to calculate activation energy of decomposition, heating rate dependency of TG curves was measured for several representative samples. Heating rate was varied 1, 2, 5, 10, 20 and 40 °C min^{-1}, respectively. Decomposition temperature (T_d) was determined from TG curve and its derivative curves [7]. When the decomposition took place in two stages, T_d was numbered from the low to high temperature.

3. Results and discussion

Apparent density (ρ_a) of composite foams was varied in a range from 0.06 to 0.16 g cm^{-3} depending on inorganic filler content, number of repeating units of ethylene glycol (n) (DEG = 2, TEG = 3 and PEG = 4) and kind of plant component. Fig. 2 shows a three-dimensional representation of apparent density (ρ_a), $BaSO_4$ content and number of repeating units of ethylene glycol of MLD/Ba, MLT/Ba and MLP/Ba. It is reasonable that ρ_a increases with increasing $BaSO_4$ content. The effect of molecular mass of ethylene glycol is not marked compared with that of $BaSO_4$ content. No large difference is found in DEG and TEG, however, as shown in Fig. 2, ρ_a values of MLP/Ba are slightly larger than those of MLD/Ba and MLT/Ba.

Bio-based PU composites filled with talc prepared using molasses polyol showed similar behaviour. The kind of plant component in polyol, kraft lignin or molasses, affected ρ_a values, although results are not shown. ρ_a values of KL-based composite foams were always higher than those of ML-based composite foams. As described in the sample preparation in Section 2, water was used as a foaming agent. Molasses is more hydrophilic than KL, and the hydroxyl groups attract water molecules. A small amount of residual water in plant component seems to affect foaming conditions.

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Fig. 3 shows representative scanning electron micrographs of biocomposite foams (MLD/Ta, MLT/Ta and MLP/Ta). As clearly seen, inorganic compound (talc) is completely covered with reacted PU. The pore diameter of PU's without fillers is from ca. 70–200 μm. By adding fillers, pore shape becomes irregular. Among three different inorganic fillers, smooth surface was observed for bio-based composites filled with $BaSO_4$ and talc. However, $CaCO_3$ powder was observed as a bulk portion that was not homogeneously mixed with PU matrix.

Biocomposite foams shown in Table 1 were measured by TG under the conditions as described in Section 2. Fig. 4 shows representative TG curves and TG derivative curves of composite foams (MLP/Ta) with various talc contents. Fig. 5 shows TG curves and TG derivative curves of KLP/Ta systems. Typical two-step decomposition curves can be seen. In both TG curves, abnormal folding is observed for the samples MLP/Ta_0 and MLP/Ta_{40} in Fig. 4a, and KLP/Ta_0 and KLP/Ta_{40} in Fig. 4b. The above observation indicates that the programmed heating rate was not attained due to large endothermic heat for thermal decomposition. A sharp peak observed in TG derivative curves is artifacts reflecting the above temperature folding. It is thought that decomposition occurs in a short time when a large amount of PU content is included. As shown in TG curves, both T_{d1} and T_{d2} values of the first and the second step decomposition shift to the high temperature side with increasing talc content. Mass residue at 500 °C linearly increased with increasing talc content. As already reported in our previous studies based on TG-Fourier

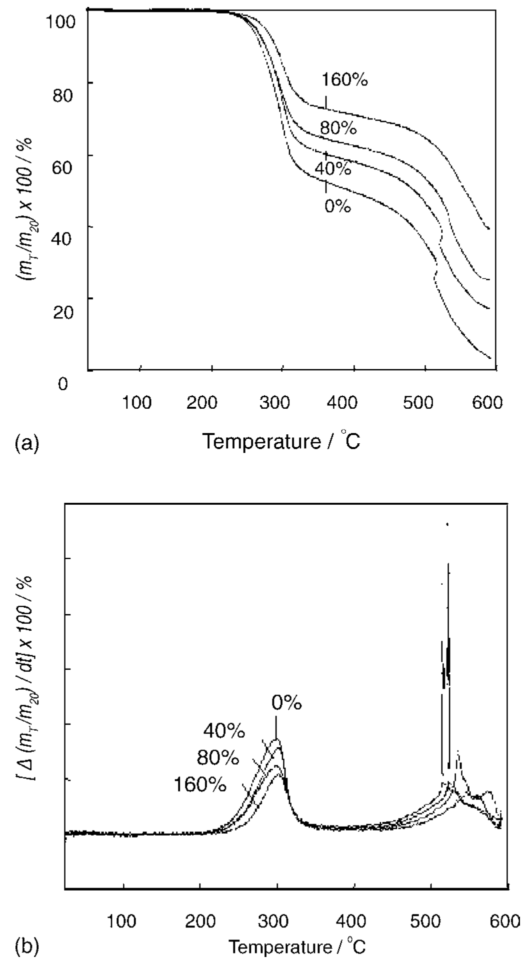

Fig. 4. Representative TG curves (a) of MLP PU, MLP/Ta_{40}, MLP/Ta_{80} and MLP/Ta_{160} and their derivative curves (b).

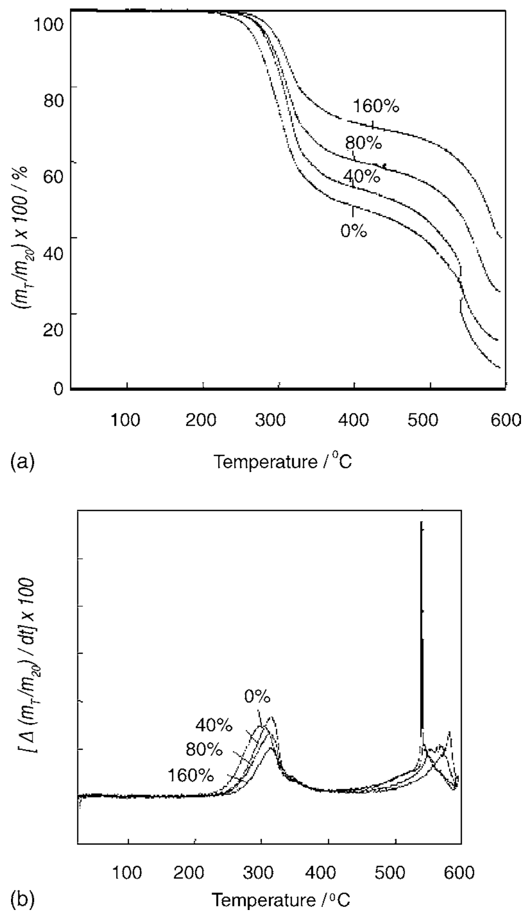

Fig. 5. Representative TG curves (a) of KLP PU, KLP/Ta_{40}, KLP/Ta_{80} and MLP/Ta_{160} and their derivative curves (b).

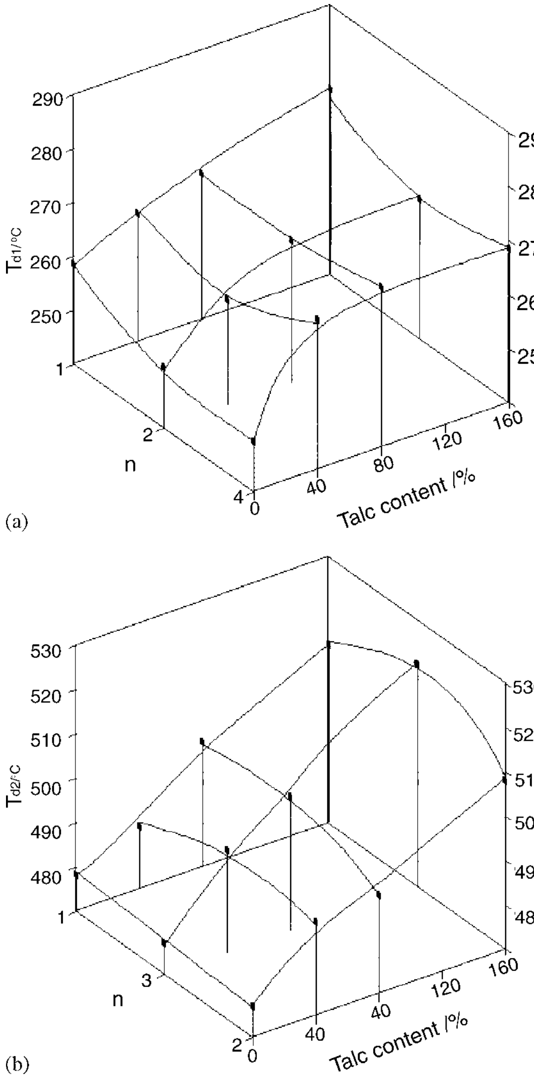

Fig. 6. Three-dimensional diagram among T_d, talc content and number of repeating units of ethylene glycol. (*n*) of ML/Ta systems: (a) T_{d1}, (b) T_{d2}.

transform infrared spectroscopy (FTIR) [1,4], the first step decomposition of molasses PU is attributed to the decomposition of pyranose rings and isocyanate, and the second step thermal decomposition is attributed to the total decomposition of organic compounds. In the case of kraft lignin PU, the first step thermal decomposition is attributed to the breakage of phenol structure of lignin.

Fig. 6 shows three-dimensional diagrams between T_{d1} (Fig. 6a) and T_{d2} (Fig. 6b) of ML/Ta systems, number of repeating units of ethylene glycol and talc content. Both T_{d1} and T_{d2} increase with increasing talc content. In contrast, the number of repeating units of ethylene glycol scarcely affects T_d. Although the results are not shown, the effect of plant components was negligible.

By observation of SEM, $BaSO_4$ and talc were homogeneously mixed with PU foams regardless of kinds of plant component, however, unmixed portion of $CaCO_3$ powder was observed. T_{d2} values of composites filled with $CaCO_3$ maintained the same T_{d2} value of PU without fillers, when $CaCO_3$ content was varied. The above results strongly suggest that molecular interaction between bio-based PU and inorganic fillers is taken place. In order to confirm the above results, biocomposites were examined by infrared spectrometry (IR). IR data indicated that no distinct absorption band due to hydrogen bonding was newly observed, although characteristic peaks of inorganic fillers shift and merged into absorption bands of PU were detected. It is thought that further investigation is necessary concerning the results of IR spectrometry.

The first step decomposition was kinetically investigated using Ozawa–Wall–Flynn method [8–10]. Fig. 7 shows heating rate dependency of T_{d1} of MLP/Ta_0 and MLP/Ta_{160}. T_{d1} values of talc filled samples are larger than those of reference sample in a whole range of heating rate. The similar tendency was obtained for T_{d2}. This suggests that intermolecular interaction exists between filler and PU components. Ozawa–Wall–Flynn method was applied to the first step decomposition:

$$\log\beta = 0.4567\left(\frac{\Delta E}{R}\right)\left(\frac{1}{T}\right) + \text{const} \tag{2}$$

where β is heating rate, ΔE the activation energy, T the absolute temperature and R the gas constant. In order to satisfy the defined conditions, the initial stage of decomposition curve was used for calculation. Fig. 8 shows relationship between heating rate ($\beta = \mathrm{d}T/\mathrm{d}t$) and reciprocal absolute temperature. Fig. 8a shows the results of MLP PU without filler and Fig. 8b shows those of MLP/Ta_{160}. It is clearly seen that gradient of straight lines is identical, although T_{d1} of MLP/Ta_{160} shifts to the high temperature side. Activation energy of MLP was 150 J mol^{-1} and that of MLP/Ta_{160} was 130 J mol^{-1}, respectively. The above facts suggest that the mechanism of the first stage decomposition is the same, regardless of inorganic filler.

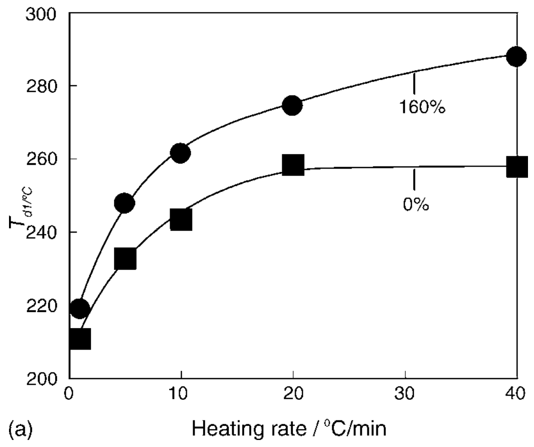

Fig. 7. Heating rate dependency on T_d's of MLP/Ta_0 and MLP/Ta_{160}.

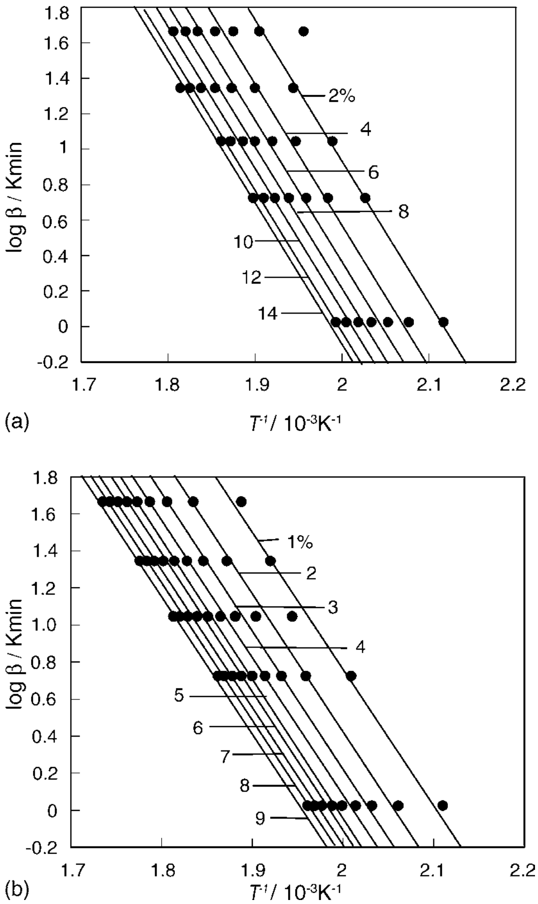

Fig. 8. Relationships between logarithmic heating rate and reciprocal absolute temperature: (a) MLP/Ta_0, (b) MLP/Ta_{160}. Numerals in the figures show mass decrease in %.

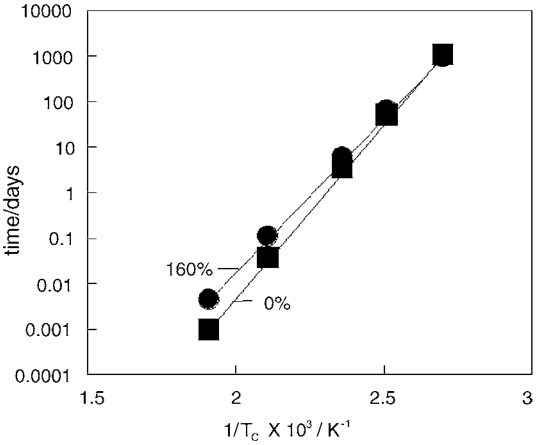

Fig. 9. Relationship between lifetime (τ) and reciprocal holding temperature of MLP/Ta_{20} and MLP/Ta_{160}. Numerals in the figure show talc content.

Lifetime at a temperature lower than T_d was predicted using Ozawa equation shown in the following equation:

$$\tau = \frac{\int_{T_2}^{T_1} \exp\left(-\frac{\Delta E}{RT}\right)}{\beta\left(-\frac{\Delta E}{RT_c}\right)} \tag{3}$$

where t is the lifetime and T_c a holding temperature. Using the initial stage of decomposition, lifetime (τ) was calculated. Fig. 9 shows relationship between τ and reciprocal absolute temperature of holding for MLP/Ta_0 and MLP/Ta_{160}. As shown in this figure, the talc filled sample is thermally durable in the high temperature region, however, when temperature decreases, difference between two samples is not observable.

4. Conclusions

Bio-based PU composite foams filled with $BaSO_4$. $CaCO_3$ and talc were prepared using polyols containing lignin or molasses. Homogeneous composites were obtained in a wide range of filler content when $BaSO_4$ and talc were used as fillers, regardless of the kinds of plant component. TG curves showed that thermal decomposition of all samples was carried out in two stages reflecting decomposition of plant components. Scanning micrographs indicated $BaSO_4$ and talc were homogeneously masked by PU matrix. Decomposition temperature increased with increasing filler content, when plant components were homogenously mixed with inorganic fillers. Activation energy calculated by Ozawa–Wall–Flynn method was ca. 130–150 J mol^{-1}. Calculated values indicate that durability of composite foams with fillers is higher than that of those without fillers at a moderate temperature region.

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