

Glass transition of rigid polyurethane foams derived from sodium lignosulfonate mixed with diethylene, triethylene and polyethylene glycols

T. Hatakeyama^{a,*}, Y. Matsumoto^a, Y. Asano^b, H. Hatakeyama^b

^a *Otsuma Women's University, 12 Sanban-cho, Chiyoda-ku, Tokyo 102-8357, Japan*

^b *Fukui University of Technology, 3-6-1 Gakuen, Fukui 910-8505, Japan*

Received 6 November 2002; received in revised form 9 December 2002; accepted 10 December 2002

Available online 1 February 2004

Abstract

Sodium salt of lignosulfonic acid (LS), which was obtained as a by-product of cooking process in sulfite pulping, was solved in diethylene-, triethylene or polyethylene glycol. Three series of polyurethane foams (LSPU) were synthesized by varying the LS content from 0 to 33 wt.%. Thermal properties of LSPU foams were studied by thermomechanometry (TMA) and differential scanning calorimetry (DSC). Main glass transition was observed in a temperature ranging from 80 to 140 °C. Glass transition temperature (T_g) increased with increasing LS content and with decreasing oxyethylene chain length. T_g values obtained by TMA accorded well with those by DSC.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Lignosulfate; Poly(ethylene glycol); Polyurethane; DSC; TMA; Glass transition

1. Introduction

Metal salts of lignosulfonic acid (LS), such as sodium (Na), calcium (Ca) and magnesium (Mg) are produced from an eluted solution obtained as a by-product of cooking process in sulfite pulping. The sulfonic group is usually introduced into α -position of the phenylpropane structure of lignin via cleavage of the side chain [1]. LS are containing Na, Ca or Mg combined with the sulfonic group in lignin. Molecular mass ranges from several hundred to several million according to the preparation conditions. Since LS consists of C6–C3 hydrophobic basic structure with hydrophilic groups such as sulfonic, hydroxyl and carboxyl groups, an aqueous solution of LS shows amphiphilic properties. On this account, LS has been used as a dispersant in a wide range of industrial fields. Due to its ionic nature, chemical modification of LS has not attempted, although a large amount of LS is produced in the world.

In our previous studies, polyurethanes in both sheet and foam shapes were derived from Kraft lignin and solvolysis (alcoholysis) lignin [2–8]. In the above synthesis, hydroxyl groups in lignin are used as reaction sites. By controlling the preparative conditions, physical properties such as mechanical and thermal properties, could be varied in a wide range. For example, glass transition temperature of polyurethane derived from solvolysis lignin are controlled in a temperature ranging from –10 to 130 °C [6], and ultimate stress was varied from 1 to 75 MPa [5]. The amount of lignin in PU is crucial in order to control the physical properties, since lignin molecules act as hard segments of the polyurethane.

In this study, we paid attention to utilization of LS. LS is water soluble, however, it is insoluble in ordinal organic solvents. On this account, LS has not been used as a reaction component. At the same time, it is known that LS can be soluble in certain kinds of organic solvents, such as diethylene-glycol, triethylene-glycol and poly(ethylene glycol). We developed novel polyurethane rigid foams using the above special characteristics of LS. Mechanical and thermal properties of LSPUs are important when they are utilized in various industrial fields. In the present study, glass transition behavior of LSPUs is investigated by thermomechanometry and differential scanning calorimetry (DSC).

* Corresponding author. Tel.: +81-3-5275-6023; fax: +81-3-5275-6932.

E-mail address: hatakeyama@otsuma.ac.jp (T. Hatakeyama).

2. Experimental

2.1. Sample preparation

Sodium (Na) lignosulfonate (commercial name Vanilex HW) was provided by the Nihon Seishi Co. Ltd. According to the manufacturer's report, the samples were purified after partial desulfonation; sulfonate group was 0.13 mol per C9–C3 and carboxyl group 0.26, alcoholic hydroxyl group 0.28 and phenolic hydroxyl group 0.42, respectively. Three series of polyurethanes from LS (LSPU) were synthesized according to the similar procedure as previously reported [9]. As a flexible component of PU, diethylene glycol (DEG), triethylene glycol (TEG) and polyethylene glycol with molecular mass of 200 (PEG200) were used. The above three oligoethylene glycol were commercially obtained from Tokai Rubber Industries Ltd. According to the manufacturer's report, each sample have molecular weight distribution, for example, TEG contains a considerable amount of DEG and tetraethylene glycol. LS was dissolved in DEG, TEG or PEG at a temperature ranged from 65 to 75 °C. LS content of the above solution was varied from 0 to 33%. LS content was calculated as follows:

$$\text{LS content (\%)} = \left[\frac{m_{\text{LS}}}{m_{\text{LS}} + m_{\text{DEG, TEG or PEG}}} \right] \times 100 \quad (1)$$

where m_{LS} is the mass of LS and $m_{\text{DEG, TEG or PEG}}$ the mass of DEG, TEG or PEG. The above polyol solution was

mixed with small amount of plasticizer (silicone surfactant), catalyst (di-*n*-butyltin dilaurate) and foaming agent (water). This premixture was reacted with diphenylmethane diisocyanate (MDI) under vigorous stirring at room temperature. NCO/OH ratio was 1.2. After foams were obtained, the samples were allowed to stand overnight at room temperature. PUs containing the above three different kinds of poly- and oligo-ethylene glycol are designated as LSDPU, LSTPU and LSPPU, respectively. Schematic chemical structure of the sample is shown in Fig. 1.

2.2. Thermomechanometry

Thermomechanical analysis was carried out using a Seiko TMA SS150 in a temperature ranging from 25 to 220 °C. A compressive type quartz sensor with surface area $9.616 \times 10^{-6} \text{ m}^2$ was used. PU foams were cut in a plate shape with $1.5 \times 10^{-5} \text{ m}^2$ surface area and thickness ca. $0.2 \times 10^{-3} \text{ m}$. The sample was placed on a quartz plate. Load applied during measurements was varied from 3.12×10^3 to $1.04 \times 10^4 \text{ Pa}$. Ordinal measurements were carried out by applying 50 mN. Heating rate was $10^\circ \text{ min}^{-1}$ and sampling time was 0.5 s. Starting temperature of expansion was defined as a point where the TMA curve deviates from the straight line (T_s). Glass transition temperature was defined as intercept point where the extrapolated straight line from T_s meets the extrapolated line of tangential line of expansion. Compression before and after transition ($-\Delta l$) was measured and

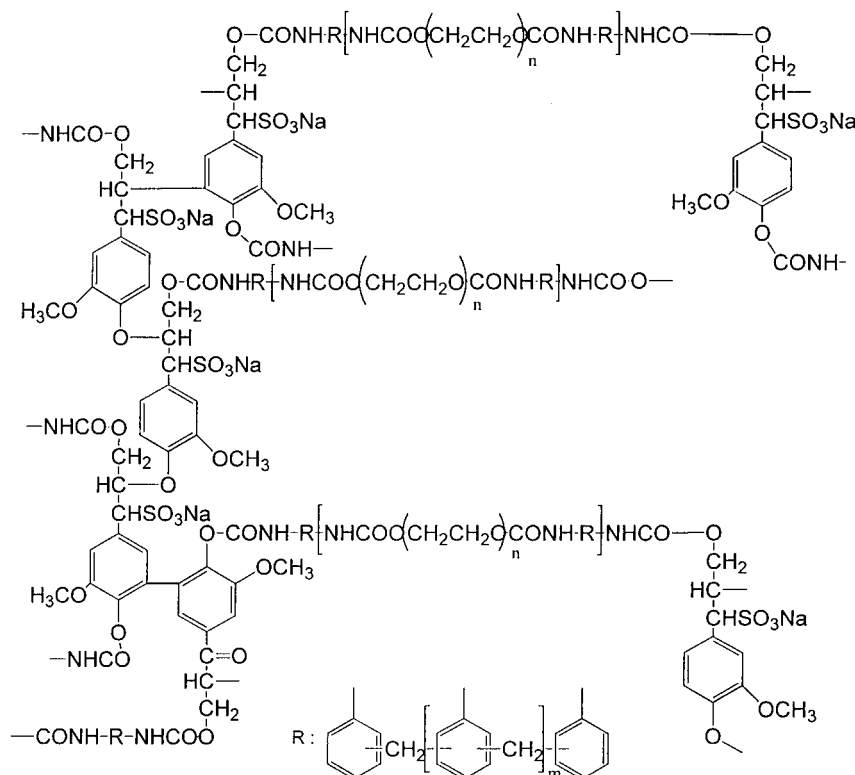


Fig. 1. Chemical structures of polyurethanes derived from lignin sulfonate Na salt (LSPU).

compression rate (ε) was calculated as follows:

$$\varepsilon (\%) = - \left(\frac{\Delta l}{l_0} \right) \times 100 \quad (2)$$

where l_0 is the thickness of the sample at 25 °C. Average compression coefficient was calculated using data obtained in a temperature ranging from T_s to $T_s - 20$ °C.

2.3. Differential scanning calorimetry

Differential scanning calorimetry was performed using a Seiko DSC 220 at a heating rate of 10 °C min⁻¹ under a nitrogen flow (flow rate = 30 ml min⁻¹). Sample mass was 5–10 mg. Aluminum open pans were used. The samples were heated to 200 °C and cooled at 40 °C min⁻¹ to -120 °C. DSC scans were repeated two times. The results of the second run were used for determination of glass transition temperature (T_g) and heat capacity gap at T_g (ΔC_p).

2.4. Thermogravimetry

Thermogravimetry (TG) was carried out in nitrogen (flow rate = 200 ml min⁻¹) using a Seiko TG 220 at a heating rate of 20 °C min⁻¹ in the temperature range from 20 to 800 °C. Sample mass was ca. 5 mg. TG curves and derivatograms were recorded.

2.5. Scanning electron microscopy

Scanning electron microscopy was carried out using a JEOL JSM-5510LV at accelerating voltage 1.0 kV. The sample was broken and coated with Au.

3. Results and discussion

Rigid polyurethane (PU) foams were prepared as mentioned in Section 2. The color of the PU foams changed from light to dark brown depending on lignin content. Apparent density ranged from 0.08 to 0.12 kg m⁻³. Diameter of pore, which was measured by scanning electron microscopy was changed from 100 to 300 × 10⁻⁶ m. No large morphological difference was observed among LSDPU, LSTPU and LSPPU samples when LS content were the same.

Fig. 2 shows representative stacked DSC curves of LSPPU and LS. A major heat capacity gap (ΔC_p) due to glass transition is observed in a temperature ranging from 80 to 100 °C depending on LS content for LSPPU samples. Glass transition temperature (T_g) linearly increases with increasing LS content. C_p difference at T_g (ΔC_p) was 0.35–0.15 J g⁻¹ K⁻¹. The C_p values are smaller than those of ordinal amorphous polymers [10], suggesting that the crosslinking points restrict the free molecular motion. When DSC curves are magnified several times, slight endothermic changes in the baseline were detected at around 50 and 180 °C. A C_p gap in the baseline measured in the low temperature side at around

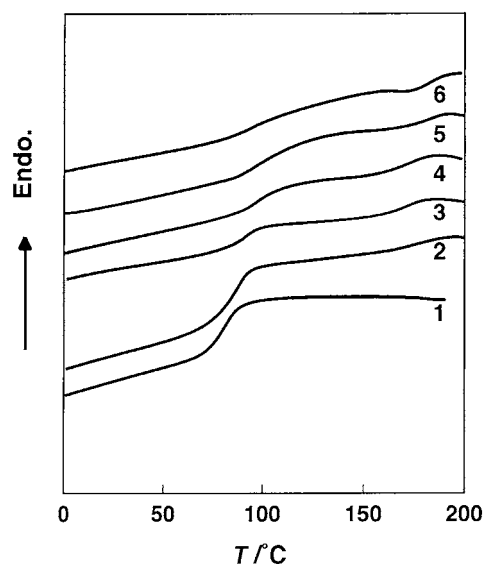


Fig. 2. Representative stacked DSC curves of LSPU with various lignin contents heated at 10 °C min⁻¹. Numerals in the figure show LS content (%)—(1) 0; (2) 7; (3) 13; (4) 20; (5) 26; (6) 33.

50 °C was so small, that reliable data could not be obtained. However, the C_p gap observed at the higher temperature side at around 80 °C could be clearly distinguished from the main T_g , although C_p difference at T_{gh} (ΔC_{ph}) was scattered in a certain range. The high temperature side T_g was designated as T_{gh} . Similar DSC curves were observed for the other two series of samples, LSDPU and LSTPU. T_g and T_{gh} values were determined as reported previously [11].

Fig. 3 shows relationships between T_g , T_{gh} and LS content of three series of LSPUs. As shown in Fig. 3, the length of ethylene glycol markedly affects T_g values, i.e. T_g values decrease with increasing chain length when LS content is

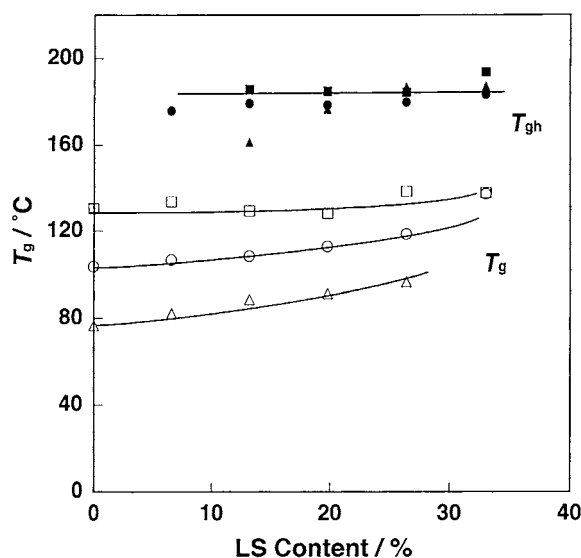


Fig. 3. Glass transition temperatures of LSPU samples measured by DSC as a function of LS content. T_g —(□) LSDPU, (○) LSTPU, (△) LSPPU; T_{gh} —(■) LSDPU, (●) LSTPU, (▲) LSPPU.

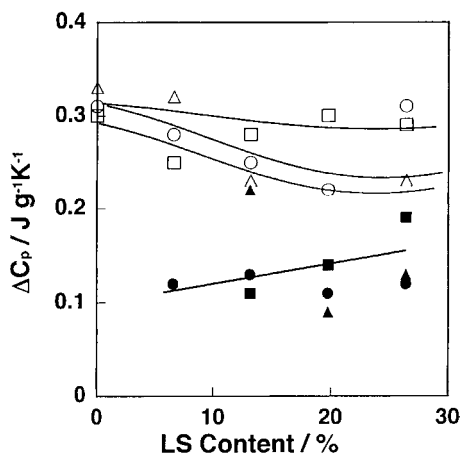


Fig. 4. Relationships between ΔC_p and LS content of LSPU samples. ΔC_p —(□) LSDPU, (○) LSTPU, (△) LSPPU; ΔC_{ph} —(■) LSDPU, (●) LSTPU, (▲) LSPPU.

the same. Among the three series of samples, T_g values of LSDPU slightly increase with LS content, in contrast T_g of LSPPU depends markedly on LS content. This indicates that the molecular mobility is affected by the length of oxyethylene chains which connect LS molecules which act as hard segments. T_{gh} of three samples are maintained at constant value of ca. 180 °C, regardless of LS content and oxyethylene chain length. When the T_g value of LS is taken into account [12], it is appropriate to consider that T_{gh} is attributed to the molecular motion of LS molecules.

Fig. 4 shows variation of ΔC_p and ΔC_{ph} as a function of LS content. Although ΔC_p values are scattered, the general tendency indicates that ΔC_p values decrease and ΔC_{ph} values slightly increase with increasing LS content. This also suggests that the main T_g is attributable to the LS connected with oxyethylene chains via urethane linkage, and T_{gh} reflects the molecular motion of LS molecules.

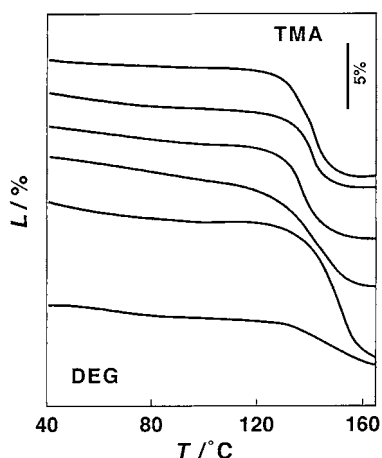


Fig. 5. Stacked TMA curves of LSPU with various LS content heated at 10 °C min⁻¹. Numerals in the figure show LS content (%)—(1) 0; (2) 7; (3) 13; (4) 20; (5) 26; (6) 33.

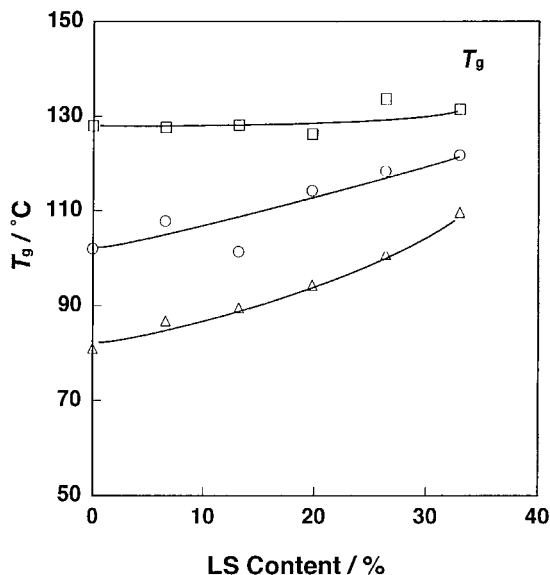


Fig. 6. Glass transition temperature of LSPU samples measured by TMA. T_g —(□) LSDPU, (○) LSTPU, (△) LSPPU.

As described in Section 2, TMA was carried out under the same conditions as DSC. In order to examine the effect of applied force on transition temperature, applied stress was varied from 3.12×10^3 to 1.04×10^4 Pa. Transition temperatures were maintained at constant values as a function of applied stress. On this account, 5.2×10^3 Pa was chosen after the TMA experiments. Representative TMA curves of LSDPU are shown in Fig. 5. Each TMA curve shows two step decreases in the linear compression curve. The first decrease

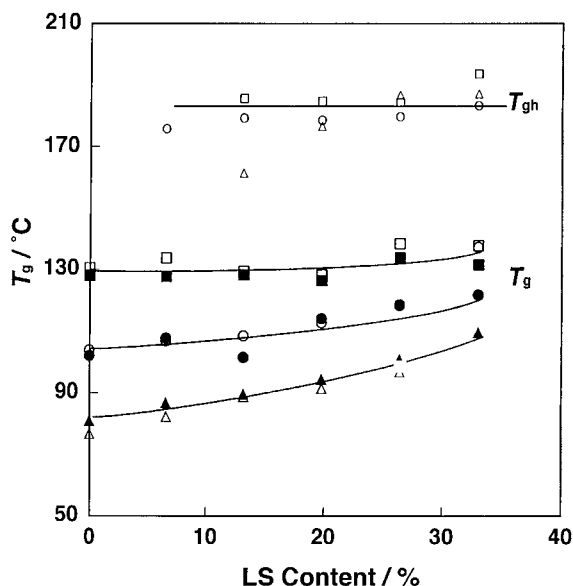


Fig. 7. Glass transition temperature of LSPU samples measured by DSC and TMA as a function of LS content. Heating rate = 10 °C min⁻¹. T_g —(□) LSDPU, (○) LSTPU, (△) LSPPU (DSC); T_g —(■) LSDPU, (●) LSTPU, (▲) LSPPU (TMA); T_{gh} —(□) LSDPU, (○) LSTPU, (△) LSPPU (DSC).

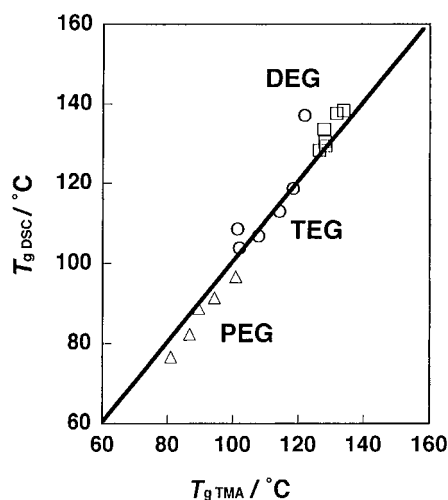


Fig. 8. Relationships between T_g measured by DSC and that of TMA: (□) LSDPU; (○) LSTPU; (△) LSPPU.

is small and was observed in a temperature range from 45 to 55 °C for all samples regardless of LS content. When TMA curves are magnified, it is clearly seen that the temperature of decrease depends on oxyethylene chain length not on LS content. On this account, the low temperature side inflection observed in TMA curves is attributed to the molecular motion of oxyethylene groups. The major increase in linear compression is large and the temperature defined as described in Section 2 agrees well with the main T_g measured by DSC. On this account, the inflection point in the TMA curve is defined as T_g .

The relationship between T_g measured by TMA and LS content was established as shown in Fig. 6. It is found that T_g values measured by TMA vary in a similar manner to T_g variation measured by DSC.

Compression rate, ε , which was defined in Section 2 was calculated for all samples. The major compression took place at T_g . At the same time, it was found that ε depends on both LS content and oxyethylene chain length. Average linear compression coefficient in a temperature between T_{gh} and T_g was from -1 to $-1.2 \mu\text{m } ^\circ\text{C}^{-1}$ for LSDPU, from -2.8 to $-4.2 \mu\text{m } ^\circ\text{C}^{-1}$ for LSTPU and from -3.8 to $-6.0 \mu\text{m } ^\circ\text{C}^{-1}$ for LSDPU. Average compression coefficient increases with increasing oxyethylene chain length and with decreasing LS content. These results are thought to be reasonable since long oxyethylene chain increases flexibility of molecular chains and LS molecules act as hard segments of PU.

Fig. 7 shows the relationships between glass transition temperatures of three series of samples determined by both

TMA and DSC and LS content. The main T_g accords well with each other. This can be clearly seen from the relationship shown in Fig. 8. A complete linear relation is found between T_g values measured by DSC and those of TMA for three series of samples. It is also clear that T_g increases in the order of oxyethylene chain length.

In this study, PU foams were successively prepared using NaLS which has been ignored due to its ionic nature. Thermal properties of LSPU are controlled through preparation. The phase transition behavior of LSPUs was investigated by TMA and DSC. The main glass transition is attributable to both LS molecules which acts as a hard segment and flexible oxyethylene chain. T_g values estimated by both methods accord well with each other. At the sample time, using two different thermal analytical methods, it was possible to detect glass transitions of NaLS, not only major molecular motion but also a small amount of inhomogeneous components. The main chain motion of NaLS which has been scarcely detected due to the ionic intermolecular bonding, could be detected as T_{gh} . This is due to the fact that a very limited number of LS molecules remain whose hydroxyl group are not fully bonded via urethane linkage. Based on the above thermomechanical properties, LSPU foams have a large potential for application in various fields.

References

- [1] D.A.I. Goring, in: K.V. Sarkanen, C.H. Ludwig (Eds.), *Lignins*, Wiley/Interscience, New York, 1971, pp. 697–768.
- [2] H. Hatakeyama, *Netsu-Solutei* 28 (2001) 183–191.
- [3] K. Nakamura, R. Morck, K.P. Kringstad, H. Hatakeyama, in: J.F. Kennedy, G.O. Phillips (Eds.), *Wood Processing and Utilization*, Ellis Horwood, Chichester, 1989, pp. 175–180.
- [4] H. Yoshida, R. Morck, K.P. Kringstad, H. Hatakeyama, *J. Appl. Polym. Sci.* 40 (1990) 1819–1832.
- [5] K. Nakamura, R. Morck, K.P. Kringstad, H. Hatakeyama, *Polym. Adv. Technol.* 2 (1991) 41–47.
- [6] K. Nakamura, T. Hatakeyama, H. Hatakeyama, *Polym. Adv. Technol.* 3 (1992) 151–155.
- [7] J. Nakano, Y. Izuta, T. Orita, H. Hatakeyama, K. Kobashigawa, K. Teruya, S. Hirose, *Sen-i Gakkaishi* 53 (1997) 416–422.
- [8] S. Hirose, K. Kobashigawa, Y. Izuta, H. Hatakeyama, *Polym. Intel.* 47 (1998) 247–256.
- [9] Y. Asano, H. Hatakeyama, *Memoirs Fukui Niv. Technol.* 32 (2002) 275–282.
- [10] T. Hatakeyama, H. Hatakeyama, *Thermochim. Acta* 267 (1995) 249–257.
- [11] T. Hatakeyama, F.X. Quinn, *Thermal Analysis*, Wiley, Chichester, 1994, pp. 107–110.
- [12] H. Hatakeyama, K. Nakamura, T. Hatakeyama, *Pulp Pap. Mag. Can.* 81 (1980) TR105–TR110.