

Synthesis of Biopolyols by Mild Oxypropylation of Liquefied Starch and Its Application to Polyurethane Rigid Foams

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ABSTRACT: The liquefaction of starch in the presence of commercial polyol resulted in liquefaction products (LPs) with much lower hydroxyl values compared to those resulting from glycerol liquefaction. With the use of the obtained LPs (as initiators) and a catalytic amount of potassium hydroxide, oxypropylation was conducted under mild conditions (at 120°C, inner pressure generation of <0.2 MPa). Urethane resin foams were prepared from the obtained biopolyols. The reactivities of the biopolyols toward isocyanates were almost the same as those of commercial polyols. The physical properties of the obtained foams were as good or better than the ones obtained with the commercial polyols, including the sucrose/glycerol polyol GR-84T. The biomass content values of the foams prepared with the biopolyols ranked among the highest in the world. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 622–630, 2013

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INTRODUCTION

During the past 40 years, oxypropylation has been extensively applied to biomass.^{1–7} Oxypropylation has been recognized as a viable and promising approach for overcoming the technical limitations and constraints imposed by the nature of biomass.² Starting solid components of biomass become a liquid polyol with the introduction of multiple ether moieties.⁷

A typical oxypropylation procedure⁶ consists of the introduction of weighed amounts of biomass and catalytic amounts of potassium hydroxide (KOH) pellets into a stainless steel reactor, followed by the addition of propylene oxide (PO). The reactor is closed, and the solid/liquid suspension is heated progressively under stirring to reach temperatures of 160°C. The oxypropylation starts in a striking manner as the temperature is increased. Then, a big increase in the temperature, which attains value of 201°C, and the pressure (up to 2.1 MPa) takes place.

These oxypropylation conditions used are considered to be too severe. Severe oxypropylation favors the liquefaction of biomass. However, it is known that under such severe conditions, monoalcoholic side products having unsaturated end groups can be

formed.^{8–10} The formation of these monoalcoholic products hinders the proceedings of crosslinking and polymerization during urethane resinification and results in a decrease in the physical properties of the urethane resins. The unsaturated end groups were shown to come from the isomerization of PO to allyl alcohol, which initiates new polymer chains.^{8–10} Thus, the conditions of oxypropylation should be constrained to a much milder range.

In a related report, Briones et al.¹ pointed out that there are two methods that can convert these solid biomasses into liquid polyols. One is oxypropylation,^{1–7} and the other is the liquefaction of biomass.^{11–14} The former is chiefly caused by the introduction of oligo (PO) grafts, partly deteriorated by severe reaction conditions, and the latter is done by solvolysis.

The liquefaction function of the oxypropylation makes it possible to convert even date seeds,¹ cork,³ rapeseed cakes,⁶ lignin,² and sugar beet pulp⁵ into liquid states. Needless to say, all of these biomasses can be liquefied by solvolysis liquefaction.^{11–14}

The combined use of liquefaction and oxypropylation are considered to be meaningful for obtaining convenient polyols.

Products obtained by only solvolysis liquefaction have high viscosities. Thus, their reactivities with isocyanates are not so good. Oxypropylation of these products can make their viscosities lower and reactivities higher. However, the reaction conditions of oxypropylation should be much milder.

In this study, we tried to make the oxypropylation conditions much milder¹⁴ compared with those adopted in Refs. 1–6 to prevent the formation of monoalcoholic products with unsaturated end groups. Even in this case, oxypropylation is an important procedure for obtaining polyols with adequate properties. We also tried to elucidate the physical and chemical characteristics of the biobased polyols before and after oxypropylation. Considering the requirements for polyols in view of their use in rigid polyurethane foams [hydroxyl value (OHV) between 500 and 300 mgKOH/g and viscosity < 10,000 mPa·s, more favorably 6000 mPa·s], we chose formulations for the synthesis of oxypropylated polyols from liquefaction products (LPs). The produced polyols were characterized in terms of their OHV and viscosity values. The mechanical and thermal properties of the polyurethane rigid foams prepared from the obtained biobased polyols were evaluated.

EXPERIMENTAL

Materials

The starch used as the starting material was corn starch obtained from Nacalai Tesque, Inc., Kyoto, Japan. Glycerol, methyl alcohol, and sulfuric acid (Nacalai Tesque) were used as the media and catalyst, respectively, for the liquefaction of starch. The commercial polyol (Actcol IR-96, OHV = 430 mgKOH/g) used as the liquefaction medium was supplied by Mitsui Chemicals, Inc., Tokyo, Japan. PO and KOH used in oxypropylation were purchased from Asahi Glass Co., Tokyo, Japan and Nacalai Tesque, respectively. Other chemicals for the measurements of OHV and gel permeation chromatography (GPC) were also obtained from Nacalai Tesque and Wako Pure Chemical Industries, Ltd., Osaka, Japan. Polymeric 4,4'-diphenylmethane diisocyanate (*p*-MDI; Cosmonate M-200, % NCO = 31.3) and other chemicals used to prepare the polyurethane foams were supplied by Mitsui Chemicals. In addition, *N,N,N',N'*-tetramethyl hexane diamine (Kaolizer no. 1) and *N,N,N',N'*-pentamethyl diethylene triamine (Kaolizer no. 3) were obtained from Kao, Inc., Tokyo, Japan. The silicone surfactant (SF-2937F) was from Toray Industries, Inc., Tokyo, Japan. The commercial polyols Actcol GR-84T, MN-400, and PE-350 (OHVs = 460, 400, and 350 mgKOH/g, respectively) used as control polyols were also obtained from Mitsui Chemicals.

Methods

Liquefaction of Corn Starch by the Use of Two Different Liquefaction Media. As the first step of this experiment, the liquefaction of starch was conducted in two ways. One was the use of a liquefaction medium of a 9 : 1 w/w mixture of glycerol and methyl alcohol (series A). The other was the use of a liquefaction medium of a 7.2 : 1.8 : 1.0 w/w mixture of Actcol IR-96, glycerol, and methyl alcohol (series B). The liquefactions were done in a pressure-resistant stainless steel reaction tube for 60 min at 120°C for the series A and 140°C for series B. Both of the LPs were neutralized and filtered to remove salts. Methanol

and the generated water were distilled off under diminished pressure before oxypropylation.

Oxypropylation Reactions of the Liquefied Starches. A definite amount of series of LP (used as the initiator) and a catalytic amount of KOH were weighed into an autoclave; this was followed by nitrogen blowing. After the distillation of water under diminished pressure (<10 mmHg at 100°C for 30 min), oxypropylation reactions were carried out with the autoclave at 120°C; we introduced PO, keeping the inner pressure less than 0.2 MPa. After introducing a calculated amount of PO, we continued the aging reactions until the inner pressure reached the normal pressure. The yields of the reactions were almost 100%. After the completion of those aging reactions, the products were neutralized by the addition of phosphoric acid at 70°C. The neutralized products were filtered to remove salt by use of a pressure filter (Advantec Co., Osaka, Japan) to obtain the intended polyols (liquefied starch PO adducts).

Preparation of the Polyurethane Rigid Foams. Polyurethane rigid foams were prepared from biobased polyols obtained through oxypropylations of the two series of liquefied starches. The prescriptions for the foam preparations are shown in Table I. Actcol GR-84T, MN-400, and PE-350 were used as control polyols.

Definite amounts of the two kinds of catalysts (Kaolizer nos. 1 and 3), silicone surfactant (SF-2937F), foaming agent (water), and polyol (one or a mixture of the biobased polyols or one commercial polyol) were mixed according to Table I and stirred severely at 3000–6000 rpm for 45 s. Then, a given amount of *p*-MDI was added quickly, stirred severely at 3000–6000 rpm for 15 s, and the cream time (CT), gel time (GT), and rise time (RT) were measured. CT is the time (in seconds) required just before the expansion of the mixed liquid (*p*-MDI, polyol and other additives), which begins to foam and becomes cloudy after mixing and agitation. GT is the time (in seconds) required for the gel strength to increase after mixing and agitation. RT is the time (in seconds) required for the foam to reach the maximum height after mixing and agitation. The prepared foams were postcured for more than 15 h at 80°C. Two types of cubic test specimens, 30 and 6 mm on a side, were cut out of the foams; the first for compression tests and the second for dynamic viscoelastic measurements (dynamic mechanical analysis). Three samples each of these specimens were conditioned at a temperature of 23°C and a relative humidity of 50% for more than 48 h before the mechanical tests were performed.

Characterization

The OHV is an important parameter in the characterization of polyols that are prepared and used as monomers for polyurethanes. By definition, this parameter is the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of polyol (mgKOH/g). OHV was determined according to JIS K 1557-1 (ISO 14900); this method consists of dissolving a weighed amount of product in pyridine, treating it with a known excess amount of phthalic anhydride under reflux for 1 h, and back-titrating the unreacted mixture of acid and anhydride. The titrations of these solutions were carried out

Table I. Formulations for the Preparation of Polyurethane Rigid Foams Tested, Foaming Reactivities, Core Densities, and Biomass Contents

Polyol used	GR-84T	A-460	B-460	B-445	MN-400	A-400	B-400	PE-350	A-350	B-350
Initiator	Sucrose	LPs ^a	LPs ^a	LPs ^a	Glycerol	LPs ^a	LPs ^a	Pentaerythritol	LPs ^a	LPs ^a
OHV ^b (mgKOH/g)	460	460	460	445	400	400	400	350	350	350
Biomass content of polyol (%)	35.1	41.7	27.4	26.6	21.9	37.1	23.5	0.00	33.2	20.1
Formulation for foam (pbw ^c)										
Polyol	100	100	100	100	100	100	100	100	100	100
Water	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Surfactant	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Catalyst	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
ρ -MDI	153	153	153	150	138	138	138	125	125	125
Reactivity										
CT (s)	25	31	42	33	30	25	35	28	28	26
GT (s)	122	120	110	87	147	112	99	121	130	96
RT (s)	232	238	272	183	244	205	230	255	223	228
Core density (kg/m ³)	66.0	66.8	54.2	55.9	65.6	69.2	53.9	72.7	65.7	57.3
Biomass content of foam (%)	13.6	16.2	10.6	10.5	9.05	15.3	9.73	0.00	14.5	8.80

^aLPs, liquefaction products; ^bOHV, hydroxyl value; ^cpbw, parts by weight.

with an automatic potentiometric titrator (AT-510; Kyoto Electronics Manufacturing Co., Ltd., Osaka, Japan).

The viscosities of the LPs and their oxypropylated polyols were measured at 25°C with an RE-80U viscometer (Toki Sangyo Co., Ltd, Osaka, Japan). The measurements were repeated twice for each sample, and their average was taken as the datum.

GPC was conducted with a high-performance GPC system (HLC-8220GPC, Tosoh Co., Osaka, Japan) with three columns, TSK SuperHZ 1000, 2000, and 3000 (Tosoh Co.), to obtain the molecular weight distribution profiles and to determine the average molecular weights of the oxypropylated products. The samples were dissolved in tetrahydrofuran and filtered before they were injected into the equipment. Calibration was done with polystyrene standards.

An Autograph AGS-5kNG (Shimadzu Co., Kyoto, Japan) was used for the compression tests. A loading speed of 2 mm/min was used, and the Shimadzu software Shikibu was used for the compressive stress and elastic modulus determinations.

Dynamic mechanical analysis measurements were performed for the aforementioned specimens with a DMS 6100 instrument (Seiko Instruments, Inc., Osaka, Japan) under compression mode (frequency = 10 Hz, rate of temperature increase = 2°C/min, temperature range = -150 to 250°C).

RESULTS AND DISCUSSION

Glycerol/Methyl Alcohol (9 : 1 w/w) Liquefaction Followed by Oxypropylation

A mixture of glycerol, methyl alcohol, and sulfuric acid (9 : 1 : 0.3 w/w) was used as the liquefaction medium and the catalyst in the liquefaction process. Among them, 50 wt % of methanol and sulfuric acid were reacted beforehand at 60°C for more than 30 min.

First, the effect of the liquefaction temperature was studied. Twelve grams (g) of corn starch and 37.1 g of the liquefaction medium and catalyst mixture [liquid ratio (LR) = 3] were fed into a 100-mL beaker and stirred under wrapping with a plastic sheet at 500 rpm for 10 min at room temperature. Then, the content was transferred to a Teflon reactor, placed inside a pressure-tight stainless steel external cylinder. The reactor was dipped in an oil bath and heated to 110, 120, 130, or 140°C with stirring for 60 min. The results of the liquefaction experiments are shown in Table II.

The liquefaction could be completed even at 110°C, in which the observed residual rate was 0.56%. There was no difference in the liquefaction achievement (residual rate) above 120°C. The OHV value showed a small decreasing tendency with increasing liquefaction temperature. A considerable decrease in the viscosity was found with increasing liquefaction temperature. This was caused by an increase in the rate of molecular weight decline.

Second, the liquefaction time dependence was studied at a liquefaction temperature of 120°C and an LR of 1.5. The result is shown in Figure 1. This figure reveals that a liquefaction time of 30 min was sufficient for attaining complete liquefaction.

Table II. Results of the Glycerol/Methyl Alcohol (9 : 1 w/w) Liquefaction^a

Sample code	Liquefaction				
	temperature (°C)	Residual rate (%)	Viscosity (mPa · s)	OHV (mgKOH/g)	Remaining water (%)
1	110	0.56	9549	991	1.16
2	120	0.03	8586	988	1.26
3	130	0.03	7337	956	1.24
4	140	0.03	4908	968	1.41

^aLR = 3.¹⁵

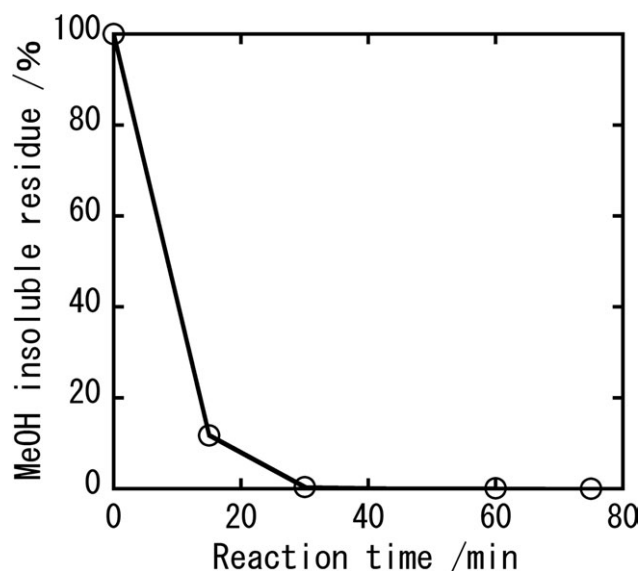


Figure 1. Liquefaction time dependence obtained at 120°C and with an LR of 1.5 (MeOH = methanol).

On the basis of these data, a liquefaction temperature of 120°C and an LR of 1.5 were selected, and about 1 L of the corresponding glycerol/methyl alcohol (9 : 1 w/w) LP was prepared. The obtained blackish brown LP had an OHV of 986 mgKOH/g, a viscosity (at 25°C) of 68,610 mPa·s, and a biomass containing degrees of 100%.

With this LP as an initiator, PO was ring-opening graft-polymerized to obtain two species of biobased polyols, which differed in their grafting amounts. To obtain these products, the added amounts of PO were calculated. As a result, two polyol products, denominated A-1 and A-2, with OHVs of 568 and 270 mgKOH/g, respectively, were synthesized. A-1 and A-2 had viscosities of 5699 and 837.2 mPa·s and biomass contents of 50.1 and 27.0%, respectively.

GPC profiles were obtained for A-1 and A-2, and the results are shown in Figure 2(1). It is known that larger the grafting amount of PO is and smaller the OHV is, the smaller the retention time will be. In fact, for the A-1 and A-2 polyols, the added PO molar values were 1.0 and 2.7 per mole of hydroxyl groups of the starting materials, respectively. It was also known that the profiles for these A-1 and A-2 had two peaks; this reflected the fact that the initiator was a mixture of different molecular weight components; one was a smaller molecular weight PO-grafted glycerol, and the other was a larger molecular weight liquefied and PO-grafted biomass component. Whether the fact that the polyol was made up of different molecular weight components affected the urethane resinification and foam formation or not was one of the studying points.

Actcol IR96/Glycerol/Methyl Alcohol (7.2 : 1.8 : 1.0 w/w) Liquefaction Followed by Oxypropylation

A mixture of Actcol IR96, glycerol, methyl alcohol, and sulfuric acid (7.2 : 1.8 : 1.0 : 0.3 w/w) was used as the liquefaction medium and catalyst in this liquefaction process. Among them, 50 wt % of methanol and sulfuric acid were reacted beforehand at

60°C for more than 30 min. A liquefaction temperature of 140°C and an LR of 1.94 was used.

The obtained blackish brown LP had an OHV of 560 mgKOH/g, a viscosity (at 25°C) of 6970 mPa·s, and a biomass content of 50.1%.

With this LP as an initiator, PO was ring-opening graft-polymerized to obtain two biobased polyols, which differed in their grafting amounts. To obtain these products, the amounts of PO added were calculated. As a result, two polyol products,

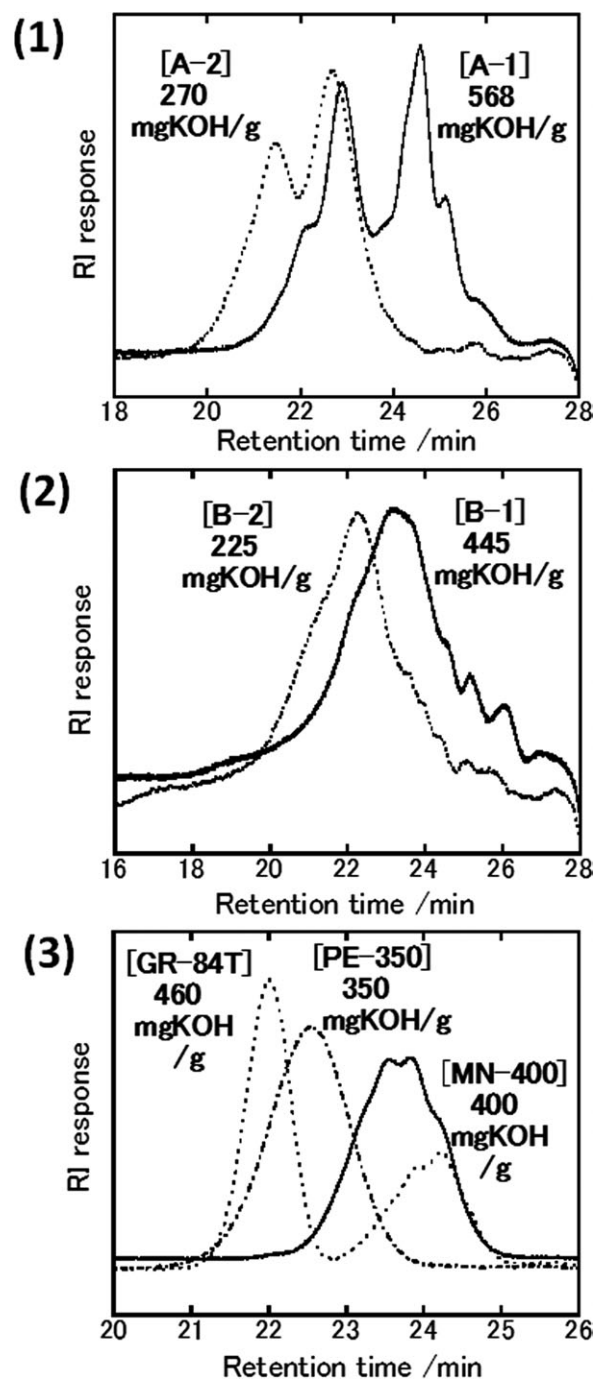


Figure 2. GPC profiles for (1) series A polyols, (2) series B polyols, and (3) the control commercial polyols. (RI = Refractive Index).

denominated B-1 and B-2, having OHVs of 445 and 225 mgKOH/g, respectively, were synthesized. B-1 and B-2 had viscosities of 2340 and 615.7 mPa · s and biomass contents of 26.6 and 11.6%, respectively.

GPC profiles were obtained for B-1 and B-2, and the results are shown in Figure 2(2). It is shown that the larger the grafting amount of PO was and the smaller the OHV was, the smaller the retention time was. In fact, for the B-1 and B-2 polyols, the added PO molar values were 0.88 and 3.3 per mole of hydroxyl groups of the starting materials, respectively. It was also known that the profiles for B-1 and B-2 had one main peak. This meant that glycerol, initially added at about 20% of the liquefaction medium, was almost completely reacted with the higher molecular weight components within the reaction liquid. Whether this fact affected the urethane resinification and foam formation or not was a checking point in this study.

GPC Profiles for the Control Commercial Polyols, Actcol GR-84T, MN-400, and PE-350

Actcol GR-84T, MN-400, and PE-350 were used as control polyols. GPC analyses were conducted for those commercial polyols, and the results are shown in Figure 2(3).

Actcol GR-84T was a mixture of PO adducts of sucrose and glycerol. Its OHV was 460 mgKOH/g, and its viscosity was 6000 mPa · s. In this case, two peaks were also observed, as shown in Figure 2(1).

Actcol MN-400 was a PO adduct of glycerol, with an OHV of up to 400 mgKOH/g and a viscosity of 410 mPa · s. Its GPC profile showed a broad single peak.

Actcol PE-350 was a PO adduct of pentaerythritol, with an OHV of 350 mgKOH/g and a viscosity of 1150 mPa · s. Its GPC profile appeared as an almost single peak with a larger molecular weight compared with that of MN-400.

Preparation and Physical Properties of Polyurethane Rigid Foams

With these synthesized novel biopolyols and control commercial polyols, polyurethane rigid foams were prepared according to the procedures described in the Experimental section and Table I. In these cases, in addition to the polyols and *p*-MDI, resinification and foaming catalysts, a blowing agent (water), and a surfactant, the amounts and species of which were selected and adjusted, were used. The amounts of *p*-MDI were calculated on the basis of the OHV of the polyol, and 1.1 times of the equivalent was used because of its self-addition.

Examples of the obtained foams are shown in Figure 3(1). In this figure, the control foam prepared from Actcol GR-84T is shown on the left side. A novel foam prepared from a mixture of polyols A-1 and A-2 is shown in the center, of which OHV was adjusted to the same value as that of GR-84T (460 mgKOH/g) by the blending of a 5.1 pbw of A-1 with a 2.9 pbw of A-2.

In the case of the series B polyol, even though the B-1 polyol had a higher OHV compared with that of B-2, its value was 445 mgKOH/g, which was lower than the value of GR-84T. Thus, to increase the OHV up to 460 mgKOH/g, a 1.1 pbw of Actcol T-300, whose OHV was 550 mgKOH/g, was blended

with a 6.9 pbw of B-1. The obtained foam is shown in the right side of Figure 3(1). As shown in the figure, its reactivity was high.

Test samples cut from the Figure 3(1) foams are shown in Figure 3(2). Compared with the control, the appearances of the foams from the novel biopolyols A-460 and B-460 were equivalent in level. B-460 was colored but within an acceptable range and gave a natural feeling.

The OHV of B-1 was 445 mgKOH/g, which was not significantly different from the corresponding value of the control GR-84T (460 mgKOH/g). Thus, foam preparation was done without blending with T-300 and was compared with those from GR-84T (control) and A-460, as shown in Figure 3(3).

The reactivity of each biopolyol for foam formation was compared with that of each control commercial polyol by the measurements of CT, GT, and RT. The measured CT, GT, and RT values are shown in Table I. The values for series B were lower than those for series A and were even lower than those each

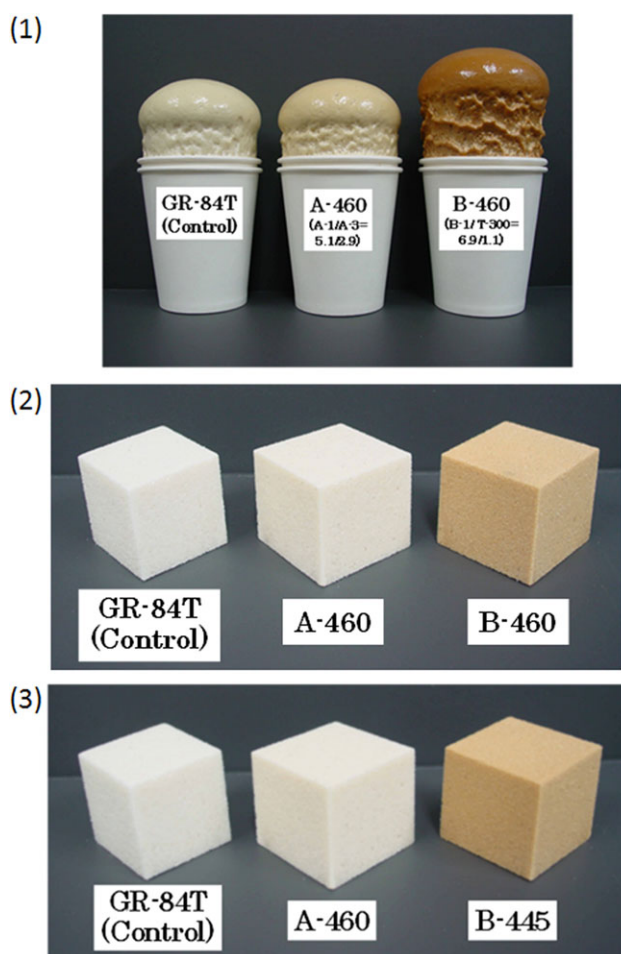


Figure 3. Appearances of (1) foams as prepared from polyols having an OHV of 460 mgKOH/g in paper cups, (2) test samples cut out of foams shown previously, and (3) test sample B-445 cut out of foam from polyol having an OHV of 445 mgKOH/g is shown instead of sample B-460. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Comparison of the Compressive Properties of the Polyurethane Foams

Sample code	OHV of polyol used (mgKOH/g)	Compressive yield strength/ D^* (MPa·m ³ /kg)	Compressive stress/ D^* (kPa·m ³ /kg)		
			At 10% strain	At 25% strain	At 50% strain
GR-84T	460	8.05	7.30	7.85	8.61
A-460	460	8.41	7.54	8.31	9.40
B-445	445	8.75	7.50	8.77	9.22
MN-400	400	6.66	5.78	6.39	7.56
A-400	400	8.08	7.02	7.72	9.40
B-400	400	8.29	7.54	8.35	8.49
PE-350	350	7.46	6.58	7.56	8.32
A-350	350	7.38	6.53	7.28	8.47
B-350	350	8.13	7.18	7.26	8.50

D^* , density of the polyurethane foam obtained (see Table I).

control, especially GT and RT; this revealed a higher reactivity toward *p*-MDI, which resulted in the foam formations. At the same time, somewhat higher values were found for CT; this indicated slight difficulties in the compatibilities of those novel biopolyols toward *p*-MDI. These results reflect the values of the core density. The use of series B polyols gave lower core-density values than that of each control. The use of series A polyols resulted in comparable values.

However, the differences in these reactivity parameters were not large, especially the differences between the series A and B polyols. This fact is interesting when we consider the previous findings, that whereas the GPC profile of series A polyols had two peaks, those of series B showed a single peak. We worried that this would have a bad effect on the reactivity of the polyols as previously mentioned, but the previous data denied these suspicions. In connection with this, the following can be pointed out. That is, the two peaks found in series A could be ascribed to the existence of small molecular weight fractions (unreacted glycerol only grafted with PO), together with larger molecular weight glycerol solvolyzed starch fractions, also grafted with PO. The fact that these two components revealed similar reactivity toward *p*-MDI means that the oxypropylation could act as an equalization tool for reactivity. Actually, the oxypropylation had the role of moving the OH groups outside the molecular core of the substrate.

The stress–strain curves measured for the foams in Table I are presented in Figure 4(1–3). Table III shows the concerning values of compressive yield strengths and compressive stresses at 10, 25, and 50% strains. The values of the stresses divided by the densities of the foams are shown in Figure 4 and Table III. Actually, the compression stresses were strongly related to the densities.

In Figure 4(1), the stress–strain curves for the foams from the A-460 and B-445 polyols were compared with those obtained for the foam from GR-84T (control). Compared with the control, curves having 4.7–8.7% higher yield strengths are obtained for the foams from the A-460 and B-445 polyols. They also revealed comparable or better compressive behavior after the yield point compared with that from GR-84T (control); this showed that they were equipped with comparable or better toughness.

Because Actcol MN-400 had an OHV of 400 mgKOH/g, the A-400 polyol, with the same OHV, was prepared by the blending of A-1 (OHV = 568 mgKOH/g) and A-2 (OHV = 270 mgKOH/g). B-400 was also prepared by the blending of B-1 (OHV = 445 mgKOH/g) and B-2 (OHV = 225 mgKOH/g). The obtained stress–strain curves are compared in Figure 4(2).

In this case, foams prepared from the novel polyols A-400 and B-400 gave much higher (21.3–24.5% higher) yield strengths compared with that from the control MN-400. From the figure, it can be also said that toughness improvements for the foams prepared from the novel polyols A-400 and B-400 were obvious.

A-350 polyol was prepared by the blending of A-1 (OHV = 568 mgKOH/g) and A-2 (OHV = 270 mgKOH/g), and B-350 was also prepared by the blending of B-1 (OHV = 445 mgKOH/g) and B-2 (OHV = 225 mgKOH/g). From those and Actcol PE-350, respective polyurethane foams were prepared, and the stress–strain curves were obtained, as shown in Figure 4(3).

In this case, the foams prepared from the novel A-350 and control PE-350 gave almost the same yield strengths. In contrast, the foam prepared from the novel B-350 gave a 9.1% higher yield strength. From the figure, the toughness of the foams prepared from the novel polyols A-350 and B-350 were found to be as good or slightly better than that of the control PE-350.

As shown in Figure 4(1–3), it can be said that foams prepared from the novel biopolyols tended to have higher yield strengths and toughnesses compared with the foams from the control commercial polyols.

As shown in Figure 2(1–3), the series A polyols had two peaks, and the series B polyols had a single peak in their GPC profiles. However, it can be said, again from Figure 4(1–3), that the difference seemed to result in no effect on the mechanical properties of the prepared foams. The foams derived from the series A polyols had strengths comparable to those of the series B polyols.

The temperature dependences of the viscoelastic properties of the foams shown in Table I were continuously measured. The results are presented in Figure 5(1–4). The logarithmic value of storage elastic modulus (E') divided by the density of the foam

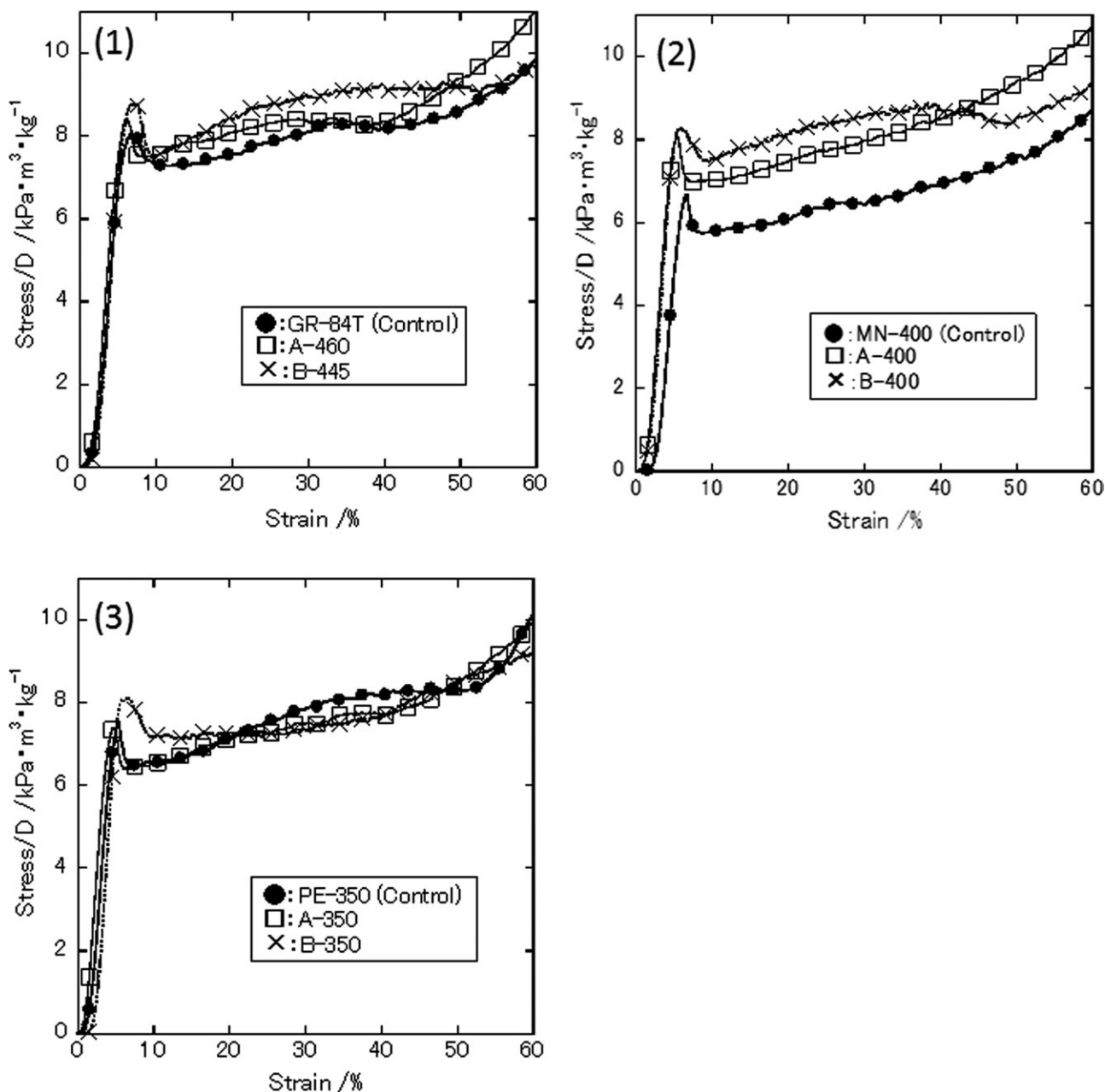


Figure 4. Stress–strain curves obtained by compression tests for the foams from the (1) GR-84T (control), A-460, and B-445 polyols; (2) MN-400 (control), A-400, and B-400 polyols; and (3) PE-350 (control), A-350, and B-350 polyols.

is shown in the vertical axis. Table IV shows the storage elastic modulus values for the polyurethane foams at the selected temperatures (−100, 50, 150, and 175°C) in the measured range of viscoelastic properties.

Figure 5(1) shows the storage elastic modulus profiles as a function of the temperature for the foams from the A-460 and B-460 polyols compared with that obtained for the foam from GR-84T (control). Compared with the control, the curve obtained for the foams from the A-460 polyol revealed slightly prominent behavior (10.4–17.6% at the selected temperatures in Table IV). In the case of B-460, the storage elastic modulus values corresponding to its glassy state were much lower (22.4 and

41.8% at −100 and 0°C, respectively), and its thermal resistance showed a little inferiority (44.2% lower at 175°C) compared with those from GR-84T (control).

Then, instead of B-460 (B-1 blended with Actocol T-300), the B-445 foam from only the B-1 polyol was used for the viscoelastic measurement. Figure 5(2) shows the results. As a result, the viscoelastic behavior of B-445 showed a substantial improvement (5.5–30.5% higher than those of B-460 at the selected temperatures in Table IV), shown by a comparison between Figures 5(1) and 5(2). This finding reveals the difficulty of blending with other types of polyols. That is, the ease of blending polyols with only various degrees of PO addition is shown.

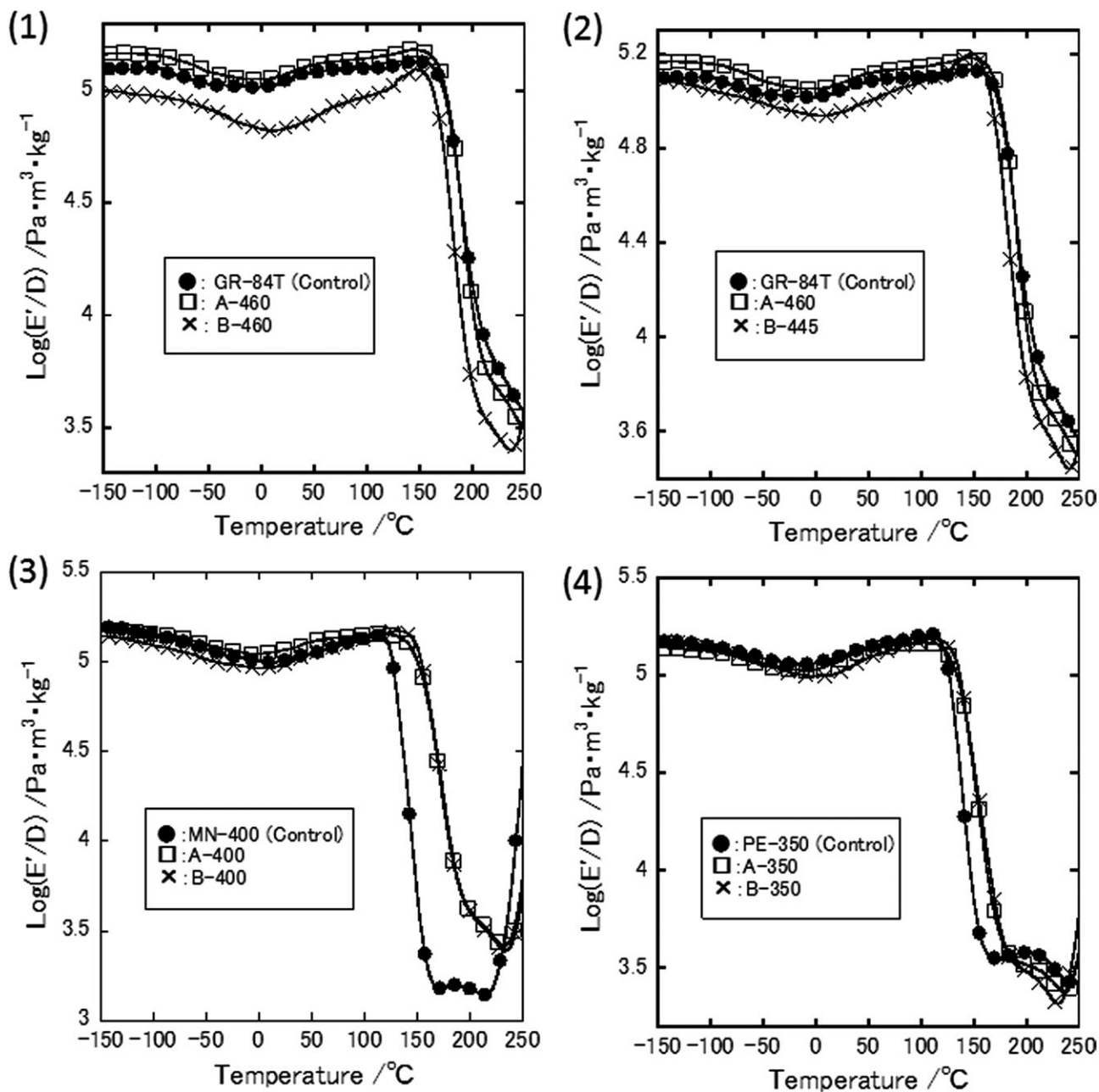


Figure 5. Temperature dependencies of E' divided by the densities of the foams from the (1) GR-84T (control), A-460, and B-460 polyols; (2) GR-84T (control), A-460, and B-445 polyols; (3) MN-400 (control), A-400, and B-400 polyols; and (4) PE-350 (control), A-350, and B-350 polyols.

In Figure 5(3), E' as a function of the temperature for the foams from the A-400 and B-400 polyols are compared with that obtained for the foam from MN-400 (control). The curve obtained for the foams from the A-400 polyol revealed almost comparable or slightly prominent behavior when compared with that of B-400. In the case of MN-400 (control), although the storage elastic modulus value corresponding to its glassy state was in the same range, its thermal resistance showed a large degree of inferiority (ca. 90% lower than those of A-400 and B-400 at 175°C) compared with those of A-400 and B-400. The starting temperature of glass transition for the MN-400 was about 20°C lower than those for A-400 and B-400. It can be said

that the latter two had not only higher degrees of biomass derivation but also enhanced viscoelastic and thermal resistance characteristics. Those effects may have been due to the more rigid cyclic structure of the pyranose ring compared to the flexible open chain of such initiators as glycerol. In this sense, the results shown in Figures 4(1) and 5(2) are attractive. The control polyol, GR-84T, was a commercial polyol and also had a rigid cyclic structure of a pyranose ring. (The initiator of the PO addition of GR-84T was sucrose.) In the previously discussed figures, at least the series A polyol indicated higher physicalities. The series B polyol was indicative of equivalence properties.

Table IV. Comparison of the Storage Elastic Modulus Values for the Polyurethane Foams at Selected Temperatures in the Measured Range of the Viscoelastic Properties

Sample code	OHV of the polyol used (mgKOH/g)	(Storage elastic modulus/ D^*) $\times 10^{-4}$ (Pa \cdot m ³ /kg)			
		At -100°C	At 50°C	At 150°C	At 175°C
GR-84T	460	12.5	11.9	13.1	9.06
A-460	460	14.6	13.3	15.4	10.0
B-460	460	9.70	6.93 (0°C) 7.74 (50°C)	12.6	5.05
B-445	445	11.2	10.1	16.0	5.33
MN-400	400	14.0	11.0	0.495	0.153
A-400	400	14.0	12.7	9.74	1.55
B-400	400	12.2	11.0	11.9	1.76
PE-350	350	13.6	13.4	0.687	0.339
A-350	350	13.1	13.4	3.06	0.461
B-350	350	13.3	11.9	3.17	0.481

* D , density of the polyurethane foam obtained (see Table I).

Figure 5(4) shows the storage elastic modulus as a function of the temperature for the foams from the A-350 and B-350 polyols compared with that obtained for the foam from PE-350 (control). The foam from A-350 resulted in a comparable viscoelasticity compared with that from B-350.

On the other hand, when the data of the foams derived from the A-350 and B-350 polyols were compared with those from control PE-350, the viscoelastic curves obtained for the glassy region showed almost comparable or slightly inferior behavior, but their thermal resistance showed a pronounced superiority. The storage elastic modulus values of A-350 and B-350 remained about 4.6 times higher than that of PE-350 (control) at 150°C (Table IV).

As shown in Figure 2(1,2), the GPC profile for the series A polyols had two peaks, and that for the series B polyols had a single peak. It can be said from the previous results shown in Figure 5(4) that this difference resulted in no effect on the viscoelasticity of the prepared foams. In the case of the data shown in Figure 5(3), the same but more highlighted ones were shown, and in the case of Figure 5(1,2), the foams from the series A polyols showed much prominent viscoelasticities compared with those from the series B polyols.

Particularly, the series A polyols had two peaks in their GPC curves and were thought to cause some time lags in reactivity toward *p*-MDI; this would have resulted in occurrences of trouble in the resinification of polyurethane. However, previous data refuted those suspicions.

Finally, the biomass contents of the prepared foams were calculated and are shown in Table I. Among them, the value of 16.2% for the A-460 polyol was thought to be the highest one as a rigid-type polyurethane foam when compared to corresponding values obtained worldwide.

The previously discussed physical properties data for the polyurethane rigid foams from novel biopolyols should give them the ability to be used in actual applications such as soundproof wall panels, tatami mats, and grinding stones.

CONCLUSIONS

The liquefaction of starch in the presence of (1) a mixed liquid of glycerol and methanol (9:1 w/w) or (2) a mixed liquid of commercial polyol, glycerol, and methanol (7.2:1.8:1.0 w/w) with catalytic amounts of sulfuric acid were developed. With obtained LPs as initiators with catalytic amounts of KOH, oxypropylations were conducted at 120°C with an inner pressure of less than 0.2 MPa. Polyurethane foams with high biomass contents were prepared from those biopolyols. The reactivities of the biopolyols toward *p*-MDI were almost equal. Thus, even though there were some differences in the structures and molecular weights of the polyol components, oxypropylation acted as an equalization tool. The physical properties of the foams were found to be as good or better than those from the control commercial polyols.

REFERENCES

- Briones, R.; Serrano, L.; Ben Younes, R.; Mondragon, I.; Labidi, J. *Ind. Crops Prod.* **2011**, *34*, 1035.
- Cateto, C.; Barreiro, M.; Rodrigues, A.; Belgacem, M. *Ind. Eng. Chem. Res.* **2009**, *48*, 2583.
- Evtiuguina, M.; Barros, A. M.; Cruz-Pinto, J. J.; Neto, C. P.; Belgacem, M. N.; Pavier, C.; Gandini, A. *Bioresour. Technol.* **2000**, *73*, 187.
- Gandini, A.; Belgacem, M. N. In *Monomers, Polymers and Composites from Renewable Resources*; Belgacem, M. N., Gandini, A., Eds.; Elsevier: Amsterdam, **2008**; Chapter 12, p 273.
- Pavier, C.; Gandini, A. *Ind. Crops Prod.* **2000**, *12*, 1.
- Serrano, L.; Alriols, M.; Briones, R.; Mondragon, I.; Labidi, J. *Ind. Eng. Chem. Res.* **2010**, *49*, 1526.
- Cateto, C. A.; Barreiro, M. F.; Rodrigues, A. E.; Brochier-Salmon, M. C.; Thielemans, W.; Belgacem, M. N. *J. Appl. Polym. Sci.* **2008**, *109*, 3008.
- Dege, G. J.; Harris, R. E.; MacKenzie, J. S. *J. Am. Chem. Soc.* **1959**, *81*, 3374.
- Steiner, E. C.; Pelletier, R. R.; Trucks, R. O. *J. Am. Chem. Soc.* **1964**, *86*, 4678.
- Wada, H. *J. Adhes. Soc. Jpn.* **2004**, *40*, 270.
- Shiraishi, N. In *Wood and Cellulosic Chemistry*; Hon, D. N. S., Shiraishi, N., Eds.; Marcel Dekker: New York, **2000**; Chapter 16, p 694.
- Yao, Y. G.; Yoshioka, M.; Shiraishi, N. *J. Appl. Polym. Sci.* **1996**, *60*, 1939.
- Kunaver, M.; Medved, S.; Cuk, N.; Jasiukaityte, E.; Poljansek, I.; Strnad, T. *Bioresour. Technol.* **2010**, *101*, 1361.
- Yoshioka, M.; Shiraishi, N. *Jpn. Pat.* 2010-184233 (**2010**).
- Horikiri, K. Bachelor's thesis, Sakyo-ku, Kyoto, Kyoto University, **2012**.