Review

Preparation and Properties of Biopolymers Based on Isosorbide (1, 4:3, 6-Dianhydro-D-sorbitol)

Makoto Kato and Chi-Han Lee

■**ABSTRACT**‖ With the continuing depletion of fossil fuel resources, much attention has been directed towards the effective utilization of plant-based biomass. 1, 4:3, 6-Dianhydro-D-sorbitol, "isosorbide," is derived from glucose and is thus a functional group-containing monomer based on natural resources. Isosorbide is thermally stable, of low cost, and available in large quantities, and may prove an interesting monomeric reagent for the synthesis of bio-based polymers. We have successfully synthesized biopolyurethanes and biopolycarbonates based on isosorbide. Biopolyurethanes were synthesized by the reaction of various isocyanates and isosorbide with an organotin oxide as a catalyst. Biopolycarbonates were synthesized by the reaction of diphenyl carbonate and isosorbide by a transesterification reaction. Prepared polyurethanes and biopolycarbonates consisted of two or three components containing isosorbide moieties in the main chain. Furthermore, in the case of biopolycarbonates, we have succeeded in preparing nanocomposites consisting of biopolycarbonates and clay mineral by treatment with organoammonium reagents. The molecular weights, thermal properties, and dynamic mechanical properties were evaluated according to the containing ratio of isosorbide. These biopolymers and biopolymer nanocomposites exhibited excellent thermal properties and high moduli because of the rigidity of isosorbide. These properties make the new industrial polymers attractive as potential high-performance materials.

■**KEYWORDS**‖ Isosorbide, Biomass, Polyurethane, Polycarbonate, Nanocomposite

1. Introduction

With the continuing depletion of fossil fuel resources, much attention has been directed towards the effective utilization of plant-based biomass, including wood, grasses, and agricultural crops and residues, in polymer synthesis.[1-3] Biomass is a renewable resource of natural products that can be used as a reliable starting material in the production of environmentally benign polymers. Among a wide variety of candidate compounds from biomass, 1, 4:3, 6-dianhydrohexitols, including isosorbide, have been shown to be promising materials for polymer synthesis.

Isosorbide as shown in **Fig. 1** is derived from glucose and is thus a functional group-containing monomer based on natural resources. It is a well-documented by-product of the starch industry, obtained by dehydration of D-sorbitol, and is produced worldwide at a rate of 650,000 tons per annum.[4,5] Isosorbide is thermally stable, of low cost, and available in large quantities, and may prove an interesting monomeric reagent for the synthesis of bio-based polymers such as polyesters,[6-14] polyamides,[15] polyurethanes,[16-21] and epoxy resins.[22]

In this review, we introduce our research on biopolyurethanes[23] and biopolycarbonates[24] based on isosorbide. The molecular weights, thermal properties, and dynamic mechanical properties were evaluated depending on the containing ratio of isosorbide. Furthermore, in the case of biopolycarbonates, we introduce our research of nanocomposites consisting of biopolycarbonates and clay mineral.[25] These biopolymers and biopolymer nanocomposites exhibited excellent thermal properties and high moduli because of the rigidity of isosorbide. These properties make these new industrial polymers attractive as potential high-performance polymeric materials.

2. Experimental Section

2. 1 General Materials

Isosorbide was obtained from Roquette, France. *N*-Butyltin oxide hydroxide hydrate [*n*-
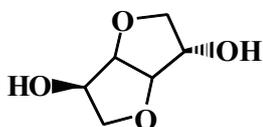
Fig. 1 1, 4:3, 6-Dianhydrosorbitol (Isosorbide).

BuSn(=O)OH·H$_2$O] was obtained from Strem Chemicals, USA.

2. 2 Materials for Biopolyurethanes

4, 4'-Isopropylidenediphenol (bisphenol A) was obtained from Wako Pure Chemicals, Japan. 1, 6-Hexamethylene diisocyanate, 1, 3-bis(isocyana-tomethyl)cyclohexane, 2, 5(2, 6)-bis(isocyanatomethyl) bicyclo[2.2.1]heptane, 4, 4'-diphenylmethane diisocyanate, and tolylene-2, 4-diisocyanate were obtained from Mitsui Kagaku Polyurethane, Japan. 1, 3-Bis(isocyana-tomethyl)benzene and 4, 4'-diisocyanato-3, 3'-dime-thylbiphenyl were purchased from Tokyo Kasei, Japan. All materials were used as received.

2. 3 Materials for Biopolycarbonates

Diphenyl carbonate was obtained from Acros, Belgium.

2. 4 Materials for Nanocomposites

Purified montmorillonite (Na-Mt, Kunipia-F) was obtained from Kunimine Ind. Co. Octadecylamine (C18) and distearyl dimethyl amine (DSDM) were obtained from Wako Pure Chemicals. Montmorillonite treated with octadecyl ammonium (C18-Mt) was obtained by ion exchange reaction with octadecylamine and Kunipia F. Montmorillonite treated with dioctadecyl ammonium was obtained by ion exchange reaction with dioctadecyl amine Kunipia F. Cloisite 30B (organic modifier Mt2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium) was obtained from Southern Clay Products. N, N-Dimethylacetamide (DMAc) was obtained from Aldrich.

3. Synthesis and Properties of Biopolyurethanes

3. 1 Polymer Preparation

In polymers **1-7**, the isosorbide and diisocyanate monomers were subjected to polymerization using polyaddition as a polymerization technique. The polymers were synthesized as shown in **Schemes 1** and **2**, with the products obtained in good to quantitative yields. In polymer **8**, the ratio of isosorbide and bisphenol A was 1:1. In polymer **9**, the ratio of 2, 5(2, 6)-bis(isocyanatomethyl)bicyclo[2.2.1]heptane and 4, 4'-diphenylmethane diisocyanate was 1:1.

3. 2 Results and Discussion

3. 2. 1 Molecular Weight, Polydispersity, and Thermal Properties

The molecular weights and dispersities of the polymers were investigated using GPC calibrated with polyethylene oxide standards, with NMP as solvent. The results are summarized in **Table 1**. The number average molecular weights (M_n) ranged from 4,000 to 7,000, and the weight average molecular weights (M_w) ranged from 8,000 to 19,000, which meant that the ratio M_w/M_n was between 1.7 and 2.8.

Thermal characterization of the polymers was carried out by DSC and TGA, and the results are also shown in Table 1. No phase transitions were recorded during the first and second heatings in the DSC experiments. The absence of melting endotherms confirmed the amorphous nature of the polymers. The glass transition temperatures (T_g) of the polymers were also determined by DSC based on the onset temperature of the first inflection point recorded during
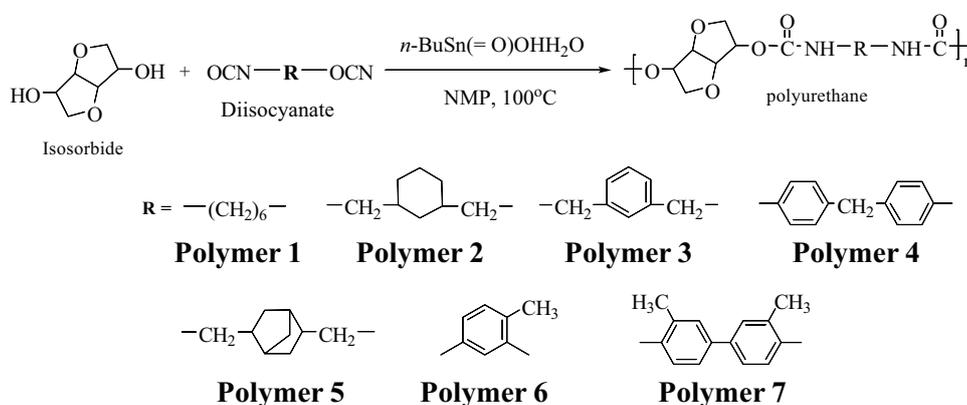
Scheme 1   Synthesis of polyurethanes with two components.
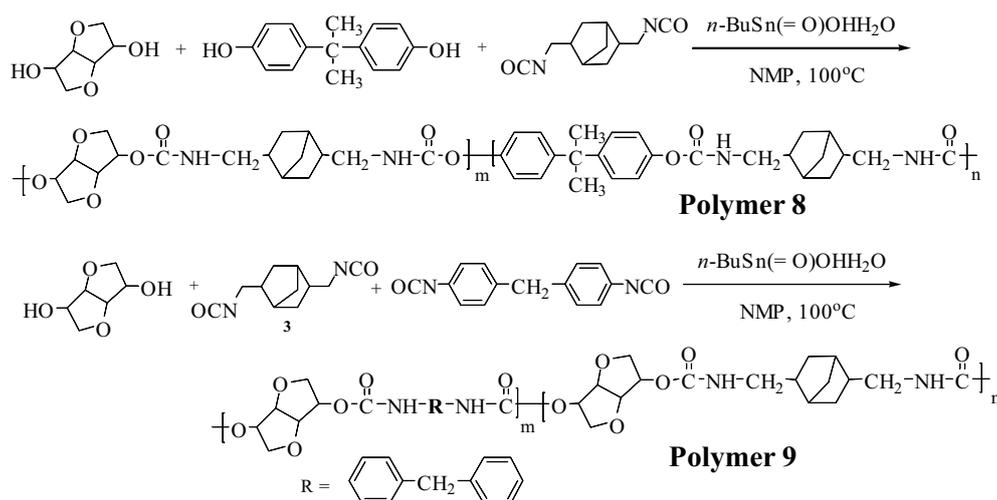
Scheme 2 Synthesis of polyurethanes with three components.

the second heating (Table 1). DSC measurements showed that all polyurethanes had T_g values between 74 and 182°C, following the decreasing order of chain flexibility. The lowest T_g, 74°C, was observed for polymer **1**, which was derived from the flexible diisocyanate hexane. In our case, the T_g of polymer **6** is remarkably high, probably due to the rigid structure of isosorbide and the aromatic ring; it can be compared to the much lower value found for a similar hard segment based on isosorbide and cyclohexane, polymer **2** (T_g = 134°C). In particular, polymers **8** and **9** showed slightly higher T_g values (168 and 178°C, respectively) than that of polymer **5** [16] (152°C). This was attributed to the increased chain rigidity caused by the bisphenol A and diphenylmethane rings and bicyclo[2.2.1]heptane (norbornane) rings along the backbones of polymers **8** and **9**. The TGA

thermograms of the polymers are also summarized in Table 1. The polymers were stable up to ~ 270–290°C in N$_2$. Polymers **8** and **9** were slightly more thermally stable than polymer **5**, and all their thermal properties were superior to those of polymer **5**.

3. 2. 2 Dynamic Mechanical Analysis (DMA) of Biopolyurethanes

The viscoelastic properties of the biopolyurethanes were investigated by dynamic mechanical analysis (DMA). Although we prepared molds for all polymers (**1–9**), molds of polymers **3**, **4**, **6**, and **7** were not obtained. Therefore, DMA analysis was carried out only for polymers **1**, **2**, **5**, **8**, and **9**. The DMA results confirmed that the properties of the polyurethanes were significantly influenced by their structures. The storage modulus values at various temperatures are summarized in **Table 2**. **Figure 2** shows the temperature dependence of the storage moduli (E') for polymers **5**, **8**, and **9**. The E' of polymer **5** decreased sharply at about 120°C because of the inherent hard segment of the polymer derived from isosorbide and

Table 1 Molecular weights and physical properties of biopolyurethanes.

polymer	molecular weight[a]			T_g[b] (°C)	T_d[c] (°C)
	M_n	M_w	M_w/M_n		
1	4,000	10,000	2.5	74	277
2	7,000	16,000	2.3	134	286
3	6,000	14,000	2.4	119	294
4	7,000	19,000	2.7	179	284
5	7,000	18,000	2.4	152	271
6	5,000	11,000	2.3	182	279
7	4,000	12,000	2.8	133	276
8	4,000	8,000	2.0	168	279
9	6,000	10,000	1.7	178	276

a) Solvent: NMP; standard: polyethylene oxide
b) Determined by DSC under N$_2$, heating rate: 10°C/min
c) 5 wt% loss temperature, measured by TGA under N$_2$, heating rate: 20°C/min

Table 2 Storage moduli (E') of biopolyurethanes.

polymer	storage modulus (GPa)		
	30°C	50°C	100°C
1	2.1	1.6	-
2	3.0	2.8	2.1
5	2.1	2.0	1.5
8	1.8	1.7	1.4
9	3.4	3.2	2.7

norbornane. The E' of polymer **8** remained constant up to 140°C then started to decreased gradually. The E' of polymer **9** was maintained up to 170°C. This increase in heat resistance of about 20–50°C from polymer **5** is due to introduction of the bisphenol A and diphenylmethane groups. Consequently, the rigidity of three component polymers **8** and **9** was increased by the introduction of bisphenol A and diphenylmethane groups compared to the two component polymer **5**.

4. Synthesis and Properties of Biopolycarbonates

4. 1 Polymer Preparation

Generally, all copolycarbonates (ISPC) **1-7** were synthesized from isosorbide, bisphenol A, diphenyl carbonate, and *n*-BuSn(=O)OH as the catalyst via a transesterification procedure (**Scheme 3**). All of the transesterification reactions proceeded successfully; random copolycarbonates were obtained in good to quantitative yields.

4. 2 Results and Discussion

4. 2. 1 Molecular Weight and Polydispersity

The molecular weights and polydispersities of the polymers were investigated using GPC calibrated with polystyrene standards with $CHCl_3$ as the solvent. The results are summarized in **Table 3**. The number average molecular weights (M_n) ranged from 1.3×10^4 to 3.3×10^4, and the weight average molecular weights (M_w) ranged from 3.1×10^4 to 9.3×10^4, giving M_w/M_n ratios between 2.4 and 2.9. As can be seen from these results, the molecular weights of the ISPCs were dependent on the content of bisphenol A. As the ratio of bisphenol A content increased, the molecular weights of the ISPCs decreased. We think this decrease is attributed to the reactivity of isosorbide and bisphenol A.
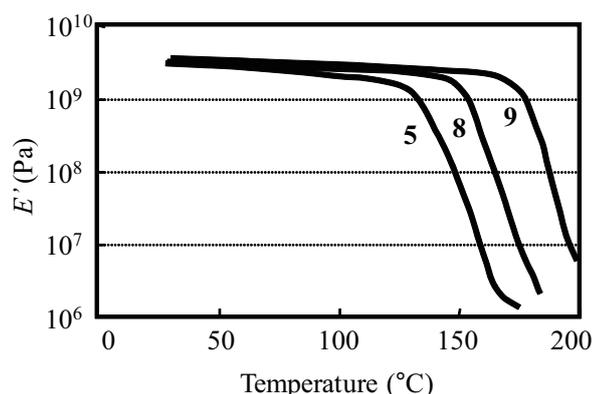
Fig. 2 Temperature dependence of E' for polymers **5**, **8**, and **9**.
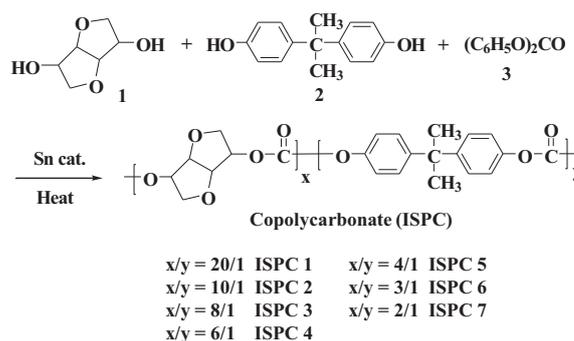
Scheme 3 Synthesis of polycarbonates with three components.

Table 3 Molecular weights and physical properties of biopolycarbonates.

polymer	x / y	molecular weight			T_g [a] (°C)	T_d [b] (°C)	E' (GPa)	T_g [c] (°C)
		M_n	M_w	M_w / M_n				
ISPC **1**	**20/1**	33,000	85,000	2.6	173	310	3.2	181
ISPC **2**	**10/1**	32,000	93,000	2.9	170	313	3.1	178
ISPC **3**	**8/1**	23,000	67,000	2.9	169	313	3.0	178
ISPC **4**	**6/1**	19,000	49,000	2.6	165	315	2.9	176
ISPC **5**	**4/1**	17,000	48,000	2.8	164	322	2.9	176
ISPC **6**	**3/1**	13,000	38,000	2.9	163	325	2.8	174
ISPC **7**	**2/1**	13,000	31,000	2.4	154	334	2.6	167

a) Determined by DSC (10°C/min). b) Measured by TGA (10°C/min). c) Determined by tan δ.

4. 2. 2　Thermal Properties

Thermal characterization of the ISPCs was carried out by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the results are listed in Table 3. No phase transitions were recorded during the first and second heatings in the DSC experiments. The absence of melting endotherms confirmed the amorphous nature of the ISPCs. The glass transition temperatures (T_g) of the ISPCs were also determined by DSC based on the onset temperature of the first inflection point recorded during the second heating (Table 3). The T_g was dependent on the content of isosorbide. As the ratio of isosorbide content increased, the T_g of ISPCs **1-7** increased gradually. In the case of bisphenol A-based polycarbonate (BPAPC), the T_g was determined to be 146°C by DSC.

The TGA thermograms of the ISPCs are also summarized in Table 3. The ISPCs were stable up to about 310 to 334°C in air. ISPCs showed decomposition temperatures [5% weight loss, (T_d)] that were dependent on the content of bisphenol A. As the content of bisphenol A increased, the T_d of ISPCs **1-7** also increased. This increase is attributed to the thermal stability of bisphenol A; the T_d of BPAPC was determined to be 413°C by TGA.

4. 2. 3　Dynamic Mechanical Analysis (DMA)

Transparent and flexible molded sheets were prepared from all of the ISPCs **1–7** by press molding. As can be seen in **Fig. 3**, the sheet prepared from ISPC **1** had rigidity, strength and flexibility, and was completely bendable.

Dynamic mechanical analysis (DMA) was carried out for ISPCs **1-7**. The DMA results confirmed that the properties of the copolycarbonates were significantly affected by isosorbide content. **Figure 4** shows the temperature dependence of the storage modulus (E'),
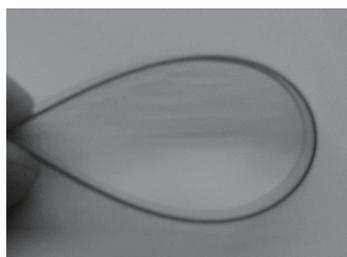
Fig. 3　The flexible molded sheet of ISPC **1**.

loss modulus (E'') and tan δ for ISPC **1**. In the temperature range from 140 to 160°C, the E' starts to decline due to the onset of softening near the glass transition. The polymers exhibited a single glass transition, the temperature of which shifted to higher values with increasing isosorbide content.

ISPCs **2-7** showed similar behavior. The E' of ISPCs **2-7** remained constant up to about 150°C and then started to decrease gradually.

Notably, ISPC **1** showed a higher T_g value than that of ISPC **7**. This difference was attributed to the increased chain rigidity caused by the isosorbide rings along the backbone of ISPC **1**. The storage modulus values are summarized in Table 3; the values obtained for ISPCs **1-7** were 2.6 to 3.2 GPa at 25°C. The E' of BPAPC was found to be 2.3 GPa under the same conditions.

Furthermore, the tan δ peak is dependent on the content of isosorbide. As the ratio of isosorbide content
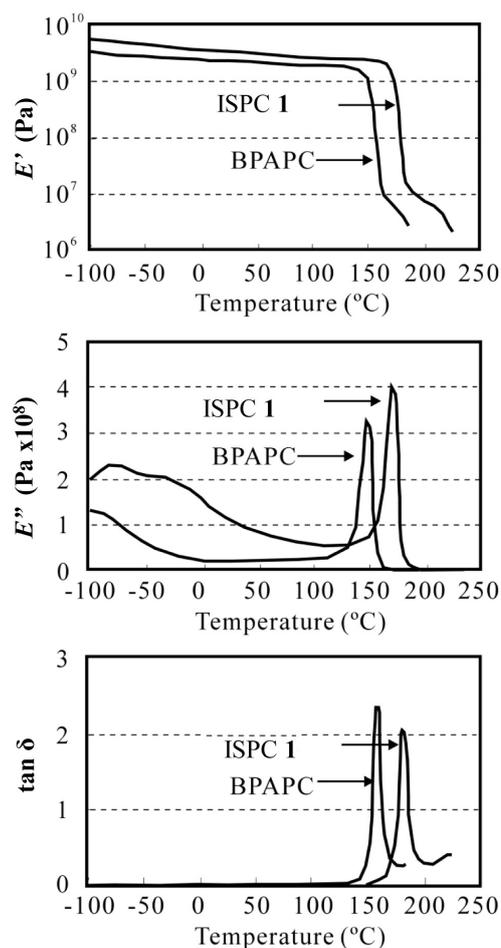
Fig. 4　The temperature dependence of E', E'', and tan δ for ISPC **1** and BPAPC.

increased, the tan δ peak increased. This result is consistent with the fact that increasing the ratio of isosorbide content increases the strength of the copolycarbonates while decreasing their flexibility. On the basis of a comparison of the results obtained for ISPCs **1-7**, it was concluded that the introduction of bisphenol A groups into the copolycarbonates resulted in an increase in thermal stability.

These viscoelastic analyses thus revealed that an increase in T_g was achieved. In the case of ISPC **1**, the increase was ca. 10°C over that for polymer **7**, indicating the beneficial effect afforded by the introduction of isosorbide groups. As has been described above, ISPC **1** possessed a T_g, rigidity and strength that were higher than those of BPAPC. Only the T_d of BPAPC was higher than that for ISPC **1**.

5. Preparation and Properties of Biopolycarbonate Clay Nanocomposites

5. 1 Preparation of Nanocomposites

The nanocomposites were prepared by mixing ISPC **1** solubilized in DMAc with an organoclay dispersed in DMAc. After removal of the solvent, the ISPC **1**/clay nanocomposites were obtained.

5. 2 Results and Discussion

5. 2. 1 Dispersion State of Silicate Layers in Biopolycarbonate Nanocomposites

ISPC **1** was prepared from isosorbide, bisphenol A and diphenyl carbonate via transesterification polymerization (Scheme 3). The nanocomposites were prepared by mixing ISPC **1** solubilized in DMAc with an organoclay dispersed in DMAc. After removal of

the solvent, the ISPC/clay nanocomposites were obtained.

TEM images of (a) the ISPC **1**/Cloisite 30B nanocomposite, (b) the ISPC **1**/Na-Mt nanocomposite, (c) the ISPC **1**/C18-Mt nanocomposite, and (d) the ISPC **1**/DSDM-Mt nanocomposite are shown in **Fig. 5**, where the dark areas represent the clay and the gray/white areas represent the ISPC **1** matrix. It can be clearly seen in Fig. 5 that the ISPC in the ISPC **1**/Cloisite 30B nanocomposite dispersed the organoclay aggregates fairly well, whereas the ISPC **1** in the ISPC **1**/Na-Mt, ISPC **1**/C18-Mt and ISPC **1**/DSDM-Mt nanocomposites did not. The organoclay (Cloisite 30B) silicate layers were exfoliated and dispersed uniformly in the ISPC **1** as monolayers and a few layers. The better dispersed the Cloisite 30B aggregates are, the larger will be the surface area of the silicate layers of Cloisite 30B, which will help increase the degree of dispersion (or exfoliation) of the Cloisite 30B aggregates.

Furthermore, the silicate layers were dispersed homogeneously in the ISPC matrix on the nanoscale, indicating that a transparent condition could likely be produced. A transparent cast film of the ISPC **1**/Cloisite 30B (5.0 wt%) nanocomposite is shown in **Fig. 6**.

5. 2. 2 Dynamic Mechanical Analysis (DMA)

To confirm the assumption that the reinforcement effect is attributed to the dispersed clays in the ISPC, the temperature dependence of the storage moduli (E') of the ISPC **1**/Cloisite 30B nanocomposites was measured. The temperature dependence of E' for the ISPC **1**/Cloisite 30B (5.0 wt%) nanocomposite compared with neat ISPC **1** is shown in **Fig. 7**. The reinforcement effect of elastic modulus at room
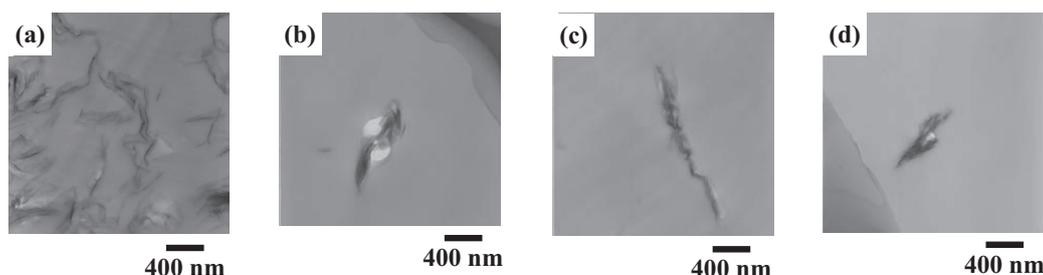
Fig. 5 TEM images of (a) ISPC **1**/Cloisite 30B, (b) ISPC **1**/Na-Mt, (c) ISPC **1**/C18-Mt, and (d) ISPC **1**/DSDM-Mt nanocomposite, where the dark areas represent the clay and the gray/white areas represent the ISPC matrix.

temperature was very high. However, such high reinforcement effect was not shown at high temperature. We suspect that this is due to the effect of organic agents (the quaternary ammonium) in the clay minerals.

The effect of the Cloisite 30B concentration on the DMA moduli of the ISPC **1**/Cloisite 30B nanocomposites at 25°C is displayed in **Fig. 8**. A very large effect of the Cloisite 30B concentration on the *E'* of the ISPC **1**/Cloisite 30B nanocomposites was observed; namely, an increase in Cloisite 30B concentration from 1.0 to 10.0 wt% led to an increase in the *E'* values of the ISPC **1**/Cloisite 30B nanocomposites.

This increase in *E'* values is attributable to the increased surface area resulting from enhanced dispersion of the layered silicate aggregates. That is, when the layered silicate aggregates are more well dispersed because of the presence of hydrogen bonds [26] between the carbonyl groups in ISPC and the hydroxyl groups in Cloisite 30B, the surface area of the layered

silicate platelets is expected to increase markedly as the amount of Cloisite 30B in the nanocomposite is increased from 1.0 to 10.0 wt%. This result is also consistent with the fact that increasing the Cloisite 30B concentration increases the rigidity of the ISPC/Cloisite 30B nanocomposites. On the basis of a comparison of the results obtained for the ISPC/clay nanocomposites, it was concluded that the dispersion of clay into the ISPC resulted in an increase in rigidity of the ISPC.

6. Conclusion

We have succeeded in the synthesis of biopolyurethanes and biopolycarbonates based on isosorbide. The biopolyurethanes were obtained by polyaddition as a polymerization technique. The biopolycarbonates were obtained by transesterification polymerization of isosorbide, bisphenol A, and diphenyl carbonate. Molecular weights (M_n) of obtained biopolyurethanes were 4,000 to 7,000. Molecular weights (M_n) of obtained biopolycarbonates were 13,000 to 33,000. These biopolyurethanes and biopolycarbonates exhibited high heat resistant properties and high moduli. Polycarbonates showed superior heat resistant properties and higher moduli than the polycarbonate based on bisphenol A (a petroleum-based polycarbonate). Furthermore, in the case of biopolycarbonates, we have succeeded in the preparation of nanocomposites consisting of biopolycarbonates and clay mineral (montmorillonite). We consider that these biopolymers and biopolymer nanocomposites have the potential to be new industrial polymers and materials.
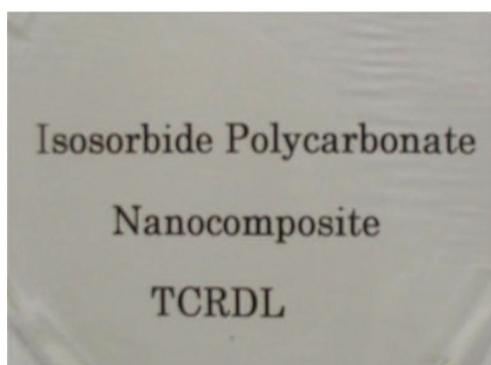
Fig. 6 Photograph of ISPC **1**/Cloisite 30B nanocomposite cast film prepared from ISPC **1** and Cloisite 30B (5 wt%).
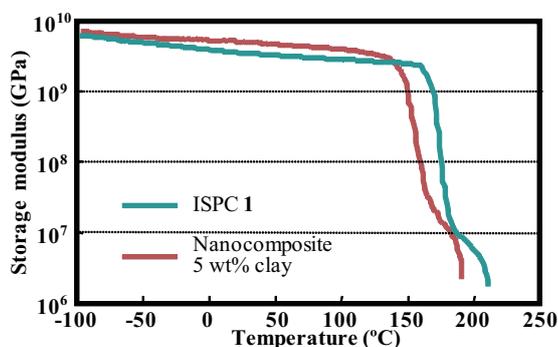
Fig. 7 Temperature dependence of storage modulus of ISPC **1**/clay nanocomposites.
Condition: heating rate 5°C/min, frequency 10 Hz.
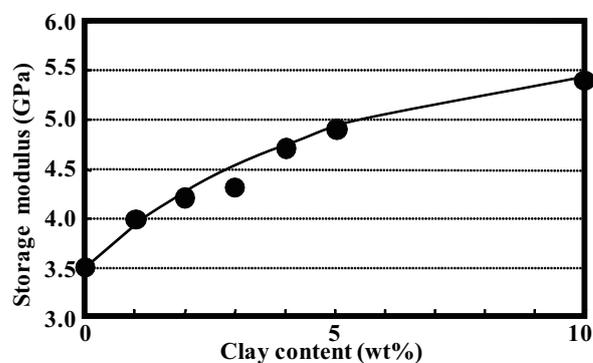
Fig. 8 The variation of the storage modulus of the ISPC **1**/clay nanocomposite at various concentrations of clay.

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- Bio-base Polymer
- Organic Synthesis
- Biofuel

Academic Degree: Ph.D.

Academic Societies:
- The Society of Polymer Science, Japan
- The Chemical Society of Japan
- Society of Automotive Engineers of Japan

Present Affiliation:
- TOYOTA BOSHOKU CORPORATION