Development of New Cellulose-based Polymers with Excellent Melt-processability

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Abstract

New cellulose-based polymers with excellent melt-processability have been developed. The effects of molecular size, functional groups and the degree of substitution on the mechanical and thermal properties of cellulose-based polymers were studied. Plasticity improved markedly with the size and number of added substituents. It was found that the balance between mechanical properties and plasticity was improved dramatically by the combined use of small and large molecules added to side chains. Furthermore, the impact strength of cellulose-based polymers was increased by the addition of ether/ester groups together. These results correlated with the degree of prevalence of soft segments as estimated from dynamic mechanical analysis and solid-state ¹H NMR, and such a specific effect is reported here for the first time. Injection molding of this material was carried out, and good rheological and processing characteristics were confirmed.

1. Introduction

Nowadays, there is increased interest worldwide in the development of materials to support a sustainable society by reducing environmental load. Conventionally, in the manufacture of products, the polymer chemical industry was completely dependent on materials originating in fossil resources. However, the industry is now striving to develop recyclable materials with biomass. As such materials, polylactic acid (hard type) and polybutylene succinate (soft type) have been commercialized, but the expectation for the development of even higher-performance, higher-functionality plastic originating in biomass has been increasing.

Among biomass, cellulose has vast output and thus stable supply can be expected. However, it is a self-cohesive energy, non-thermoplastic material, having very strong hydrogen bonds within and between molecular chains. To add thermoplasticity to cellulose materials, the following two methods have been discussed: external plasticization utilizing the denaturation of hydroxyl groups in combination with plasticizers; and internal plasticization utilizing the denaturation solely. Acetylcellulose and nitrocellulose are cellulose-based polymers with low molecular plasticizers added that can be produced using the former technique. On the other hand, cellulose acetate propionate and cellulose acetate butyrate are materials made with the latter technique. However, in spite of the above-described development activities, the thermoplasticity of cellulose-based polymers alone is still insufficient.

Under such circumstances, focusing on the unique property of cellulose, the industry has been vigorously working on the improvement of cellulose materials by utilizing denaturation. In recent years, some case examples have been reported, such as the commercialization of melt-spin fibers with thermoplastic-enhanced, cellulose-based polymers; and the development of strong, thermoplastic cellulose-based polymers with excellent water and heat resistance from acetylcellulose with cardanol (a main ingredient of cashew nuts) grafted on.

In the meantime, we reached the idea of developing high-performance biomass plastic materials having excellent thermoplasticity from cellulose-based polymers by controlling their strong hydrogen bonds within and between molecular chains.

Thus, we developed new strong, cellulose-based polymers with excellent thermoplasticity and heat resistance. In this paper, we explain their capabilities and report the results of investigations of their applicability as injection molding materials.

2. Thermoplasticity and Mechanical Properties of New Cellulose-based Polymers

On considering the thermoplasticity of new cellulose-base polymers, we focused on the following factors: binding species, molecular sizes and the degree of substitution. Among them, it is molecular sizes and the degree of substitution that are directly related to the control of the hydrogen bonds of cellulose. Binding species function to
change the rigidity of portions connected to cellulose. Fig. 1 illustrates the idea of binding species and molecular sizes that we considered.

2.1 Properties of Cellulose-based Polymers Denatured with A Single Substituent

We first considered the impact of molecular sizes and the degree of substitution on the expression of thermoplasticity and discovered that those factors are closely related to it. As shown in Fig. 2, using bulky substituents was more effective to enhance thermoplasticity, and binding species had an influence on the mechanical properties of the new cellulose-based polymers. Fig. 3 exemplifies the relationship between the degree of substitution and glass transition temperature of materials that have molecule sizes of four-carbon atoms and eight-carbon atoms. The use of bulky substituents promoted the expression of thermoplasticity but it also tended to soften the polymers. That means, to balance the mechanical performance and melt moldability of polymers, controlling molecular sizes and the degree of substitution alone is not sufficient.

2.2 Properties of Cellulose-based Polymers Denatured with Multiple Substituents

With only a single substituent, it was difficult to balance thermoplasticity and material performance. Therefore, we considered modification in the higher-order structure achieved by the substitution of three hydroxyl groups in the cellulose repetition cycle. Then, we designed polymers with a method in which binding species, molecular sizes and the degree of substitution were combined within the chemical structure, incorporating molecular motion in the cellulose molecular form (higher-order structure) and side chains during the modification.

Fig. 4 shows the dependence of modulus on the degree of substitution in the cases where the following materials with multiple substituents were used: a combination of the methyl group and the 2-ethylhexanoyl group (MC-2Eh); and a combination of the acetyl group and the 2-ethylhexanoyl group (CA-2Eh). Compared with the case where materials with the single substituent 2-ethylhexanoyl (Cel-2Eh) are used, materials with multiple substituents expressed thermoplasticity in the high modulus area and had a better balance of material performance. In this way, they exhibited performance that materials with a single substituent cannot achieve. In addition, further consideration of various combinations of substituents found that specific substituent combinations exhibit an excellent balance of rigidity, impact resistance and heat resistance, based on which Article A was developed. The results of an analysis of newly discovered materials retaining excellent performance balance are described in the following paragraphs.
3. Impact -Resistance Factors of New Cellulose-based Polymers

We investigated the reason that the cellulose-based polymers having the aforementioned specific combination of substituents exhibit excellent impact resistance. As a result, it was discovered that impact resistance is closely related to the molecular motion in the higher-order structure and side chains of the cellulose-based polymers incorporated as an additional element. More specifically, we discovered the following three scientific facts related to the increase of the volume of the molecular chains of cellulose and to molecular motion at low temperature: i) at the velocities used in high-speed destruction tests such as impact tests at room temperature, there exist a constant number of molecular motion elements that can absorb energy; ii) the increased degrees of freedom in space allow molecular chains to move within gaps in response to impact; iii) weakened hydrogen bonds let the higher-order structure transform from a molecular chain layered structure that consists of general cellulose materials to a symmetrical uniaxial cylindrical structure (pseudo). Putting these results together, we propose a model shown in Fig. 5.

As far as we know, this correlation between impact resistance and the molecular structure had not been recognized as a property originating in the structure of cellulose-based polymers. We believe that these findings are significant.

Table 1 shows the summary of the properties of Article A, polylactic acid (PLA), cellulose acetate propionate (CAP), acrylonitrile-butadiene-styrene copolymer (ABS). Article A far surpassed PLA, which is now commonly used as a biomass material, in heat distortion temperature, impact resistance and hydrolysis resistance and CAP, the cellulose-based polymer on the market, in moldability, impact resistance and absorbency. In addition, although not listed in the table, it is worthy of note that, for a biomass material, the physical properties of Article A are less likely to be changed by heating. In our opinion, Article A has achieved a level of heat flow kinesis close to that of resin on the market. It has excellent thermoplasticity for a cellulose-based polymer created with the internal plasticization technique.

![Photo 1](image)

Table 1 Characteristics of the development material.

<table>
<thead>
<tr>
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<th>Biomass plastic</th>
<th>Petroleum resin</th>
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<tr>
<td>Article A</td>
<td>Commercial materials</td>
<td></td>
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<tr>
<td>Flexural modulus (GPa)</td>
<td>2.2</td>
<td>1.8</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>76</td>
<td>78</td>
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<tr>
<td>Heat distortion temperature (°C)</td>
<td>93</td>
<td>78</td>
</tr>
<tr>
<td>Charpy impact strength (kJ/m²)</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Moisture absorption coefficient (%)</td>
<td>0.9</td>
<td>2.3</td>
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<tr>
<td>Hydrolysis resistance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molding cycle (s)</td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td>Moldability</td>
<td></td>
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<tr>
<td>Injection</td>
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<td>Solidification</td>
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<td>Measuring</td>
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4. Molding with Test Molds

We conducted injection molding on Article A, which is one of the materials with excellent performance, at a temperature of 210°C (Photo 1). From the resin-filling condition of the thin portions and ribs of the molded articles, we could confirm its high fluid capability. In addition, it exhibited high performance in the molding cycle and was amenable to pigment coloring.
5. Conclusion

We developed new cellulose-based polymers with high thermoplasticity. It was confirmed that those introduced in this paper also retain a good balance of rigidity, impact resistance and heat resistance and are suitable as molding materials. In the future, we are going to consider technology that enables the low-cost mass production of those new materials and to extend their usage to other possible domains. We intend to systematize the findings obtained via this activity into a basic technology to unleash the various practical properties of cellulose materials.

References