

# Bio-Based Polymers

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*(Manuscript received February 8, 2005)*

**Poly(lactic acid (PLA) is a resin that is synthesized by fermenting the raw plant material (biomass) that has been fixed within living plants such as corn and potatoes by photosynthesis. PLA is biodegradable and does not generate harmful gases during combustion. Also, because it is derived from plants, it can be produced using only small amounts of fossil fuel. PLA, therefore, is a material with a low environmental burden. We developed a PLA-based material for the housings of notebook computers using flameproofing and polymer-alloy technologies. This material has optimal physical properties for use in notebook computer housings. We use this material in the FMV-BIBLO NB notebook computer that went on sale in January 2005. This paper describes the development of this material and Life Cycle Assessment (LCA) evaluation.**

## 1. Introduction

Interest in bio-based polymers has increased recently, and manufacturers have been closely examining their applications. Fujitsu is very interested in bio-based polymers such as polylactic acid (PLA), which is made from raw plant materials, in its efforts to decrease oil consumption and the environmental burden.<sup>1)</sup> We have been researching the use of PLA for the housings of portable word-processors and other devices since before 1996 and were the first in the world to apply this material in the electronics field.

In 2000, we developed a PLA carrier tape for transporting and mounting LSIs.<sup>2)</sup> Then, in March 2002, we optimized the composition of this material and used the new composition for the IR mask cover of notebook personal computers.<sup>3)</sup> Because the IR mask cover weighs only 0.2 g, it does not have to meet non-flammability or moldability requirements. However, computer housings must be non-flammable, heat-resistant, highly moldable, and yet impact resistant.

The temperature range of notebook computers is from  $-10$  to  $65^{\circ}\text{C}$ . To improve the heat resistance of PLA, the required deflection temperature under load (DTUL) to attain crystallization is  $110^{\circ}\text{C}$ . The glass transition point ( $T_g$ ) is about  $60^{\circ}\text{C}$ . Therefore, PLA is of sufficient quality for applications in notebook computers. To meet the non-flammability requirements for the housings, we must achieve a rating of UL94 standard V-2 or more. The rating of PLA is UL94 standard HB; therefore, we need to apply a flame retardant. Halogen flame-retardants cannot be used because they create environmental problems, but the rigidity and moldability decrease when other flame-retardants are used. Therefore, achieving a balance in the material's properties is extremely important.

## 2. Material technology

### 2.1 Flame-proofing technology

The non-flammability rating of PLA is UL94 standard HB. To improve the flammability rat-

ing of a composition consisting of 50 wt% PLA and 50 wt% PBS (PLA: Mitsui Chemicals, Inc. H-100J and PBS: Showa Highpolymer Co., Ltd. 1020), we added various combinations of the flame-retardants listed below.

### 2.1.1 Flame retardants

- 1) Aromatic silicon resin J-052: Dow Corning Toray Silicone Co., Ltd.
- 2) Polydimethylsiloxane DC4-708: Dow Corning Toray Silicone Co., Ltd.
- 3) Dimethyl siloxane MB50-315: Dow Corning Toray Silicone Co., Ltd.
- 4) Methylphenyl system silicone resin X-40-9805: Shin-Etsu Chemical Co., Ltd.
- 5)  $\text{Al}(\text{OH})_3$  Pairoraizar HG: Ishizuka Glass Co., Ltd.

The resultant compositions were injected using a twin-screw extruder, and the injection conditions were changed according to the composition being injected.

### 2.1.2 Non-flammability test

We used the non-flammability test of the UL94V standard. In the test, we fixed the test sample perpendicularly. The non-flammability is evaluated by testing five rectangular specimens. A burner flame is applied to the free end of the

specimen for 10 seconds and then a further 10 seconds after flaming combustion ceases. The following are evaluated for the non-flammability:

- 1) The duration of flaming combustions after the first and second burner applications.
- 2) The generation of flaming drips below the specimen.

### 2.1.3 Results

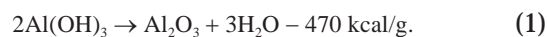
**Table 1** shows the evaluation results. We achieved the V-2 rating of the UL94V standard using a 5 wt% solution of methylphenyl-silicone resin and a 20 wt% solution of  $\text{Al}(\text{OH})_3$ . When PLA burns, it forms a barely visible carbonization layer. Moreover, as the heat is increased, the resin rapidly liquefies, drips, and then combusts. In one example of a test that showed satisfactory results, two of the five samples stopped burning at between 10 and 12 seconds during the second testing. A composition to which a silicone flame retardant had been added continued to burn even after 35 seconds and therefore had poor self-extinguishing properties. When we observed the burning of this composition, we found that only a small number of carbonized layers were formed. As a result, the resin's surface area was increased, which increased the steam pressure within the composition and therefore accelerated combustion.

Table 1  
Non-flammability test.

Flame retardants	Loading (wt%)	Extinction time (s)		UL94 standard rank
		1st test	2nd test	
None	–	3 to 8	28 (1), 31 to 32 (4)	NOT 94V
Aromatic silicone resin: J-052	5	23 to 26 (3), 31 to 32 (2)	27 to 32	NOT 94V
Polydimethylsiloxane: DC4-708	5	35 or more	–	NOT 94V
Dimethyl siloxane: MB50-315	5	3 to 6 (3), 35 or more (2)	35 or more	NOT 94V
	10	4 to 5 (3), 35 or more (2)	35 or more	NOT 94V
	20	4 (1), 35 or more (4)	35 or more	NOT 94V
Methylphenyl silicone resin: X-40-9805	5	2 to 15	5 to 19	V-2
	10	2 to 7	5 to 15	V-2
$\text{Al}(\text{OH})_3$	10	2 to 30 (4), 35 or more (1)	10 to 35 or more	NOT 94V
	20	3 to 6	10 to 19	V-2
	30	2 to 8	3 to 16	V-2

However, when X-40-9805 (Shin-Etsu Chemical Co., Ltd.) was added to the PLA, it attained a rating of UL94V standard V-2. This flame retardant is used in polycarbonate (PC). Both PLA and PC have a common COO structure; therefore, an alloy of PLA and PC might also be effective.

Moreover, the flame-retardant properties of aluminum hydroxide are high. During combustion, it retards combustion through the following endothermic reaction:



Additionally, a carbonized layer is formed by the generation and evaporation of water and an insulation layer is formed by the aluminum oxide generated by the reaction.

## 2.2 Polymer-alloy technology

In PLA, the degree of crystallinity is only 30 to 40 wt%; therefore, even when it completely crystallizes, its amorphous-to-crystallized ratio is high and the characteristics of the amorphous part become dominant. Because the glass transition point of PLA is about 60°C, it has low rigidity at high temperatures. Therefore, it has a low thermal resistance and is difficult to mold. We therefore tried to improve the physical properties of PLA by adding the resins listed below.

### 2.2.1 Resin additives

- 1) PLA H-100J: Mitsui Chemicals, Inc.
- 2) Polystyrene (PS) 685: PS Japan Corporation
- 3) High-impact polystyrene (HIPS) H-9152: PS Japan Corporation
- 4) Polyethylene (PE) 3000B: Mitsui Chemicals, Inc.
- 5) Polypropylene (PP) MA-410: Japanese polyolefine
- 6) Modified polyphenylene ether (mPPE) 200H: Asahi Kasei Corporation
- 7) Acrylonitrile-butadiene-styrene (ABS) 121: Asahi Kasei Corporation
- 8) Polybutylene terephthalate (PBT) 1401: Toray Industries Inc.

- 9) Polymethyl methacrylate (PMMA) VH001: Mitsubishi Rayon Co., Ltd.
- 10) Polycarbonate/Acrylonitrile-butadiene-styrene (PC-ABS) S1100: Daicel Polmer Ltd.
- 11) Polycarbonate (PC) A1900: Idemitsu Kosan Co, Ltd.

### 2.2.2 Experimental methods

The compositions were made using a twin-screw extruder. The mixture rate of each resin was set to 10, 30, 50, and 70 wt%.

#### 1) Izod impact strength

Testing using a JISL-D machine (Toyo Seiki Seisaku-sho, Ltd.) showed that the Izod impact-strength of these compositions conformed to ASTM D-256.

#### 2) Flexural strength

Testing using a versatile testing machine (model 1195 from Instron Corporation) showed that their flexural strength conformed to ISO 178 standards.

#### 3) Deflection temperature under load (DTUL)

Testing using a DTUL tester (model 148 from Yasuda Seiki Seisakusho, Ltd.) showed that their DTUL conformed to ISO 75. The deflection temperature under load was defined as the temperature at which the load deflection point was 0.26 mm.

### 2.2.3 Results

#### 1) Izod impact strength

**Figure 1** shows the results of Izod impact-strength testing. At 70 wt%, the strength of PLA was increased by adding PC, PE, and PP. Especially, in the case of PLA-PC alloy, the alloy rapidly became stronger than PLA at PC concentrations above 50 wt%. Because PLA and PMMA can easily be mixed together, the Izod impact strengths of PLA-PMMA alloys were basically the same regardless of the amount of PMMA. Also, the Izod impact strengths of compositions containing the other resins were lower than those of the pure resins.

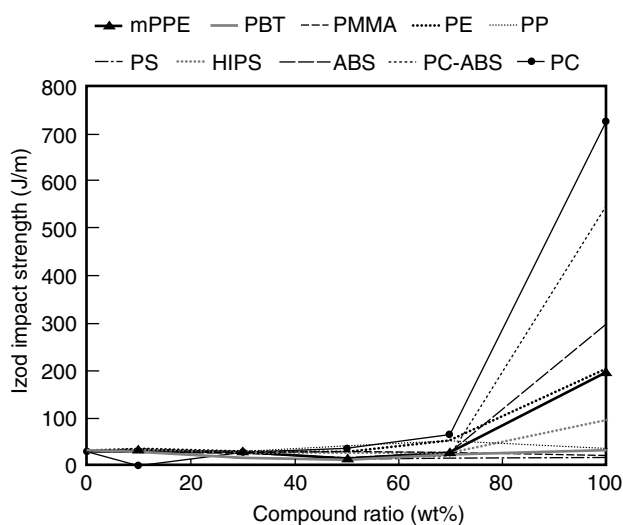


Figure 1 Results of Izod impact-strength test.

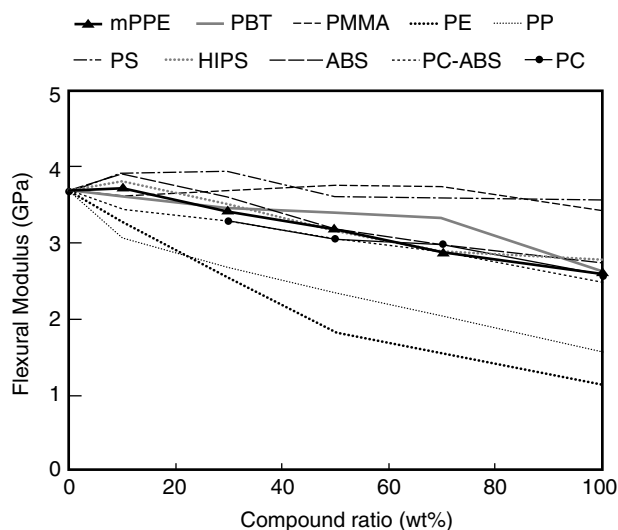


Figure 2 Results of flexural modulus test.

## 2) Flexural strength

**Figure 2** shows the measurement results. The flexural strengths of alloys with PMMA were better than those of pure PMMA. In the other compositions, the flexural modulus decreased in proportion to the amount of resin, particularly when the decrease in PE and PP was large.

## 3) DTUL

**Figure 3** shows the DTUL test results. When compositions were formed with 70 wt% PP, PE, or PBT resin, the DTUL exceeded that of PLA.

The DTUL of PP, PE, and PBT is low; therefore, even if they are added to PLA, a large effect might not be obtained. When a PLA alloy containing 70 wt% or more PC is made, the physical properties of PLA are greatly improved because the alloy consists of small islands of PLA surrounded by a sea of PC. Furthermore, we believe that this effect is enhanced by adding a compatibilizer and nucleating agent.

## 2.3 Summary

We have developed a new plant-based resin based on the flame-proofing and polymer-alloy technologies described above (**Table 2**). This new material has been used in the housing of the FMV-BIBLO NB personal computer since January 2005 (**Figure 4**).

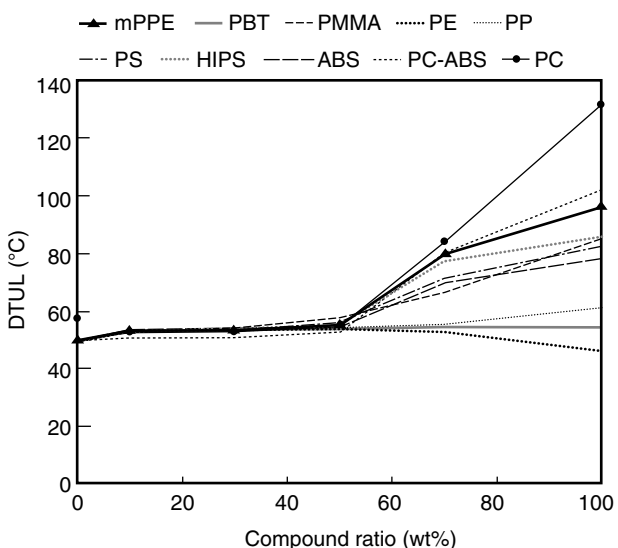


Figure 3 Results of DTUL test.

## 3. Life Cycle Assessment (LCA)

**Figure 5** shows the life cycle of the housing for a personal computer made from plant resin. Because its primary materials are lactic acids extracted from corn, the process begins with agricultural production. Bio-based polymer is chemically synthesized from the extracted lactic acid. The housing is manufactured by injection-molding from a mixture of bio-based polymer, polycarbonate resin, and some additives. At the

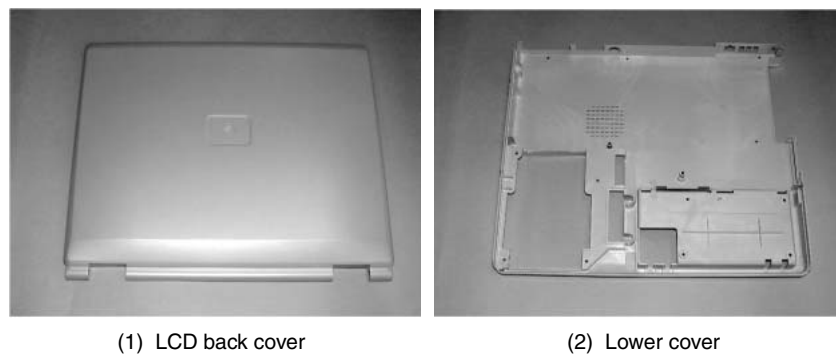


Figure 4  
FMV-BIBLO NB.

Table 2  
Physical properties of new composition.

	Test method	Unit	value
DTUL	ASTM D648	°C	85
Tensile strength	ASTM D638	MPa	65
Tensile strain	ASTM D638	%	60
Flexural strength	ASTM D790	MPa	100
Flexural modulus	ASTM D790	GPa	4.4
Flame retardancy (1.5 mm)	UL94	-	V-1
Flame retardancy (3.0 mm)	UL94	-	V-0

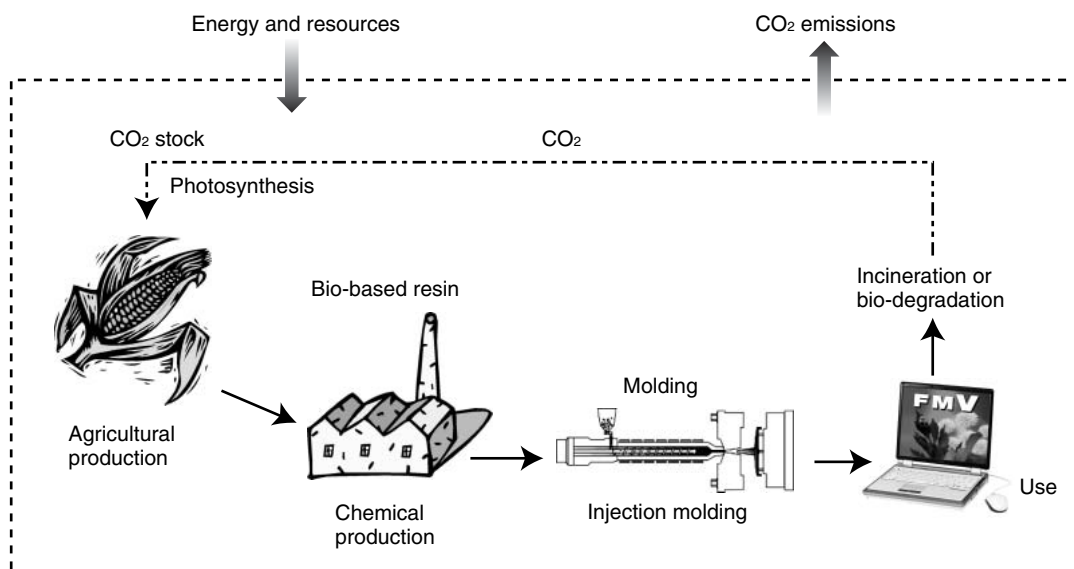


Figure 5  
Life cycle of PC housing.

end of the computers' lives, the housings are recycled for use as a reducing agent in a blast furnace. The various inputs such as energy and resources in this life cycle affect the environment in the form of CO<sub>2</sub> emissions, which are a cause of global warming.

We analyzed the environmental impact of these housings by taking into consideration the CO<sub>2</sub> emissions and various inputs such as energy and resources during the life cycle.

1) Material production process

The use of pesticides, fertilizers, water, and heavy oil in agricultural production affects the environment in the form of CO<sub>2</sub> emissions.<sup>4)</sup> However, CO<sub>2</sub> is absorbed from the atmosphere by growing crops (e.g., corn) by photosynthesis. In addition, extracting starch from corn and synthesizing it into a bio-based polymer requires the input of electricity and fossil fuel for energy (Figure 6). CO<sub>2</sub> emissions from the production of this material were estimated by deducting the CO<sub>2</sub> absorbed from the atmosphere due to crop photosynthesis from the CO<sub>2</sub> emitted during synthesis of the material. The CO<sub>2</sub> emission and absorption values such as the “kg of CO<sub>2</sub> per kg”

value were taken from Cargill Dow data that was released in 2003.

We compared the CO<sub>2</sub> emissions from a bio-based polymer with the CO<sub>2</sub> emissions from PC-ABS (Figure 7). The CO<sub>2</sub> levels emitted during the production of the bio-based polymer were higher than those for plastics, which use up non-renewable resources. However, when CO<sub>2</sub> absorption by photosynthesis is taken into consideration, the overall CO<sub>2</sub> emissions from the manufacture of a bio-based polymer are 14% less than for PC-ABS.

2) Housing production process

The injection-molding process involves the consumption of electricity (energy) and the mold material. Then, the housings are transported by truck from the molding factory to the assembly factory, which is assumed to be 500 km from the molding factory. The energy consumption and transportation processes both emit CO<sub>2</sub>. The CO<sub>2</sub> emissions during this housing production process (excluding transportation) were only 8% of the total CO<sub>2</sub> emissions during the entire life cycle. Although the cycle time for injection-molding using the bio-based polymer is 20% longer than

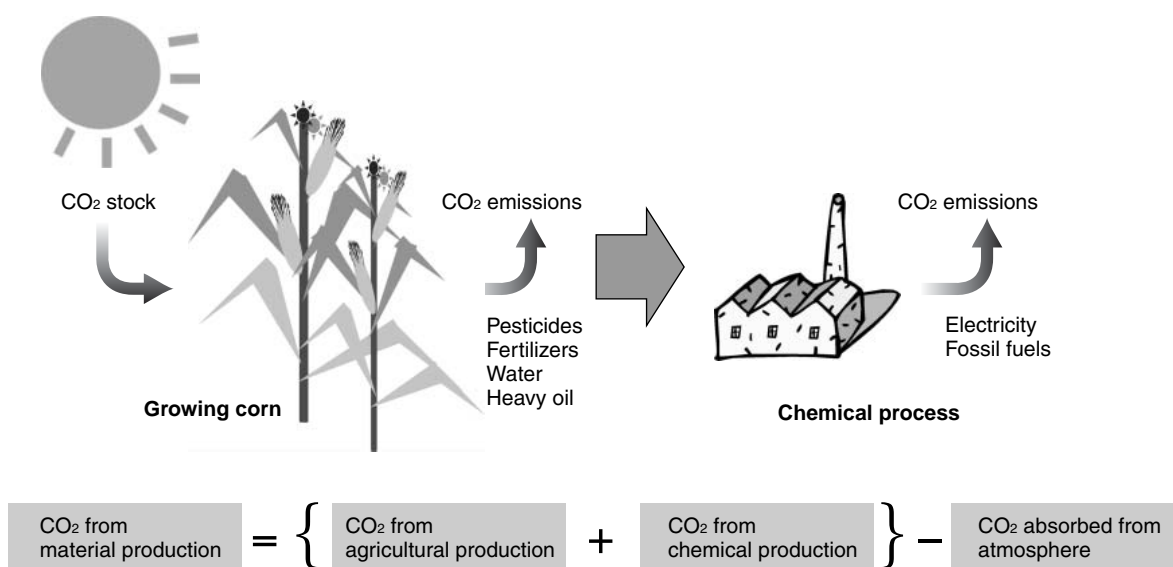


Figure 6 Assessing bio-based polymer.

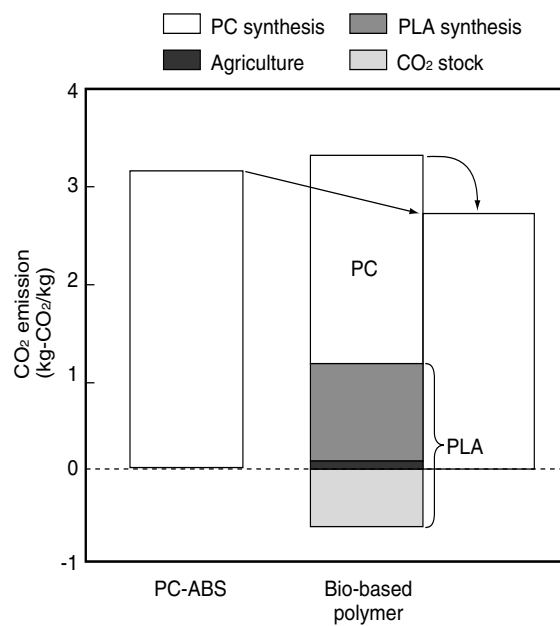


Figure 7  
Comparing CO<sub>2</sub> emissions from bio-based polymer production with CO<sub>2</sub> emissions from PC-ABS production.

the cycle time for PC-ABS, the resulting increase in environmental impact due to the increased energy consumption is small.

### 3) Recycling process

After use, discarded housings are recycled as a reducing agent in a blast furnace. Consequently, the CO<sub>2</sub> emissions generated during this process are as large as those generated during incineration. The CO<sub>2</sub> emissions during this process are estimated by calculating them from the carbon content based on the chemical composition of the material. When a bio-based polymer is used for housings, less CO<sub>2</sub> is emitted during the recycling process than when PC-ABS is used because bio-based polymers have a lower carbon content.

**Figure 8** shows the level of CO<sub>2</sub> emission from housings made of bio-based and fossil-based (PC-ABS) polymers throughout their life cycles. There were differences in CO<sub>2</sub> emissions from the two materials during the material production and incineration processes. The overall results showed that using the bio-based polymer provided an environmental advantage equal to a 14.8%

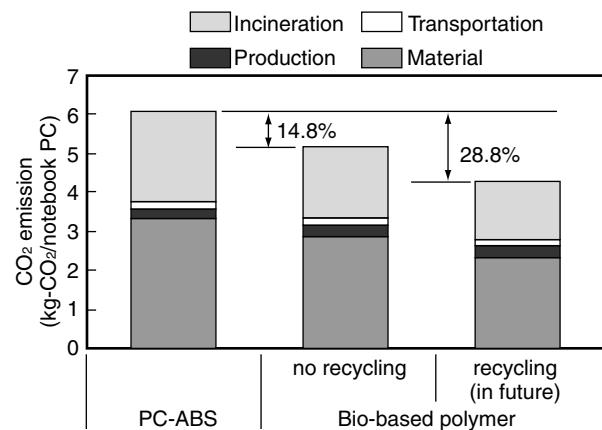


Figure 8  
Comparing CO<sub>2</sub> emission from the bio-based polymer and plastic from non-renewable sources.

decrease in CO<sub>2</sub> emissions over the entire life cycle.

In the future, discarded personal-computer housings will be recycled as a raw material for new housings. Some electrical power is required to recycle used housings into raw material. However, because of the decrease in consumption of virgin material, the CO<sub>2</sub> emissions during the life cycle of bio-based polymers are 28.8% lower than those of PC-ABS.

## 4. Final remarks

In the Kyoto Protocol, Japan is asked to decrease its CO<sub>2</sub> emissions by 6%. We believe that using bio-based polymers is a positive step towards decreasing our CO<sub>2</sub> emissions. Bio-based polymers can reduce oil consumption, and that will help to conserve our non-renewable resources. We will continue to work on further improvements in the properties of bio-based polymers so that their applications can be expanded in the future.

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