

Future directions for the research and development of polyesters: From high-performance to environmentally friendly*

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Abstract: We discuss the future directions for the research and development of polyester-based materials. In the discussion of polyesters as industrial materials, one direction is the development of high-performance materials. Poly(ethylene terephthalate) (PET), known as one of the most important polyesters, was developed early in the 1940s. We discuss two approaches to the development of high-performance materials suitable for injection-molding applications using PET units. The first approach is development of high-performance materials by copolymerization with bibenzoic acid (BB), which has a rigid structure, and the second approach is development of liquid-crystal polyesters (LCPs) with superior thermal resistance and excellent flowability using PET units.

The other future direction for research and development is the targeting of environmentally friendly materials. Poly(lactic acid) (PLA), derived from bio-based materials, is a very important material because it can realize the carbon neutral cycles. Nevertheless, the practical properties of PLA itself are unsatisfactory compared to other plastics derived from fossil resources. We have developed PLA-based polymer alloys with various practical properties by utilizing a newly developed nanoalloy technology.

Keywords: polyesters; high-performance; environmentally friendly; liquid-crystal polyesters; nanoalloys.

HIGH-PERFORMAMNCE MATERIALS

Poly(ethylene terephthalate) (PET) was developed in the early 1940s and industrialized in 1949 by ICI. PET is the most widely known and important polyester especially for fiber and film applications. However, PET has a very low crystallization rate and is not suitable for injection-molding applications. We have studied the new high-performance polyesters suitable especially for injection molding by utilizing PET units. In this paper, we discuss two types of high-performance polyesters.

The first type of high-performance polyester has been developed by using bibenzoic acid (BB) with rigid structure as a dicarboxylic acid. We describe this type of polyester as BB polyester. Schiraldi et al. reported excellent mechanical properties of BB polyesters [1]. We have focused our attention on the BB polyesters and have studied them [2].

The second type of high-performance polyester is liquid-crystal polyester (LCP). A new LCP called “SIVERAS”, which has outstanding flowability and high thermal resistance and contains PET units, has been developed by controlling the self-condensation of *p*-hydroxy benzoic acid (HBA).

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BB polyesters

Although poly(ethylene naphthalate) (PEN) is well known as a high-modulus polyester, it has a lower crystallization rate than PET and is very difficult to use for injection-molding applications. In contrast to PEN, the polyester derived from BB and ethylene glycol (EG) seemed to have a high crystallization rate because it has excellent packing of molecules due to its rod-like molecular structure. We describe it as BB-EG polyester. But it is also very difficult to obtain injection-molded articles because of its too high melting point (Table 1). Consequently, we investigated the copolymerization of BB-EG polyester with other dicarboxylic acids such as terephthalic acid (TA), isophthalic acid (IA), and tetrahydroterephthalic acid (TH). And we finally selected TA as a comonomer because the T_g of the copolymer is higher than PET (Fig. 1). We describe it as BB/TA-EG polyester.

Table 1 Thermal and mechanical properties and crystallinity of polyesters.

	Thermal properties		Fiber	Injection molding	
	T_g (°C)	T_m (°C)	Young's modulus (g/d)	Half-crystallization time (s) at 180 °C	Moldability
PBT	35	228	20–40	<10	Very good
PET	85	252	129–121	60	Poor
2,6-PEN	122	269	217	>400	Not good
BB-EG	–	330–355	–	–	–

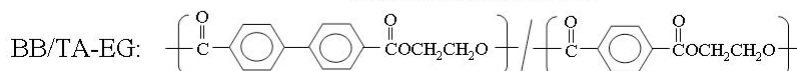
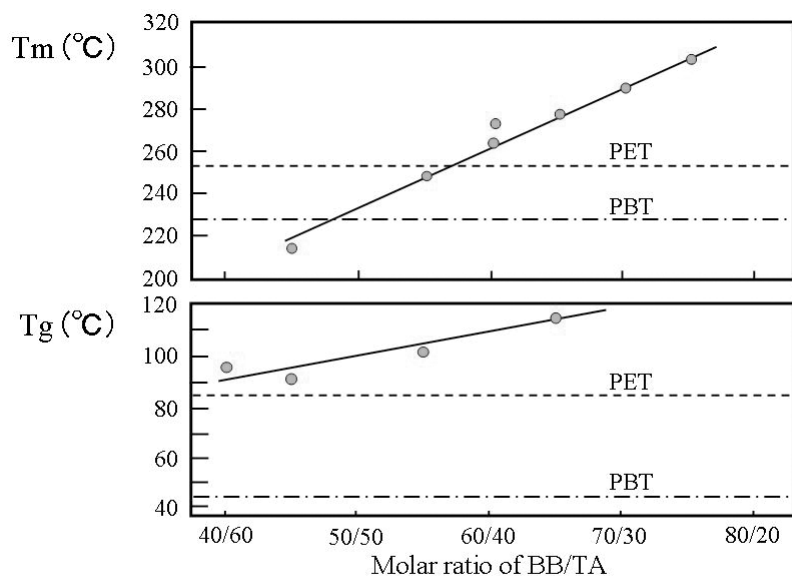
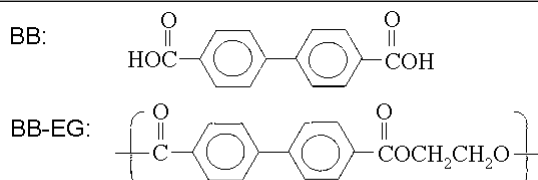


Fig. 1 Thermal properties of BB/TA-EG polyesters.

BB/TA-EG polyesters

BB/TA-EG polyesters show the same crystal structure as PET, and the range of copolymerization ratio of BB/TA is 0/100 to 20/80. In the case of the copolymerization ratio of 30/70, BB/TA-EG polyester shows an amorphous X-ray diffraction pattern. In the case of the ratio of 45/55 of BB/TA, the polymer shows good crystallinity, and in the range of 45/55 to 65/35, the BB/TA-EG polyesters show almost the same X-ray diffraction patterns (Fig. 2).

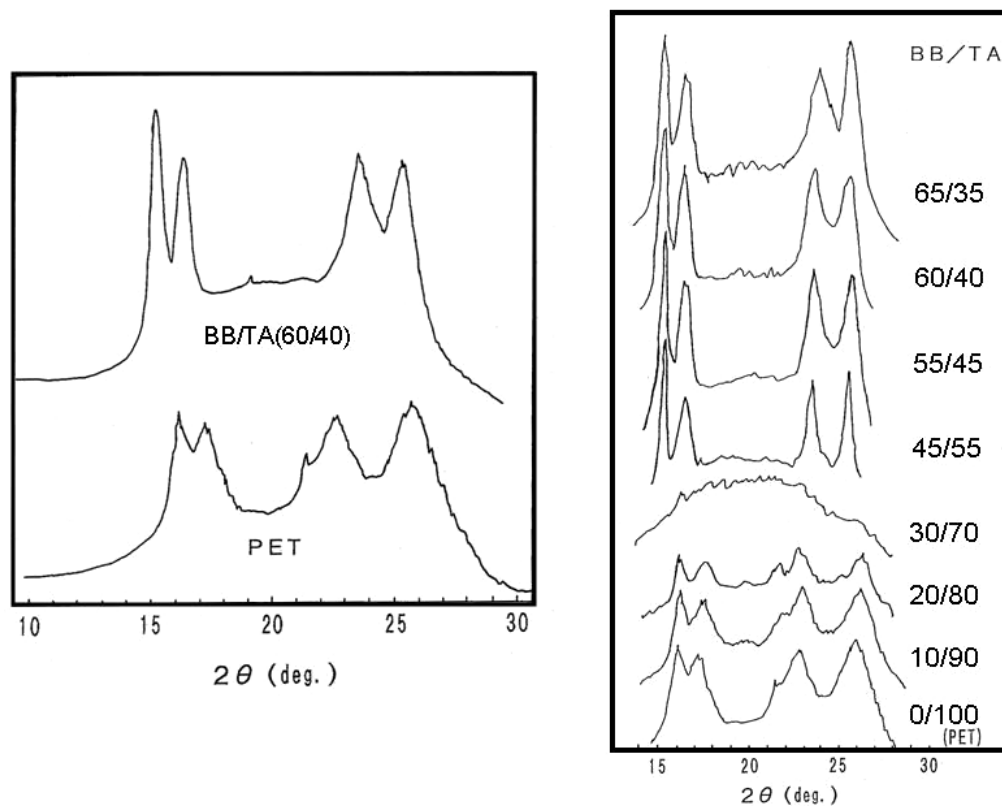


Fig. 2 X-ray diffraction patterns of BB/TA-EG polyesters.

Among these polymers with different BB/TA ratios, BB/TA-EG polyesters with the ratio of 50/50 to 60/40 have a crystallization rate as high as poly(butylene terephthalate) (PBT) in spite of copolymers (Fig. 3).

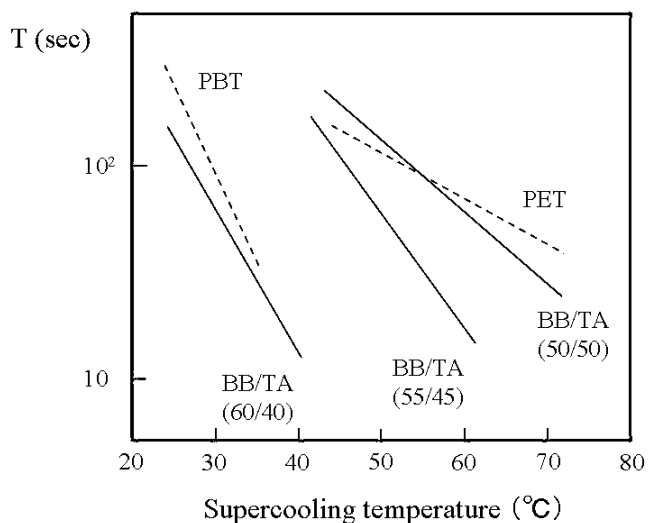


Fig. 3 Rate of crystallization of BB/TA-EG polyesters.

The tensile strength and modulus of BB/TA-EG polyesters with the copolymerization rate of 60/40 to 65/35 are higher than those of PET and PBT, especially in a molded article with very small thickness (Fig. 4).

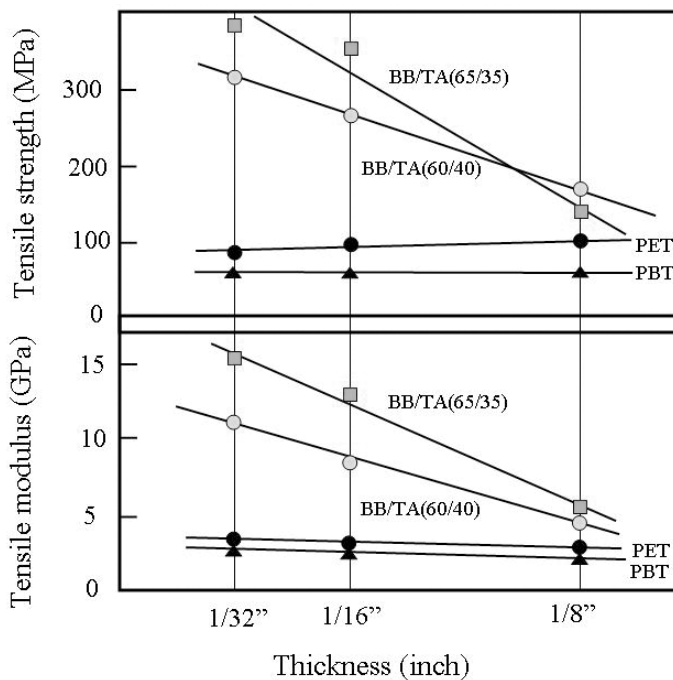


Fig. 4 Tensile properties vs. thickness of BB/TA-EG polyesters.

The high mechanical properties of BB/TA-EG polyesters are due to their highly oriented skin layer observed in thin wall molded articles. Figure 5 shows the highly oriented fibrils observed on the

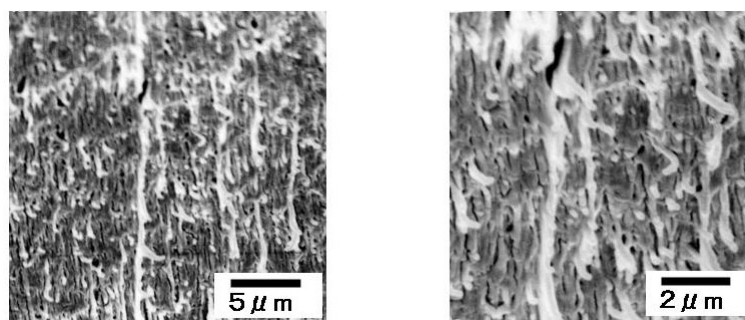


Fig. 5 SEM images of flexural fractured BB/TA(60/40)-EG polyester injection-molded test pieces.

fractured skin layer of the injection-molded test piece of BB/TA(60/40)-EG polyester. BB/TA-EG polyesters show much higher thermal and chemical resistance than those of PET and PBT.

Thus, we have obtained high-modulus, injection-molded articles from BB/TA-EG polyesters.

LCP with HBA and PET units

It is well known that the melting points of LCP consisting of HBA/PET units depend on the molar ratio of HBA/PET units. In order to increase the melting points of those polyesters, it is necessary to reduce the content of PET units. But it is difficult to polymerize HBA/PET LCP with homogeneous composition if the PET content is less than 20 mole %. In other words, solidification occurred during the polymerization of HBA/PET LCP with the PET content of less than 20 mole % (Fig. 6). In order to make the mechanism of the solidification clear, we investigated the polymerization reaction and determined that the reaction rate of self-condensation of HBA was much higher than that of the acidolysis reaction of PET by HBA [3] (Scheme 1). Thus, we reached the idea of controlling the self-condensation of HBA by copolymerization of the third unit, which reacts competitively with HBA unit (Scheme 2). Finally, we obtained the high-heat-resistant new LCP containing less than 20 mole % of PET units by copoly-

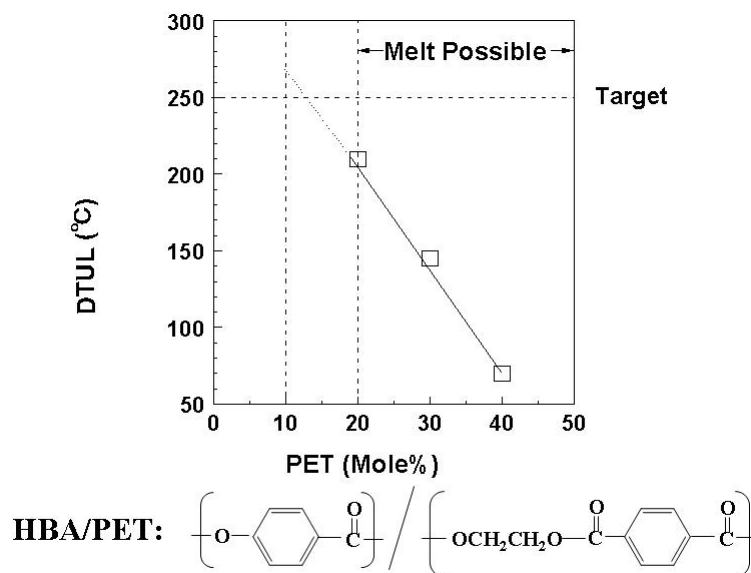
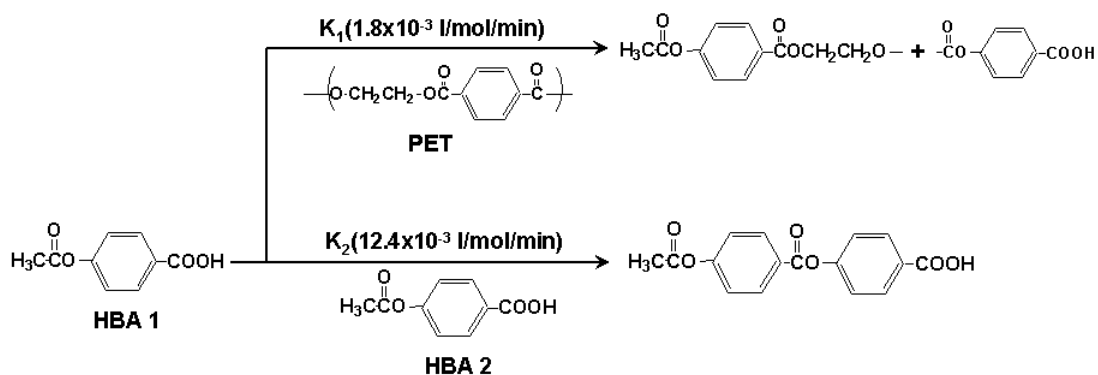
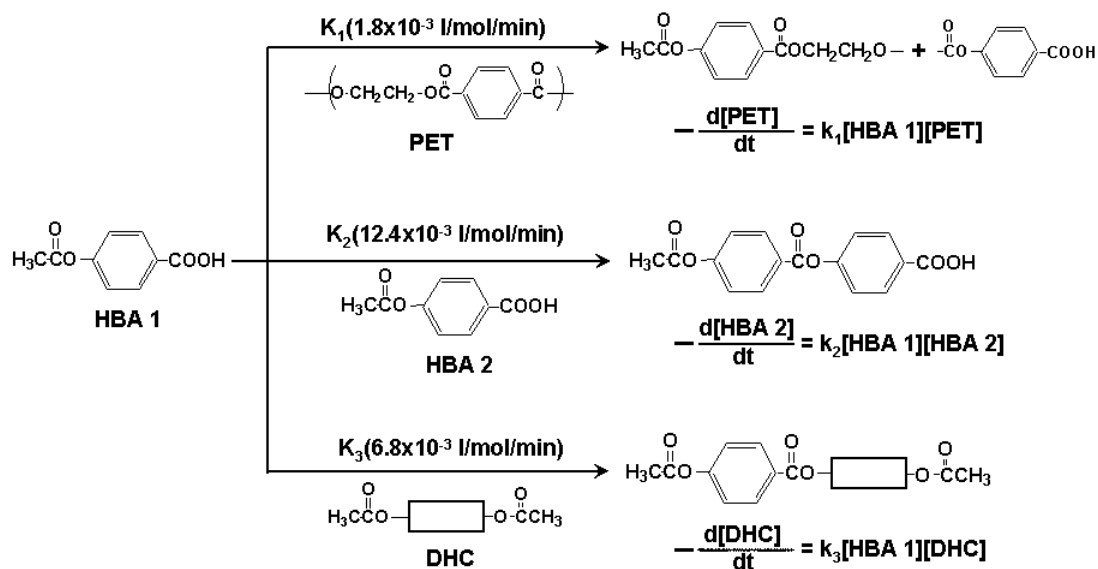


Fig. 6 DTUL as a function of PET content in HBA/PET LCP.

merization of a small amount of the third unit (Fig. 7). This LCP has better balance of crystallinity and homogeneity compared to other LCPs (Fig. 8).



Scheme 1 Relative mechanism of HBA/PET LCP.



Scheme 2 Relative mechanism of HBA/PET LCP with the third unit.

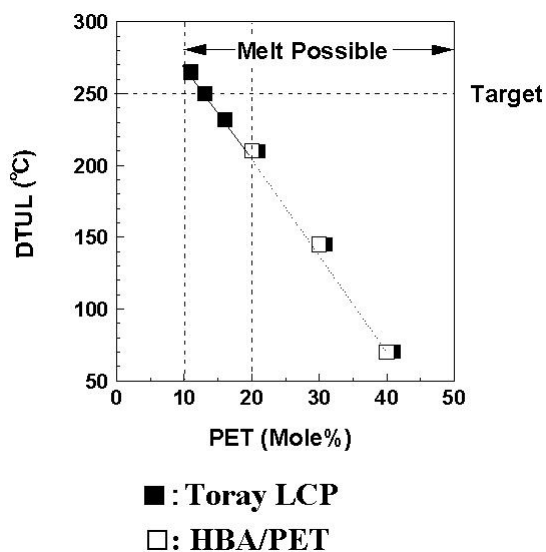


Fig. 7 DTUL as a function of PET content in HBA/PET LCP and Toray LCP.

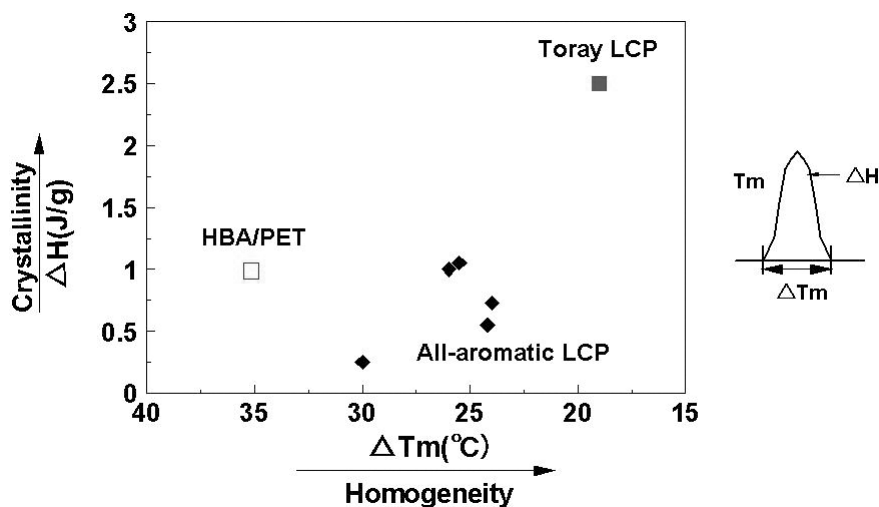


Fig. 8 Crystallinity (ΔH) vs. homogeneity (ΔT_m) measured by differential scanning calorimetry (DSC).

Figure 9 shows the relation between the flowability and the heat resistance of several types of LCP. We developed our original LCP, SIVERAS, from the above-mentioned molecular designing, which shows an excellent balance of flowability and heat resistance.

SIVERAS has high soldering heat resistance and fast cycle time in injection molding due to its high crystallinity, and also has excellent low flash, excellent flowability, and high weld line strength due to its high homogeneity. SIVERAS is used in electrical and electronic (E&E) areas such as flexible printed circuit connectors or hard disk drive parts.

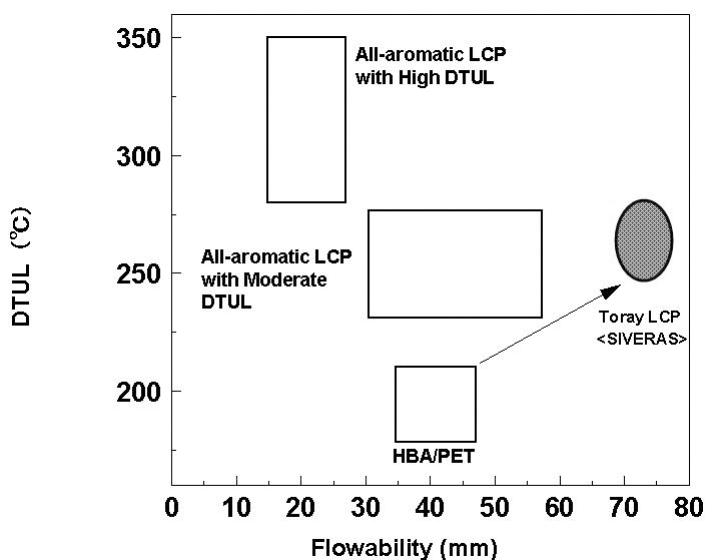
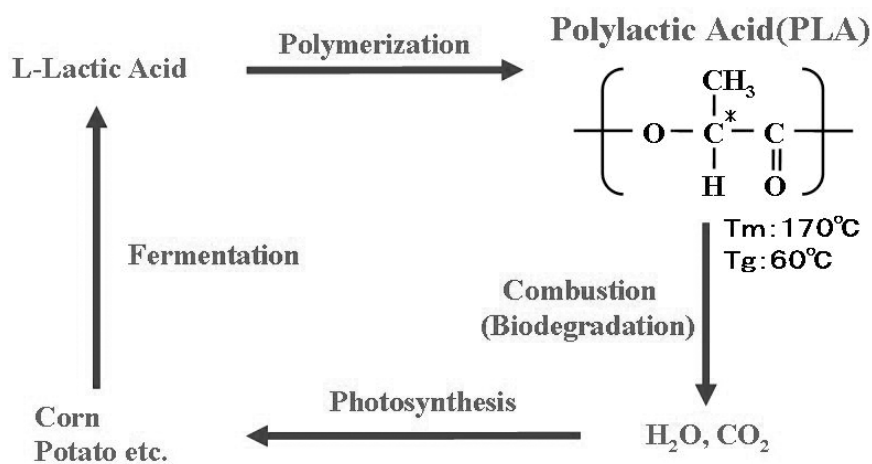


Fig. 9 DTUL and flowability of Toray LCP SIVERAS.

ENVIRONMENTALLY FRIENDLY MATERIALS

In recent years, environmental issues such as ozone depletion, air pollution, environmental pollution, and rapid increase of industrial and toxic waste, have emerged worldwide. Our society depends on fossil resources, and the drying up of fossil resources in this century is a concern. To address these problems, there is a need for the development of a recycling-based society. As for plastics, there is a need for materials with low fossil resource consumption and environmental impact.

The evaluation of poly(lactic acid) (PLA) in the marketplace has increased as a representative of bio-based polymers, whereas most plastics are manufactured from fossil resources. PLA has been expected as a practical bio-based polymer because of its high melting temperature (around 170 °C) and the compatibility to melt processing, and it has been utilized mainly for food containers and agriculture or forestry materials (Scheme 3).



Scheme 3 Life cycle of PLA.

However, the performance of PLA was insufficient for high-end uses such as E&E or automobile applications. Therefore, the improvement of the properties of PLA has been in strong demand in order to reduce the use of fossil resources and environmental impact.

High-performance technology for PLA

To use PLA widely, its disadvantages, such as heat resistance, moldability, durability, toughness, and flame retardancy, must be improved. We have developed a new polymer alloy technology called “nanoalloy” to improve these disadvantages.

Improvement of heat resistance by nanoalloy

PLA has disadvantages such as low crystallization rate, heat resistance, and durability. We succeeded in improving heat resistance, moldability, and durability drastically by the original nanoalloy technology.

As for the conventional polymer alloy, the second polymer component is dispersed at micrometer scale in PLA. We have developed a new PLA alloy in which the high-performance component is dispersed at nanometer scale (Fig. 10).

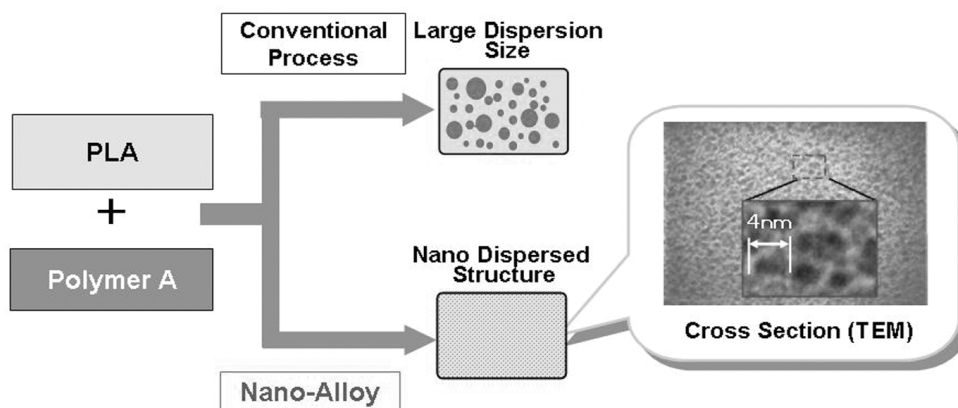


Fig. 10 Concept of PLA nanoalloy.

By the effect of nanoscale dispersion of high-performance polymer component in PLA, many advantages (such as improved crystallinity, enabling injection molding, and improved short- and long-term heat resistance) were obtained.

To improve the crystallization rate, nucleating agents are generally used. For PLA, the effect of the nucleating agents is low and deflection temperature under load (DTUL) is not improved. For the new alloy, DTUL over 100 °C was obtained. On the other hand, DTUL of the ordinary PLA was as low as 50 °C. The mold temperature of the test specimens was 90 °C. The new alloy can be used at high temperature, for example, in automobiles.

Moreover, long-term heat resistance was improved drastically by this nano-dispersion structure. After 300 h and immersion at 120 °C, the retention of tensile strength of the PLA nanoalloy was as high as 70 %, compared to 20 % for PLA itself. This material can be used as E&E and automobile parts due to the improvement of heat resistance and durability of PLA.

Improvement of toughness

One of the problems of PLA is its insufficient toughness. To use plastics for electronic equipment, high impact strength is required so that the equipment can endure assembly, transport, and use. So, high-im-

compact plastics such as high-impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS) have been used.

We succeeded in improving impact strength drastically by dispersing the impact modifier which was designed especially for PLA. The Izod impact strength of the modified PLA is more than 10 times higher than that of the original PLA. In addition, by combining with the above-mentioned nanoalloy technology, we developed a new material with high heat resistance, impact strength, and moldability equal to ABS or more. The use of this material as housing, etc. has just started.

Transparent PLA with high heat resistance

PLA is a transparent material if it is molded in the noncrystalline state. However, because of the low T_g of 60 °C, the heat generated from the equipment and the heat exposed in transit may deform the noncrystalline PLA. Moreover, there is a problem in the use of PLA as a transparent material because it becomes opaque when it is crystallized to improve heat resistance.

We also succeeded in developing a new PLA alloy material with high transparency and heat resistance by alloying the high T_g polymer with PLA and by controlling the dispersion size. Because the dispersion size of the high T_g polymer is smaller than the wavelength band of light, it is possible to use it for a lot of applications, including optical media.

When this material is used for DVDs, the heat resistance should be improved about 15 °C without ruining the optical characteristics of DVDs using homo PLA. This disk showed excellent static optical properties and satisfied the fundamental specifications of physical and signal characteristics. The newly developed transparent PLA alloy is also applicable to all other types of optical disk, such as compact disks and Blu-ray disks, using the same injection-molding technique with mass production capability.

Flame-retardant technology

Because of an aliphatic polyester structure, PLA is easily burnt and is not sufficient to use for applications where flame resistance is required. Moreover, it is necessary to satisfy the characteristics such as heat resistance, moldability, durability, toughness, etc. in addition to flame resistance to be used for electronic equipment.

To solve such problems, we improved the characteristics of PLA by nanoalloy technology and the original non-halogenated flame-retardant technology. That is, a non-halogenated flame-retardant PLA material was created with advanced flame retardancy without using the halogenated flame retardant, which may generate poisonous substances such as dioxin. Moreover, it shows good heat resistance, moldability, durability, and toughness.

As a large amount of flame retardant was necessary to improve the flame retardancy of PLA, the properties of the obtained material became low and it was not sufficient to be used as a plastic housing. Therefore, we have developed a new flame-retardant technology for PLA by using carbonized layer formation polymer in addition to non-halogen flame-retardant agent (Fig. 11). By the migration of the material to the surface, a carbonized layer selectively forms, insulates effectively, and restricts the diffusion of the combustible gases.

Moreover, we solved the problem of bleeding of flame retardant by confining it in carbonized layer formation polymer and by designing so that the non-halogen flame-retardant agent moves to the surface only when burning. The developed flame-retardant technology achieved advanced flame resistance by using a small amount of flame retardant with the appropriate carbonized layer formation.

Then, we developed a nanoalloy technology blending polycarbonate having higher T_g with PLA. In this alloy, special morphology at nanometer order was formed by a newly developed compatibilizer and an original processing technology. Also, we realized advanced flame-retardant PLA with excellent heat resistance, moldability, durability, and toughness. It is applicable to a large-scale plastic housing.

This material achieved the performance and productivity equal with the polycarbonate/acrylonitrile-butadiene-styrene resin alloy for the large-scale plastic housing, and it was the world's first plastic adopted as housing for notebook computers.

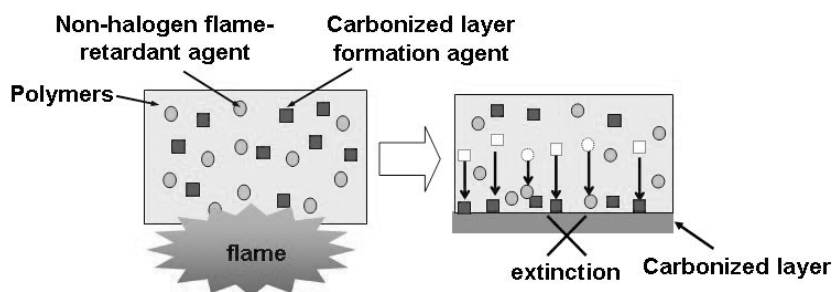


Fig. 11 Concept of flame-retardant technology.

This material is also applicable to various E&E products other than notebook computers, and the commercialization for a lot of applications has already been started.

CONCLUSION

We showed two future directions for the research and development of polyesters. As high-performance materials, we developed a high-performance polyester suitable for injection molding utilizing BB as a dicarboxylic acid unit and also a new LCP with outstanding flowability by controlling molecular structure. As environmentally friendly materials, we focused on PLA and developed PLA-based nanoalloys with excellent thermal, mechanical, and practical properties such as flame retardancy or transparency.

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