

Development of Elastic Polylactic Acid Material Using Electron Beam Radiation

Shinichi KANAZAWA

Sumitomo Electric Fine Polymer has developed a technology for fabricating a brand new elastic material made of electron-beam (EB) irradiated polylactic acid (PLA) in the joint research with the Japan Atomic Energy Agency (JAEA). This new technology enables PLA to be cross-linked by EB irradiation and then swollen in hot plasticizer solution, resulting into a "PLA organogel with plasticizer". Even though this was performed under a temperature condition of 80 degrees C, the PLA gel contains 40 to 60 wt% plasticizer and keeps softness for at least half a month. Using this technology, several products are under development as materials or components for electronics and automotive applications.

1. Introduction

Since measures for solving global environmental problems are recently being demanded with greater urgency, bio-based plastics has been widely studied as alternatives to petroleum-based plastics that can reduce carbon dioxide emissions.

Among various bio-based plastics, polylactic acid (PLA) has material properties nearest to those of general plastics. Because PLA can be industrially mass produced, it can be priced cheaper, and therefore early practical utilization is expected.

However, PLA is not without shortcomings. Its crystallization speed is extremely slow and it becomes almost noncrystalline within the standard processing time, which means that at 60°C and above PLA become so soft that it cannot retain its original shape.

In the joint research with the Japan Atomic Energy Agency (JAEA) on property modification of PLA using electron beam (EB) irradiation technology, the author had revealed that EB irradiation improves PLA's heat resistance and prevents whitening due to heating⁽¹⁾⁻⁽⁴⁾. In the course of studying the substitution of PLA for petroleum-based plastics, it had been noticed that another problem of PLA is that PLA is stiff and lacks flexibility. In this paper the author reports on the solution to this problem.

2. Problems in plasticization of PLA

Plasticizers are usually used for plasticization of plastics, and several plasticizers for PLA are already available in the market. By adding 20% to 30% by weight of plasticizer, the glass transition temperature (T_g) of PLA can be brought down to around the room temperature (RT).

In order to make PLA sufficiently soft at RT, between 35% to 40% by weight of plasticizer needs to be added to bring down PLA's T_g under RT. However, it is difficult to uniformly blend more than 30% by weight of

plasticizer with PLA.

A further problem is that even if plasticizer over 30% by weight is successfully mixed with PLA and PLA is formed into such shapes as film, sheet or pellet, the bleeding out of plasticizer starts to occur as soon as it is cooled. In many cases, PLA products harden and become white, or adhere with each other. (Fig. 1)

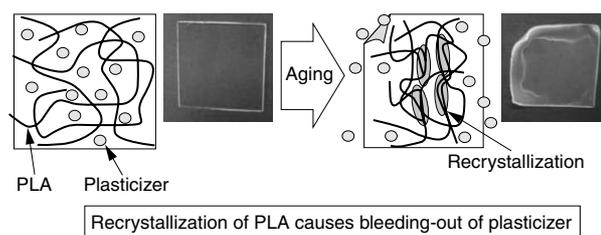


Fig. 1. Problem in PLA plasticization

3. Recrystallization of PLA

The phenomenon of bleeding of plasticizer is caused by the recrystallization of PLA. Recrystallization means that PLA transits from a non-crystalline state into a crystalline state at temperatures higher than T_g but not exceeding the melting point temperature (T_m). In the differential scanning calorimetric (DSC) curve of PLA (Fig. 2(a)), it is shown as a heat evolution peak at around 100°C.

Normally, the recrystallization of PLA only takes place at temperatures above PLA's T_g of 60°C (for example 100°C), but in the case where T_g becomes lower than RT as a result of mixing enough amount of plasticizer, PLA recrystallizes even at RT.

PLA in a crystalline state loses flexibility and its molecules cannot respond to further deformation. In addition to this, the spaces between the PLA molecules where plasticizer can be contained decreases, and plasticizer bleeds out from the surface of PLA.

The author previously reported that EB radiation

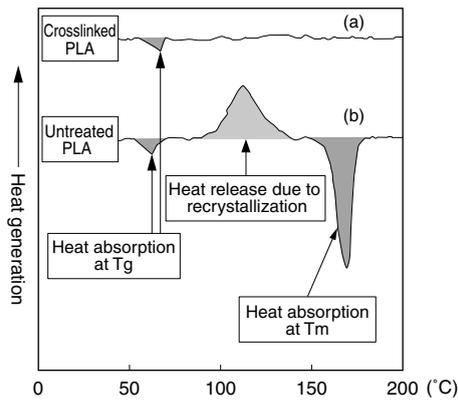


Fig. 2. DSC analysis of crosslinked PLA

crosslinking using triallylisocyanurate (TAIC) as a crosslinker can crosslink and bind PLA molecules and prevent the recrystallization of PLA^{(5), (6)}. (Fig. 3)

Restraining the molecular movement of PLA by crosslinking prevents PLA's transition from a noncrystalline state to a crystalline state. As shown in Fig. 2(b), crosslinked PLA shows neither the heat evolution peak due to recrystallization observed at around 100°C nor the absorption peak of Tm observed at around 160°C.

The author has found that this mechanism of restraining PLA molecules by EB crosslinking can prevent the bleeding of plasticizer from PLA. (Fig. 4)

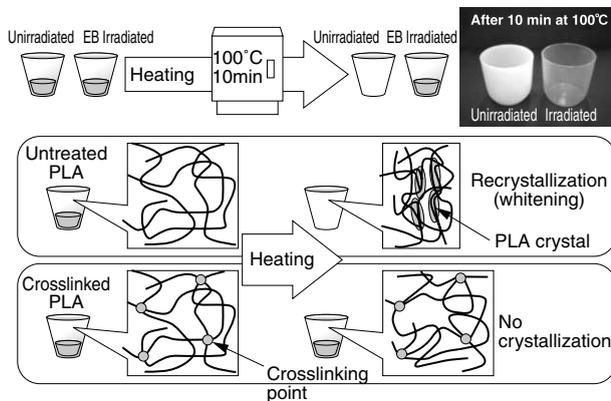


Fig. 3. Prevention of PLA recrystallization by EB crosslinking

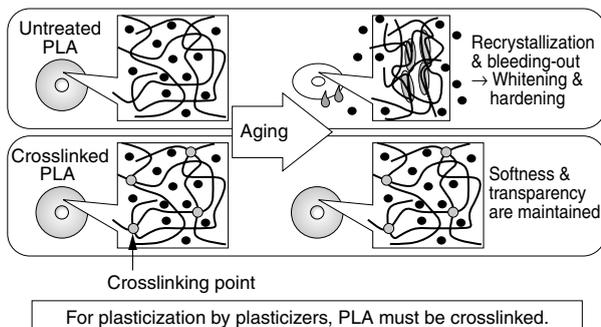


Fig. 4. Effect of crosslinking in maintaining softness

4. Addition of plasticizer to PLA

The effect of EB crosslinking has been theoretically understood, but verification was difficult. This was because the bleeding of plasticizer begins as soon as the forming process starts and before the EB irradiation process.

The typical manufacturing process of EB-irradiated products is shown in Fig. 5(a). All contents are first melted and blended, then formed, and lastly subjected to EB radiation. EB crosslinking links separate molecules together and makes them non-heat-meltable, so the hot-melt forming process must be done prior to the EB irradiation process. When the processes are in this order, the EB irradiation process cannot prevent the bleeding of plasticizer.

Prevention of the bleeding of plasticizer was seen in a PLA sample containing 20% by weight of plasticizer⁽⁷⁾. However, it was unable to prepare PLA samples having enough softness, such as PLA containing more than 40% by weight of plasticizer.

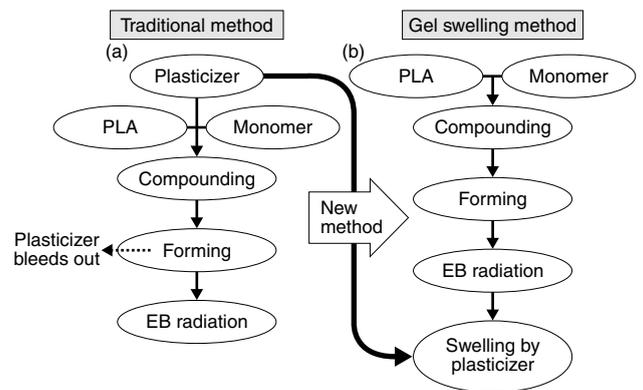


Fig. 5. Improvement of plasticizer blending method

As a solution to this problem, the author has developed a method of gel swelling of PLA by using plasticizer. Contrary to the conventional method of adding the plasticizer in advance (Fig. 5(a)), this brand new method soaks cross-linked PLA in a heated plasticizer liquid, then composite it with the plasticizer by the gel swelling mechanism (Fig. 5(b))⁽⁸⁾.

The most popular case of gel swelling phenomenon is the absorption of water by acrylic polymer hydrogel (crosslinked acrylic acid) used in disposable diapers and sanitary napkins. (Fig. 6) Crosslinked acrylic acid can absorb several hundred times its volume of water without bleeding.

The PLA gel developed by the author has a gel structure just like hydrogel, but it is an organogel absorbing plasticizer instead of water. Therefore, the plasticizer absorbance of the PLA gel is around 100% and not very high, but it can hold a maximum of 70% by weight of plasticizer.

For efficient swelling of this PLA gel, heating at above Tg is necessary. The author also found out that PLA must be almost 100% crosslinked because non-

crosslinked PLA melts or recrystallizes in a heated plasticizer liquid⁽⁸⁾. (Fig. 6)

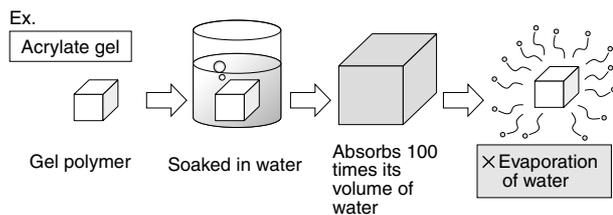


Fig. 6. Water absorption by hydrogel

5. Properties of plasticized PLA

5-1 Materials and fabrication method

A mixture of 100 phr of PLA (LACEA H-440 manufactured by Mitsui Chemicals, Inc.) and 5 phr of TAIC (TAICROSS manufactured by Degussa Japan Co., Ltd.) was blended at 180°C by a two-axis extruder and molded into compound pellets using a pelletizer. Then each pellet was formed into a sheet with 0.5 mm thickness by a hot press machine. The PLA sheets were irradiated with an EB dose of 90 kGy at 10 MeV and 12 mA in a vacuum packed state, and were verified by an extraction test using chloroform to be almost 100% crosslinked. The sheets were swollen in two different kinds of heated plasticizers (RIKEMAL PL-710 manufactured by Riken Vitamin Co., Ltd. and DAIFATTY-101 manufactured by Daihachi Chemical Industry Co., Ltd.) at 120°C for 6 hours, and then cooled to RT. The plasticizer content in the PLA sheets was 40wt% and 50wt%, respectively.

A mixture of PLA and plasticizer was also prepared at 180°C, but compounds containing more than 30wt% of plasticizer could not be made. Therefore, a sheet containing 20 wt% of plasticizer and not crosslinked was regarded as control sample.

The test results are as follows.

5-2 Inhibition of bleeding of plasticizer

The bleeding test result of the newly developed elastic PLA gel at 80°C is shown in Fig. 7.

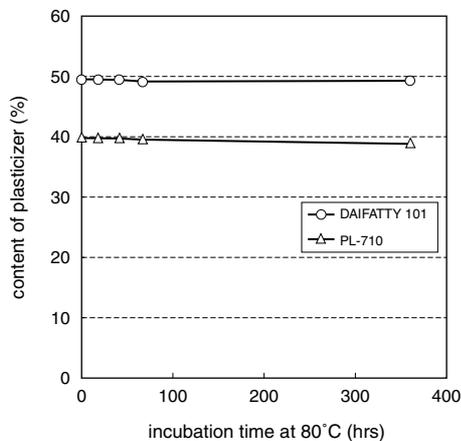


Fig. 7. Plasticizer retention effect

All of the test samples maintained their softness and showed neither whitening nor deformation. Weight loss after 15 days at 80°C was less than 1 wt%.

On the other hand, in the case of the control sample containing 20 wt% of plasticizer, most of plasticizer bled out within 10 minutes.

Since it is difficult to achieve a plasticizer content of 40 wt% without EB crosslinking, it is understood that EB crosslinking is an extremely efficient method for inhibiting the bleeding out of plasticizer.

5-3 Mechanical properties

Figure 8 shows the results of the dynamic mechanical analysis (DMA) test for measuring storage elastic modulus E' and $\tan \delta$ conducted on the elastic PLA gel swollen with 60 wt% of DAIFATTY-101 and on a crosslinked PLA sample with no plasticizer content.

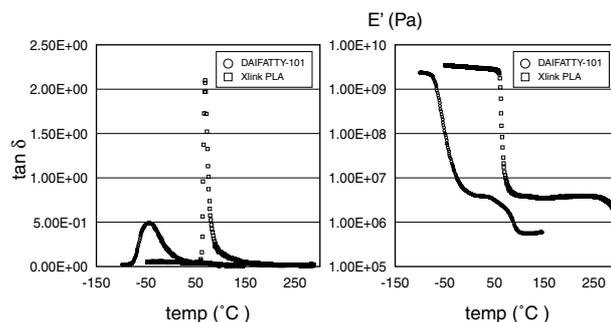


Fig. 8. DMS properties of crosslinked PLA

Although crosslinking has an effect of providing PLA with heat resistance against high temperatures exceeding T_m , it cannot inhibit a severe decline of elasticity at around $T_g = 60^\circ\text{C}$.

As T_g of the new elastic PLA gel is below -50°C , it is understood that its softness is caused by the reduction of T_g . The developed PLA gel shows little elasticity decline at around 60°C , and exhibits stable elasticity and strength in a range from 0°C to 100°C , which is the general use temperature range for plastics.

Figure 9 shows the stress-strain curve in the tensile strength test.

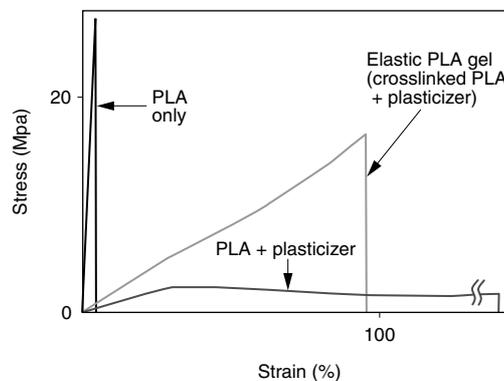


Fig. 9. Mechanical properties

Untreated PLA has high strength but exhibits little strain (percentage change in length). On the other hand, non-crosslinked PLA containing 30% by weight of plasticizer has low strength but shows large strain.

Unlike these two PLA samples, the new elastic PLA gel (a sample containing 40 wt% of PL-710) shows about 100% strain and moderate strength, and its stress-strain curve is similar to that of elastomers.

It is assumed that these elastomer-like properties are caused by a phenomenon similar to the heat-induced shape recovery behavior of EB crosslinked heat shrinkable tubes. In other words, the PLA gel plasticized by adding plasticizers has the shape memory and recovery ability against deformation by crosslinking, which is similar to the shape memory and recovery mechanism of heat-shrinkable products. (Fig. 10)

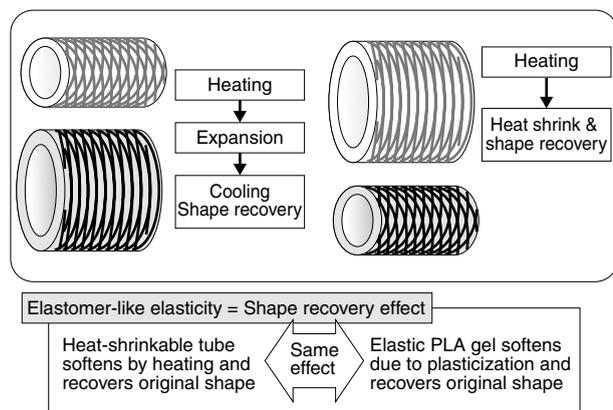


Fig. 10. Mechanism of elasticity

5-4 Microstructure of elastic PLA gel

Photo 1 was taken using transmission electron microscope (TEM) photography to observe the microstructure of the new PLA gel. The sample was prepared as follows. The crosslinked PLA gel sheet was soaked into styrene monomer at 70°C instead of into liquid plasticizer that is unsuitable for TEM observation, and then irradiated at 60 kGy by EB in a vacuum packed seate. After styrene monomer was changed into polystyrene (PS) polymer in the PLA gel, an interpenetrating polymer network (IPN) was formed between PLA and PS⁽⁹⁾.

In Photo 1, PLA is shown as white areas and PS is shown as black areas. This microstructural study reveals that the newly developed PLA gel has a nano-scale network structure with pores about 20 nm in size.

This microstructure suggests that the reason why the newly developed PLA gel exhibits high absorptance and less bleeding of plasticizers is that plasticizers are contained inside the nano-scale sponge-like structure of the gel.

The affinity between PLA and plasticizers is stronger than that between PLA and PS. Therefore, the microstructure of the newly developed PLA gel does not show typical phase separation like that shown in Photo 1. However, the microstructure of PLA swollen with plasticizer is assumed to have a similar size as that of the

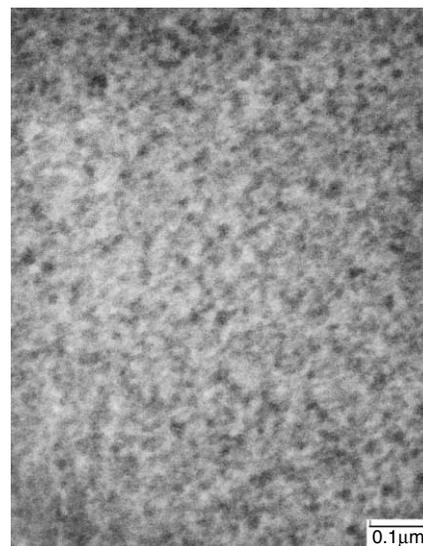


Photo 1. TEM image of elastic PLA gel

blend of PLA and PS, because the structures of the two are both based on the crosslinked network of PLA.

6. Conclusion

A brand new PLA material having softness and elastomer-like properties was successfully developed by using a new method for compositing PLA with plasticizer. Using this new technology, PLA is irradiated with EB to have a nano-scale crosslinked structure and then swelled with a hot plasticizer solution so that it becomes a "PLA organogel with plasticizer" that features a high level of plasticizer absorption and retention. Development of materials and components for electronics and automotive applications using this new technology is underway.

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Contributor

S. KANAZAWA

- Assistant General Manager, Research & Development Department, Sumitomo Electric Fine Polymer Inc.