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Studies on Reactive Blending of Poly(lactic acid) and Poly(trimethylene terephthalate) and Its Composite

Katanyu Kultravut (Academic Supervisor: Professor Toshiaki Ougizawa)

[Introduction]

The increasing demand for plastic use causes serious environmental problems because decomposition of petroleum-based plastic wastes requires long period of time. Moreover, carbon dioxide generation during production and incineration of plastics is also the main cause of the global warming. Poly(lactic acid) (PLA), which is biodegradable and bio-based plastic, has been gained popularity for use in many applications such as agricultural, biomedical, and packaging applications. However, PLA is impossible to be used in some applications of commodity and engineering plastics because of its inferior properties such as brittleness and low thermal stability. In this research, development of the inferior properties of PLA was studied by melt blending with poly(trimethylene terephthalate) (PTT) because PTT is synthesized from 1,3-propanediol that is derived from renewable resources and shows good mechanical properties. Poly(ethylene-*co*-glycidyl methacrylate) (PEGMA) was also added in the blends as a reactive compatibilizer in this system because the epoxy ring in PEGMA can react with both of carboxyl and hydroxyl groups in both of the polyesters which was improve the interfacial adhesion between PLA and PTT.

[Experimental]

PLA and PTT were blended by melt mixer with 1 phr of PEGMA at 240 ˚C and 90 rpm for 5 min under N_2 gas. The blend compositions of PLA and PTT were assigned as ratios of 90/10, 80/20, 70/30, 60/40, and 50/50 by weight to make PLA rich blends. The sample was denoted as "PLA/PTT/PEGMA blend by one-step blending". For tensile test, a sample was prepared by compression molding at 240 ˚C. Then quenched immediately to obtain amorphous PLA phase structure in the blends. Mechanical, morphological, structural, thermal, and rheological were investigated. Moreover, the crystallization of the samples was achieved by annealing at several temperatures (80 ˚C, 90 ˚C, 100 ˚C, 110 ˚C, and 120 ˚C) for 1 h, for complete crystallization. Furthermore, the applied PLA/PTT blend was investigated to make a conductive composite by using an interfacial localization of the poly(glycidyl methacrylate) (PGMA) grafted reduced graphene oxide (rGO-PGMA) at the interface between immiscible co-continuous PLA/PTT blend.

[Results and Discussion]

Stress-strain curves of neat amorphous PLA and PLA/PTT/PEGMA (70/30/1) blend by one-step blending are shown in Fig. 1 as a representative of the blends with different compositions. All the blends prepared by one-step blending showed low stain at breaks in the same manner as neat PLA, brittle manner, even though PEGMA was added as a compatibilizer. To clarify the reason of the low mechanical properties of the blend, morphology of the blend was observed by transmitted electron microscope (TEM) as shown in Fig. 2 (a). It was observed that PEGMA particles (black regions) dispersed mainly in PLA matrix phase (white regions) but not in PTT dispersed phase (gray regions). To make PEGMA act as a compatibilizer effectively, it is desirable to form graft copolymer of PLA-*g*-PEGMA-*g*-PTT and the copolymer should exist at the interface between PLA and PTT phases. Therefore, PTT was pre-mixed with PEGMA for 2.5 minutes, then PLA was added and continued the blending process (two-step blending) more 2.5 minutes (totally 5 minutes same as the normal blending). The sample was denoted as "PLA/PTT/PEGMA blend by two-step blending". Stress-strain curve of PLA/PTT/PEGMA (70/30/1) blend by the two-step blending was also shown in Fig. 1. Strain at break of the blends with all compositions prepared by two-step blending method were much improved even though PLA was a matrix phase in the blend. Fig. 2 (b) shows a TEM micrograph of the two-step blending sample. It was found that the size of PTT dispersed phase was decreased compared with the blend prepared by the normal blending. The PEGMA particles (black region) were located at the interface between PLA matrix and PTT dispersed phases. Moreover, the PLA-*g*-PEGMA-*g*-PTT copolymer formation was confirmed by FTIR measurement. These results indicate that PEGMA played a role as an effective compatibilizer by forming PLA-*g*-PEGMA-*g*-PTT graft-

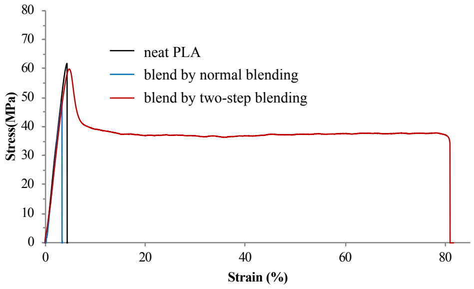

Fig. 1 Stress-strain curves of neat PLA, PLA/PTT (70/30) blend and PLA/PTT/PEGMA (70/30/1) blends.

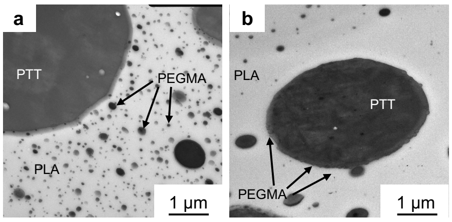

Fig.2 TEM micrographs 70/30/1 of PLA/PTT/PEGMA blends by (a) normal and (b) two-step blending methods.

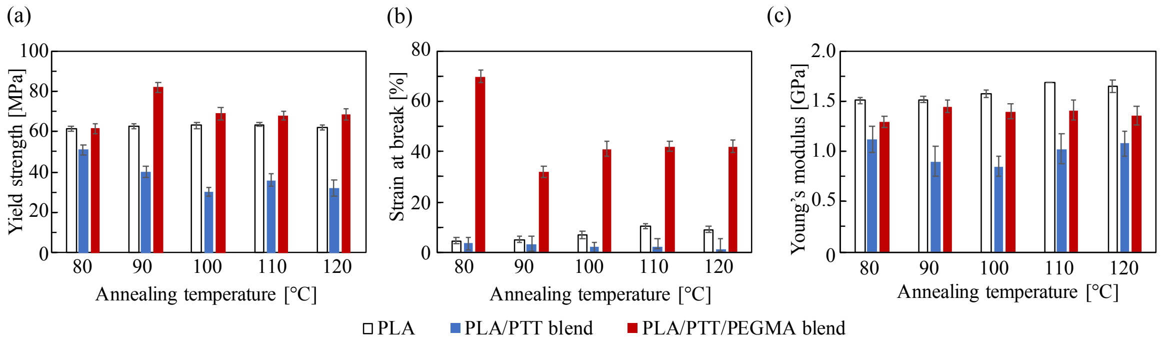

Fig. 3 (a) Yield strength, (b) strain at break, and (c) Young's modulus of annealed neat PLA (white), PLA/PTT blend (blue), and PLA/PTT/PEGMA (red) blend as a function of annealing temperature.

copolymer at the interface between two phases. To enhance a thermal stability, PLA/PTT/PEGMA blends by the two-step blending was annealed for 1 h to crystallize both PLA and PTT phases in the blend. Although the crystallized polymer generally behaves more brittle manner than the amorphous one, the blends by the two-step blending behaved as ductile manner as shown in Fig. 3. By observation by polarized optical microscope and laser light scattering, crystal formation without spherulitic morphology was observed in the blends which is the main reason of the tensile improvement due to the reduction of the stress concentration. This must be the reason why the strain at break of the crystallized blends prepared by two-step blending were still higher than neat PLA. It indicates that the two-step blending was an effective method for making a high thermal stability PLA blends.

Moreover, the applied PLA/PTT blend was investigated in this research. Interfacial localization of conductive fillers in co-continuous polymer blends is an effective method to enhance a conductivity of the composite with low filler content by forming a conductive path at interfaces. PLA was blended with PTT to make a co-continuous immiscible blend. Glycidyl methacrylate (GMA) was grafted on reduced graphene oxide (rGO-PGMA) because epoxy group of rGO-PGMA was expected to react with both PLA and PTT and localize at interface by two-step blending procedure to make the conductive paths between PLA and PTT. Firstly, rGO-PGMA was blended with PTT to make a masterbatch. Then the masterbatch was blended with neat PLA, respectively. From transmission electron microscopy (TEM), it was observed that rGO-PGMA localized between PLA and PTT. Moreover, the DC electrical volume resistivity of the composite was remarkably improved, compared with neat polymers. It was due to the reason that the rGO-PGMA at the interface between PLA and PTT in PLA/PTT/rGO-PGMA blend by two-step blending could effectively work for conductive application. PLA/PTT/rGO-GMA composites were produced by two-step blending procedure same as before. rGO-PGMA located at the interface between PLA and PTT, confirmed by TEM micrograph. It was suggested that rGO-PGMA was an effective filler to locate at the interface between PLA/PTT blend after blending by two-step blending procedure because epoxy group of GMA at the surface of rGO-PGMA could reacted with both PLA and PTT. To investigate the effect of the location of conductive filler, the DC electrical volume resistivity was measured. Fig. 4 shows the relation between DC electrical volume

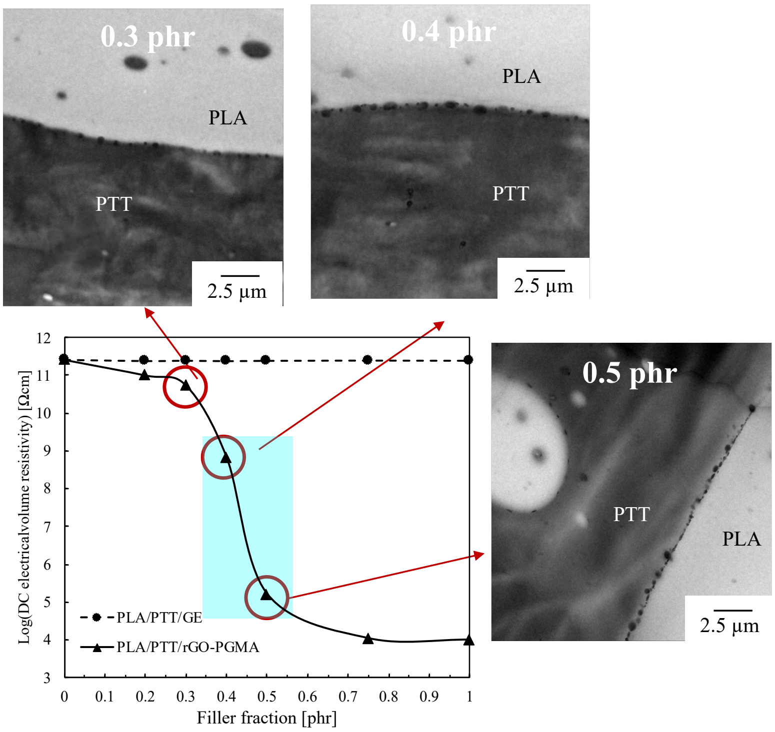

Fig. 4 Relation between DC electrical volume resistivity and rGO-PGMA content in PLA/PTT/rGO-PGMA composite and TEM micrographs.

resistivity and rGO-PGMA content in PLA/PTT/rGO-PGMA composite and TEM micrographs. Neat PLA and PTT show the values of DC electrical volume resistivity as normal polymer, insulation material. The same result was obtained in PLA/PTT blend without conductive filler. PLA/PTT/rGO-PGMA composite showed the improved DC electrical volume resistivity around 1.65 x 10^4 Ωcm. Only a very small amount of rGO-PGMA could form the percolated conduction network at the continuous interface of the PLA/PTT blend. It was confirmed that the selective localization of the rGO-PGMA was significantly affected to both DC electrical volume resistivity. It was well known that conductive properties of composite around percolation threshold is sensitive to variation of filler content. Little change of filler content will affect suddenly because of the construction of conductive network. In the content between 0 and 0.25 phr, PLA/PTT/rGO-PGMA composites showed the high DC electrical volume resistivity around 1.04 x 10^{12} Ωcm. Then, it was shown that the percolation threshold of the PLA/PTT/rGO-PGMA composite which made the DC electrical volume resistivity change drastically was observed in the range of 0.25–0.5 phr of rGO-PGMA. It was clearly indicated that the conductive properties of PLA/PTT/rGO-PGMA composite could be enhanced with the small amount of rGO-PGMA, less than 0.5 phr.

[Conclusions]

In this study, PLA/PTT blends with PEGMA, reactive compatibilizer, with improved elongation at break were prepared with different composition of PLA and PTT. The effects of blending procedure were examined. As the result, it was found that two-step blending procedure was a successful method to enhance the elongation at break because PEGMA located at the interface between PLA and PTT phases which was confirmed by morphologies, FTIR, and η^*. The result of elongation at break of the PLA/PTT/PEGMA (70/30/1) was 80.9% where the elongation at break of PLA/PTT/PEGMA blend produced by one-step blending was 3.5% in the same composition. It was due to the location of PEGMA and the craze formation which was occurred only the blend produced by two-step blending. Moreover, PLA/PTT/PEGMA blend was crystallized using an annealing treatment, and we succeeded in obtaining a ductile but highly crystallized blend. The tensile properties of the annealed PLA/PTT/PEGMA blend were clearly improved compared with the annealed neat PLA and PLA/PTT blend. Even though the PLA/PTT/PEGMA blend was highly crystallized from the annealing, craze formation was observed; this is one of the dominant toughening mechanisms. The high crystallinity of PLA in the PLA/PTT/PEGMA blend could be prepared at a lower annealing temperature than the neat PLA due to the reduced cold crystallization temperature. Crystals without spherulitic structures in the PLA/PTT/PEGMA blend contributed to the tensile improvement due to the reduction of the stress concentration. Furthermore, the applied PLA/PTT blend with rGO-PGMA as a conductive filler was a successful method to enhance DC electrical volume resistivity of the composite because rGO-PGMA was located at the interface and formed a percolation threshold with low content of the filler. DC electrical volume resistance of the PLA/PTT/rGO-PGMA composite were dramatically increased compared to neat polymer. Moreover, the percolation threshold of rGO-PGMA in the PLA/PTT/rGO-PGMA was observed in the low content of rGO-PGMA in the range of 0.4−0.5 phr. Therefore, the PLA/PTT/PEGMA blends and PLA/PTT/rGO-PGMA composites produced by two-step blending show high potential for the application in the commercial and engineering fields they exhibit with excellent tensile properties, thermal stability, and conductive properties.

[Publication Lists]

1. Katanyu Kultravut, Keiichi Kuboyama, Toshiaki Ougizawa, “Annealing effect on tensile property and hydrolytic degradation of biodegradable poly(lactic acid) reactive blend with poly(trimethylene terephthalate) by two-step blending procedure”, *Polymer Degradation and Stability.* 2020, *179*, 109228. DOI: https://doi.org/10.1016/j.polymdegradstab.2020.109228
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[Academic Conference]

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