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# Compatibilization of PLA/starch composite with electron beam irradiation in the presence of a reactive compatibilizer

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The aim of this study is to improve the compatibility of poly (lactic acid) (PLA)/starch composite by electron beam irradiation in the presence of glycidyl methacrylate (GMA) as a reactive compatibilizer. Compatibilization process has been done by melt mixing the PLA/starch and GMA with a twin screw extruder and exposing the PLA/starch/GMA mixture to electron beam at room temperature. The exposure process was carried out to induce definite interfacial adhesion at the interface between PLA and starch through electron beam-initiated graft copolymerization by the medium of the GMA. To testify the effect of this compatibilization strategy, rheological, mechanical, and morphological properties of the composite were analyzed. The scanning electron micrographs of the cryofracture and tensile fracture surfaces of the composites revealed that the interfacial adhesion between PLA and starch was greatly improved by this strategy. Fourier transform infrared study confirmed the grafting reaction between PLA and starch. The reaction schemes were proposed to understand the reaction mechanisms at the interface.

**Keywords:** poly (lactic acid); composite; electron beam radiation; compatibility; morphology



## 1. Introduction

Biodegradable polymer has attracted an increasing amount of interest due to the environmental requirements on the safe and effective disposal of used plastics into the waste stream.[1] Poly (lactic acid) (PLA) is one of the important bio-based biodegradable polymers which now can be found in most of the single-use disposable items and is produced from nonfossil renewable resources by fermentation of polysaccharide. Thus, PLA is an environmentally and ecologically sound polymer, which hence would not cause the carbon dioxide accumulation in the earth. Furthermore, other environmentally friendly materials include renewable natural polymers such as starch and cellulose.[2–4]

Since starch can improve the biodegradability and lower the cost while PLA can control the mechanical properties, the composite of both would exhibit advantages in environmental, ecological, and economic aspects, and also improved properties than each of the individual components. However, the main drawback of the composite is the lack of compatibility between PLA and starch, resulting in the reduced PLA mechanical properties. Thus, to improve both the compatibility between PLA and starch and the performance of the final composite, some different strategies were introduced.

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[5,6] The preferred strategy of compatibilization of the PLA/starch composite is introducing a grafting reaction between PLA and starch at the interface. There are two distinct processes available for the grafting reaction at the interface, which are a direct process for the PLA that has reactive functionalities such as maleated PLA [7] and a mediation process by addition of a reactive compatibilizer.[8] Frequently, however, the added reactive compatibilizer reacts with the matrix polymer of PLA. Therefore, self-copolymerization or cross-linking of PLA may compete with grafting reaction at the interface between PLA and starch. For the case of the PLA/starch composite, the mediation process by addition of a reactive compatibilizer was preferred for compatibilization strategy in recent studies.[8]

In more recent years, high-energy radiation exposure on a polymer and a polymer blend at room temperature have been newly introduced to modify their properties by changing the structure of a polymer molecule or improving the compatibility of a polymer blend and a polymer composite.[8,9] It was reported that PLA is a kind of chain scission dominated polymer.[10,11] For this reason, high-energy radiation exposure for PLA composite has not applied for the compatibilization of PLA/starch composite. However, in our previous work [11], we found that PLA could be modified with minimal amount of radiation-induced chain scission by addition of a functional monomer.

Therefore, in this paper, we adopted the high-energy radiation exposure strategy with a reactive compatibilizer to improve the compatibility between PLA and starch. After mixing PLA, starch, and GMA by using a twin screw extruder, various doses of electron beam were irradiated on the mixture. To testify the results of this new compatibilization trial for the compatibilization of PLA/starch composite, SEM study of composite and Fourier transform infrared (FTIR) analysis of starch extracted from the composite were carried out. Also changes in rheological and mechanical properties of the composite were observed. We also proposed electron beam-initiated reaction mechanisms, which were believed to be occurred at the interface, to explain the interfacial phenomena.



## 2. Experimental

### *2.1. Materials*

PLA (NatureWorks® PLA Polymer 2100D) with specific gravity of 1.3 and a melt flow index of 5–15 g/10 min (measured at 190 °C at a load of 2.16 kg) was obtained from NatureWorks LLC. Glycidyl methacrylate (GMA) was provided by Sigma-Aldrich (WI, USA). Corn starch (11% inherent moisture) was obtained from Shindongbang Inc. Korea. Starch dried in convection oven at 90 °C for 24 h before use. The moisture content of starch was reduced to about 3%.

### *2.2. Preparing PLA/starch composite containing GMA*

The composite ratio of the PLA and starch was chosen to be 80/20 in weight percent and the amount of GMA content was fixed at three parts per hundred resin (phr) basis on the total mass of PLA and starch. PLA, starch, and GMA were mixed in a plastic bag before being extruded in a twin screw co-rotating extruder (SM PLATEK Co. Ltd., TEK 30, Korea). The screw diameter was 30 mm with an L/D ratio of 36. The extruder was operated at 150 rpm with a constant feed rate of 10 kg/h. The barrel and die temperatures were set at 160–190 and 185 °C, respectively. The extrudates of the

specimens were pelletized and then dried for 24 h at 50 °C prior to the electron beam irradiation. The diameter and length of pellet were less than 1 and 3 mm, respectively. In addition, pristine PLA was extruded under the same preparation conditions as the composite for comparison purpose.

### 2.3. Electron beam irradiation

The mixture of the PLA/starch and the GMA with maximum chip diameter of 1 mm was irradiated using a commercial electron beam accelerator (ELV-0.5, BINP, Russia, with a maximum beam current of 40 mA and beam energy of 0.5–0.7 MeV) under a nitrogen atmosphere. The irradiation doses were 5, 10, 30, and 100 kGy, which were controlled by varying both the beam currents of 0.5–10 mA and the conveyor speeds of 1–2 m/min, and the irradiation dose was measured by dosimetry film (B3 WIN dose Dosimetry, GEX Co.) and dosimeter (GENESYS 20, Thermo SCIENTIFIC Co.). Acceleration energy was 0.7 MeV and the effective penetration depth was about 2 mm for the substrate with 1 g/cm$^3$ of density.[12,13] The irradiated samples were dried in an oven at 50 °C for 12 h to eliminate any residual radicals. The electron beam-irradiated PLA/starch composites are designated as PS-0 (unirradiated composite), PS-5, PS-10, PS-30, and PS-100 where numbers denote irradiation dose with the unit of kGy.

### 2.4. Characterization

The morphology of the composites was investigated by studying the cryofracture and tensile fracture surfaces using a scanning electron microscope (SEM, Hitachi model s-4200, Japan). To testify the chemical reaction between starch and PLA, PLA was extracted from both the unirradiated and irradiated PLA/starch composites with boiling chloroform in a soxhlet extractor. The remaining starch was rinsed with chloroform and dried in oven at 100 °C, before it was analyzed by Fourier transform infrared spectroscopy (FTIR, Excalibur Spectrometer FTS 3000MX, BIO RAD, USA). The mechanical properties of the composites were determined using a MICRO 350 tensile tester (Testometric Co., Ltd.). Tests were performed on tensile bars (type II) that were compression molded according to the KS M3600 test method using a hot press (Model 3851-O, Carver Inc.) at a set temperature of 200 °C and a molding pressure of 10 MPa. Prior to experiment, the tensile specimens were conditioned at room temperature with 50% relative humidity for 24 h. The experiments were then performed at room temperature with a gage speed of 10 mm/min and a gage length of 35 mm. The average value determined from the six tests was employed as the tensile value. The rheological property was measured using an ARES (Advanced Rheometric Expansion System: Rheometric Scientific Co. Ltd US) rotational rheometer. The equipment was run in the parallel plate configuration at a strain of 2% in the frequency range of 0.1–100 rad/s.

## 3. Results and discussion

### 3.1. Morphology and compatibilization mechanisms

It is well known that morphology study is the most frequently used method to determine the interfacial phenomena in the field of polymer composite. Therefore, the morphology of PLA/starch composite with and without electron beam irradiation was observed. Figure 1 exhibits the SEM micrographs of starch, the cryofracture surfaces of the PLA, and the PLA/starch composites with and without irradiation. The starch

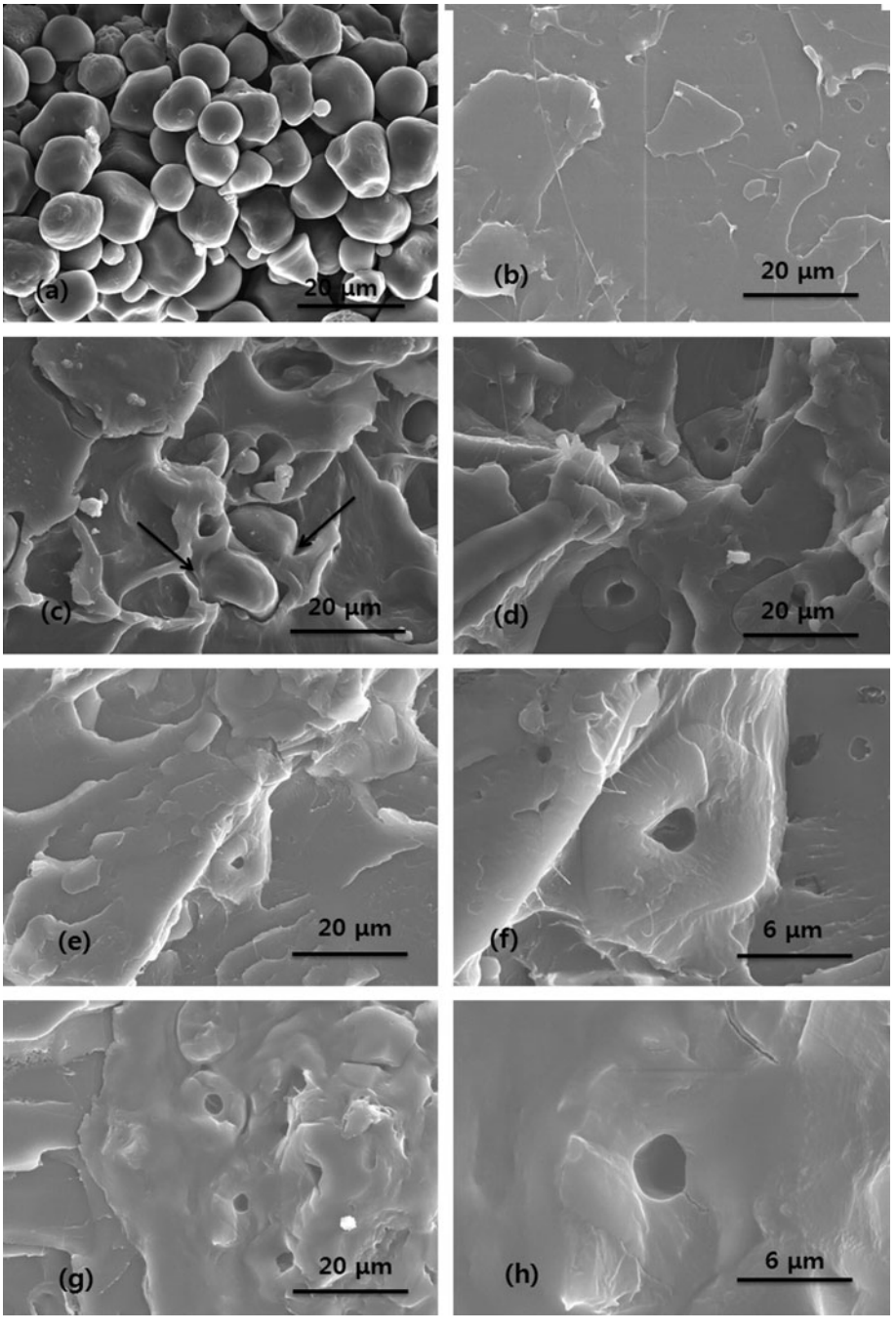



Figure 1. SEM images of starch (a), cryogenic fracture surface of pure PLA (b), PS-0 (c), PS-5 (d), PS-30 (e), magnified view of (e) in the region with broken starch (f), PS-100 (g), and magnified view of (g) in the region with broken starch (h).

granules vary in the size range from approximately 5 to 20 μm and their shape is roughly spherical (Figure 1(a)). As shown in Figure 1(b), a brittle fracture was observed on the smooth PLA surface. Figure 1(c) is the micrograph of the cryofracture surface for the unirradiated PLA/starch composite. As shown in Figure 1(c), the parts labeled in arrows exhibit an improved adhesion compared to the morphology of the PLA/starch simple composite, which was reported in the previous work.[14] From this morphology, we can expect that the GMA locates at the interface between PLA and starch. However, there are still sharp edges and big cavities at the interface, which means that the compatibility of unirradiated PLA/starch composite is still poor compared to the PLA/starch composite compatibilized by the mediation process.[8]

Accordingly, the electron beam radiation method was applied to the PLA/starch composite to get definite interfacial adhesion in expectation of grafting reaction between PLA and starch by the medium of the GMA, which was located at the interface. From the decreased cavity size between the starch granule and PLA matrix, the interfacial adhesion is much improved comparison with the unirradiated PLA/starch composite, as shown in Figure 1(d)–(h). The dramatic morphological change was observed when the composite was irradiated at doses higher than 30 kGy. Figure 1(e) and (g) display broken starches at the center and there is no clear edge or cavity between the PLA matrix and broken starch. Micrographs in Figure 1(f) and (h) are the magnified micrographs of Figure 1(e) and (g). As shown in the magnified micrographs, it is impossible to draw a line between starch and PLA like a single phase. These morphologies confirm that the compatibility of the PLA/starch composite was definitely enhanced by the electron beam irradiation in the presence of the GMA.

Likewise, Figure 2 exhibits the tensile fracture surfaces of the PLA/starch composites with and without irradiation. As seen in Figure 2(a), the micrograph of unirradiated PLA/starch composite also exhibits voids between PLA and starch like the cryofracture morphology. On the other hand, the tensile fracture morphology of 10 kGy irradiated composite is very different from the unirradiated composite. As can be seen in Figure 2 (b), the voids between PLA and starch are filled with a certain substance, which is elongated and torn by the tensile stress (see the arrows in Figure). The substance filled the voids between PLA and starch seems to be newly formed copolymer, which is produced through electron beam-initiated graft copolymerization by the medium of the GMA, which is located at the interface. The tensile fracture behavior of the substance looks like ductile material and is much different from that of the brittle PLA. Moreover, the parts labeled in arrows, which are shown in the micrograph of 30 kGy irradiated composite, exhibit clear evidence of the newly formed material, which covers the surface of the starch and connects PLA matrix and starch granule. From the results of the cryofracture and the tensile fracture morphologies of the composites, we can clearly confirm that the interfacial adhesion between the PLA matrix and the starch was greatly enhanced by the electron beam irradiation. This excellent interfacial adhesion, in turn, seems to be caused by the electron beam radiation-initiated graft copolymerization with the medium of the GMA placed at the interface.

Therefore, we proposed the reaction mechanisms of the electron beam radiation-initiated graft copolymerization with the medium of the GMA at the interface in Schemes 1–5. The GMA bears a double bond (free-radical reactivity) and an epoxy group (functional reactivity). The double bond can perform free-radical grafting and the epoxy group possesses reactivity toward various functional groups such as –COOH, –OH, –SH, and $–NH_2$. Thus, GMA can react with both the chain ends of PLA and hydroxyl groups in starch. Scheme 1 illustrates the etherification and esterification reactions that

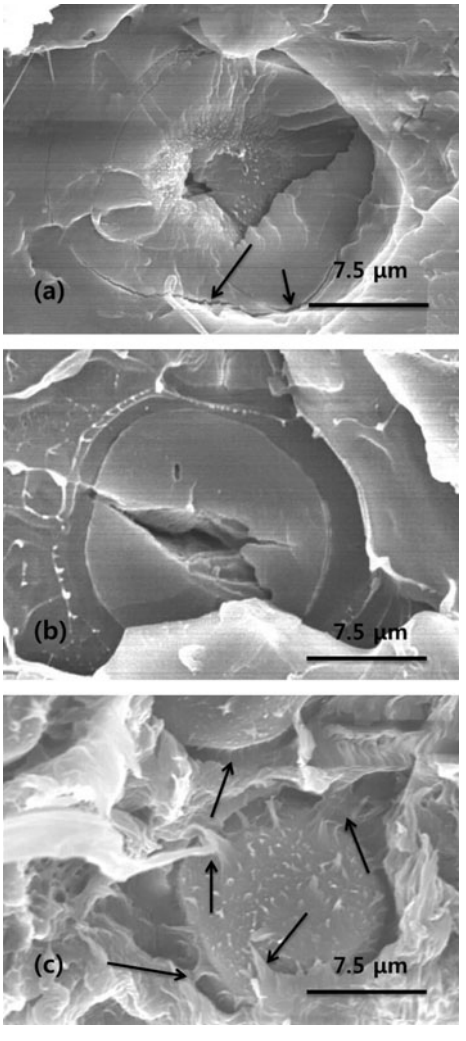
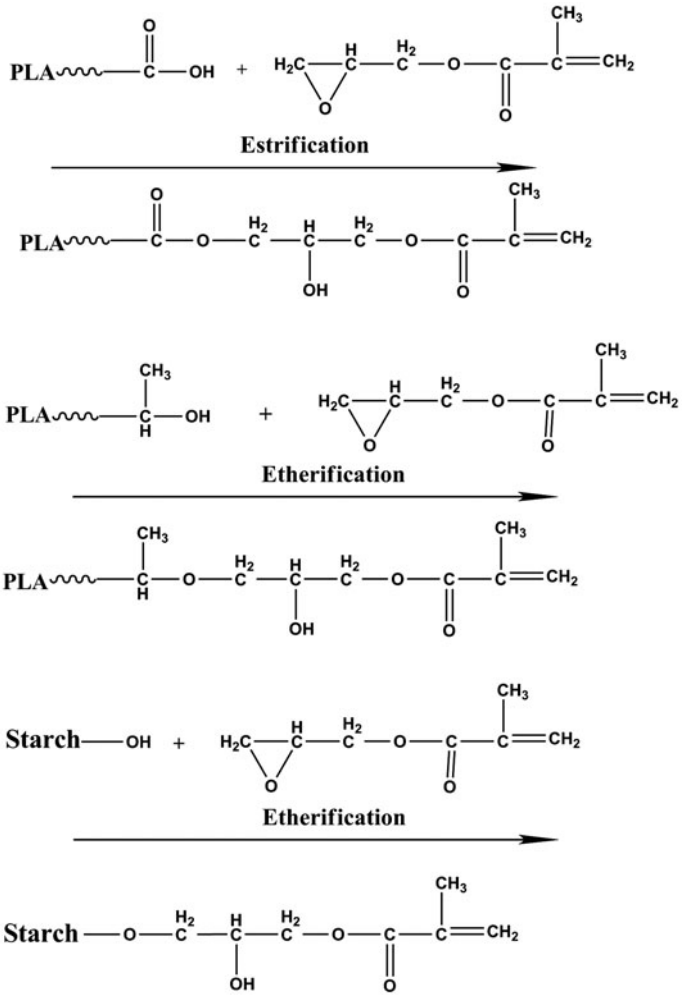



Figure 2. SEM images of tensile fractures of composites irradiated at PS-0 (a), PS-10 (b), and PS-30 (c).



could occur between GMA and both the PLA and starch during the melt mixing.[15] As can be seen in Scheme 2, PLA• represents the free radicals formed by hydrogen abstraction at the quaternary carbon atom sites of PLA.[16] The double bonds of grafted GMA onto starch and PLA are easily initiated by the electron beam irradiation. Thus, the PLA–GMA• and the starch–GMA• represent the free radicals formed by radiolysis of the GMA. Scheme 3 estimates graft copolymerization at the interface, which can be taken place between the PLA• and the starch–GMA•. It is also possible that there are free GMAs, which are only wetting the interface without any reaction with both the PLA and the starch at the interface. Scheme 4 estimates schematics of homo-polymerization of the free GMA and grafting reaction between PLA• and free GMA•. As shown in Scheme 5, the PLA-g-GMA and the GMA homopolymer (PGMA) can also contribute to enhancing the compatibility of composite through graft reaction between the epoxy groups of the PLA-g-GMA and the hydroxyl groups of the starch or

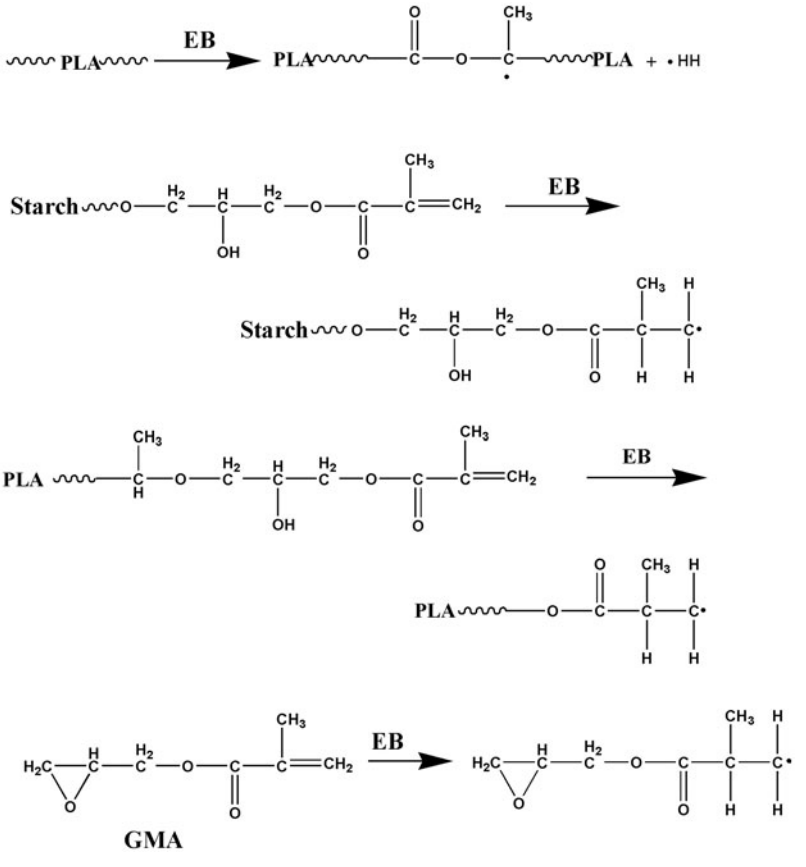



Scheme 1. Schematics of esterification and etherification reactions between the GMA and both the PLA and starch during melt mixing.

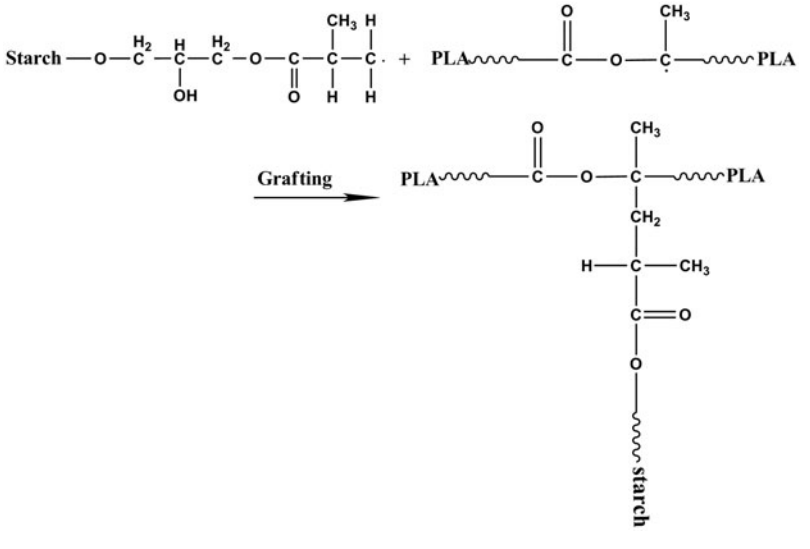
the end groups of the PLA and between the epoxy groups of the PGMA and the hydroxyl groups of the starch and the end groups of the PLA. Here, the GMA plays very important role of mediator for cross-copolymerization between PLA and starch. Therefore, if there is no GMA between PLA and starch, the cross-copolymerization would not occur and the chain scission of PLA by electron beam irradiation would not be suppressed, as reported in previous work.[11]

### *3.2. FTIR spectroscopy*

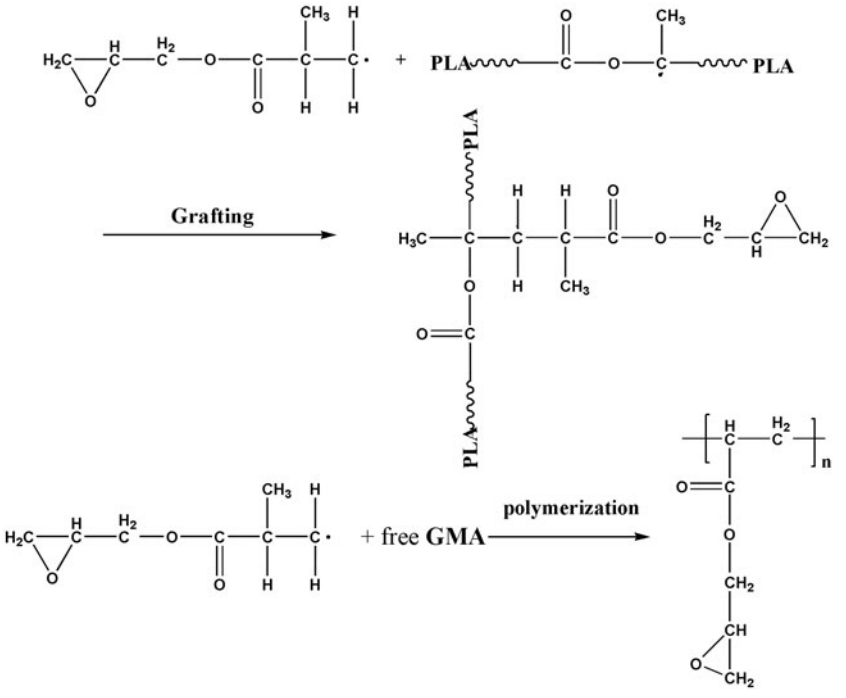
To observe the compatibilization reaction between PLA and starch, the FTIR spectra of granule starch, PLA, and extracted starches from PS-0, PS-10, and PS-100 were investigated. As shown in Figure 3, the characteristic absorption ranges of starch include the absorption bands at O–H (3300–3900 $cm^{-1}$), C–H (2927 $cm^{-1}$), C–H stretching (1250–900 $cm^{-1}$), and the band of water absorbed in the amorphous region




Scheme 2. Expected schemes for the induction of radical by electron beam irradiation.




Scheme 3. Schematics of grafting reaction between GMA-grafted starch and PLA during irradiation.

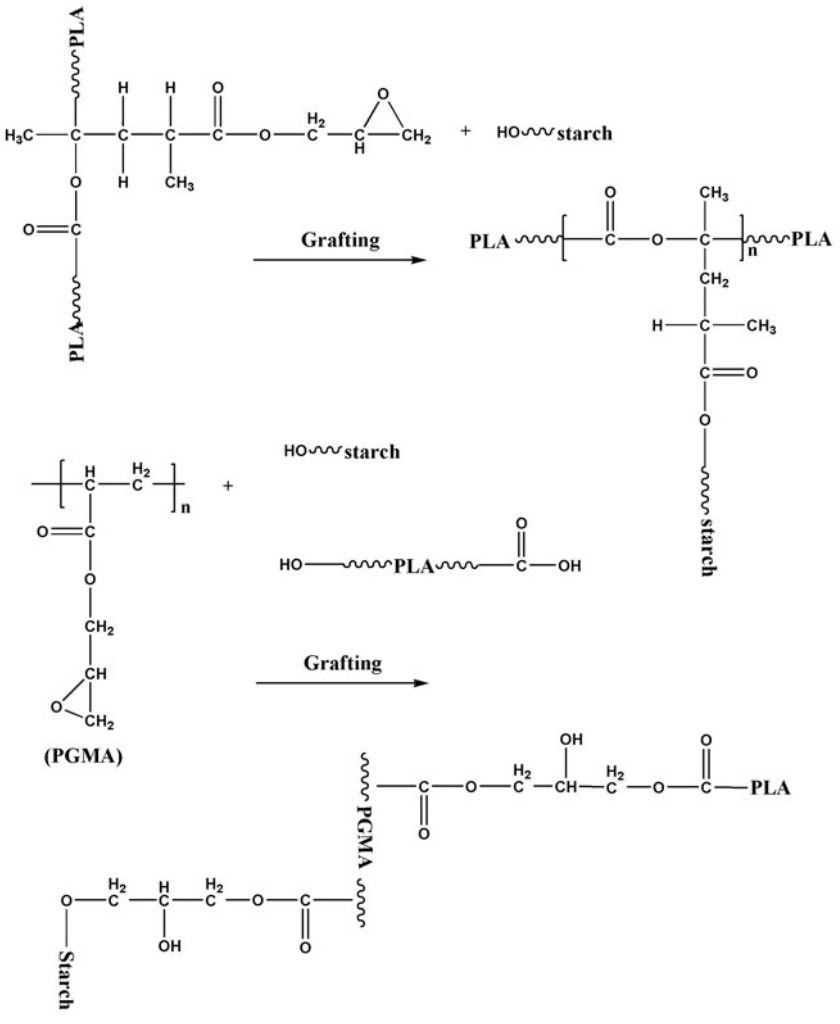



Scheme 4. Schematics of grafting reaction between PLA and starch by means of free GMA and homo-polymerization of the free GMA during irradiation.

of starch (1634 $cm^{-1}$). The spectrum of PLA displays the strong C=O absorption band at 1748 $cm^{-1}$. All the FTIR spectra of the extracted starches from PS-0, PS-10, and PS-100 have C=O characteristic band. This result confirms that the compatibilization reaction should have been occurred at the interface. Moreover, the C=O absorption band at 1748 $cm^{-1}$ is shifted to 1759 $cm^{-1}$ and another C=O characteristic peak at around 1700 $cm^{-1}$ is newly appeared and shifted slightly to higher wavenumber by electron beam irradiation. This new C=O absorption band at around 1700 $cm^{-1}$ seems to be contributed from carbonyl stretching of GMA. The band observed at 1634 $cm^{-1}$ was not changed.

### *3.3. Rheological properties*

Generally, the rheological properties of polymers are very sensitive to their molecular weights, molecular distribution, and chain structure as branching and cross-linking. Complex viscosity ($\eta^*$) and storage modulus ($G'$) of pure PLA and PLA/starch composites irradiated at various doses are shown in Figures 4 and 5, respectively. As shown in Figure 4, both PLA and the unirradiated composite (PS-0) have very long Newtonian viscosity plateau region; while, all the irradiated composites have shear thinning flow curves and more viscous characteristics. Complex viscosity and storage modulus of the composite are generally increased with increasing irradiation dose up to 10 kGy, but decreased at higher doses. It is reported that the complex viscosity and the modulus of the filled polymer are higher than the neat polymer; moreover, those of the compatible composite are higher than the incompatible one. In this composite system, the change in the rheological properties by irradiation in the presence of a reactive compatibilizer




Scheme 5. Expected schemes that the epoxy group in PLA-g-GMA reacts with hydroxyl group in starch and the epoxy groups in GMA homopolymer react with both the hydroxyl group in starch or hydroxyl and carboxyl groups in PLA.



was very complex because the compatibility of the composite as well as the grafting reaction and chain scission of PLA molecule can affect the viscoelastic properties of the composite all together. However, PS-10, which was irradiated at a lower dose, has higher complex viscosity and storage modulus by a factor of nearly 10 and 73 at the frequency of 0.1 rad/s compared to those of the unirradiated composite, respectively. Though it is difficult to interpret the exact relationships between the effect factors and the enhancement of the complex viscosity and modulus, it is certain that the increased compatibility does partially contribute to the enhanced rheological properties.

### *3.4. Mechanical properties*

It is well known that the mechanical properties of the simple PLA/starch are very poor due to the brittleness and also the lack of compatibility between PLA and starch.

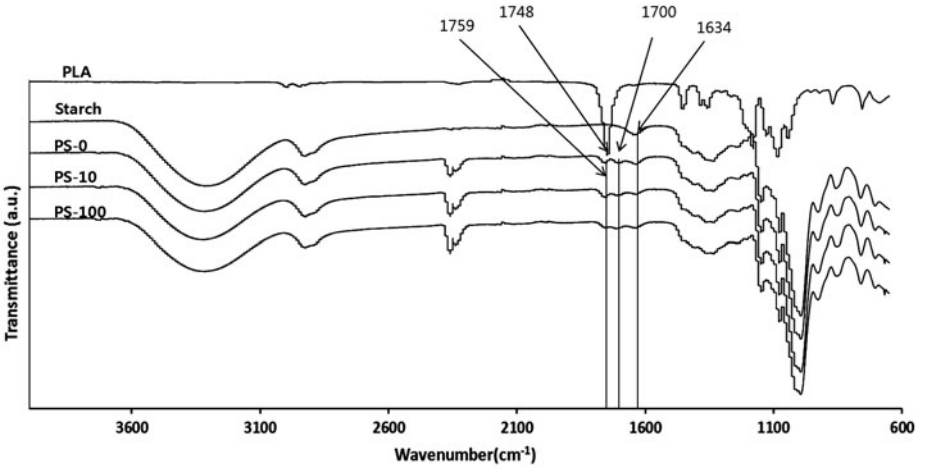



Figure 3. FTIR spectra of PLA and extracted starches from the composites.

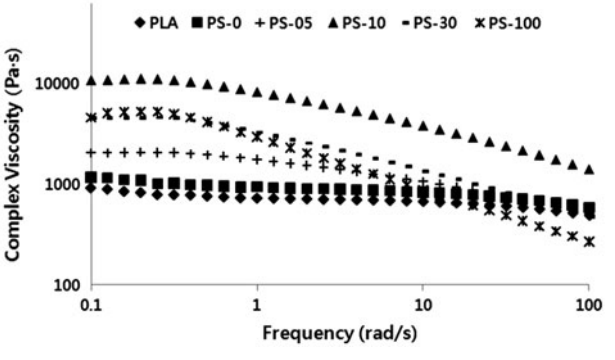



Figure 4. Complex viscosity vs. frequency for PLA and irradiated composites measured at 190 °C.

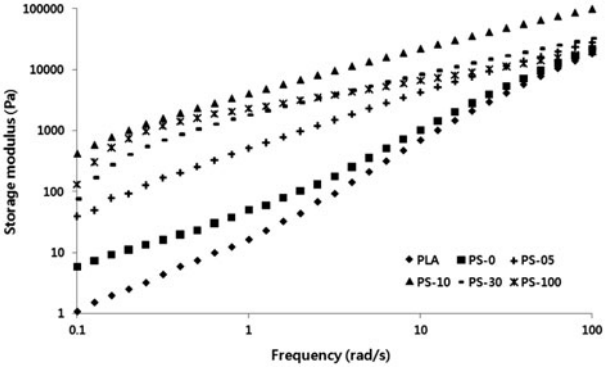



Figure 5. Storage modulus vs. frequency for PLA and irradiated composites measured at 190 °C.

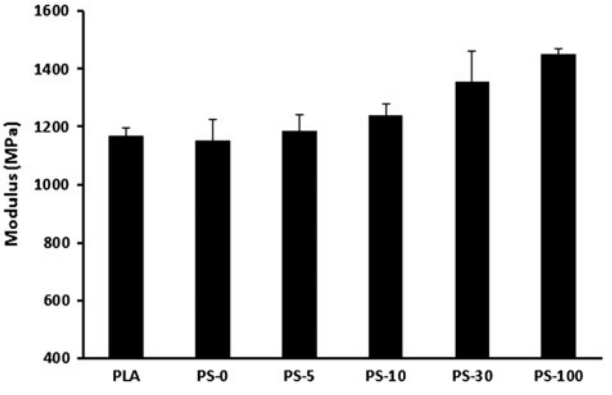



Figure 6. Tensile modulus of PLA and irradiated composites.

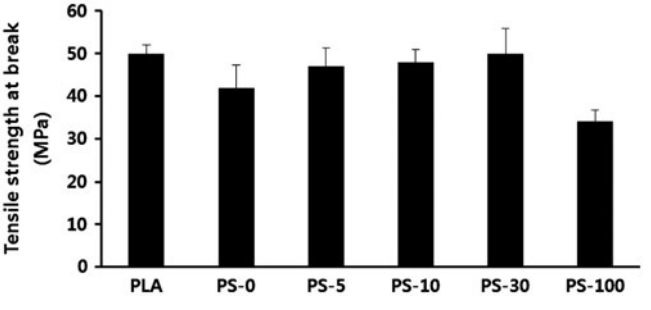



Figure 7. Tensile strength at break of PLA and irradiated composites.

Figures 6 and 7 plot the modulus and tensile strength at break as a function of irradiation dose, respectively. As shown in Figure 6, the modulus of PLA/starch composite increases with the increasing irradiation dose due to the improved compatibility. The tensile strength at break is decreased by the addition of GMA due to the plasticizer behavior of the GMA,[17] however it is retrieved to the level of PLA by 30 kGy irradiation.

## 4. Conclusions

In this study, we studied the effects of the electron beam irradiation in the presence of GMA on the compatibility of the PLA/starch composite by observing the morphological, mechanical, and rheological properties of the composite and the FTIR spectrum of the starch, which was extracted from the composite. The morphology study clearly indicated that the interfacial adhesion between the PLA matrix and the starch was greatly enhanced by the electron beam irradiation with the presence of the GMA. The SEM micrograph of tensile fracture showed a newly formed substance, which covered the starch granules and connected the starch to the PLA matrix. The FTIR study confirmed that a compatibilization reaction occurred at the interface between PLA and starch. The rheological properties and the modulus were enhanced due to improved compatibility. The proposed reaction schemes explained well the electron beam

radiation-initiated graft copolymerization with the medium of the GMA, which was placed at the interface during the melt mixing. Overall, this new compatibilization strategy was very successful. Furthermore, the compatibility of the PLA/starch composite might be eventually controlled by varying the irradiation dose.

**Acknowledgment**

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