

ORIGINAL ARTICLE

Effects of a Compatibilizer on the Tensile Properties of Low-Density Polyethylene/Modified Starch Blends

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Abstract

In this study, thermoplastic starch (TPS), cross-linked starch (CS), and cross-linked starch modified with glycerol (CTPS) were prepared, and the mechanical properties of the compatibilized low-density polyethylene (LDPE) blends (LDPE/TPS, LDPE/CS, and LDPE/CTPS) were investigated and compared with those of uncompatibilized LDPE/TPS, LDPE/CS, and LDPE/CTPS blends. Maleic-anhydride-grafted polyethylene was used as the compatibilizer. The enhanced tensile strength and elongation at break for the compatibilized LDPE/modified starch blends are a result of the improved compatibility between LDPE and the modified starch, which was confirmed by torque measurements and scanning electron microscopy.

Key words : Modified starch, Polyethylene, Compatibilizer, Compatibility, Scanning electron microscopy

1. Introduction

Most lightweight plastic packaging materials are discarded after being used only once. Plastic waste has an adverse effect on the environment; thus, legislative threats and increasing public concern surrounding the garbage crisis have generated much interest in biodegradable packaging materials. Two separate approaches towards the production of biodegradable packaging materials are currently under investigation: the first being the development of completely biodegradable packaging materials, and the other being the development of partially biodegradable polymers obtained through the blending of biodegradable polymers and non-biodegradable polymers. Currently, partially biodegradable polymers are more useful

than completely biodegradable polymers as a result of their economic advantages and more desirable properties.

Among the various biodegradable polymers, starch has recently received much attention with respect to its use as the biodegradable component in partially biodegradable packing materials because it is readily available, inexpensive, and has a very fast biodegradability (Gupta et al., 2008; Kiatkamjornwonga et al., 2001; Sangeeta and Asim, 2010). The potential advantages of starch polymers, in addition to their environmental compatibility, include the abundance of the raw materials used in their manufacture, which are derived from renewable sources.

One major disadvantage of existing starch polymers is their limited processability, because their melting

Received 5 June, 2013; Revised 13 August, 2013;

Accepted 21 October, 2013

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point is greater than the decomposition temperature. Therefore, it is difficult to make blown thin films for packaging applications. In order to enable the melting point of the starch polymer to be below its decomposition temperature, thermoplastic starch (TPS) has been developed by gelatinizing the starch with 6–10% plasticizer in the presence of elevated heat and pressure (Bikiaris and Panayiotou, 1998; Hulleman et al., 1998; Ma et al., 2009; Ma and Yu, 2004; Rodriguez-Gonzalez et al., 2004; Sailaja and Seetharamu, 2008).

Low-density polyethylene (LDPE) is one of the most widely used polymers and is used extensively in packaging materials. However, the incompatibility between hydrophilic TPS and hydrophobic LDPE often leads to larger non-degradable portions and diminished mechanical properties of the LDPE/TPS blends (Kiatkamjornwong et al., 2001; Ma and Yu, 2004). In order to enhance the compatibility between the two immiscible polymers, two methods have recently been employed. The first method involves the use of compatibilizers such as maleic-anhydride-grafted polyethylene (PE-g-MAH), and the second method involves the use of chemically modified starch.

Recently, it has been reported that the tensile strength and elongation at break of LDPE/cross-linked starch modified with glycerol (CTPS) blends are higher than those of LDPE/cross-linked starch (CS) and LDPE/native starch blends (Sangeeta and Asim, 2010). However, there have been relatively few studies on the effects of a compatibilizer on the

mechanical properties of LDPE/CTPS and LDPE/CS blends. In this work, the effects of a compatibilizer (PE-g-MAH) on the mechanical properties of LDPE/TPS, LDPE/CS, and LDPE/CTPS blends were investigated.

2. Experimental

2.1. Materials and preparation of modified starch (MS)

The important characteristics of the materials used in this study are summarized in Table 1. The grafting ratio of MAH in PE-g-MAH was 0.5 wt%, as reported by the commercial producers. Commercially available tapioca starch (TS) was used in this study, and CS was prepared from TS by treating it with the cross-linking agent epichlorohydrin under alkaline conditions. TS was suspended in distilled water at 60 wt%, and the slurry was agitated with a high-speed stirrer for 1 h. Epichlorohydrin at 2 wt% (based on the starch weight) was added to the slurry, and the pH was adjusted to 10.5 with a 1N NaOH solution. After the mixture was stirred for 24 h at room temperature, the pH of the mixture was adjusted to 5.5 with acetic acid, and the mixture was subsequently washed with distilled water and 85% acetone. The mixture was then immediately cooled using a refrigerator, and the obtained CS was then dried in a vacuum oven at 50°C until the moisture content was around 1%.

TPS and CTPS were prepared by applying both glycerol and water to TS and CS, respectively. The

Table 1. Important characteristics of the materials used in this study

Class of materials	Materials	Supplier	Characteristics
Polymer	Low-Density Polyethylene (LDPE)	Han-Wha Petrochem., Korea	Melt Index(g/10min) :4 Density(g/cm ³) : 0.923
Polymer	Tapioca starch (TS)	Sam-Yang Chem., Korea	Density(g/cm ³) : 1.65 Moisture(%) : < 14
Compatibilizer	PE-g-MAH (Fusabond 493D)	Dupont, USA	Melt Index(g/10min) : 1.6 Density(g/cm ³) : 0.87
Cross-linking agent	Epichlorohydrin	Acros Chem., Belgium	Density(g/cm ³) : 1.18
Plasticizer	Glycerol	KCI Chem., Korea	Density(g/cm ³) : 0.87

TS/glycerol/water (5/3/2 ratio by weight) and the CS/glycerol/water (5/3/2 ratio by weight) mixtures were maintained for 1 h at room temperature in order to allow the plasticizers (water and glycerol) to swell the granular starch molecules. The mixtures were then agitated with a high-speed stirrer for 1 h, and the obtained TPS and CTPS were further cooled within a refrigerator. The TPS and CTPS were subsequently dried in a vacuum oven at 50°C until the moisture content was around 1%. The obtained CS, TPS, and CTPS were then ground with a mortar and pestle in order to obtain a powder with relatively small granules (100–300 μm). The preparation of the modified starch is summarized in Fig. 1.

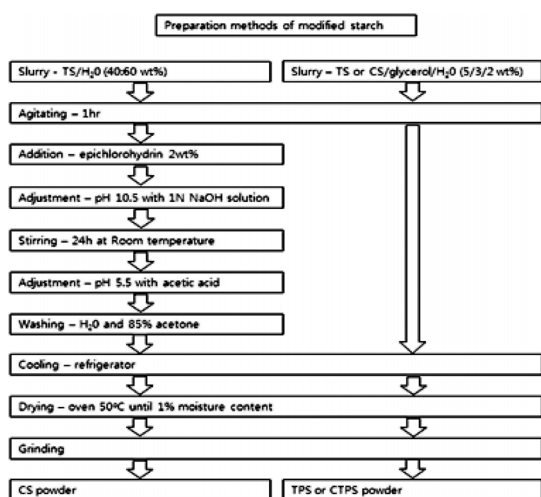


Fig. 1. Preparation methods of modified starch.

2.2. Preparation of LDPE/MS/PE-g-MAH blends

TPS, CS, and CTPS were melt-blended with LDPE and PE-g-MAH. Before melt-blending, all materials were pre-dried at 40°C for 4 h within a vacuum oven. The LDPE was then mixed with varying quantities (5, 15, and 30 wt%) of modified starch (CS, TPS, and CTPS) with or without PE-g-MAH (5 wt%) at 100 rpm and 140°C for 10 min in a Hakke internal mixer with the temperature and torque being monitored

during the mixing process. The obtained bulk specimens were compression-molded in order to fabricate sheets under the following conditions: 150°C for 5 min at a pressure of 150 bar, followed by treatment with a cooling press at room temperature at a pressure of 100 bar in order to fix the shape of sheets. The produced samples were stored at 23°C for 24 h in a desiccator at 50% relative humidity, which was regulated by ASTM standards (D638).

2.3. Testing

A universal testing machine (Model 4466, Instron Co.) was used to obtain the tensile strength and elongation at break of the samples at room temperature. The crosshead speed was 50 mm/min. All measurements were repeated five times on bone-shaped specimens (ASTM D638) and averaged to obtain the final result.

X-ray diffraction (XRD) studies were conducted on a Rigaku D/max 2200H X-ray diffractometer (40 kV, 50 mA) with a scanning rate of 2°/min. In order to study the morphology of the samples, cross sections of the blends were cryogenically fractured and examined using a field-emission scanning electron microscope (FE-SEM, HITACHI S-4200, Japan).

3. Results and discussion

Fig. 2 shows the tensile strength of the LDPE/modified starch blends. The tensile strength of LDPE was 12.8 MPa, which is higher than the tensile strength of all the blends. When increasing the content of modified starch in the blends, the tensile strength typically decreases, with the exception of the LDPE/CS/PE-g-MAH blend. This decrease is due to the low tensile strength of TPS and CTPS. Because glycerol was used as a plasticizer in the preparation of TPS and CTPS, it contributes to the low tensile strength of TPS and CTPS. The tensile strength of the LDPE/CS blend remains nearly unchanged as the CS content increases from 15 wt% to 30 wt%. This result

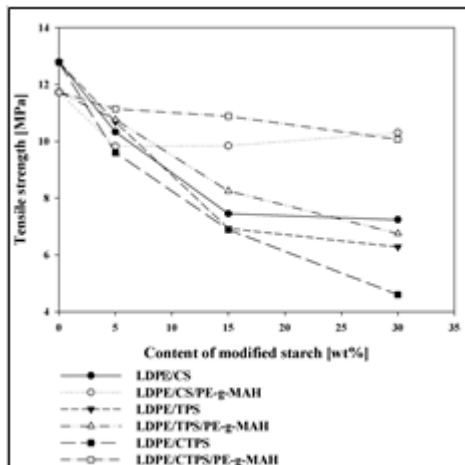


Fig. 2. Tensile strength of the LDPE/modified starch blends.

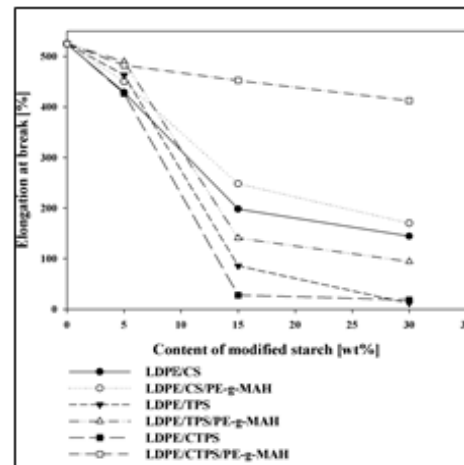


Fig. 3. Elongation at break of the LDPE/modified starch blends.

could be attributed to the fact that CS does not contain a plasticizer. Interestingly, the tensile strength of the LDPE/CS/PE-g-MAH blend increases as the CS content increases from 5 wt% to 30 wt%. In general, the tensile strength of elastomers increases as the degree of cross-linking increases, up to an optimum amount. Because CS is a cross-linked starch that does not contain a plasticizer, the number of cross-linked polymers in the blend increases as the CS content increases in the LDPE/CS/PE-g-MAH blend; thus, the tensile strength increases. The tensile strength of the LDPE/CS blend decreases as the CS content increases, which is due to the poor compatibility between CS and LDPE.

When the modified starch content was 30 wt%, the tensile strengths of the LDPE/CS/PE-g-MAH, LDPE/TPS/PE-g-MAH, and LDPE/CTPS/PE-g-MAH blends were higher than that of the LDPE/CS, LDPE/TPS, and LDPE/CTPS blends, respectively. The addition of a compatibilizer (PE-g-MAH, 5 wt%) led to improved compatibility between the LDPE and the modified starch (CS, TPS, and CTPS), which produces an increase in tensile strength. The tensile strength of the LDPE/CS/PE-g-MAH blend was the highest among all blends and nearly 81% of the tensile strength of

pure LDPE. The second highest tensile strength was achieved by the LDPE/CTPS/PE-g-MAH blend.

Fig. 3 displays the elongation at break of the LDPE/modified starch blends. The elongation at break of LDPE was 525%, which was higher than that of all other blends. As the content of modified starch increased, the elongation at break decreased. When the modified starch content was 30 wt%, the elongations at break of the LDPE/CS/PE-g-MAH, LDPE/TPS/PE-g-MAH, and LDPE/CTPS/PE-g-MAH blends were higher than that of the LDPE/CS, LDPE/TPS, and LDPE/CTPS blends, respectively. The elongation at break of the LDPE/CTPS/PE-g-MAH blend was the highest among all blends and was nearly 79% of elongation at break of pure LDPE. The higher elongation at break for the compatibilized LDPE/modified starch blends, relative to the uncompatibilized LDPE/modified starch blends, is due to the improved compatibility between the LDPE and the modified starch. Poor compatibility between LDPE and the modified starch may lead to premature failure, starting at the interface between the LDPE and the modified starch. Therefore, improved compatibility between the LDPE and the modified starch due to the presence of the compatibilizer results in an increase in both

tensile strength and elongation at break.

The torque applied to the blends during the blending of the LDPE and modified starch was investigated using a Haake Rheomix 600P. Fig. 4 displays the torque curves of the LDPE/CS blend. For the uncompatibilized blends [Fig. 4(a)], the torque of the LDPE/CS (70/30 wt%) blend was lower than that of the LDPE/CS (95/5) blend because the melt viscosity of CS was lower than that of LDPE. However, in the compatibilized blends [Fig. 4(b)], the torque of LDPE/CS/PE-g-MAH (65/30/5) was higher than that of LDPE/CS/PE-g-MAH (90/5/5). The higher torque of LDPE/CS/PE-g-MAH (65/30/5) is a result of the reaction and/or the interactions between the hydroxyl groups of CS and the anhydride groups of PE-g-MAH. The concentration of the hydroxyl groups of the LDPE/CS/PE-g-MAH (90/5/5) blend was smaller than that of LDPE/CS/PE-g-MAH (65/30/5); therefore, the reaction and/or the interactions between the hydroxyl groups of CS and the anhydride groups of PE-g-MAH are also minimal in the LDPE/CS/PE-g-MAH (90/5/5) blend. The torque behavior of the uncompatibilized and compatibilized LDPE/TPS (Fig. 5) and LDPE/CTPS (Fig. 6) blends also exhibit similar trends. Because the melt viscosity of TPS and CTPS is lower than that of LDPE, the torque of the uncompatibilized LDPE blend containing 30 wt% TPS or CTPS is lower than that of the uncompatibilized LDPE blend containing 5 wt% TPS or CTPS. However, the torque of the compatibilized LDPE blend containing 30 wt% TPS or CTPS is similar to or higher than the torque of the compatibilized LDPE blend containing 5 wt% TPS or CTPS, respectively.

For various polymer blends, the study of their morphology is crucial because their physical properties often depend upon their morphology. Fig. 7 shows the morphology of the LDPE/modified starch blends containing 30 wt% modified starch. Because the major component of the polymer blends typically forms the matrix, LDPE is the matrix in the LDPE/

modified starch blend containing 30 wt% modified starch. In the LDPE/CS (70/30) blend, the dispersed spheres are comprised of CS. In the LDPE/TPS (70/30) and LDPE/CTPS (70/30) blends, many cavities are observed, and these cavities are attributed to the locations where TPS and CTPS were initially present. This result indicates poor adhesion between the LDPE and the modified starch. However, in the compatibilized LDPE/modified starch blends, the size of the spheres and cavities decreases. The compatibilizer (PE-g-MAH) functions as an emulsifier at the interface between the LDPE and the modified starch. The polyethylene portion is compatible with the LDPE and MAH portions as well as with the modified starch. The reaction and/or interactions between the hydroxyl groups of the starch and the

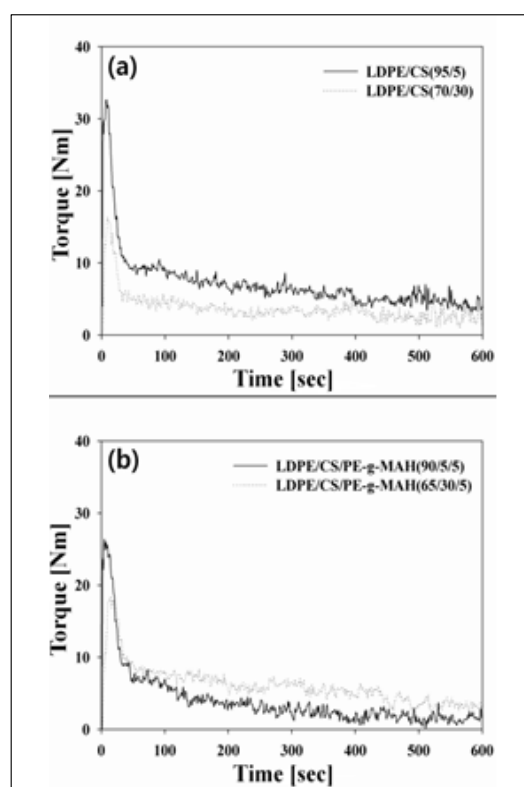


Fig. 4. Torque curves of (a) the uncompatibilized LDPE/CS blends and (b) the compatibilized LDPE/CS blends.

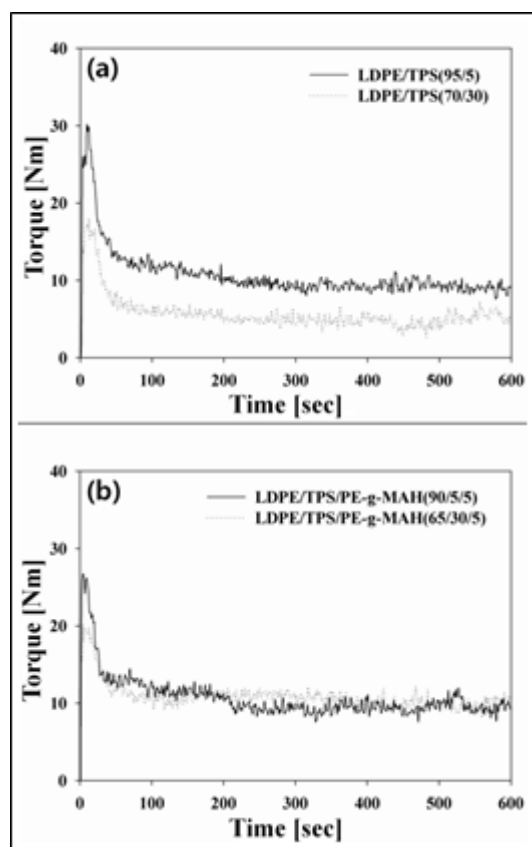


Fig. 5. Torque curves of (a) the uncompatibilized LDPE/TPS blends and (b) the compatibilized LDPE/TPS blends.

anhydride groups of PE-g-MAH were reported in a previous study (Bikiaris and Panayiotou, 1998). This phenomenon leads to a reduction in interfacial tension, and the sizes of the spheres and cavities subsequently decrease.

Fig. 8 displays the XRD patterns of TS and the modified starches. Prior to the XRD measurements, all the samples were melted and remained at room temperature during the cooling process. TS exhibits the A-type crystal pattern with peaks at about $2\theta = 15^\circ$ and 23° as well as a doublet at 17° and 18° (Atichokudomchai and Varavinit, 2003; Bogracheva et al., 1998; Veregin et al., 1986; Zobel, 1988). The CS pattern was similar to the TS pattern; however,

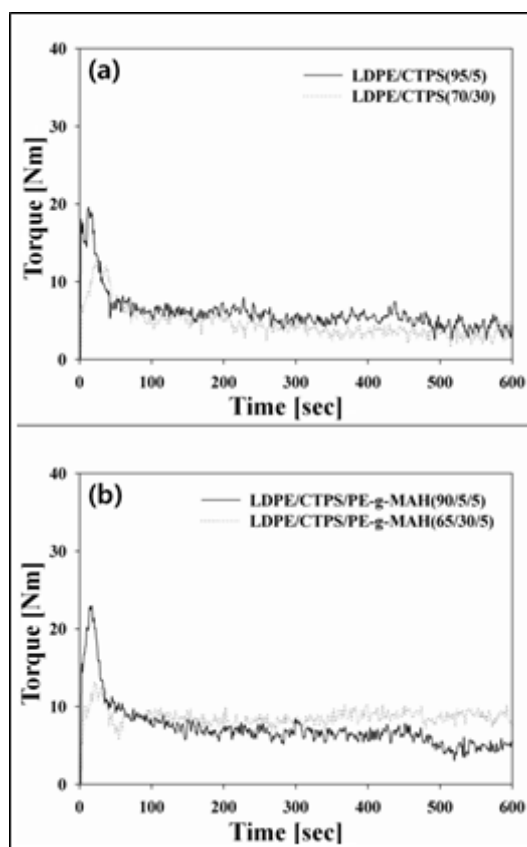


Fig. 6. Torque curves of (a) the uncompatibilized LDPE/CTPS blends and (b) compatibilized LDPE/CTPS blends.

the TPS and CTPS patterns become broader, indicating a decrease in crystallinity. Because glycerol was used as a plasticizer in preparing TPS and CTPS, glycerol molecules replace intermolecular hydrogen bonds arising from the starch, thus leading to a decrease in crystallinity.

4. Conclusions

When the content of the modified starch was 30 wt%, the tensile strengths and elongations at break of the LDPE/CS/PE-g-MAH, LDPE/TPS/PE-g-MAH, and LDPE/CTPS/PE-g-MAH blends were higher than those of the LDPE/CS, LDPE/TPS, and LDPE/CTPS blends, respectively. The tensile strength of the

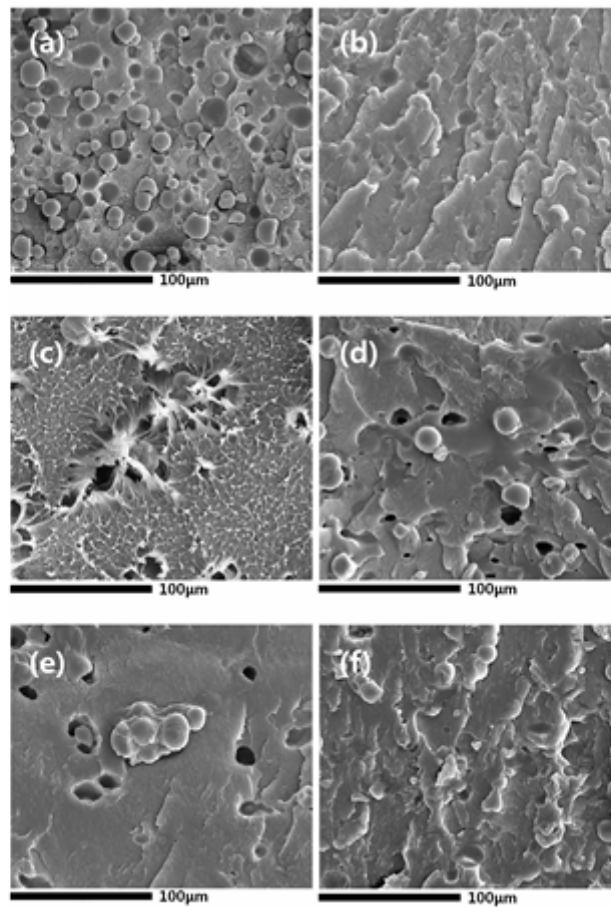


Fig. 7. SEM photographs: (a) LDPE/CS(70/30) blend, (b) LDPE/CS/PE-g-MAH(65/30/5) blend, (c) LDPE/TPS(70/30) blend, (d) LDPE/TPS/PE-g-MAH (65/30/5) blend, (e) LDPE/CTPS (70/30) blend, (f) LDPE/CTPS/PE-g-MAH (65/30/5) blend.

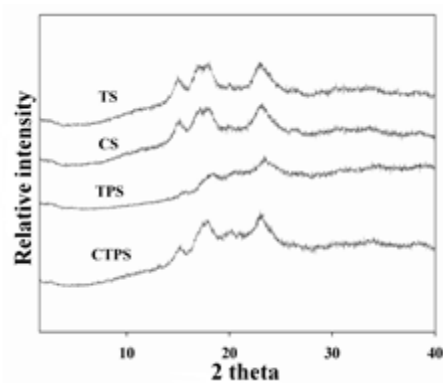


Fig. 8. XRD patterns of TS and the modified starches.

LDPE/CS/PE-g-MAH blend was the highest among all blends and was nearly 81% of the tensile strength of LDPE. The elongation at break of the LDPE/CTPS/PE-g-MAH blend was the highest among all blends and was nearly 79% of the elongation at break of LDPE. The improved tensile strength and elongation at break for the compatibilized LDPE/modified starch blends, compared to the uncompatibilized LDPE/modified starch blends, are a result of the improved compatibility between the LDPE and the modified starch. This improved compatibility was also confirmed by torque measurements and SEM

observations, which confirmed the decreased size of the domains, and was due to the reaction and/or the interactions between the hydroxyl groups of the modified starch and the anhydride groups of PE-g-MAH.

Acknowledgement

This paper is part of Jin-Woo Park's Master's thesis, which was accepted by Dongseo University.

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