

PROCESSABILITIES & MECHANICAL PROPERTIES OF THE BIODEGRADABLE LDPE/MODIFIED STARCH BLENDS

Young Jin Kim, Yong Man Lee*, Hyang Mok Lee and O Ok Park†

Dept. of Chem. Eng., Korea Advanced Institute of Science & Technology,
373-1, Kusung-Dong, Yusung-Gu, Taejon 305-701, Korea

*Environment Project Department, Lucky Engineering Co., Ltd., 275, Kongdok-Dong, Mapo-Gu, Seoul, Korea
(Received 20 August 1993 • accepted 21 March 1994)

Abstract—An investigation of the biodegradable polymers based on starch has been accomplished. Starch needs to be modified before blending with low density polyethylene (LDPE) because of its hydrophilicity. Three kinds of modification methods were applied to obtain the compatibility to starch-LDPE blends. The first one was the esterification of the hydroxyl group of starch with acetic anhydride. The second was the copolymerization of acrylonitrile and styrene onto starch. The last was the esterification reaction of the hydroxyl group of starch with three kinds of ionomers. The tensile strength, % elongation, Young's modulus, and shear viscosities of blends of the modified starch and LDPE were examined. Ionomer-treated starch showed better compatibility with LDPE to give better performances than other blends.

INTRODUCTION

Starch is perhaps one of the most abundant and the cheapest natural polymer on the market. It is also known to be completely biodegradable. Today, there is an increasing necessity to develop biodegradable polymers to preserve the environments. The biodegradable polymer based on starch is very useful for products ranging from disposable diapers, shopping bags to fast food containers. However, the starch-based materials usually have poor strengths and impact properties. In the case of blending with synthetic polymers, starch needs to be modified before blending since starch with three hydroxyl groups is hydrophilic and synthetic polymers are usually hydrophobic. There have been many reports on the modified starch-polyethylene blends. Otey and co-workers [1,2] reported a technique for blending gelatinized starch with poly (ethylene-co-acrylic acid) to produce flexible blown films which contains high levels of starch. Griffin [3] prepared the biodegradable film filled with more than 50% starch using auto-oxidants such as unsaturated fatty acids and fats. Maddaver and Campbell [4] proposed the biodegradation mechanism of the blend of the modified starch with the general purpose polymer, low density polyethylene. The biodegrada-

tion mechanism is consisted of two steps. The first step is the degradation of starch by microorganism like fungi or bacteria, which not only weakens the polymer matrix but also generates new surfaces to be exposed to the microorganism. The next step is the degradation by the auto-oxidant, which produces peroxides, when contacts with metallic salts in the environment. The peroxides can attack and degrade the polymer chains. Our concerns were to examine the mechanical properties, rheological properties, and morphologies of starch based polymer blends. It was assumed that they are biodegradable.

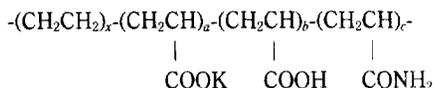
EXPERIMENTAL

1. Materials

Low density polyethylene, LDPE 5301 was kindly supplied by Hanyang Chemical Co. It had a melt index (MI) of 0.3 and its density was 0.920 g/cm³. The unmodified corn-starch was obtained from Sunil Glucose Co. It contains about 15% moisture by weight. It was dried at oven that kept 100°C for 2 hours. Three kinds of ionomers were also used in this experiment. Ionomers were prepared at Korea Research Institute of Chemical Technology (KRICT) for other purposes. They are in an emulsion state and the solid weight percent is 20%. Each ionomer has a different portion of the functional groups (-COOH, -COOK, and -CO-

†To whom all correspondences to be addressed.

NH₂). The portions of functional group of ionomer-1 are all 20%. Ionomer-2 has 50% of -COOK and 50% of -CONH₂, and ionomer-3 has only -COOK functional group. The structure of ionomers is such that,



2. Modification of Starch

The esterification of the hydroxyl group of starch with acetic anhydride (Esterified starch; ES) was done as follows. The reaction was carried out in the three neck flask at 50°C for six hours. These conditions are adopted from those of Lemmerling et al. [5]. The mechanical stirring bar and the water bath heated by hot plate was used. After the reaction materials were washed by 500 mL ethanol four times, it was dried in the oven at 80°C for two hours. The copolymerization of acrylonitrile and styrene onto starch (Grafted starch; GS) was performed with the procedure of Gugliemelli et al. [6, 7]. In this case, ceric ammonium nitrate (CAN) was used as an initiator. After water and starch were agitated at 50°C, the temperature was raised to 60°C. At this temperature, monomers, acrylonitrile and styrene, were added before dropping the initiator at 65°C. The starch had gelatinized and initiated simultaneously at 70°C for 30 minutes, then the reaction material was cooled to 50°C. The polymerization was carried out in the water bath with nitrogen atmosphere at 50°C for 6 and half hours more. After polymerization, the reaction material was poured and washed in 1 L methanol and then it was filtered four times. The esterification reactions of the hydroxyl group of starch with three kinds of ionomers (ionomer-1, 2, 3) were done with the similar procedures except reaction device and conditions. The reaction device used was the highly efficient PET polymerization reactor in Fig. 1, which was originally designed as a finisher. The distilled water and starch were mixed in the beaker at the room temperature, then ionomer and sulfuric acid were added in. Each condition was different. The ionomer-1 and starch was esterified on stirring 60 rpm at 50°C for eight hours. In case of ionomer-2, the reaction temperature was 50°C and the pressure was 0.9 atm. The reaction was done with rotational speed, 60 rpm for 12 hours. The ionomer-3 was esterified with starch at 70°C, 1 atm with the same rotational speed and reaction time of ionomer-2. In this case, the reaction temperature was higher than the gelatinization temperature, 60°C of starch.

3. Testing of Mechanical Properties

Each modified starch was mixed with LDPE by Bra-

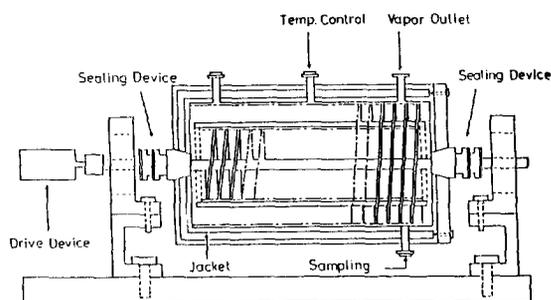


Fig. 1. The schematic diagram of apparatus for esterification reaction between the hydroxyl groups of starch and the side groups of ionomer.

bender batch mixer at 190°C for 10 minutes. For the first 2 minutes the rotation rate was 25 rpm and for the last 8 minutes kept 37.5 rpm. Blends were made into sheets by hot press following the ASTM method. The first heating was done for 3.5 minutes and the second one was heated with 200 Kgf/cm² pressure. The thickness of sheet was 2 mm. The samples for tensile strength test were cut by mold whose length was 19.2 mm, width was 2.7 mm, and thickness was 2.2 mm. Universal tensile tester (Instron model 4202) was used at the room temperature.

4. Viscosity

The blend was crushed into small size and the viscosity was measured by capillary rheometer Rosand model D10B as molten state at 170°C.

5. Morphology

The morphologies of the samples were looked into by scanning electron micrograph (Hitachi model 510). The samples were broken for clean surfaces after quenched by liquid nitrogen.

RESULTS AND DISCUSSION

Six starch-LDPE blends prepared in this study were not much different in their appearance. Differences in mechanical properties were able to be observed, however, when they were examined by the universal tensile tester. If starch is successfully modified, then they can be expected to have better properties than native starch. In general, tensile strength refers to resistance to stretching and it is determined by stretching a strip of dimensionally uniform polymer. It is one of the important properties to characterize polymeric materials. Tensile strengths are plotted as a function of their compositions of blends in Fig. 2. Blends of native starch & ionomer-treated starch with LDPE shows a similar trend; tensile strengths de-

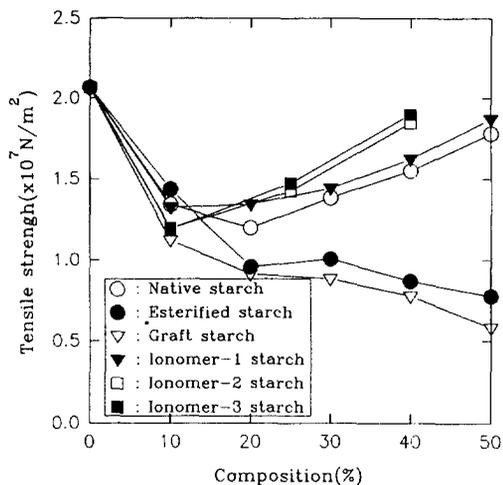


Fig. 2. Tensile strength versus composition of native, esterified, graft, ionomer-1, 2 and 3 starch.

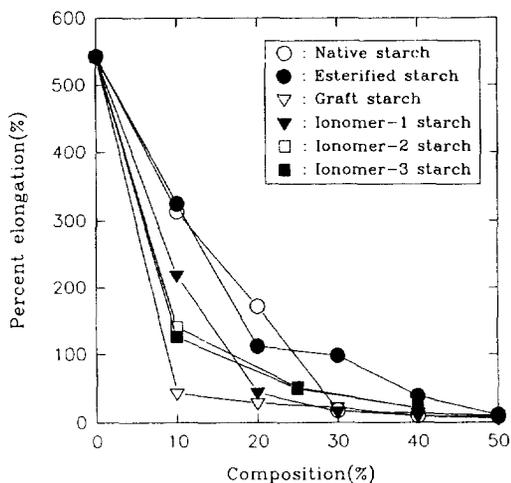


Fig. 3. % elongation versus composition of native, modified, graft, ionomer-1, 2 and 3 starch.

crease a little at low composition of starch, then increase at higher composition. If there exist only few starch particles, then they do not have any contribution on mechanical strengths except weakening them a little bit. However, if there exist enough numbers of starch particles in LDPE matrix, then they can have a role as fillers to show high mechanical strengths. In case of blends of grafted starch & esterified starch with LDPE, strengths decrease continuously as the composition increases. The tensile strength of ionomer grafted starch-LDPE blends are somewhat large throughout all compositions except 10% esterified starch.

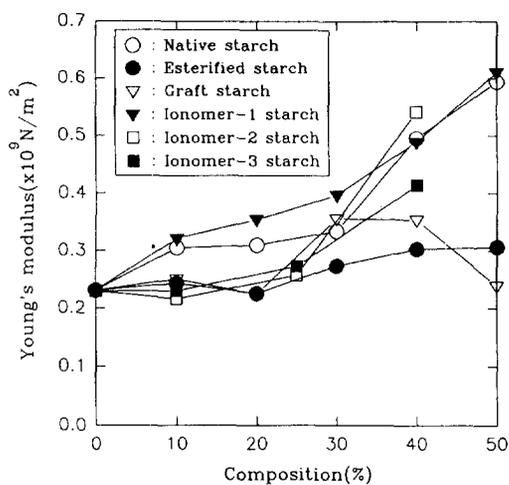


Fig. 4. Young's modulus versus composition of native, esterified, graft, ionomer-1, 2 and 3 starch.

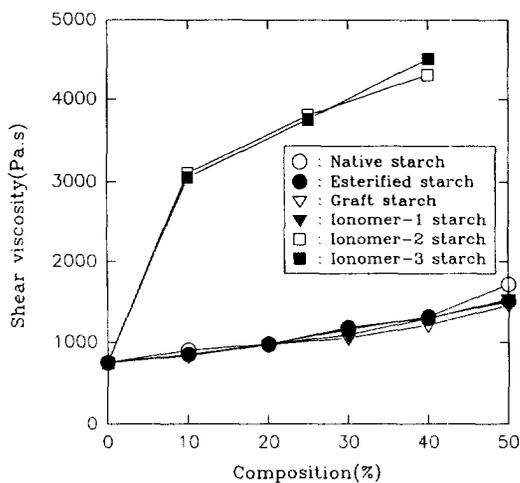


Fig. 5. Shear viscosity versus composition of native, esterified, graft, ionomer-1, 2 and 3 starch at the constant shear rate, 150 s⁻¹.

ch.

The % elongation is generally determined to measure how much polymers can be stretched until they are broken. % elongation (Fig. 3) decreases rapidly as starch is added in LDPE. The reason is that starch weakens the LDPE matrix when it penetrates into LDPE phase, and ionomer-treated starch blends show relatively lower values due to its hydrophobic nature.

Young's modulus is measured as a slope of the elastic region in which polymer acts elastically. Young's modulus is shown in Fig. 4. When the composition of starch increased, blends of ionomer-treated starch

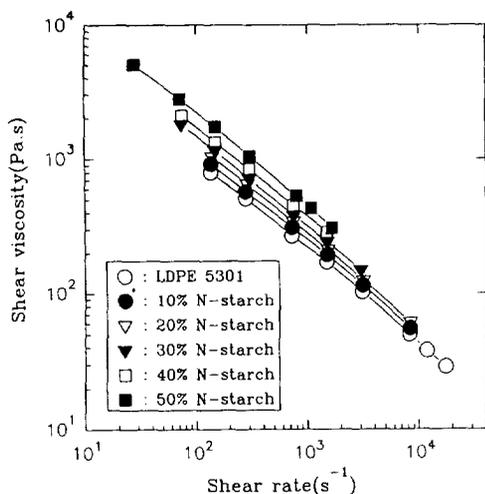


Fig. 6. Shear viscosity versus shear rate of pure LDPE 5301, 10%, 20%, 30%, 40% and 50% native starch-LDPE blend at 170°C respectively.

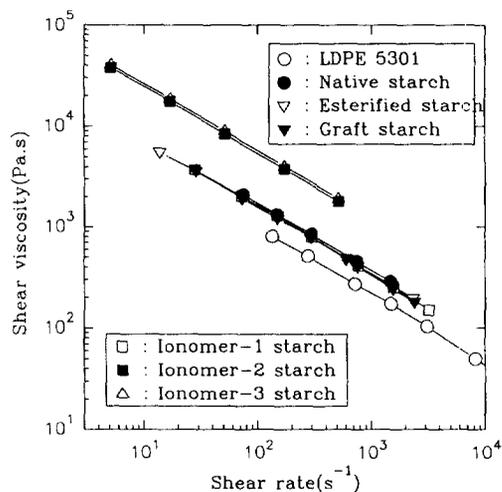


Fig. 8. Shear viscosity versus shear rate of pure LDPE 5301 40% native, esterified, graft, ionomer-1, 2 and 3 starch-LDPE blend at 170°C.

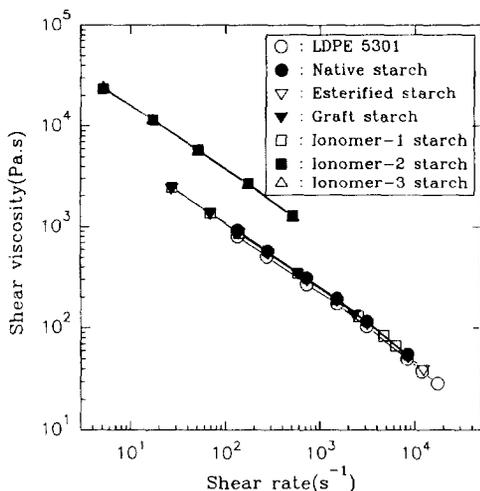


Fig. 7. Shear viscosity versus shear rate of pure LDPE 5301 and 10% native, esterified, graft, ionomer-1, 2 and 3 starch-LDPE blend at 170°C.

and native starch are becoming harder and more brittle whereas blends of esterified starch & grafted starch are getting softer and weaker. As far as the mechanical properties are concerned, it might be concluded that ionomer-treated starch blend is superior to others.

In processing polymers, it is necessary to know the shear viscosity of polymer since it largely affects the processability of polymer. Fig. 5 shows the changes of shear viscosities of each blend. Viscosities increase

gradually when starch is added in, as expected. For an example, the shear viscosity of 50% composition is the highest in Fig. 6 because the hydroxyl group of starch can have the hydrogen bonding. Blends of ionomer-2 & ionomer-3-treated starch with LDPE exhibit larger shear viscosities than others as shown in Figs. 7 and 8. It implies that ionomer-2 and ionomer-3 starch are successfully modified to obtain proper hydrophobic properties. Reaction conditions during the ionomer treatment of starch are very crucial to determine the rheological properties of their blends. Therefore optimal reaction conditions should be carefully considered before processing, which is now under consideration in this laboratory.

Now let us look into the morphologies of blends in order to determine whether the modifications are successful. Fig. 9 shows SEM micrographs. Native starch-LDPE blend has the most distinct boundary between starch and LDPE due to their immiscibility. Blends of ionomer-treated starch and LDPE are fairly well mixed since ionomer-treated starch has better compatibility with LDPE. There is a problem, though, to take SEM since the starch in the LDPE matrix could be broken by the SEM electrons.

CONCLUSIONS

In this study, it has been shown that modified starch-LDPE blends using various methods apparently possess better properties than the native starch-LDPE blend. To obtain the good properties of starch-LDPE

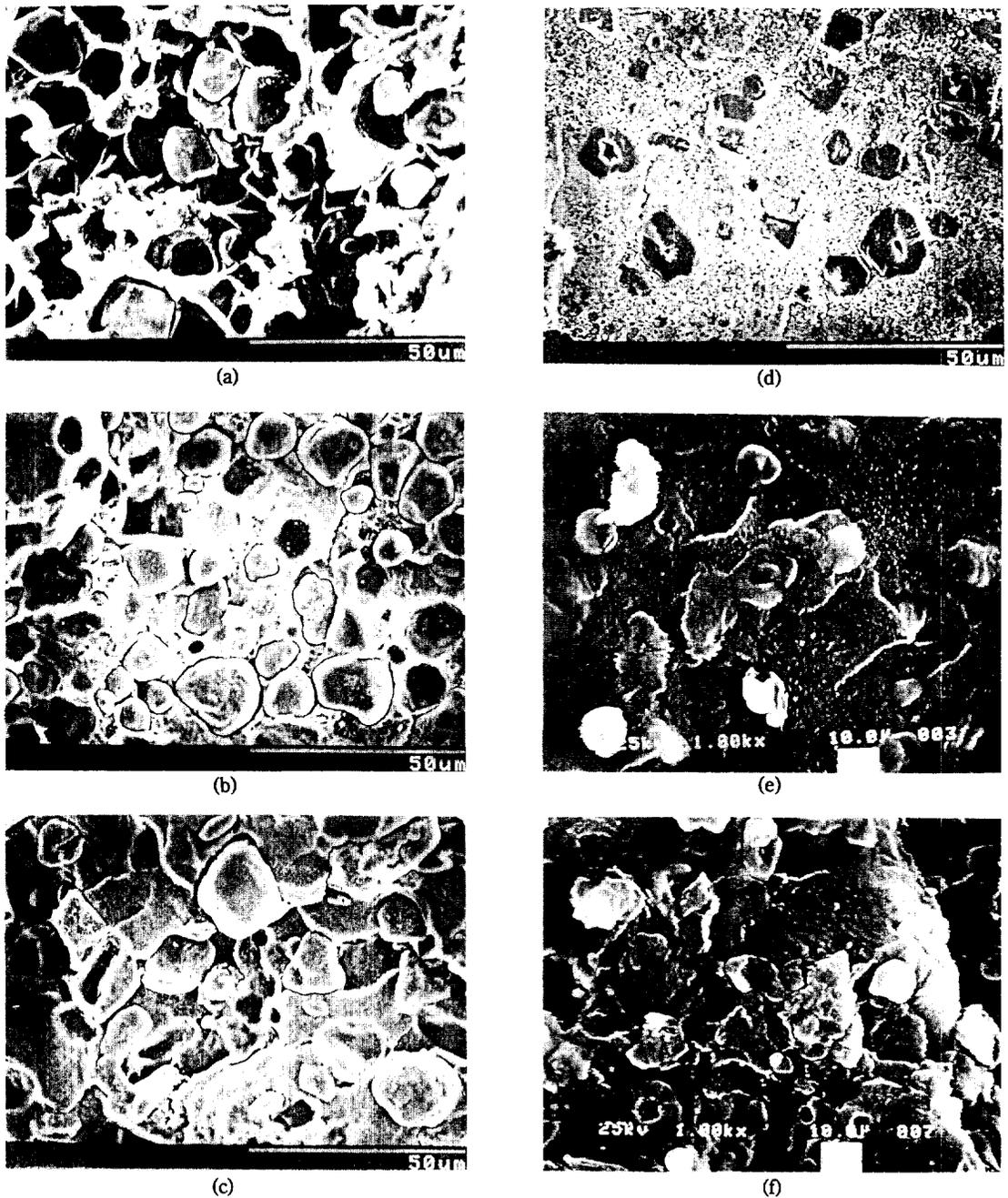


Fig. 9. SEM photograph of blends between LDPE and 40% (a) native starch ($\times 1,000$); (b) esterified starch ($\times 1,000$); (c) graft starch ($\times 1,000$); (d) ionomer-1 starch ($\times 1,000$); (e) ionomer-2 starch ($\times 1,000$); (f) ionomer-3 starch ($\times 1,000$).

blends, the hydrophilic starch should be changed to hydrophobic one for the compatibility. Most modification methods used here are useful to improve the pro-

cessability of blends. The fact that ionomer-2 & 3 treated starch blends reveal especially high viscosities implies that the properties are largely influenced by the

reaction conditions during the treatment of starch. Considering all aspects above, ionomer-treated starch blends can be said to possess superior properties than others.

ACKNOWLEDGMENT

The authors are grateful to Bioprocess Engineering Research Center, BPERC headed by Professor Ho Nam Chang for the financial support, and thankful to Dr. Jae Heung Lee for the supply of ionomers.

REFERENCES

1. Otey, F. H., Westhoff, R. P. and Doane, W. M.: *Ind. Eng. Chem. Prod. Res. Dev.*, **26**, 1659 (1987).
2. Otey, F. H. and Mark, A. M.: US Patent, 3,949,145 (1976).
3. Griffin, G. J. L.: US Patent, 4,016,117 (1977).
4. Maddaver, W. J. and Campbell, P. D.: "Current Status of Starch Based Degradable Plastics", Proceedings of the Corn Utilization Conference III (1990).
5. Lemmerling, J. T.: US Patent, 3,281,411 (1966).
6. Gugliemelli, L. A., Swanson, C. L., Doane, W. M. and Russel, C. R.: *Polym. Sci. Polym. Letters Ed.*, **15**, 739 (1977).
7. Gugliemelli, L. A., Weaver, M. O., Russel, C. R. and Rist, C. E.: *J. Appl. Polym. Sci.*, **13**, 2007 (1969).

1. Otey, F. H., Westhoff, R. P. and Doane, W. M.: *Ind. Eng.*