Morphology and Properties of Low-Density Polyethylene and Rice-Starch Composites

Y.-J. Wang, and W. Liu

ABSTRACT

Blends of rice starch, glycerol, polyethylene graft maleic anhydride (PE-g-MA) and low-density polyethylene (LDPE) with different rice starch contents were prepared using a lab-scale twin-screw extruder. The morphology and properties of the blends were evaluated by using a scanning electron microscope (SEM) and a Universal Testing Machine, respectively. The dispersion of rice starch in the LDPE matrix was homogeneous and tensile strength and elongation at break were improved after protein removal. The interfacial adhesion between rice starch and LDPE was further improved by the addition of PE-g-MA according to the morphology structure by SEM, thus resulting in a greater tensile strength and elongation at break.

INTRODUCTION

Fillers have been extensively used in polymer materials for several decades. The materials and size/shape of fillers and the interaction between filler particles and polymeric matrix affect morphological structure, rheological properties, and solid state mechanical properties (Nielsen, 1966). Although inorganic substances are still the main filler materials, some natural biopolymers such as starch, cellulose, and lignin are being widely used in the development of biodegradable products with increased biodegradability (Mayer and Kaplan, 1994; Kaplan, 1998). Much research on biodegradable polymers focuses on blending starch with other polymers (Lim et al. 1992; Aburto et al.

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1 This is a completed study.
Different starches have different granule sizes and other intrinsic properties, which will affect the properties of polymeric composites. Lim et al. (1992) studied the effect of starch granule size on physical properties of starch-filled polyethylene. Film made with small particle corn starch (2-µm average diameter) had the highest elongation rate and tensile strength and rice starch-filled polyethylene had better tensile properties than corn starch-filled polyethylene. Rice starch potentially offers a good source of filler for biodegradable plastics with desirable mechanical properties because of its smaller granular size. However, little research has been done on the use of rice starch in biodegradable materials. Our previous report showed that the dispersion of rice starch in LDPE matrix was inhomogeneous and the addition of glycerol improved the dispersion of rice starch in LDPE and tensile properties of the composites. The addition of compatibilizer would improve the interaction between filler and matrix and enhance their interfacial adhesion (Bikiaris and Panayiotou, 1998). Therefore, in this study PE-g-MA was incorporated into rice starch/LDPE/glycerol blends to improve the properties of the resulting blends and protein-removed rice starch was blended with LDPE to improve the dispersion of rice starch in LDPE matrix.

**PROCEDURES**

**Materials**

Low-density polyethylene (LDPE) was a product of Dow Chemical Co. (Midland, MI), LDPE 640I, with a melt flow index of 2g/10min. Native rice starch was obtained from A&B Ingredients Inc. (Fairfield, NJ). The residual protein in the native rice starch was removed according to the method of Yang et al. (1984). Rice starch was dried at 120ºC for 24 hr to a moisture content of less than 1% prior to specimen preparation. PE-g-MA with an approximate maleic anhydride content of 3wt % was purchased from Aldrich Chemical Company Inc. (Milwaukee, WI). Glycerol was reagent grade obtained from EM Science (Gibbstown, NJ).

**Preparation of Starch and LDPE Blends**

Rice starch, glycerol (25% of rice starch weight), PE-g-MA (10% of rice starch weight), and LDPE were blended at room temperature with a Kitchen Aid mixer (St. Joseph, MI) at starch to LDPE ratios of 5%, 10%, 20%, and 30% (w/w). These blends were then melt-blended in a lab-scale twin-screw counter-rotating extruder (PolyLab, ThermoHaake, Madison, WI) at a processing temperature of 170ºC and a processing speed of 50 rpm.

**Morphology Observation**

The blend samples were fractured in liquid nitrogen and the fracture surface of the samples was observed using a Hitachi S-2300 Scanning Electron Microscope.
(Tokyo, Japan) at an accelerating voltage of 25KV. The fracture surfaces were sputter coated with gold prior to examination.

**Tensile Properties**

Five dumbbell-shaped specimens were prepared from each extruded sample. The tensile tests were carried out using an Instron Universal Testing Machine (Model 1011, Instron, Canton, MA) at 23°C with a crosshead speed of 20 mm/min.

**RESULTS AND DISCUSSION**

The phase morphology of LDPE/starch blends reflects the dispersion of starch filler in LDPE matrix. Figure 1 shows the SEM micrographs of LDPE/protein-removed rice starch blends. It had been reported that the dispersion of native rice starch in LDPE matrix was inhomogeneous. After the protein removal, the dispersion of rice starch was improved, indicating that the presence of protein contributed to the inhomogeneous dispersion of native rice starch in LDPE matrix. The protein in rice starch might have increased the interaction between rice starch granules, which in turn hindered the dispersion of rice starch in LDPE matrix. Figure 2 shows the morphology of LDPE/rice starch/glycerol/PE-g-MA blends with different starch contents. It was noted that the distinction between rice starch and LDPE was not clear and the surface of rice starch became coarse, which is a typical character of compatibilized blends. The rice starch surface was not smooth but was covered with materials that adhered to the LDPE matrix. Because LDPE had little interaction with rice starch, the materials on the starch surface were assumed to be PE-g-MA. The improved interfacial adhesion was attributed to the chemical reaction between hydroxyl groups in rice starch and anhydride groups in PE-g-MA under an extrusion condition of high temperature and high shear (Bikiaris and Panayiotou, 1998) and the strong physical interaction between LDPE and PE-g-MA.

For polymer blends, the dispersion of the dispersed phase in the matrix phase and the interfacial adhesion between dispersed phase and matrix are key factors to determine the mechanical properties (Paul, 1978). The use of a smaller particle size for the dispersed phase and a more homogeneous dispersion will improve the ability of the material to tolerate load, which consequently results in improved distribution of stress and better mechanical properties of the material. Figure 3 shows tensile properties of the rice starch composites with different starch contents. The tensile properties of LDPE/protein-removed rice starch were higher than those of native rice starch composites as a result of a homogenous dispersion of starch in LDPE matrix based on SEM observation. The homogeneous dispersion of rice starch in LDPE matrix would reduce the chance of a significant stress concentration, which led to the formation of initial craze at higher displacement and load during deformation (Kramer, 1990). Consequently, materials were fractured at higher ultimate strength and displacement. The tensile strength of LDPE/rice starch/glycerol/PE-g-MA blends was significantly greater than that of LDPE/native rice starch blends. It was believed that PE-g-MA increased adhe-
sion between the LDPE matrix and the starch filler because PE-g-MA was situated at the interface between starch and LDPE and integrated with both constituents based on SEM results. The improved interfacial adhesion played an important role in the stress transfer, thus reducing the chance of interfacial debonding and leading to improved tensile strength. The elongation at break of LDPE/rice starch/glycerol/PE-g-MA blends was significantly greater than that of LDPE/rice starch blends at lower starch contents but their differences became smaller at higher starch contents. The elongation at break of the composites was predominately controlled by the interfacial properties of starch in LDPE at lower starch contents and by the distance between starch granules at higher starch contents, respectively. In addition, these results also supported the finding that the interaction between starch and PE-g-MA was similar to that between hydroxyl groups in rice starch and anhydride groups in PE-g-MA (Bikiaris and Panayiotou, 1998).

**SIGNIFICANCE OF FINDINGS**

The results of this study demonstrate that after removing proteins from rice starch, the dispersion of rice starch in LDPE matrix was improved and subsequently led to improving the tensile properties of LDPE/rice starch blends. PE-g-MA improved the interfacial properties between rice starch and LDPE so as to improve tensile properties of LDPE/rice starch blends.

**ACKNOWLEDGMENTS**

The authors thank the Arkansas Rice Research and Promotion Board for financial support.

**LITERATURE CITED**


Fig. 1. SEM micrographs of fracture surface of LDPE/rice starch (protein removed) blends with different weight fractions of starch to LDPE for (a) 5%, (b) 10%, (c) 20%, and (d) 30%.
Fig. 2. SEM micrographs of fracture surface of LDPE/rice starch/glycerol/PE-g-MA with different weight fractions of starch to LDPE for (a) 5%, (b) 10%, (c) 20%, and (d) 30%.
Fig. 3. Tensile properties of rice starch composites. Starch (RP): removed protein starch.