

# Effects of Glycerol and PE-g-MA on Morphology, Thermal and Tensile Properties of LDPE and Rice Starch Blends

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**ABSTRACT:** The effects of glycerol and polyethylene-grafted maleic anhydride (PE-g-MA) on the morphology, thermal properties, and tensile properties of low-density polyethylene (LDPE) and rice starch blends were studied by scanning electron microscopy (SEM), differential scanning calorimetry, and the Instron Universal Testing Machine, respectively. Blends of LDPE/rice starch, LDPE/rice starch/glycerol, and LDPE/rice starch/glycerol/PE-g-MA with different starch contents were prepared by using a laboratory scale twin-screw extruder. The distribution of rice starch in LDPE matrix became homogenous after the addition of glycerol. The interfacial adhesion between rice starch and LDPE was improved by the addition of PE-g-MA as demonstrated

by SEM. The crystallization temperatures of LDPE/rice starch/glycerol blends and LDPE/rice starch/glycerol/PE-g-MA blends were similar to that of pure LDPE but higher than that of LDPE/rice starch blends. Both the tensile strength and the elongation at break followed the order of rice starch/LDPE/glycerol/PE-g-MA blends > rice starch/LDPE/glycerol > LDPE/rice starch blends. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 344–350, 2004

**Key words:** polyethylene; mechanical properties; morphology; rice starch; polyethylene-grafted maleic anhydride (PE-g-MA); glycerol

## INTRODUCTION

Research on biodegradable polymers has been very active owing to environment pollution concerns by nondegradable plastic wastes. Although many pure biodegradable polymers such as polycaprolactone, polyhydroxyalkanoates, and poly(lactic acid) possess the required properties and can be used for the production of blown film and injection-molded materials, they are not widely used because of their high costs.

Starches from various sources are among the most abundant, renewable, and inexpensive natural biopolymers. The use of starch to partially replace synthetic plastics will reduce the dependence on petroleum and plastic waste. However, biodegradable plastics from starch cannot compete with conventional plastics because of their poor mechanical properties. It is generally accepted that starch must be combined with other materials, such as synthetic polymers, to produce satisfactory plastics because starch alone is brittle and sensitive to water.<sup>1</sup> However, common polymers such as polyethylene are immiscible with starch because of their differences in polarity. The most effective way to enhance the compatibility and mechanical properties of starch and polymers is to improve the dispersion and interfacial

properties between starch and synthetic polymer with addition of compatibilizer.<sup>2–7</sup>

Currently, corn starch is the predominant starch used in biodegradable materials because of its availability and low cost; however, polyethylene plastics containing corn starch generally have undesirable mechanical properties, possibly because of the large granular size of corn starch. The average granular size of corn starch is 25  $\mu\text{m}$  compared with 4  $\mu\text{m}$  for rice starch. Rice starch potentially offers a good source of filler for biodegradable plastics with desirable mechanical properties<sup>8</sup> because of its small granular size and commercial availability. However, rice starch tends to form multigranular agglomerates and the intraagglomerate void volume reduces the packing fraction, resulting in low maximum packing fraction, which is called fractional solid content,<sup>9</sup> and will lead to decreases in mechanical properties.<sup>10</sup> In the present study, glycerol was used as a dispersing agent to improve the dispersion of rice starch in LDPE and to reduce the agglomeration phenomenon. The effects of incorporating a commercially available compatibilizer, polyethylene-grafted maleic anhydride (PE-g-MA), on the morphology, thermal, and tensile properties of LDPE/rice starch blends were also investigated.

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## EXPERIMENTAL

### Materials

Low-density polyethylene (LDPE, LDPE 640I, Dow Chemical Co., Midland, MI) with a melt flow index of

2 g/10 min was used. Native rice starch was obtained from A&B Ingredients Inc. (Fairfield, NJ). Rice starch was dried at 120°C for 24 h to a moisture content of less than 1% prior to sample preparation. PE-g-MA with an approximate maleic anhydride content of 3 wt % was purchased from Aldrich Chemical Company Inc. (Milwaukee, WI). Glycerol was reagent grade from EM Science (Gibbstown, NJ).

### Samples preparation

Rice starch, glycerol (25% of starch weight), PE-g-MA (10% of starch weight<sup>11</sup>), and LDPE were premixed at room temperature by using a KitchenAid mixer (St. Joseph, MI) at starch-to-LDPE ratios of 5, 10, 20, and 30% (w/w). These mixtures were then melt-blended in a laboratory scale twin-screws counter-rotating extruder (PolyLab, ThermoHaake, Madison, WI) at 170°C and 50 rpm. The plain LDPE was subjected to same procedure as the LDPE starch composites.

### Morphology observation

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

### Thermal analysis

The thermal properties of the blends were determined by using a Perkin-Elmer Pyris-1 Differential Scanning

Calorimeter (DSC, Norwalk, CT). Samples were heated from 25 to 180°C, cooled to 25°C, and reheated to 180°C at a rate of 10°C/min. The peak temperature of the first cooling curve was termed the crystallization temperature ( $T_c$ ) and the peak temperature of the second heating curve was termed the melting temperature ( $T_m$ ).

### Tensile properties

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

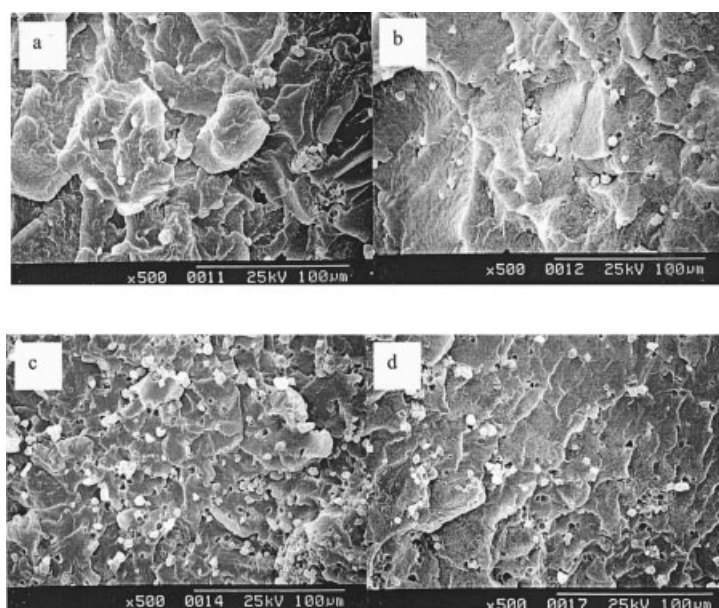
### Statistical analysis

The general linear model procedure (SAS Software Institute, Cary, NC, 1999) was used to identify a difference among data. All significant differences were reported at the 95% confidence level.

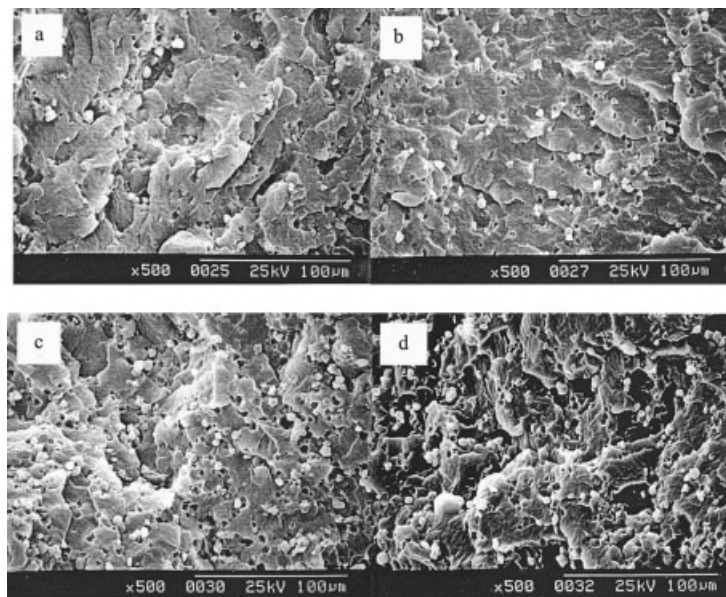
## RESULTS AND DISCUSSION

### Morphology

The morphology structure of polymer blends is very important because it ultimately determines many properties of the polymer blends, such as viscoelastic properties and solid mechanical and adhesive properties.<sup>12</sup> For LDPE/rice starch blends, starch was the filler because the granular structure of starch was neither destroyed nor melted during processing. Thus,



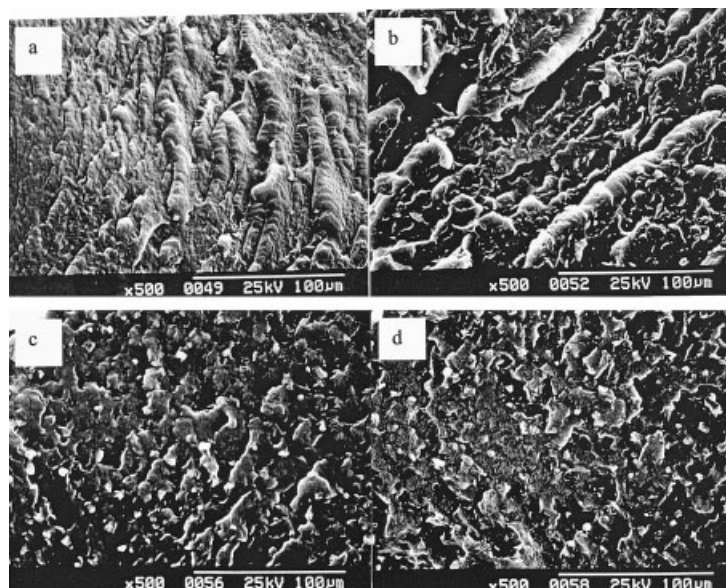
**Figure 1** SEM micrographs of fracture surface of LDPE/rice starch blends with different starch to LDPE ratios (w/w) (a) 5%, (b) 10%, (c) 20%, and (d) 30%.



**Figure 2** SEM micrographs of fracture surface of LDPE/rice starch/glycerol blends with different starch-to-LDPE ratios (w/w) (a) 5%, (b) 10%, (c) 20%, and (d) 30%.

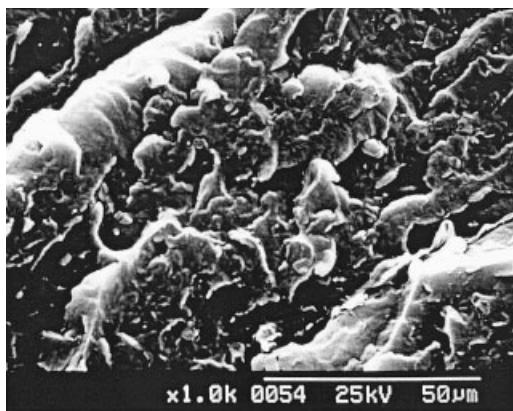
the dispersion of the rice starch in the LDPE was critical, which affected the mechanical properties of the resulting blends. Figure 1 shows the SEM micrographs of LDPE/rice starch blends with different rice contents. The rice starch was still granular in structure and agglomerates were noted even at low rice starch contents, which was indicative of heterogeneous dispersion of rice starch in LDPE. The smooth surface of rice starch and the distinct interfacial appearance between rice starch and LDPE suggested that there was little interaction but large interfacial tension between

them. The SEM micrographs of LDPE/rice starch/glycerol blends are shown in Figure 2. The amount of glycerol addition was 25% of rice starch weight based on our preliminary results. In comparison with Figure 1, the dispersion of rice starch in the LDPE was greatly improved after the addition of glycerol and few starch agglomerates were observed, indicating that glycerol was a good dispersing agent for rice starch in the LDPE. The improved dispersion was attributed to a stronger interaction between starch and glycerol than the interaction between starch granules under the pro-



**Figure 3** SEM micrographs of fracture surface of LDPE/rice starch/glycerol/PE-g-MA blends with different starch-to-LDPE ratios (w/w) (a) 5%, (b) 10%, (c) 20%, and (d) 30%.





**Figure 4** SEM micrograph of fracture surface of LDPE/rice starch/glycerol/PE-g-MA blends with starch content of 20%.

cessing conditions, thus decreasing rice starch agglomeration. Although glycerol improved the dispersion of rice starch in the LDPE matrix, the interfacial adhesion between rice starch and LDPE remained poor because the interface between starch and LDPE was still distinct.

Figure 3 shows the morphology of LDPE/rice starch/glycerol/PE-g-MA blends with different starch contents. The amount of PE-g-MA addition was 10% of rice starch weight based on our previous results.<sup>11</sup> With the addition of PE-g-MA, the distinction between rice starch and LDPE became unclear as compared with the blends without it (Figs. 1 and 2), and the surface of rice starch became coarse, which is a typical characteristic of compatibilized blends. The improved interaction between starch and PE-g-MA is evident, as shown in Figure 4. The rice starch surface was not smooth but covered with materials, which adhered to the LDPE matrix. Because LDPE had little interaction with rice starch as demonstrated in Figures 1 and 2, the materials on the starch surface were assumed to be PE-g-MA. The improved interfacial adhesion was attributed to chemical reaction between hydroxyl groups in rice starch and anhydride groups in PE-g-MA under extrusion conditions of high temperature

and high shear<sup>5,6</sup> and the strong physical interaction between LDPE and PE-g-MA.

**Thermal properties**

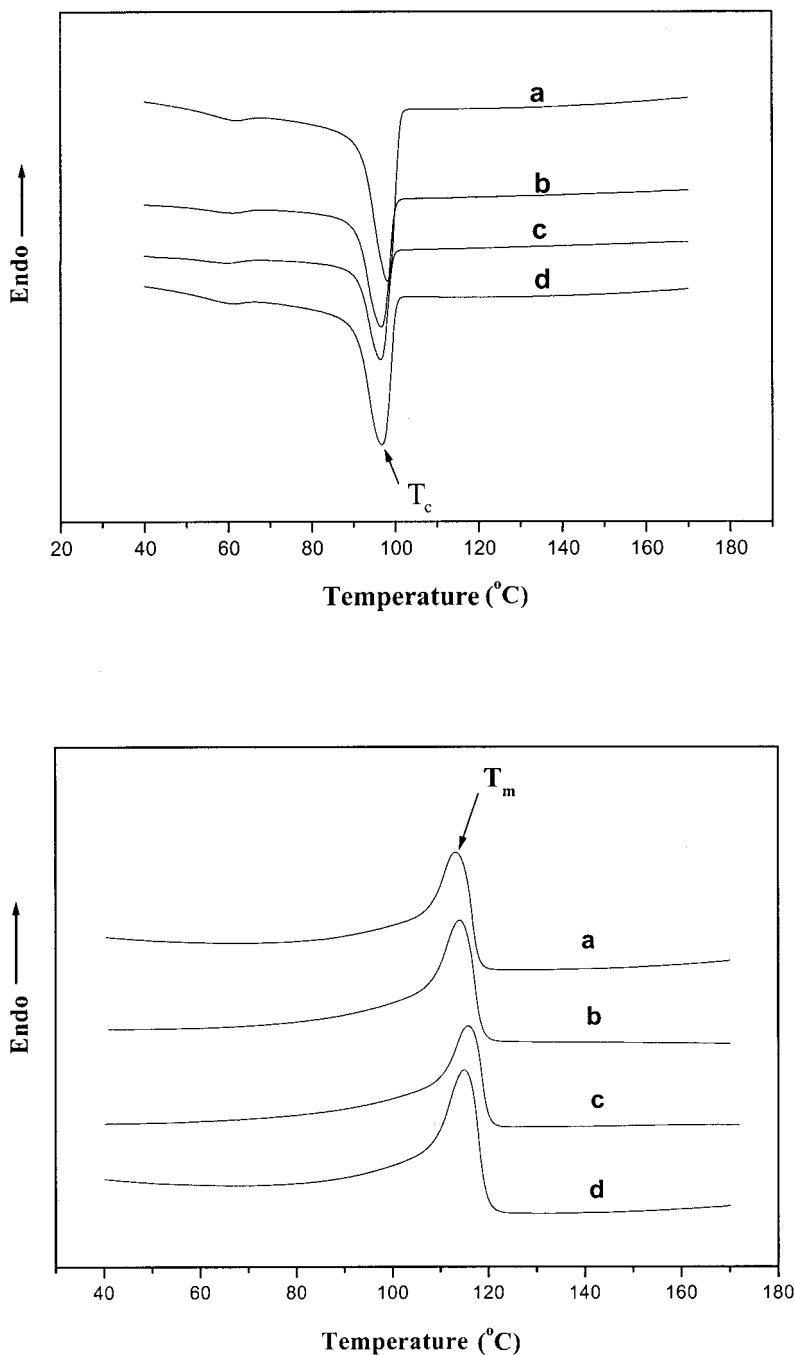
The crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) of different rice starch and LDPE blends are summarized in Table I. Both  $T_c$  and  $T_m$  were properties of LDPE because starch was not gelatinized nor melted during extrusion (Figs. 1–3). The  $T_c$  of LDPE decreased with the addition of rice starch, which agreed with our recent study of corn starch and LDPE.<sup>11</sup> The negative effect on the crystallization of LDPE from starch can be possibly explained by the following two reasons. The addition of starch hindered the crystallization of LDPE, which is branched in nature,<sup>13</sup> resulting in more complex and less perfect crystallization of LDPE during cooling. The other possible reason was that the migration and diffusion of molecular chains of long-chain branched polyethylene to the crystal surface of short-chain branched polyethylene was limited by interfacial tension between starch and LDPE, thus depressing the crystallization of LDPE during cooling. The  $T_m$  of LDPE in the blends increased with increasing starch content, agreeing with the corresponding decreasing  $T_c$ . Hence, rice starch not only affected crystallization but also melting behavior of LDPE.

The significantly increased  $T_c$  after the addition of glycerol as compared with blends without glycerol suggested that glycerol reduced the negative impact on crystallization of LDPE from rice starch, resulting in  $T_c$  closer to pure LDPE. However, the trend in  $T_m$  was not as clear. This result was possibly attributed to the interaction between starch and glycerol. After the addition of PE-g-MA, the  $T_c$  did not change but  $T_m$  decreased significantly, except for the 5% starch fraction, compared with blends without PE-g-MA. The curves of LDPE/rice starch blends (100/30) without and with PE-g-MA as well as pure LDPE are presented in Figure 5. The addition of PE-g-MA did not further increase the  $T_c$  of LDPE/rice starch/glycerol blends to be close to pure LDPE but did decrease the  $T_m$  to be close to pure LDPE.

**TABLE I**  
**Thermal Properties of LDPE/Rice Starch Blends**

Starch fraction (w/w, %)	Crystallization temperature ( $T_c$ )			Melting Temperature ( $T_m$ )		
	LDPE/rice starch	LDPE/rice starch/glycerol	LDPE/rice starch/glycerol/PE-g-MA	LDPE/rice starch	LDPE/rice starch/glycerol	LDPE/rice starch/glycerol/PE-g-MA
0	98.05 <sup>a*</sup>	—	—	113.14 <sup>a</sup>	—	—
5	96.88 <sup>b</sup>	97.72 <sup>a</sup>	97.37 <sup>a</sup>	114.13 <sup>b</sup>	113.80 <sup>a</sup>	114.29 <sup>a</sup>
10	96.54 <sup>c</sup>	97.21 <sup>b</sup>	97.21 <sup>b</sup>	115.13 <sup>c</sup>	114.97 <sup>b</sup>	114.47 <sup>b</sup>
20	96.54 <sup>c</sup>	96.96 <sup>c</sup>	97.06 <sup>c</sup>	115.13 <sup>c</sup>	115.80 <sup>c</sup>	114.30 <sup>a</sup>
30	96.54 <sup>c</sup>	96.80 <sup>d</sup>	96.80 <sup>d</sup>	115.13 <sup>c</sup>	115.82 <sup>c</sup>	114.96 <sup>c</sup>

\* Mean values in the same column with same letters are not significantly different ( $P < 0.05$ ).

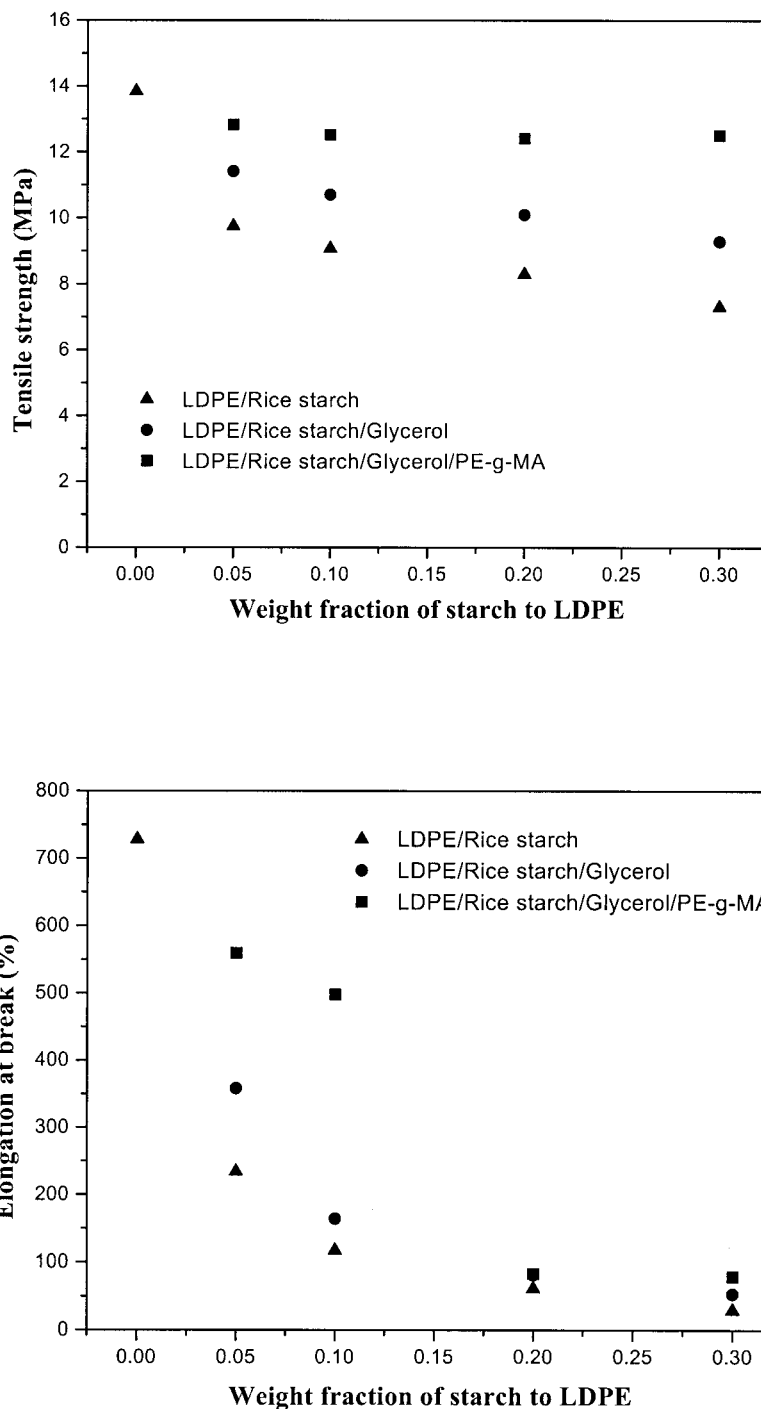


**Figure 5** DSC curves for (a) LDPE, (b) LDPE/starch (100/30, weight basis), (c) LDPE/starch/glycerol (100/30/7.5, weight basis), and (d) LDPE/starch/glycerol/PE-g-MA (100/30/7.5/3, weight basis).

### Tensile properties

The distribution of a dispersed phase in the matrix phase and the interfacial adhesion between a dispersed phase and the matrix are key factors determining the mechanical properties of polymer blends.<sup>14</sup> A dispersed phase with a small particle size and a homogenous distribution will improve the ability of the resulting blend to tolerate external force, resulting in a more homogenous distribution of stress and better

mechanical properties of the blend. The tensile properties of different LDPE and rice starch blends are shown in Figure 6. When rice starch content increased, the tensile strength and elongation at break of LDPE/rice starch blends decreased, presumably because of heterogeneous dispersion of starch in LDPE matrix and incompatibility of LDPE and starch. The heterogeneous dispersion of starch in the LDPE matrix would cause a very significant stress concentration,



**Figure 6** Tensile properties of LDPE/rice starch blends, LDPE/rice starch/glycerol blends, and LDPE/rice starch/glycerol/PE-g-MA blends.

which led to initial microvoids or craze and quick development into crack during deformation.<sup>15,16</sup> Consequently, the material would break at a low load and displacement. After the addition of glycerol, the tensile properties of LDPE/rice starch blends were improved from the homogenous dispersion of rice starch in the LDPE matrix, which was supported by SEM and DSC results. Nevertheless, because the interfacial

properties between starch and LDPE were not improved so much with addition of glycerol as demonstrated by SEM morphology structure (starch granules were not coated by matrix), the tensile strength improved, but not to a great extent.

When PE-g-MA was added to rice starch/LDPE/glycerol blends, the tensile strength and elongation at break of the resulting blends were further improved,

particularly tensile strength at high starch contents and elongation at break at low starch contents. When rice starch content was 20% or higher, there was no difference among the different blends, presuming the distance between the starch particles was the predominant factor determining the property of elongation at break. Both dispersing agent and compatibilizer did not exert a significant effect on this property when starch content was equal or over 20%. It is believed that PE-g-MA increased the interfacial adhesion between the LDPE matrix and the starch filler by locating between them and interacting with them. The improved interfacial adhesion played an important role in the process of stress transfer, thus reducing the chance of interfacial debonding and leading to improved tensile properties. In addition, these results also provided support that the starch and PE-g-MA interaction was between hydroxyl groups in rice starch and anhydride groups in PE-g-MA.<sup>5</sup>

### CONCLUSION

Although rice starch has a small granular size, the tensile properties of LDPE/rice starch blends were inferior due to inherent multigranular agglomeration. The addition of glycerol improved the dispersion of rice starch in LDPE matrix and consequently their tensile properties, presuming a result of a stronger interaction between starch and glycerol under the processing conditions. Nevertheless, glycerol did not improve the interfacial properties between rice starch and LDPE because of no interaction between LDPE

and glycerol. The interfacial adhesion between rice starch and LDPE was improved with the addition of PE-g-MA. Results from DSC, SEM, and tensile properties suggest that the improved compatibility between rice starch and LDPE from PE-g-MA was attributed to the chemical reaction between hydroxyl groups in starch and anhydride groups in PE-g-MA and the physical interaction between the PE in PE-g-MA and LDPE.

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### References

1. Roper, H.; Koch, H. *Starch/Starke* 1990, 42, 123.
2. Willett, J. L. *J Appl Polym Sci* 1994, 54, 1685.
3. Vaidya, U. R.; Bhattacharya, M. *J Appl Polym Sci* 1994, 52, 617.
4. Prinos, J.; Bikiaris, D.; Theologidis, S.; Panayiotou, C. *Polym Eng Sci* 1998, 38, 954.
5. Bikiaris, D.; Panayiotou, C. *J Appl Polym Sci* 1998, 70, 1503.
6. Sailaja, R. R. N.; Chanda, M. *J Polym Mater* 2000, 17, 165.
7. Sailaja, R. R. N.; Chanda, M. *J Appl Polym Sci* 2001, 80, 863.
8. Lim, S.; Jane, J.; Rajagopalan, S.; Seib, P. A. *Biotechnol Prog* 1992, 8, 51.
9. Willett, J. L. *Cereal Chem* 2001, 78, 64.
10. Wang, Y.-J.; Liu, W.; Sun, Z. *J Mater Sci Lett* 2003, 22, 57.
11. Liu, W.; Wang, Y.-J.; Sun, Z. *J Appl Polym Sci* 2003, 88, 2904.
12. Paul, D. R.; Newman, S. in *Polymer Blends*; Academic Press: New York, 1978; p. 35.
13. Drummond, K. M.; Hopewell, J. L.; Shanks, R. A. *J Appl Polym Sci* 2000, 78, 1009.
14. Jang, B. Z.; Uhmman, D. R.; Sande, J. B. V. *Polym Eng Sci* 1985, 25, 643.
15. Kramer, E. J. *Adv Polym Sci* 1990, 91/92, 1.
16. Liang, J. Z.; Li, R. K. Y.; Tjong, S. C. *Polym Eng Sci* 2000, 40, 2105.