

# Effects of Polyethylene-Grafted Maleic Anhydride (PE-g-MA) on Thermal Properties, Morphology, and Tensile Properties of Low-Density Polyethylene (LDPE) and Corn Starch Blends

W. Liu\*, Y.-J. Wang, Z. Sun

Department of Food Science, University of Arkansas, Fayetteville, Arkansas 72704

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**ABSTRACT:** The effects of polyethylene-grafted maleic anhydride (PE-g-MA) on the thermal properties, morphology, and tensile properties of blends of low-density polyethylene (LDPE) and corn starch were studied with a differential scanning calorimeter (DSC), scanning electron microscope (SEM), and Instron Universal Testing Machine, respectively. Corn starch-LDPE blends with different starch content and with or without the addition of PE-g-MA were prepared with a lab-scale twin-screw extruder. The crystallization temperature of LDPE-corn starch-PE-g-MA blends was similar to that of pure LDPE but higher than that of

LDPE-corn starch blends. The interfacial properties between corn starch and LDPE were improved after PE-g-MA addition, as evidenced by the structure morphology revealed by SEM. The tensile strength and elongation at break of corn starch-LDPE-PE-g-MA blends were greater than those of LDPE-corn starch blends, and their differences became more pronounced at higher starch contents. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2904–2911, 2003

**Key words:** polyethylene (PE); mechanical properties; morphology; thermal properties

## INTRODUCTION

Plastics have become one of the most important materials in our daily life over the past four decades. However, with time, environmental pollution from consumed plastics becomes serious, particularly from package materials, disposable containers, and agriculture mulch films. With tighter environmental regulations and increasing waste disposal costs, plastic manufacturers are forced to seek solutions or alternatives. Polymer recycling is an environmentally attractive solution but has not been successful on a worldwide scale. It is estimated that only 1% of the produced plastics is recycled worldwide, whereas the remaining majority portion goes to municipal burial sites. Thus, in the last 20–30 years, there has been an increased interest in the production and use of fully biodegradable polymers with the main goal of replacing nonbiodegradable plastics. Commercially available biodegradable synthetic plastics include polycaprolactone (PCL), polyhydroxyalkanotes, poly(3-hydroxybutyrate) (PHB),

poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), poly(lactic acid) (PLA), poly(butylene succinate), poly(butylene succinate-co-adipate), and poly(vinyl alcohol). Although many of these polymers 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 botanical sources are among the most abundant, renewable, and inexpensive natural biopolymers. Using starch to partially replace synthetic plastics will not only reduce the dependence on petroleum but also reduce plastic waste. However, biodegradable plastics from starch cannot compete with conventional petroleum-based plastics because of their poor mechanical properties. It is known that starch must be combined with other materials, like synthetic polymers, to produce satisfactory plastics because starch alone is brittle and sensitive to water.<sup>1</sup> Two major technologies for starch addition to plastics have been developed. One is based on the use of thermoplastic starch (gelatinized starch) as an integral part of the polymeric structure, and the other one is based on the use of native starch (granular starch) as the filler. In the last 30 years, various synthetic polymers have been combined with starches to prepare more biodegradable plastics,<sup>2–6</sup> such as ethylene-propylene copolymers, PCL, PLA, polyethylene (PE), and polystyrene (PS).

Correspondence to: Y.-J. Wang (yjwang@uark.edu).

\*Permanent address: State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Peoples Republic of China

Most research on starch and synthetic polymers blends has been focused on common plastics such as PE. However, PE and starch are immiscible because of their differences in polarity; that is, starch is hydrophilic whereas PE is hydrophobic. To improve their compatibility, various attempts have been made to modify either starch or PE.<sup>7-10</sup> It was found that plasticizers, coupling agents, or modified starch only partially improved the dispersion of starch in PE and their interfacial properties because of their limited interaction. Another approach was to use poly(ethylene-co-acrylic acid), poly(ethylene-co-vinyl alcohol), or oxidized PE as a compatibilizer in PE-starch composites, but the composites had unsatisfactory mechanical properties.<sup>11-13</sup> The inferior mechanical properties were a result of weak interaction (e.g., hydrogen bonding) between starch and compatibilizer and limited opportunities for compatibilizer to interact with PE.

More recently, an increased interest has appeared in the use of polymers containing reactive groups (e.g., maleic anhydride) as compatibilizers.<sup>14-17</sup> It was discovered that anhydride groups could react with the hydroxyl groups in starch to produce chemical bonding, thus improving the dispersion of starch, the interfacial adhesion, and, subsequently, the mechanical properties of the resultant blends. Nevertheless, most research involving blending with PE employs thermoplastic starch<sup>15-17</sup> that consists of reactive groups because thermoplastic starch has been shown to improve processing properties.<sup>18</sup> In recent studies, Sailaja and Chanada concluded that PE-plasticized starch blends performed better than dry starch blends,<sup>15,16</sup> however, the dry starch blends exhibited a greater tensile strength than the plasticized starch blends.

This work was undertaken to study the effects of PE-grafted maleic anhydride (PE-g-MA) as a compatibilizer on the thermal properties, morphology, and tensile properties of low-density PE (LDPE) and granular corn starch blends.

## EXPERIMENTAL

### Materials

Low-density polyethylene (LDPE; LDPE 640I, Dow Chemical Company, Midland, MI) with a melt flow index of 2 g/10 min was used. Common corn starch was obtained from Cerestar USA, Inc. (Hammond, IN). Corn starch was dried at 120°C for 24 h to a moisture content of <1% prior to sample preparation. PE-g-MA with an approximate MA content of 3 wt % was purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI).

### Sample preparation

Corn starch and LDPE (25:100) were pre-mixed at room temperature with a KitchenAid mixer (St. Joseph, MI) with different amounts of compatibilizer (PE-g-MA at 0, 5, 10, 15, 20, 25, and 35%, w/w, based on starch) to determine the critical saturated interfacial concentration of PE-g-MA for the corn starch and LDPE system. These mixtures were then melt-blended in a lab-scale twin-screw counter-rotating extruder (PolyLab, ThermoHaake, Madison, WI) at 170°C and 50 rpm.

Once the critical saturated interfacial concentration of PE-g-MA was identified, corn starch, PE-g-MA (the critical value based on starch weight), and LDPE were blended at starch-to-LDPE ratios of 5, 10, 15, 20, and 25% (w/w) according to aforementioned procedure.

### Thermal analysis

The thermal properties of the blends were determined with a Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC). Samples were heated from 25 to 180°C, cooled to 25°C, and then 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 curves was termed the melting temperature ( $T_m$ ).

### Morphology observation

The blends were fractured in liquid nitrogen, and the fracture surface was observed with a Hitachi S-2300 scanning electron microscope (Tokyo, Japan) at an accelerating voltage of 25 KV. The fracture surfaces were sputter coated with gold prior to examination.

### Tensile properties

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

### Statistical analysis

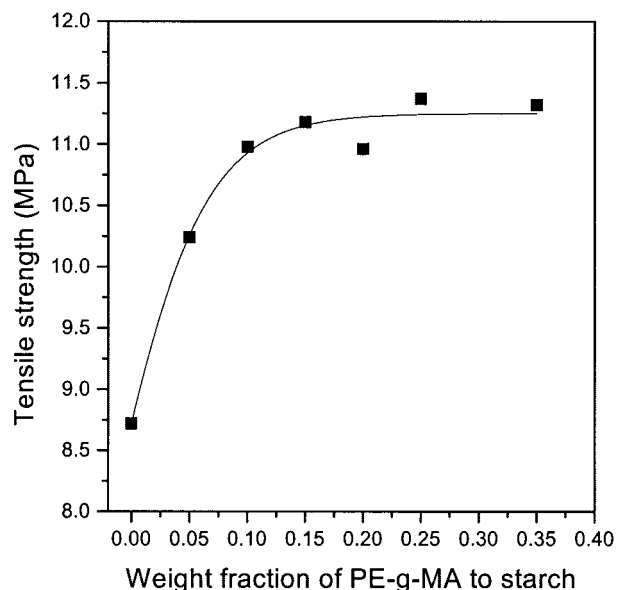
The general linear model procedure (SAS Software Institute, Cary, NC, 1999) was used to identify difference among data. All significant differences were reported at the 95% confidence level.

## RESULTS AND DISCUSSION

### Critical interfacial concentration

An interfacial agent (i.e., compatibilizer) is needed to increase the compatibility and reduce the interfacial tension between components in immiscible polymer blends to obtain desired final properties. The concentration of compatibilizer in the interface of two immiscible components will determine the efficacy of compatibilization. The critical interfacial concentration is the minimum value of interfacial saturation of an interfacial agent in the dispersed phase, which is an important parameter for the interfacial state between polymer components.<sup>19</sup> When the concentration is above or below this critical value, the compatibilizer is not effective in improving the compatibilization of the polymer blends. The critical interfacial concentration is generally obtained from the emulsification curves, which relate the average dispersed phase particle diameter to the amount of added compatibilizer in the blends.<sup>20–22</sup> This method is useful to characterize the morphology and the efficacy of a compatibilizer for a given interface. The curves of tensile strength and impact strength versus the concentration of the compatibilizer also exhibit the same trends as the emulsification curves.<sup>21,22</sup> In fact, the dispersed phase particle size, tensile strength and impact strength all reflect the interfacial state (e.g., interfacial tension and adhesion). For the LDPE and starch blends, the emulsification curves were not suitable to determine the critical concentration because the starch granular size did not change with composition and with the addition of the compatibilizer. Therefore, the curve of tensile strength versus the amount of compatibilizer was used in the present study to characterize the interfacial state between starch and LDPE.

The curve of tensile strength of starch and LDPE (25/100) blends versus the fraction of compatibilizer-to-starch is shown in Figure 1. When the PE-g-MA content was <10%, the tensile strength increased rapidly, indicating that the interface between starch and LDPE was not saturated and their interfacial adhesion was still weak. When the PE-g-MA content was >10%,



**Figure 1** Plot of tensile strength of starch and LDPE (25:100) blends versus the concentration of PE-g-MA.

the tensile strength leveled off, implying that the interface between starch and LDPE was saturated by PE-g-MA and the interfacial tension reached a minimum value. This result indicates that the critical saturated interfacial concentration of PE-g-MA was ~10% of starch weight for the starch and LDPE (25:100) blends. Because the ratio of surface area-to-corn starch weight was constant and the starch granule size did not change with the composition of starch and LDPE blends, the critical interfacial concentration of PE-g-MA was only related to the starch weight. Thus, the critical interfacial concentration of PE-g-MA used 10% of the starch weight in all corn starch and LDPE systems.

### Thermal properties

The crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) of corn starch-LDPE blends with and without PE-g-MA are summarized in Table I. Both  $T_c$

**TABLE I**  
Thermal Properties of LDPE-Corn Starch Blends

Starch-to-LDPE (w/w, %)	Crystallization temperature ( $T_c$ )		Melting temperature ( $T_m$ )	
	Without PE-g-MA	With PE-g-MA	Without PE-g-MA	With PE-g-MA
0	98.05 <sup>a</sup>		113.14 <sup>a</sup>	
5	97.70 <sup>b</sup>	98.04 <sup>a</sup>	114.12 <sup>b</sup>	114.21 <sup>a,b</sup>
10	97.37 <sup>c</sup>	97.88 <sup>b</sup>	114.95 <sup>c</sup>	114.13 <sup>c,b</sup>
15	97.13 <sup>d</sup>	97.87 <sup>b</sup>	114.87 <sup>c</sup>	114.38 <sup>a</sup>
20	96.87 <sup>e</sup>	97.88 <sup>b</sup>	114.95 <sup>c</sup>	114.27 <sup>a,b</sup>
25	96.86 <sup>e</sup>	97.83 <sup>b</sup>	114.88 <sup>c</sup>	113.95 <sup>c</sup>

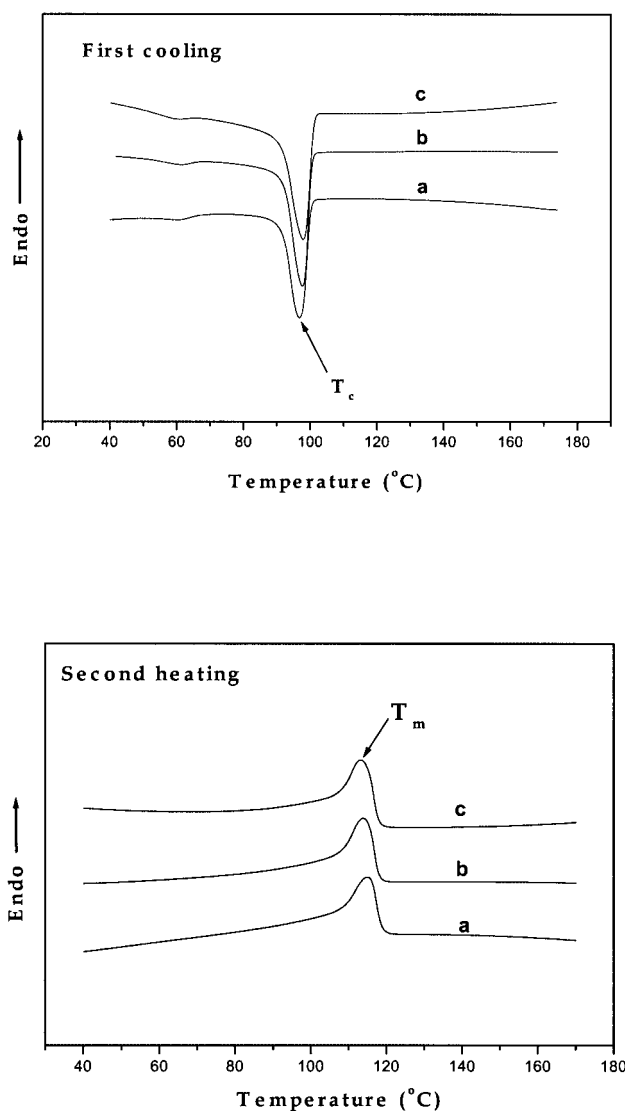
<sup>a–e</sup> Mean values in the same column with same letters are not significantly different ( $p < 0.05$ ).

and  $T_m$  were properties of LDPE because starch was neither plasticized nor melted in the absence of plasticizer during extrusion. The  $T_c$  of LDPE decreased with increasing corn starch content. This result has not been previously reported for PE and starch blends, but a similar phenomenon was noted for blends of starch with biodegradable polyesters, such as PHB and PHBV.<sup>23</sup> The negative effect on the crystallization of LDPE from starch can be possibly explained by the following two reasons. First, the addition of starch hindered the molecular motion of LDPE in the supercooling melt during cooling. Because of the branched nature of LDPE,<sup>24</sup> the crystallization of LDPE is more complex and less perfect. When starch was added, the crystallization of LDPE became even more complex. On one hand, the dispersion of starch in LDPE matrix decreased the nucleus density of LDPE.<sup>25</sup> On the other hand, the presence of starch hindered the migration of the nucleus of LDPE. The other possible reason is that the interfacial tension between starch and LDPE limited the migration and diffusion of molecular chain of long-chain branched PE to the crystal surface of short-chain branched PE, thus depressing the crystallization of LDPE during cooling. In other words, interfacial tension limited the motion of LDPE to the nucleus and hindered the crystal growth on the surface of starch.<sup>26</sup> When the starch content increased, the interface between starch and LDPE increased and the depression on LDPE from starch became more pronounced. The  $T_m$  of LDPE in the blends increased with increasing the starch content. Hence, starch not only affected crystallization but also the melting behavior of LDPE.

When PE-g-MA was added to LDPE-starch blends, the  $T_c$  was largely unaffected but the  $T_m$  showed a trend similar to that for blends without PE-g-MA. The curves of corn starch-LDPE (25:100) blend without and with PE-g-MA, as well as pure LDPE, are shown in Figure 2. The  $T_c$  in the blends was close to that of pure LDPE with the addition of PE-g-MA, indicating that PE-g-MA reduced the effects of starch on crystallization of LDPE. It is assumed that PE-g-MA interacted with starch during extrusion and reduced the interfacial tension between starch and LDPE so that the nucleus would migrate to the interface and LDPE crystals would grow on the compatible interface between LDPE and PE-g-MA.<sup>27</sup>

### Morphology

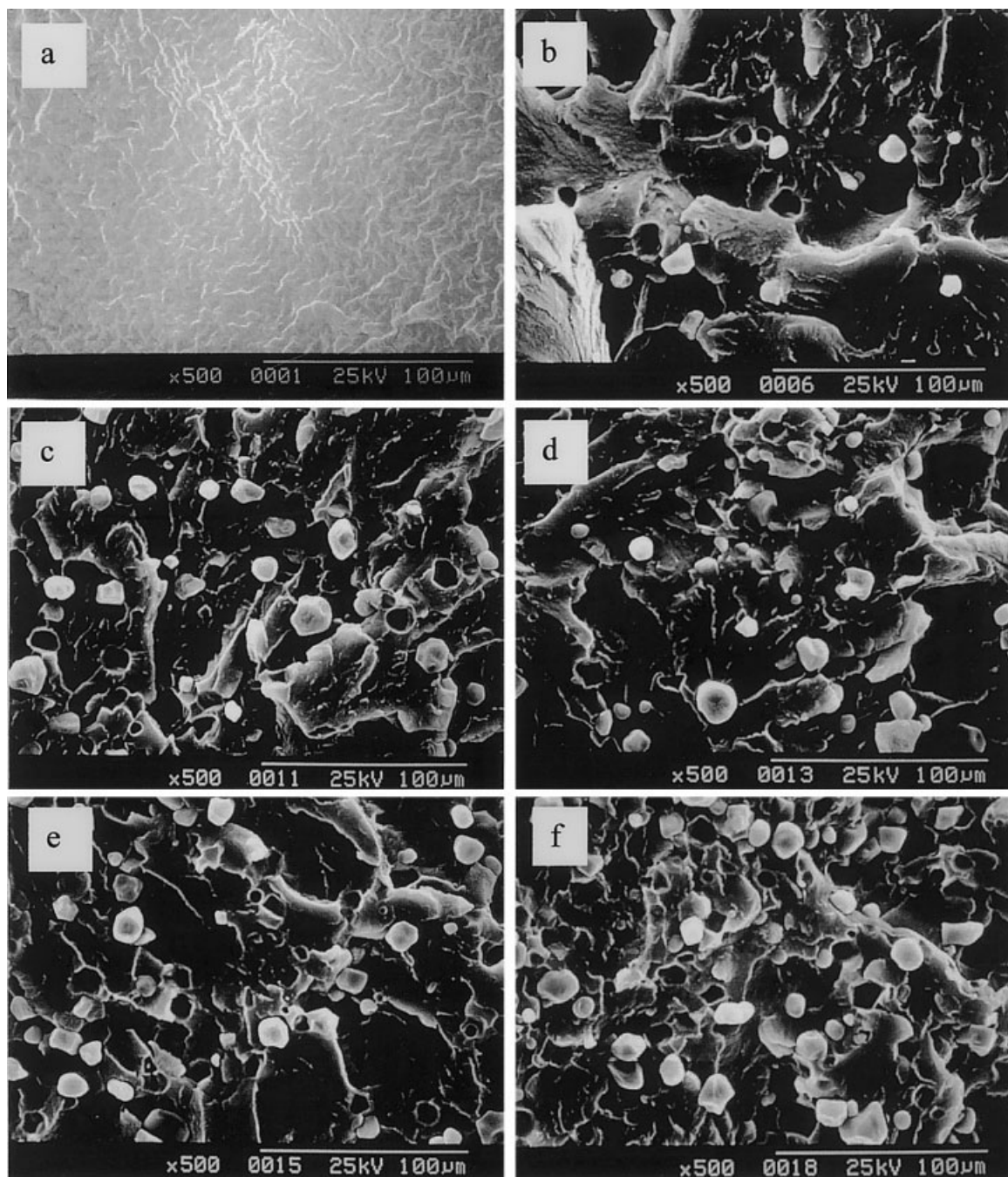
The morphology structure of polymer blends is a very important characteristic because it ultimately determines many properties of the polymer blends, such as solid mechanical and adhesive properties.<sup>28</sup> In the present study, starch functioned as a filler because the granular structure of starch was retained after extrusion (Figure 3) and was homogeneously dispersed in



**Figure 2** DSC curves for (a) LDPE-corn starch (100:25), (b) LDPE-corn starch (100:25) with PE-g-MA, and (c) pure LDPE.

the LDPE matrix. The smooth surface of corn starch and the distinct interfacial appearance between corn starch and LDPE suggests that there was little interaction between them. Therefore, their interfacial tension was large and their interfacial adhesion was low, which agreed with recent results of Sailaja and Chanda.<sup>15,16</sup>

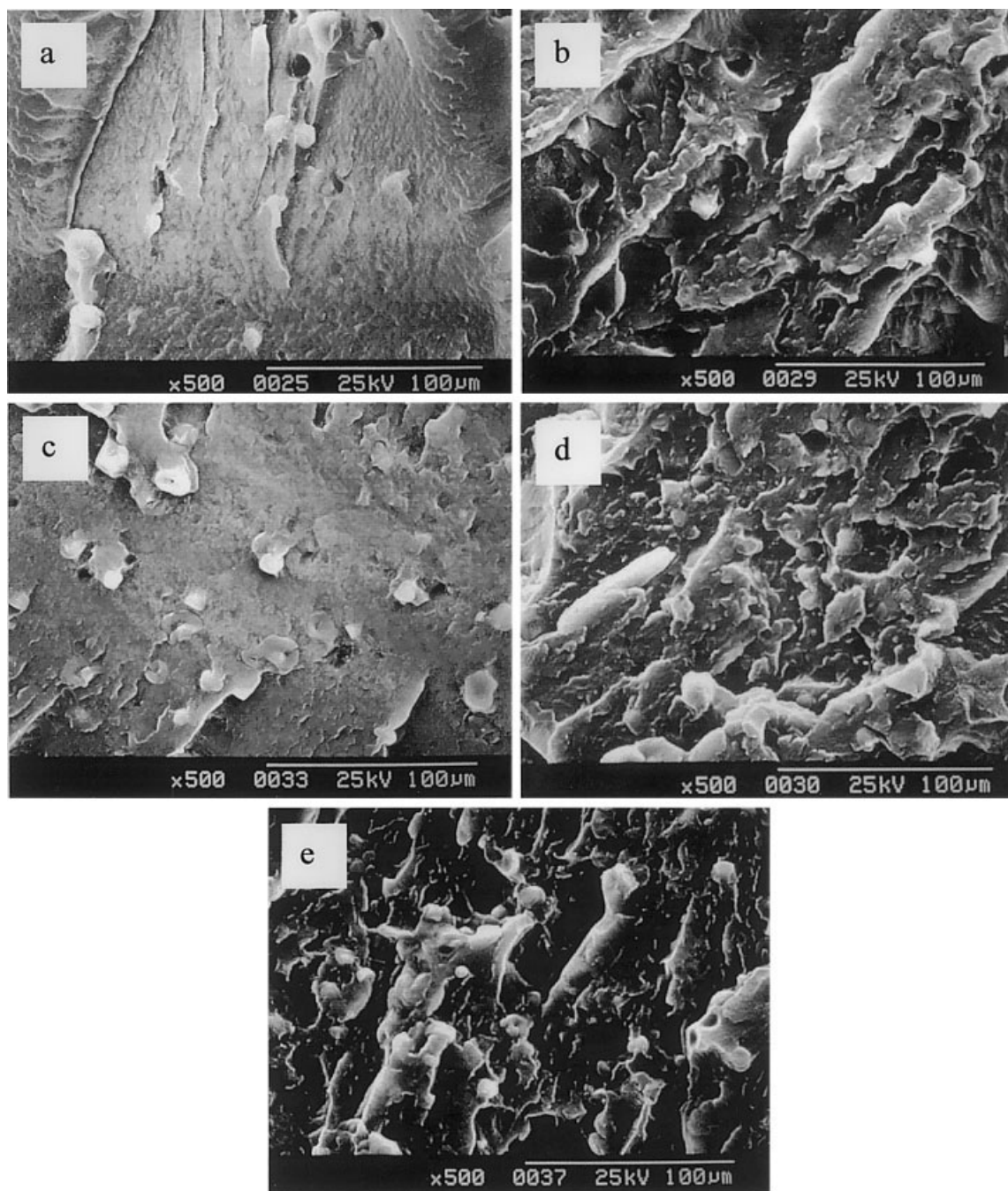
The morphology of LDPE-corn starch-PE-g-MA blends with different starch contents is shown in Figure 4. The distinction between corn starch and LDPE is not as clear as that of the blends without PE-g-MA (Figure 5), and the surface of corn starch becomes coarse. These characteristics are typical of compatibility, suggesting the occurrence of an interaction between starch and LDPE. However, in recent similar studies, Sailaja and Chanda<sup>15,16</sup> did not report these



**Figure 3** SEM micrographs of fracture surface of LDPE–corn starch blends with different starch fractions: (a) 0%, (b) 5%, (c) 10%, (d) 15%, (e) 20%, and (f) 25%.

compatibility characteristics in granular starch/PE blends nor did they show any improvement in interfacial adhesion from morphology results. The improved interaction between starch and PE-g-MA is evident in Figure 5. The corn starch surface was not smooth but covered with materials, which adhered to the LDPE matrix. Because LDPE had little interaction with corn starch, the materials on the starch surface were assumed to be PE-g-MA. PE-g-MA improved the

interfacial adhesion between LDPE and corn starch, and the improved interfacial adhesion resulted in increased miscibility. The improved interfacial adhesion was attributed to the strong chemical interaction between corn starch and PE-g-MA and the strong physical interaction between LDPE and PE-g-MA. The chemical interaction presumably resulted from reaction of hydroxyl groups in corn starch with anhydride groups in PE-g-MA under the extrusion conditions of



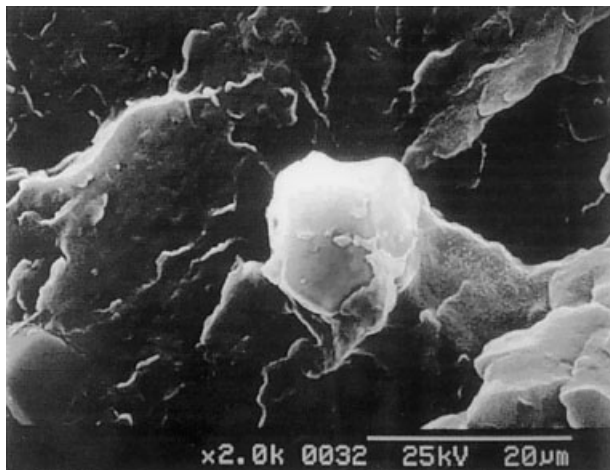
**Figure 4** SEM micrographs of fracture surface of LDPE-corn starch-PE-g-MA blends with different starch fractions: (a) 5%, (b) 10%, (c) 15%, (d) 20%, and (e) 25%.

high temperature and high shear,<sup>17</sup> with some minor interaction from their hydrophilic interaction.

When PE-g-MA was situated at the interface between starch and LDPE and interacted with both, the interfacial tension was reduced and compatibility was increased. The morphology results support the DSC results that the interaction between starch and PE-g-MA reduced the interfacial tension between starch and PE-g-MA, which in turn reduced the influence of starch on the crystallization of LDPE.

### Tensile properties

The ability of a polymeric material to resist deformation under an applied force depends on the mobility of the molecule, and the ability to deform determines the mechanical properties of the material. The molecular mobility of multiphase polymeric materials is determined by the interfacial properties because molecular mobility is discontinuous at the interface. Therefore, interfacial adhesion



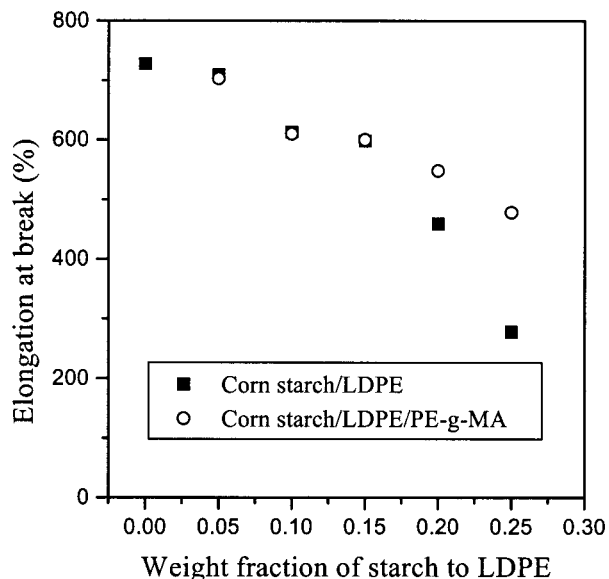
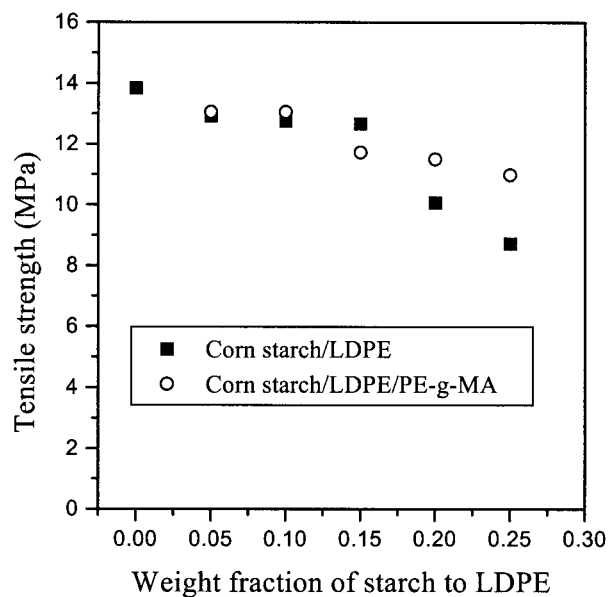
**Figure 5** SEM micrographs of the fracture surfaces of LDPE-corn starch-PE-g-MA blends.

is a very important factor for controlling the mechanical properties of multiphase materials. The tensile properties of LDPE-corn starch blends with and without PE-g-MA are shown in Figure 6. When the corn starch content increased, the tensile strength and elongation at break of LDPE-corn starch blends decreased, presumably because of incompatibility of LDPE and starch. It is possible that the inclusion of corn starch in a LDPE matrix would cause a very significant stress concentration. Therefore, fracture would be initiated from the weak interface of the blend due to their poor interfacial adhesion, thus resulting in reduced tensile properties.

When PE-g-MA was added to the blends, the tensile strength and elongation at break of the blends were improved, and the improvement was more pronounced at higher starch contents. It is believed that PE-g-MA increased adhesion between the LDPE matrix and the starch filler, which is in agreement with DSC and SEM results. The improved interfacial adhesion between LDPE and corn starch has a positive impact on the stress transfer, thus reducing the chance of interfacial debonding and leading to improved tensile properties. In addition, these results also support the assumption that the interaction between starch and PE-g-MA was a chemical one between hydroxyl groups in corn starch and anhydride groups in PE-g-MA because a polar interaction between them would not improve their properties to any significant extent.<sup>17</sup>

## CONCLUSIONS

The miscibility between granular corn starch and LDPE was improved by the addition of a commercially available compatibilizer, PE-g-MA. Results from



**Figure 6** Tensile properties of LDPE-corn starch blends with and without PE-g-MA.

DSC, SEM, and tensile analyses suggest that the improved compatibility was attributed to a 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. Therefore, it is possible to blend a high percentage of granular corn starch with LDPE while keeping comparable tensile properties.

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