

# Use of Maleic Anhydride–Grafted Polyethylene as Compatibilizer for HDPE–Tapioca Starch Blends: Effects on Mechanical Properties

R. R. N. SAILAJA, MANAS CHANDA

Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India

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**ABSTRACT:** Tapioca starch in both glycerol-plasticized and in unplasticized states was blended with high-density polyethylene (HDPE) using HDPE-*g*-maleic anhydride as the compatibilizer. The impact and tensile properties of the blends were measured according to ASTM methods. The results reveal that blends containing plasticized starch have better mechanical properties than those containing unplasticized starch. High values of elongation at break at par with those of virgin HDPE could be obtained for blends, even with high loading of plasticized starch. Morphological studies by SEM microscopy of impact-fractured specimens of such blends revealed a ductile fracture, unlike blends with unplasticized starch at such high loadings, which showed brittle fracture, even with the addition of compatibilizer. In general, blends of HDPE and plasticized starch with added compatibilizer show better mechanical properties than similar blends containing unplasticized starch. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 863–872, 2001

**Key words:** HDPE; HDPE–starch blends; HDPE-*g*-maleic anhydride; biodegradable polyethylene

## INTRODUCTION

Polyethylene is widely used as a packaging material because of its good mechanical properties and low cost. However, these qualities have been overshadowed by its highly nonbiodegradable nature, leading to waste-disposal problems, particularly in short-term packaging applications. It has been estimated that nearly 2% of all plastics ultimately reach the environment, leading to acute pollution problems.<sup>1</sup> In addition, dwindling petroleum resources have inspired consideration of various alternatives. In this context biodegradable plastics have gained considerable importance as a viable

alternative. Polyhydroxybutyrate (PHB) and polyhydroxybutyrate–valerate (PHBV) are fully biodegradable polymers that have found use in packaging applications. However, its high cost (about seven times that of conventional packaging polymers) has restricted<sup>2</sup> their use.

Another alternative is to blend conventional packaging polymers such as polyolefins with biopolymeric renewable resources including starch, chitin, chitosan, and cellulose, all of which are fully biodegradable.<sup>3–5</sup> Of these, starch is an abundantly available renewable resource. However, because it is a polar material, starch is incompatible with polyolefins, and blending the latter with starch leads to significant reduction in mechanical properties, thereby making the blend unsuitable for packaging applications.

In an early work Otey et al.<sup>6</sup> blended starch with polyethylene-*co*-acrylic acid (EAA). Griffin<sup>6</sup>

Correspondence to: M. Chanda (chanda@chemeng.iisc.ernet.in).

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patented a process of blending linear low-density polyethylene with starch (6–9%). Willett<sup>7</sup> studied the effect of this on mechanical properties and found that the addition of EAA compatibilizer significantly increased the composite tensile modulus.

In order to reduce either the hydrophobicity of polyethylene or the hydrophilicity of starch, attempts were made to modify one or the other. Thus, Evangelista et al.<sup>8</sup> were able to load up to 25% of starch that had been modified with octenyl succinate. These blends showed better mechanical properties than unmodified polyethylene–starch blends. Jane et al.<sup>9</sup> incorporated oxidized polyethylene as compatibilizer for blending polyethylene with starch. However, the modification was quite expensive, and the blends still had inferior mechanical properties. The effect of the granule size of rice starch, potato starch, and cornstarch on blend properties was also studied.<sup>10</sup> It was found that mechanical properties of the blend decreased with increasing particle size. Thus, potato starch 35- $\mu\text{m}$  in diameter showed lower mechanical properties than either cornstarch (14.3  $\mu\text{m}$ ) or small-particle cornstarch (2  $\mu\text{m}$ ).

Unmodified starch is not thermoplastic by nature and degrades on heating. However, treatment with glycerol and water induces thermoplasticity in starch. Pierre et al.<sup>11</sup> studied the mechanical properties of low-density polyethylene–thermoplastic starch (LDPE–TS) and linear low-density polyethylene–thermoplastic starch (LLDPE–TS) blends. These blends had better processibility and mechanical properties than untreated starch. However, at higher loadings of TS, there was a drastic reduction in mechanical properties. Hence, Bikiaris et al.<sup>12,13</sup> studied the effect of incorporating LDPE-*g*-maleic anhydride as a compatibilizer along with 30% of native cornstarch, emphasizing that the biodegradation of compatibilized blends was only slightly lower than that of uncompatibilized blends. Ultra-high-molecular-weight polyethylene and starch blends with high modulus and high strength were prepared by Nakashima et al.<sup>14</sup> The studies revealed reduction of drawability with an increase in starch content.

In keeping with the trend in the development of biodegradable polyethylene, high-density polyethylene (HDPE) was blended with cornstarch<sup>15</sup> modified with cholesterol units. HDPE loaded with modified starch up to 20% showed better

mechanical properties than untreated starch-loaded polyethylene.

Increasing the amount of starch loading with polyethylene increases the biodegradability of the blend. However, loading higher percentages of starch leads to poor mechanical properties, notably those of elongation at break and tensile strength. Since this effect is mainly a result of poor adhesion between starch and polyethylene, addition of a suitable compatibilizer that improves the interfacial adhesion could prove to be beneficial. However, a detailed study has not been made of starch-filled HDPE, nor has a study been done on the use of plasticized starch with HDPE along with a suitable compatibilizer. In the present work HDPE with grafted maleic anhydride (HDPE-*g*-MAH) has been used as a compatibilizer for both HDPE–starch and HDPE–TS blends. The blends were then tested for different mechanical properties such as impact strength and elongation at break.

## EXPERIMENTAL

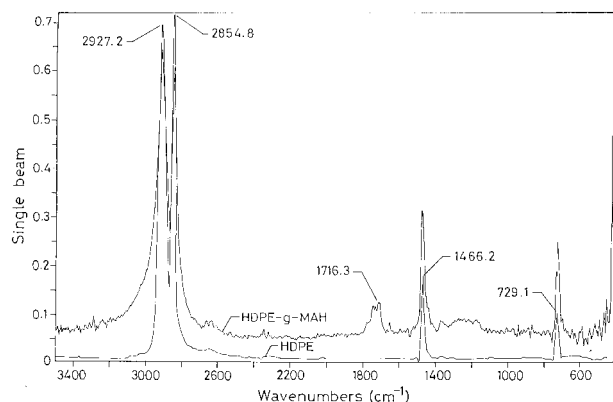
### Materials

High-density polyethylene (HDPE; 50MA180 grade; from IPCL, Baroda, India) with a melt flow index of 18 g/10 min was used. Tapioca starch (14.7  $\mu\text{m}$ ) used in this work was obtained from the roots of tapioca plants grown in the south Indian state of Kerala. Plasticized tapioca starch was prepared following the method described by Pierre et al.<sup>11</sup> In this method 48% starch, 33% glycerol, and 19% water were first mixed for 15 min. The starch granules were allowed to swell by leaving the mixture for 1 h. The plasticized starch was then made by stirring this mixture for 30 min at 70°C.

Maleic anhydride was purified by refluxing a solution in chloroform and recrystallizing to remove any trace of maleic acid.

### Preparation of Compatibilizer

To a solution of 5 g of HDPE in boiling toluene under reflux was added an equal amount of maleic anhydride along with 2 mL of dimethyl sulfoxide (DMSO) additive. Benzoyl peroxide initiator (0.15 g)<sup>16</sup> was added to this solution, and refluxing continued for 5 h. The solution containing maleic anhydride–grafted polymer was slowly precipitated in methanol after cooling. Unreacted



**Figure 1** FTIR spectrograph of HDPE-g-MAH polymer.

maleic anhydride was removed by repeatedly washing with methanol followed by further extraction with acetone before drying the copolymer. The residue, HDPE-g-MAH copolymer, was then finely powdered in a ball mill. An FTIR spectrum of the copolymer revealed a carbonyl (C=O) peak at  $1700\text{ cm}^{-1}$ , as shown in Figure 1. The titration procedure as described by Gaylord et al.<sup>17</sup> was used to determine the percentage of grafting, which was found to be 4.93% (w/w).

### Melt Blending

Blends of HDPE and starch or TS with HDPE-g-MAH compatibilizer were made in an Minimax injection molder (Model No. CS-183MMX, Custom Scientific Instruments, New Jersey) in varied proportions. Blending was done at  $210^{\circ}\text{C}$  in an open cup fitted with a spiked rotor, and dumbbell-shaped specimens for property measurements were then prepared by injection molding into standard dies provided with the Minimax molder. Dumbbell specimens of HDPE and starch or TS with no added compatibilizer were also prepared for comparison. The compatibilizer was added on the basis of weight percent of starch or TS in all cases throughout the study.

### Blend Morphology

The morphology of the blends was studied using a scanning electron microscope [SEM (JEOL, JSM-840A)]. The fractured surfaces of the specimens were sputtered [JEOL, JSM-1100E] with gold prior to microscopy. Thin slices of the unfractured blend specimens were cut with a sharp blade, and the smooth surfaces so obtained were then sputtered with gold for scanning electron microscopy.

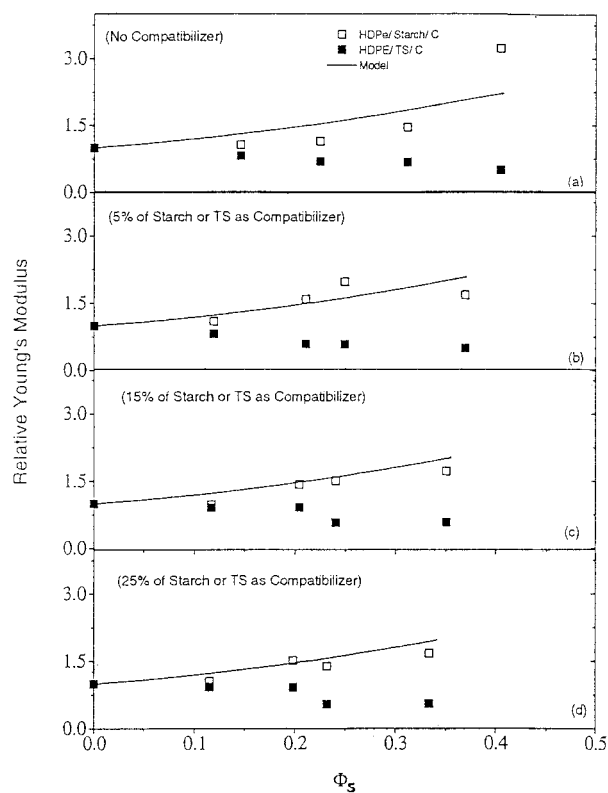
### Mechanical Properties of the Blend

The mechanical properties of the dumbbell-shaped blend specimens were tested with a Minimax impact tester (Model No. CS-183T1-079) and a Minimax tensile tester (Model No. CS-183). The impact and tensile tests were carried out according to the ASTM D1822 and ASTM D1708 methods, respectively. The average of the values for five tested specimens for each test was used as the result.

## RESULTS AND DISCUSSION

### Young's Modulus

The variation of relative Young's modulus with the volume fraction of starch with and without compatibilizer is shown in Figure 2. Relative Young's modulus represents the ratio of the Young's modulus value of the blend to that of pure HDPE. All relative properties are similarly defined throughout this article. Young's modulus calculated from Kerner's model is plotted in the



**Figure 2** Relative Young's modulus of HDPE-starch and HDPE-TS blends with and without compatibilizer versus starch volume fraction ( $\phi_s$ ).

same figure, showing a comparison with the experimental values. The simplified Kerner's equation of the form as suggested by Willett<sup>7</sup> has been used.

$$E_{(b)} = E_{(0)} \left[ 1 + \left( \frac{\phi_S}{1 - \phi_S} \right) \left\{ \frac{15(1 - \nu)}{8 - 10\nu} \right\} \right] \quad (1)$$

where  $E_b$  and  $E_0$  are the Young's modulus of the blend and of pure HDPE, respectively;  $\nu$  is the Poisson's ratio of HDPE (taken to be 0.43); and  $\phi$  is the volume fraction of starch and is evaluated by converting the weight fraction into volume fraction by using the following equation:

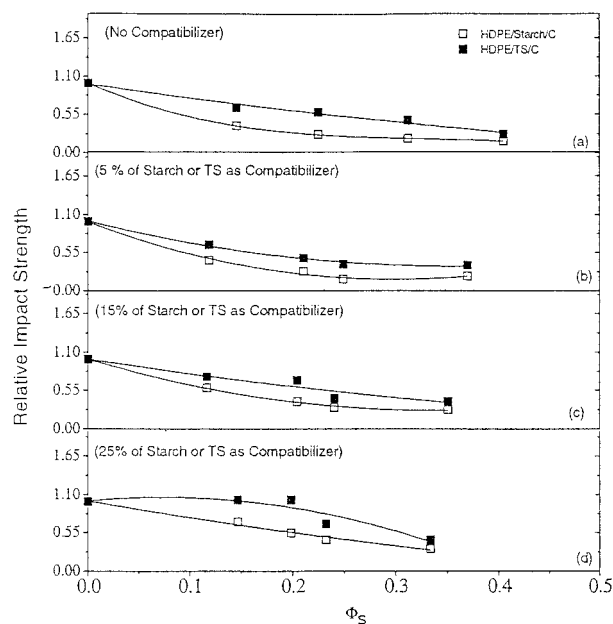
$$\phi_i = \frac{(W_i/\rho_i)}{\sum(W_i/\rho_i)} \quad (2)$$

where  $W_i$  and  $\rho_i$  are, respectively, the weight fraction and the density of component  $i$  in the blend. Density values of  $1400 \text{ kg/m}^3$  and  $940 \text{ kg/m}^3$  have been used for starch and HDPE, respectively.

It has been found that relative modulus increases with increased starch loading [Fig. 2(a)]. The increase is mainly the result of the stiffness of starch chains. The effect of adding 5%, 15%, and 25% compatibilizer in the HDPE–starch blends is shown in that order in Figure 2(b–d). The experimental data agree well with the theoretical values when compatibilizer is added to the blend. A similar trend in the results was obtained by Willett<sup>7</sup> on using EAA as compatibilizer for blends of LDPE–cornstarch and LDPE–potato starch. This is because of the improved adhesion between HDPE and starch in the blend. The HDPE-*g*-MAH compatibilizer anchors its nonpolar HDPE part to the HDPE matrix in the blend, while the maleic anhydride units react with the hydroxyl groups of the starch, thereby forming a chemical bond. Thus, the effect is to increase the flexibility of starch chains.

#### HDPE–TS Blends

The addition of glycerol-plasticized starch reduces the Young's modulus of the HDPE–TS blend when no compatibilizer is added, as shown in Figure 2(a). Relative modulus versus  $\phi_S$  is shown in Figure 2(b–d) for 5%, 15%, and 25% compatibilizer loading. There is no marked improvement in the Young's modulus values for low compatibilizer loading. However, with 20% compatibilizer, the modulus values of the blend attain



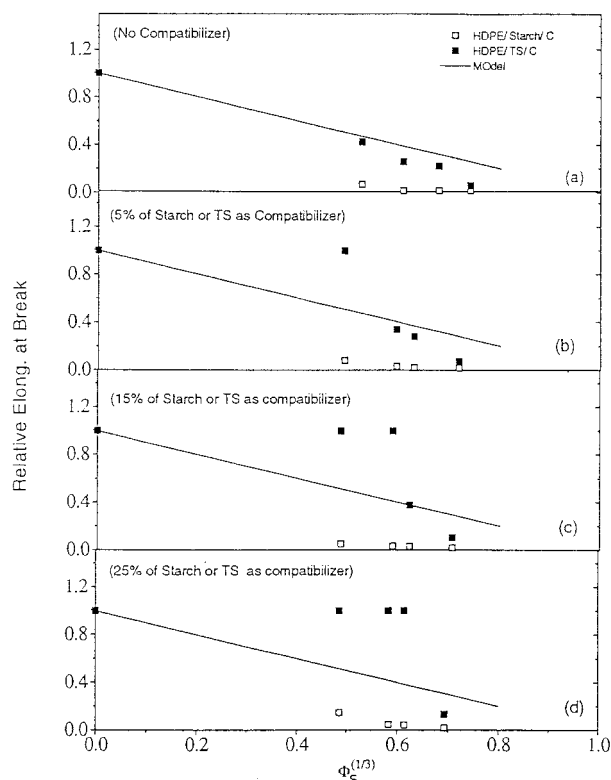
**Figure 3** Relative impact strength of HDPE–starch and HDPE–TS blends with and without compatibilizer versus starch volume fraction ( $\phi_S$ ).

nearly 90% of that of pure HDPE. For 40 wt % TS loading (corresponding to a  $\phi_S$  value of 0.2362), the Young's modulus increases to 74% of that of virgin HDPE ( $2.31 \times 10^8 \text{ N/m}^2$ ) for the same compatibilizer loading. However, there is no significant improvement in the relative modulus at a still higher loading of starch, even with an increase of compatibilizer loading to 25%. The improvement in the modulus values can be attributed mainly to improved adhesion between starch and HDPE.

#### Impact Strength

##### HDPE–Starch Blends

Figure 3 shows the effect of compatibilizer on the impact strength of HDPE–starch blends. Figure 3(a) shows the variation of the relative impact strength with the increasing volume fraction of starch. The relative impact strength drops to 16.7% of virgin polyethylene at a volume fraction of 0.40 (corresponding to 50 wt % starch). Impact strength decreases with an increase in starch loading when no compatibilizer is added, as shown in Figure 3(a). Figure 3(b–d) shows in that order the variation of relative impact strength with increasing volume fraction of starch for 5%, 15%, and 25% compatibilizer loading. The impact strength values improve only slightly with the



**Figure 4** Relative elongation at break of HDPE-starch and HDPE-TS blends with and without compatibilizer versus starch volume fraction ( $\phi_S^{1/3}$ ).

addition of compatibilizer. Thus, even with the addition of 25% compatibilizer, the relative impact strength at 50 wt % starch loading increases to only about 31%. For the same compatibilizer loading as stated above and 20 wt % starch loading, the impact strength is about 70% of that of pure HDPE ( $1.142 \times 10^5 \text{ J/m}^2$ ). This can be attributed mainly to the poor adhesion between starch and HDPE. Moreover, starch also degrades during melt blending with HDPE in the mixer.

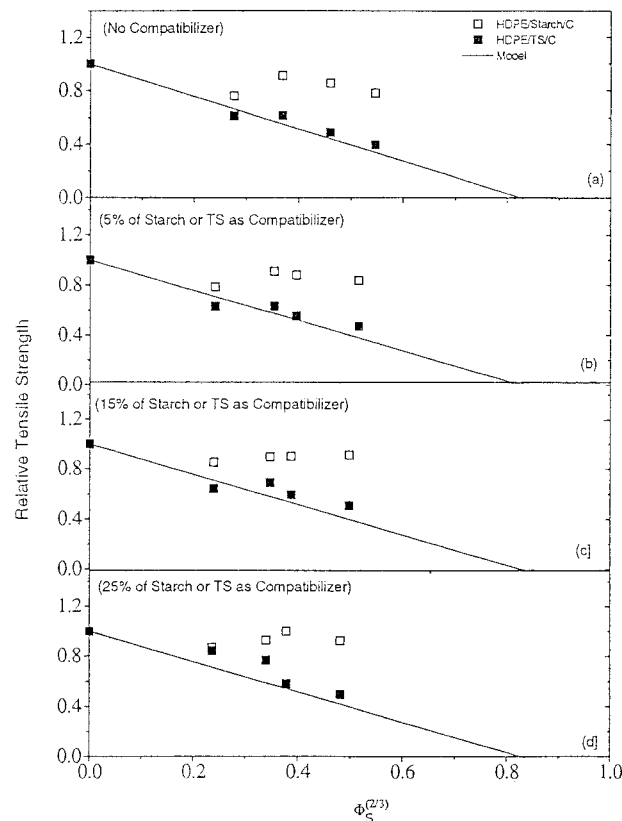
#### HDPE-TS Blends

Figure 3 shows the variation of relative impact strength with and without compatibilizer [Fig. 3(a)] with the volume fraction,  $\phi_S$ , of thermoplastic starch. It can be seen that relative impact strength decreases with an increase in starch loading and reduces to 26.6% when starch loading is 50 wt % (corresponding to 0.40 value of  $\phi_S$ ), and no compatibilizer is added. It has been found that impact strength values for these blends are always higher than those of HDPE-starch blends. In Figure 3(a-d) is presented the impact strength

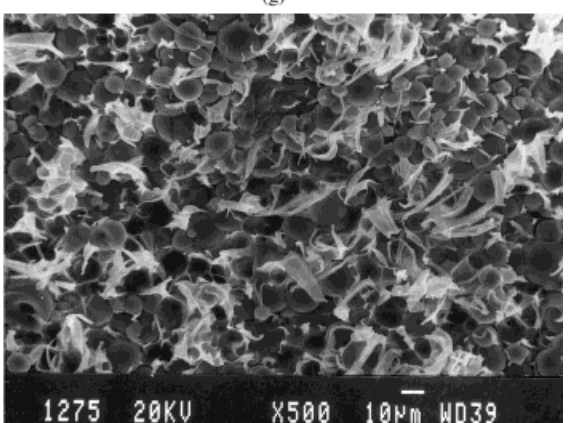
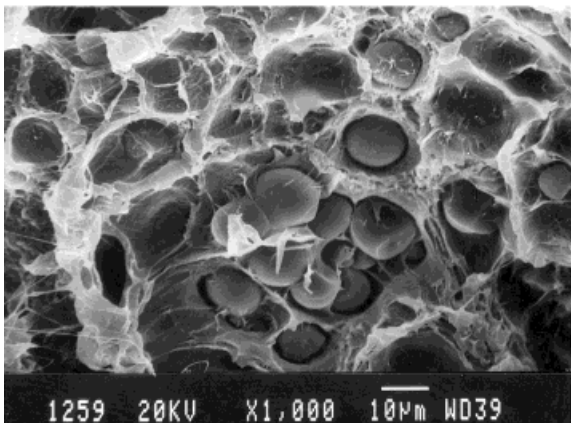
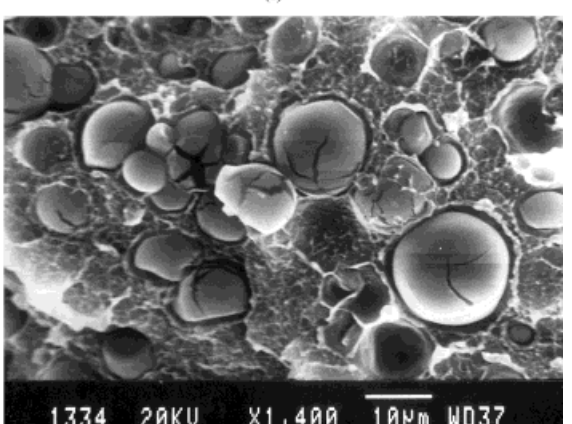
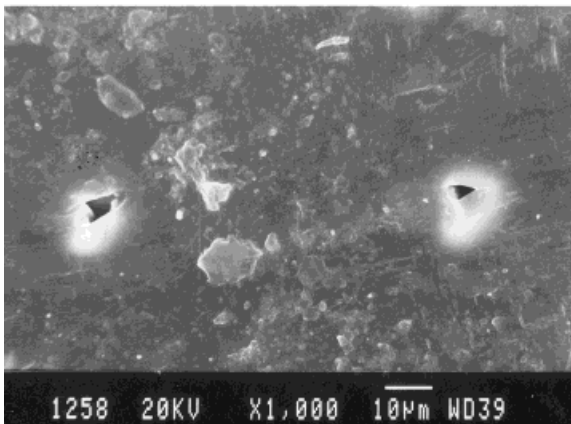
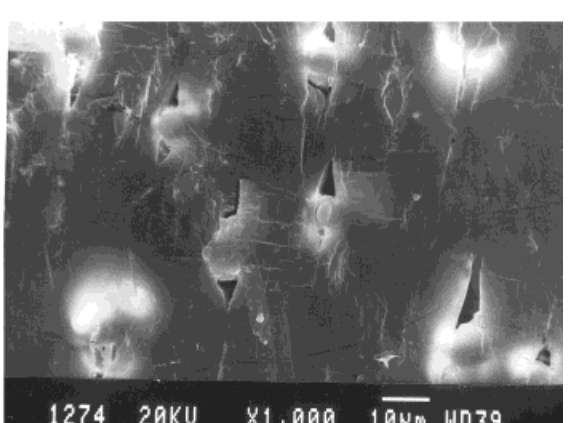
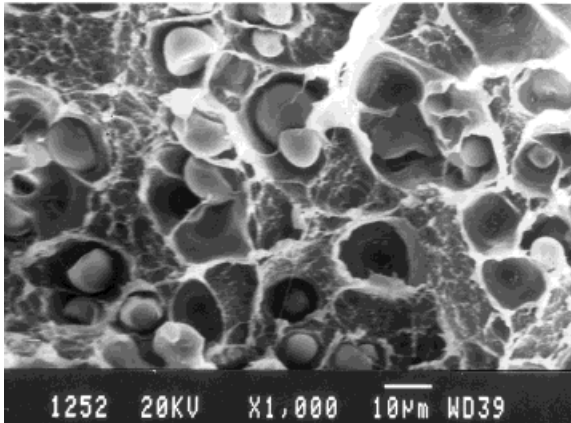
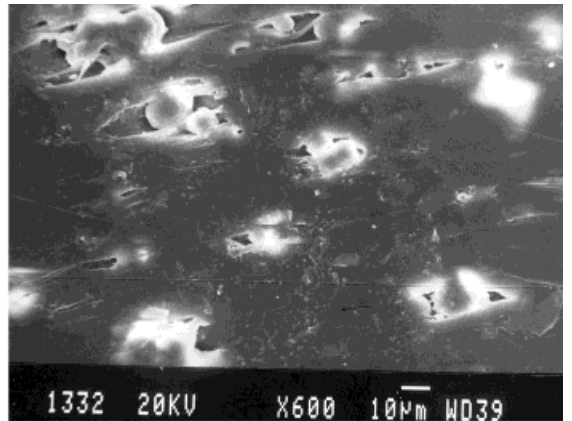
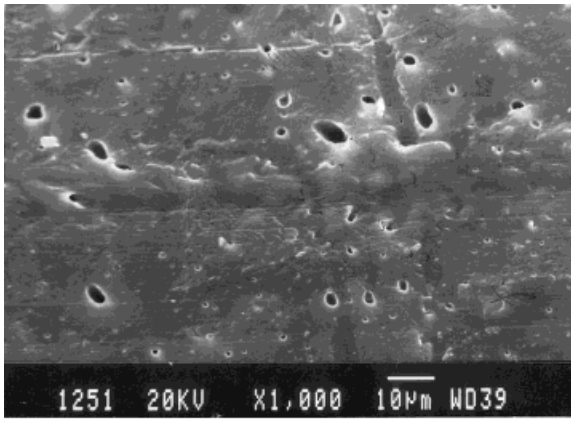
versus TS volume fraction ( $\phi_S$ ) for blends containing compatibilizer to the extent of 5%, 15%, and 25%. It has been found that the addition of compatibilizer progressively increases the impact strength of the blend. Thus, with the addition of 25% compatibilizer for 20 wt % and 30 wt % TS loading, the impact strength is the same as that of virgin HDPE. For a higher percentage, that is, 40 wt % TS loading, the impact strength is nearly 78% of pure HDPE. However, with further increase in the TS loading, there is very little improvement in the impact strength of the blend, even after addition of compatibilizer.

#### Elongation at Break

Figure 4 shows the effect of compatibilizer on elongation at break with  $(\phi_S)^{1/3}$ . The Nielsen model has been used to determine the theoretical values of relative elongation at break. The model assumes perfect adhesion between the rigid filler (starch) and matrix (HDPE) and gives the following relation<sup>7</sup>:



**Figure 5** Relative tensile strength of HDPE-starch and HDPE-TS blends with and without compatibilizer versus starch volume fraction ( $\phi_S^{2/3}$ ).



$$\epsilon_b = \epsilon_0(1 - (\phi_s^{1/3})) \quad (3)$$

where  $\epsilon_b$  and  $\epsilon_0$  are the elongation at break for the blend and pure HDPE, respectively. The theoretical values of elongation at break decrease with an increase in starch loading, as can be seen from Figure 4(a). The observed values are far lower than the theoretical values, indicating practically no adhesion [Fig. 4(a)] between starch and HDPE. The increase in elongation-at-break values on the addition of compatibilizer is very marginal because of poor adhesion, as has also been observed by Willett.<sup>7</sup> In all cases, the theoretical values calculated are much higher than the observed values of elongation at break (Fig. 4).

#### HDPE-TS Blends

The elongation at break for HDPE-TS blends decreases with an increase in TS loading, as shown in Figure 4. The elongation at break decreases to 43% of that of pure HDPE, even with a low loading of 20 wt % TS (corresponding to a  $\phi_s$  value of 0.1451), when no compatibilizer is added to the blend, as shown in Figure 4(a). However, an addition of just 5% compatibilizer to this blend increases the value to that of virgin HDPE [531.17%; Fig. 4(b)]. The effect of adding 5%, 15%, and 25% compatibilizer on the elongation at break is shown in that order in Figure 4(b-d). With the addition of 20% compatibilizer, the value of elongation at break attains the same value as that of pure HDPE with a TS loading as high as 40 wt %. However, the improvement is very marginal at still higher TS loading. An additional increase in compatibilizer loading to 25% has no effect on the above trend.

#### Tensile Strength

##### HDPE-Starch Blends

Figure 5 shows the change in tensile strength with  $\phi_s^{2/3}$  with and without compatibilizer. The tensile strength values decrease with an increase in starch loading when no compatibilizer is added

to the blend, as shown in Figure 5(a). The effect on relative tensile strength of adding 5%, 15%, and 25% compatibilizer loading is shown in Figure 5(b-d) in that order. The theoretical values of relative tensile strength have been calculated from the Nicolais and Narkis model<sup>7</sup> using the equation

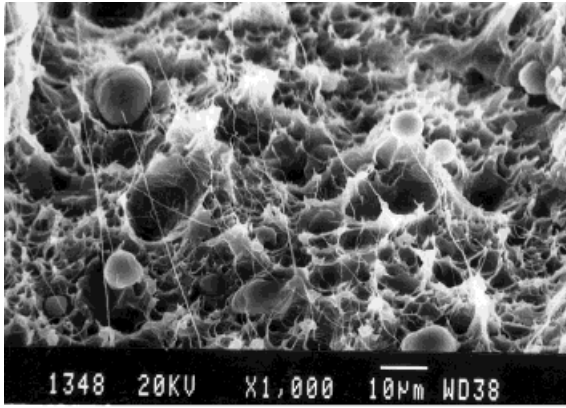
$$\sigma_{(b)} = \sigma_0(1 - 1.21\phi_s^{2/3}) \quad (4)$$

where  $\sigma_b$  and  $\sigma_0$  are the tensile strength of HDPE-starch blend and pure HDPE, respectively; and  $\sigma_b/\sigma_0$  is the relative tensile strength. The model assumes no adhesion between the matrix and the rigid filler particle. However, in all the cases the observed experimental values are found to be higher than the predicted values. This indicates a certain degree of adhesion between HDPE and starch, as was also observed in LDPE-starch blends by Willett.<sup>7</sup> It can be seen from Figure 5(b-d) that there is only a marginal improvement in relative tensile strength upon the addition of increasing amounts of compatibilizer.

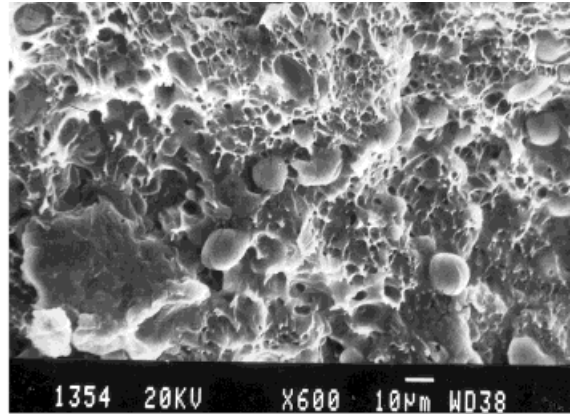
##### HDPE-TS Blends

Figure 5 shows the variation in relative tensile strength versus  $\phi_s^{2/3}$  for HDPE-TS blend. Relative tensile strength decreases with an increase in TS loading, as shown in Figure 5(a). Figure 5(b-d) shows the effect of 5%-25% compatibilizer with  $\phi_s^{2/3}$ . There is no significant improvement in the tensile strength up to a compatibilizer loading of 5% and 15%, as shown in Figure 5(b-c). However, it can be seen in Figure 5(d) that the tensile strength is 84% and 77% of that of pure HDPE ( $0.1664 \times 10^8$  N/m<sup>2</sup>) for a loading of 20 wt % and 30 wt % TS, respectively. At still higher TS loading, however, the tensile strength values do not improve significantly [Fig. 5(d)]. This may be because of the reduced effective cross-sectional area in HDPE-TS blend for higher loadings of TS.

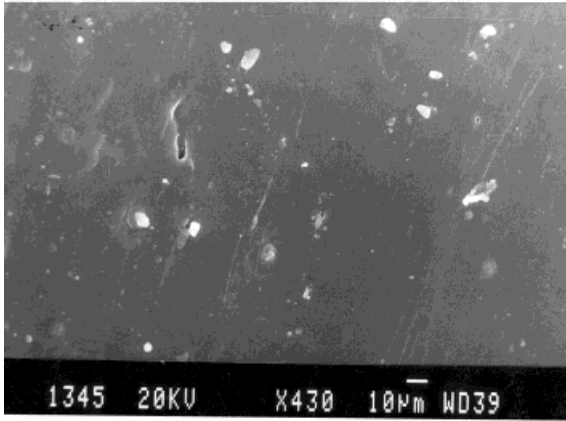
**Figure 6** SEM photographs of blends containing (a) HDPE and Starch (20 wt %); (b) fractured surface of HDPE-starch (20 wt %), (c) HDPE-starch (20 wt %) compatibilized with 25% HDPE-g-MAH, (d) fractured surface of HDPE-starch (20 wt %) compatibilized with 25% HDPE-g-MAH, (e) HDPE and starch (40 wt %), and (f) HDPE-starch (40 wt %) compatibilized with 25% HDPE-g-MAH, (g) fractured surface of HDPE-starch (20 wt %), and (h) fractured surface of HDPE-starch (20 wt %) compatibilized with 25% HDPE-g-MAH.



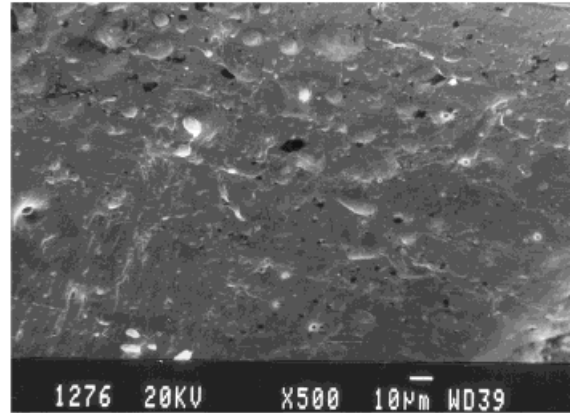
(a)



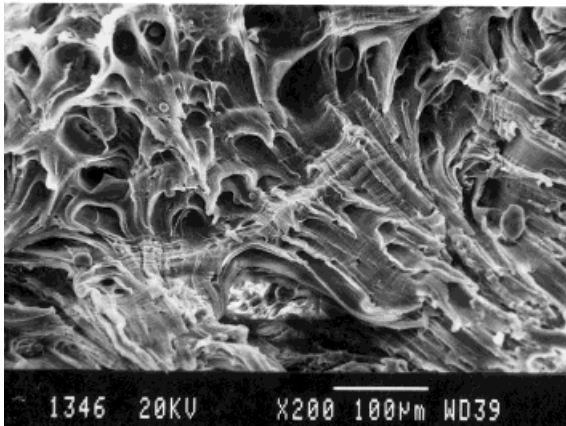
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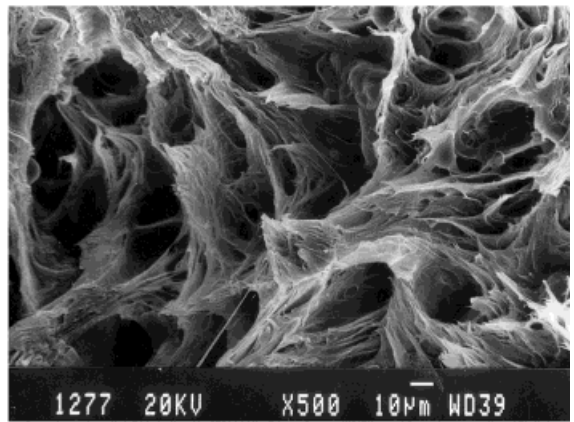
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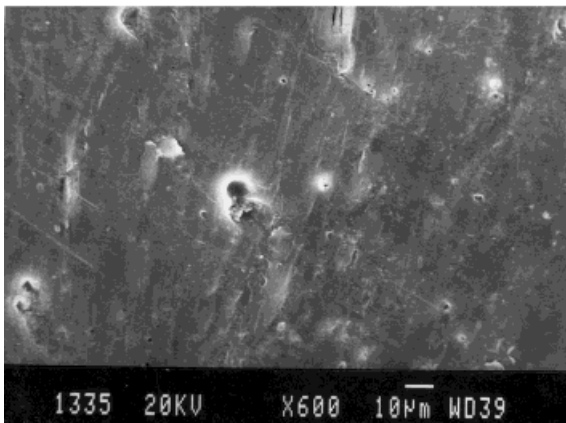
(f)



(c)



(g)



(d)



## Morphology of Blends

### HDPE-Starch Blends

The blend morphology of both impact-fractured and unfractured specimens loaded with 20 wt % and 40 wt % starch is shown in Figure 6. Figure 6(a) shows the SEM photograph of HDPE blended with 20 wt % starch. The poor dispersion of starch in HDPE leads to brittle fracture, as revealed in Figure 6(b). The dispersion improves slightly on the addition of 25% compatibilizer to this blend [Fig. 6(c)]. The fractured surface of this blend with an interfacial modifier, as shown in Figure 6(d), reveals a slight deformation prior to fracture as compared to that without compatibilizer [Fig. 6(b)], though the fracture is still predominantly brittle. The above behavior is also reflected in the impact strength values of the blend as will be seen later. There is, however, no marked improvement, even after the addition of compatibilizer for a still higher loading of starch (40 wt %), as shown with no compatibilizer [Fig. 6(e)] and with 25% compatibilizer [Fig. 6(f)]. The corresponding fractured surfaces shown in Figure 6(g,h) indicate that there has been only a very marginal improvement in the morphology of the fractured surface, with which the impact strength values corroborate.

### HDPE-TS Blends

The blend morphology of HDPE-TS blends is shown in Figure 7 for both impact-fractured and unfractured surfaces. The fractured surface of HDPE blended with 20 wt % TS with no added compatibilizer is shown in Figure 7(a). The dimpled structure reveals a predominantly semiductile fracture because of cavitation and craze of the plasticized starch and HDPE matrix, respectively. The partially brittle nature of impact-fractured surface lowered the impact strength value to 65% compared to that of virgin HDPE. The addition of 25% compatibilizer to this blend [Fig. 7(b)] shows that the starch domains in the compatibilizer blends are smaller than those in the uncompatibilized blends. Since blending was

done under identical conditions, this difference may be attributed to a better dispersion of starch caused by the compatibilizer. However, a quantitative evaluation of the compatibilizing effect could not be made. Since starch contains a large number of —OH groups, may it may be postulated that formation of ester groups by reaction with the anhydride groups of the compatibilizer promotes better dispersion of starch in the polyethylene matrix. The impact-fractured surfaces in different sections of the entire fractured surface are shown in Figure 7(c). The large plastic deformation of the polyethylene matrix combined with cavitation initiated by plasticized starch particles (which act as stress concentrators) and crazing of the HDPE matrix<sup>18</sup> delay the crack growth leading to ductile failure. This leads to high-impact strength values equaling that of pure polyethylene. For higher TS loadings of 40 wt % [Fig. 7(d)] and no compatibilizer, the mode of failure is brittle fracture [Fig. 7(e)]. The poor mechanical properties of plasticized starch predominantly contributes to the brittleness of the blend. The above blend when blended with 25% compatibilizer greatly improves the dispersion of TS in the blend as shown in Figure 7(f). The impact fractured surface of this compatibilized blend shown in Figure 7(g) reveals large plastic deformation prior to ductile fracture. The relative impact strength values are found to increase from 20% for the uncompatibilized blend to 68% for the compatibilized blend with 40 wt % TS loading.

The blend morphology of HDPE-TS blend shows better dispersion than HDPE-starch blends, mainly due to greater processibility of plasticized starch and favorable interaction with the polar groups of the compatibilizer.

## CONCLUSIONS

Both plasticized and unplasticized tapioca starch were blended separately with HDPE using HDPE-g-MAH as compatibilizer. Better dispersion of plasticized starch in the HDPE matrix was

**Figure 7** SEM photographs of blends containing (a) HDPE and TS (20 wt %), (b) HDPE-TS (20 wt %) along with 25% HDPE-g-MAH compatibilizer, (c) fractured surface of HDPE-TS (20 wt %) compatibilized with 25% HDPE-g-MAH, (d) HDPE and starch (40 wt %), (e) fractured surface of HDPE-TS (40 wt %), (f) HDPE-starch (40 wt %) compatibilized with 25% HDPE-g-MAH, and (g) fractured surface of HDPE-TS (40 wt %) with 25% compatibilizer.

observed by SEM as compared to that of the HDPE–starch blends. A high degree of ductility may be achieved for HDPE–TS blends by the use of compatibilizer, which seems to promote better adhesion between starch and the HDPE matrix.

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