

Use of Poly(ethylene-*co*-vinyl alcohol) as Compatibilizer in LDPE/Thermoplastic Tapioca Starch Blends

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ABSTRACT: Poly(ethylene-*co*-vinyl alcohol) (EVOH) was used as a compatibilizer to make blends of low-density polyethylene (LDPE) and plasticized starch (TS). The tensile properties and impact strength were measured and compared with those of neat LDPE. The morphology of the blend specimens, both fractured and unfractured, was observed by scanning electron microscopy. Comparison of the properties showed that the impact strength of the blend improves significantly by the addition of a compatibilizer even with a high TS loading of 40 and 50% (by weight). A

high elongation at break almost matching that of neat polyethylene was also obtained. The blend morphology of the etched specimens revealed fine dispersion of the starch in the polyethylene matrix, while the fracture surface morphology clearly indicate that the failure of compatibilized blends occurs mainly by the ductile mode. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3126–3134, 2002

Key words: blends; compatibilization; polyethylene

INTRODUCTION

The development of biodegradable materials has been gaining considerable importance over the years. It has been estimated that 2% of all plastics reach the municipal wastes.¹ This has become a major waste-disposal problem particularly for certain applications like waste bags, agricultural mulch films, and food packaging. Further, replacement of petroleum-based plastics with materials from renewable resources is useful from the stand-point of conservation of petroleum resources. Attempts have been made to use fully biodegradable polyhydroxyalkanoates like PHB and PHBV but their use has been limited due to high production costs.² Hence, another alternative, that is the blending of synthetic packaging polymers like polyethylene and polypropylene with a low-cost biopolymer, was investigated by many researchers.^{3–5} Starch, being an inexpensive and renewable product, has good potential as a biodegradable filler for synthetic polymers. The biodegradability of the polyethylene/starch blends used for packaging films is based on the concept that if starch is present in sufficient amounts and if it is removed by microorganisms in the waste-disposal environment the residual plastic film should lose its integrity, disintegrate, and disappear.

Blending of polyethylene with starch, however, leads to blends of poor mechanical properties owing to poor interfacial adhesion between the hydrophilic starch and hydrophobic polyethylene. Ultrahigh molecular weight polyethylene and starch blends with high module and high strength were studied.⁶ It was revealed that the drawability of the blends decreased with an increasing starch content. To overcome this problem, attempts have been made to impart hydrophobicity to starch by esterification. Octanoated starch,⁷ for example, has been found to impart hydrophobicity to starch. However, a higher loading of this modified starch in low-density polyethylene (LDPE) is found to cause significant reduction in the mechanical properties as compared to neat LDPE. Jane et al.⁸ thus could load only to 25% of starch octenyl succinate without a significant decrease in mechanical properties.

Introduction of a third component as a compatibilizer, such as poly(ethylene-*co*-acrylic acid), has been found to improve the mechanical properties of the blend.^{9,10} To improve the processability and to reduce the degradation of starch, thermoplastic starch obtained by treating starch with glycerol has been used for blending with LDPE and LLDPE rather than dry starch powder.¹¹ However, these blends show poor mechanical properties at higher loadings of plasticized starch. The present authors,¹² in their earlier work, also found similar behavior with blends containing thermoplastic tapioca starch. However, the use of maleic anhydride-grafted copolymers as compatibilizers^{12–14} was found to improve the mechanical properties of

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LDPE/plasticized starch blends as compared to blends without a compatibilizer.

The biodegradability of starch/polyethylene blends increases with a higher loading of starch. However, as mentioned earlier, increased starch loading leads to blends with inferior mechanical properties, particularly, elongation at break. In the work reported in the present article, the effect of the poly(ethylene-co-vinyl alcohol) copolymer (EVOH) as a compatibilizer was studied and a detailed and systematic analysis of the mechanical properties of the blends in comparison with those of neat LDPE was made.

EXPERIMENTAL

Materials

LDPE (grade 24FS040 with an MFI of 4g/10 min from IPCL, Vadodara, India) was used for blending with tapioca starch (10.2 μm). The starch is obtained from the roots of the tapioca plant grown in the south Indian state of Kerala. Plasticized starch (TS) was prepared by mixing 48% starch, 33% glycerol, and 19% water for 15 min and then allowing the mixture to stand for 1 h. This mixture was then stirred for 30 min at 70°C. Iron stearate was used as the autooxidant. The poly(ethylene-co-vinyl alcohol) (EVOH) copolymer was obtained by the hydrolysis of an ethylene vinyl acetate copolymer (from NOCIL, Mumbai, India) of 43% (by weight) vinyl acetate content and a molecular weight of 1,50,000. The degree of hydrolysis was measured to be 89%. The FTIR spectrum of the hydrolyzed product is shown in Figure 1.

Melt blending

Blends of LDPE, TS, EVOH, and an autooxidant, that is, iron stearate 0.1% (by weight), were blended at 210°C. Blending was carried out in a stainless-steel cup fitted with a spiked rotor and extruded for cutting into small pellets, which were subsequently molded into standard dies to make dumbbell-shaped specimens using a Minimax molder (Custom Scientific Instruments, Cedar Knolls, NJ, Model CS-183MMX). The compatibilizer was added as weight percent of TS in all cases.

Morphology

The morphology of the blends was studied by scanning electron microscopy (SEM, JEOL, JSM-840A). The specimens (unfractured and fractured) were sputtered with gold prior to microscopy (JEOL, JSM-1100E). Thin slices of unfractured specimens were heated in water at 80°C for 24 h to remove the TS.

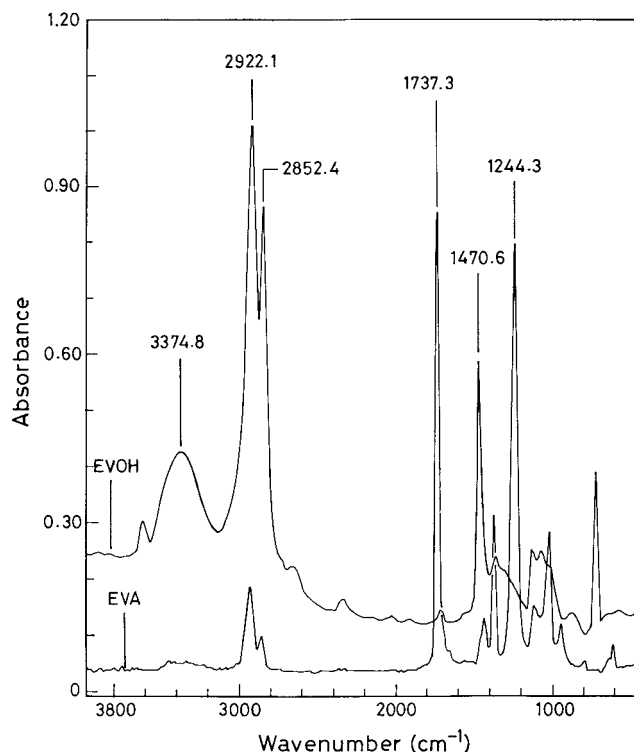


Figure 1 FTIR spectra of EVA copolymer and hydrolyzed EVA copolymer.

Mechanical properties of the blend

A minimax impact tester (Model CS-183T1-079) and Minimax tensile tester (Model no. CS-183TTE) were used to measure the impact and tensile properties of the molded dumbbell-shaped specimens. The impact and tensile tests were carried out according to the ASTM D1822 and ASTM D1708 methods, respectively. At least eight specimens were tested for each variation of composition and property measurements. The measurements are reported as the relative mechanical property (i.e., ratio of a mechanical property of the blend to that of neat LDPE) in all cases.

RESULTS AND DISCUSSION

Impact strength

Figure 2 shows the relative impact strength (RIS) of the LDPE/TS blends with different compatibilizer contents for each TS loading, which, itself, was varied in the range of 20–50% (by weight). For 20% TS loading, an optimum is reached at 10% (based on TS) compatibilizer, yielding an RIS value of 1.02, which is essentially the same impact strength as that of pure LDPE. An optimal RIS value of 1.01 is obtained for blends of LDPE with 30% TS loading and 15% (based on TS) compatibilizer. For higher TS loadings of 40 and 50%, the impact strength attains that of neat LDPE when 15% (based on TS) compatibilizer is used. The

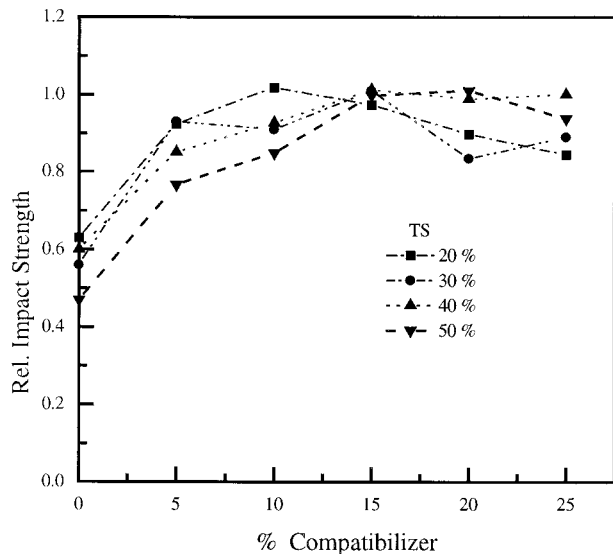


Figure 2 Plot of relative impact strength versus percent compatibilizer (based on TS) in the blend.

improvement in impact strength on the addition of the EVOH copolymer as the compatibilizer may be attributed to better interfacial adhesion that assists in stress transfer from the LDPE matrix to the dispersed TS phase. An improvement in the interfacial adhesion is reflected in the interlocking of phases that are observed in the etched blend specimens due to addition of the compatibilizer (Fig. 6). The effectiveness of this copolymer as a compatibilizer is shown by the high impact strength values obtained even for high TS loadings of 40 and 50%.

It may be noted that, for 20 and 30% TS loadings, a significant decrease in the RIS value occurs when the optimal compatibilizer content is exceeded. This may be attributed to a phenomenon described as saturation of the interface. Such a phenomenon has been reported for several blend systems using reactive compatibilizers. It has been argued^{15,16} that when the interface becomes "saturated" with the compatibilizer the latter forms micelles or remain trapped in one of the two immiscible phases. For higher TS loadings also, that is, for 40 and 50%, there is very little improvement in the impact strength at high compatibilizer levels beyond 15% (based on TS).

A factorial analysis was performed on the experimental data for two factors, namely, TS loading and

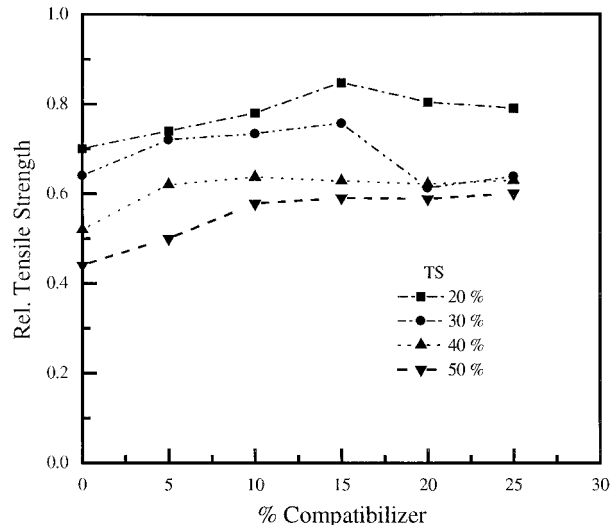


Figure 3 Plot of relative tensile strength versus percent compatibilizer (based on TS) in the blend.

compatibilizer content at four and five levels, respectively. The significant terms from the *F*-test using ANOVA were collected and nonlinear regression using Sigmaplot software (version 2.0) on the experimental data was performed to obtain an equation for the relative impact strength (RIS) in terms of the weight percent TS and the compatibilizer content (*C*). The equation is represented by

$$\text{RIS} = a_1 + b_1(C) + c_1(\text{TS}) + d_1(\text{TS})(C) + e_1(C)^2(\text{TS})^2 \quad (1)$$

The coefficients a_1 to e_1 are given in Table I. The multiple correlation coefficient, *R*, given in the Table shows that there is a good fit with the equation as it is closer to 1.

Tensile strength

Figure 3 shows the effect of the compatibilizer addition on the relative tensile strength of LDPE/TS blends. The variation in the tensile strength with an increase in TS loading from 20 to 50% is also shown in the figure.

As observed in Figure 3, the relative tensile strength improves with the addition of the EVOH compatibilizer as compared to the uncompatibilized blends. For

TABLE I
List of Coefficients for Eqs. (1)–(4)

Equation	a_1	b_1	c_1	d_1	e_1	f_1	g_1	Standard error
1	1.203	-0.023	-0.011	0.001	^a	0.000	0.000	0.067
2	0.926	-0.009	-0.000	0.019	^a	-0.007	0.000	0.036
3	1.326	-0.020	^a	0.001	-0.013	0.000	0.000	0.051
4	1.493	-0.088	0.004	^a	0.023	0.002	-0.002	0.054

^a Values less than 1.0×10^{-4} .

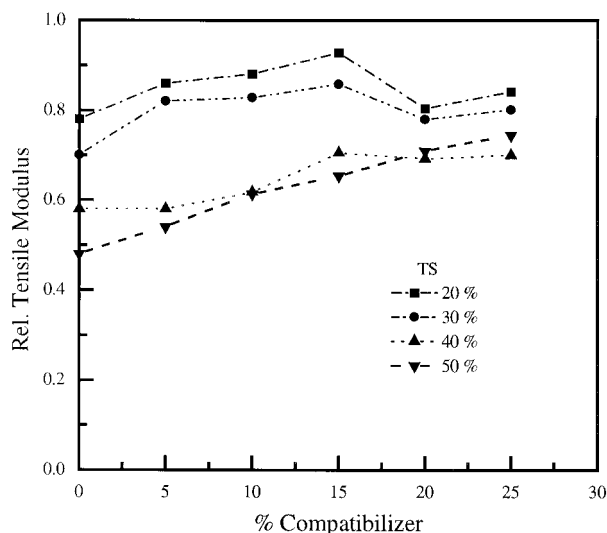


Figure 4 Plot of relative tensile modulus versus percent compatibilizer (based on TS) in the blend.

20 and 30%, the optimal tensile strength values corresponding to 85 and 76%, respectively, of that of neat LDPE were obtained with a compatibilizer content of 15% (based on TS). The improvement in tensile strength was examined by the highly ductile failure observed for the blends (Fig. 7) due to necking and drawing. The compatibilizer acts as an efficient emulsifier between the two immiscible phases. However, a further increase in the compatibilizer contents reduces the tensile strength, possibly due to the accumulation of the compatibilizer at the interface when the saturation concentration is exceeded.

For higher TS loadings of 40 and 50%, saturation seems to occur at a lower compatibilizer content. Thus, no significant improvement occurs in the tensile strength of the blend when the compatibilizer content exceeds 10% (based on TS). This may be due to the higher interaction of the compatibilizer with the TS phase than with the LDPE matrix.¹⁷

Factorial analysis of the experimental data was performed and a nonlinear regression equation for the relative tensile strength (RUS) was obtained:

$$\text{RUS} = a_1 + b_1(\text{TS}) + c_1(C)^2 + d_1(C) + e_1(C)(\text{TS})^2 + f_1(\text{TS})(C) \quad (2)$$

The values of the coefficients of the above equation are given in Table I.

Tensile modulus

Figure 4 shows the plot of the relative tensile modulus versus the percent compatibilizer for LDPE/TS blends with 20 to 50% TS loading. For lower TS loading that is, 20 and 30%, there is an improvement in the tensile modulus with the compatibilizer addition, reaching

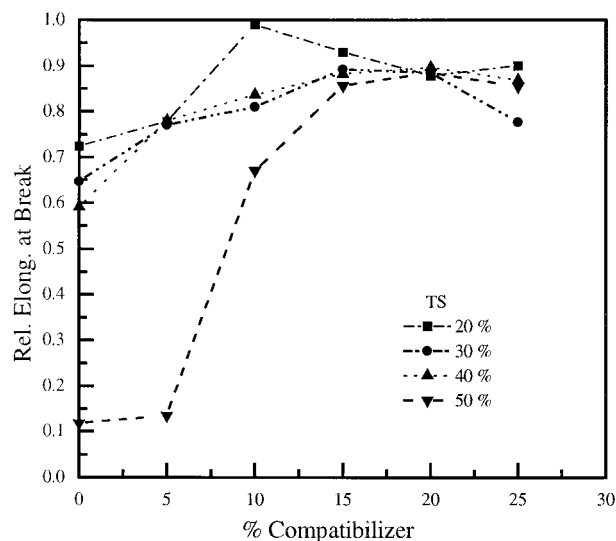


Figure 5 Plot of relative elongation at break versus percent compatibilizer (based on TS) in the blend.

optimal relative tensile modulus values of 0.93 and 0.86, respectively. In our earlier work,¹² it was observed that increasing the loading of granular starch increases the tensile modulus due to the stiffness of the starch chains. In contrast, an increased thermoplastic starch loading reduces the modulus due to the plasticizing effect of glycerol in TS. The improvement in the modulus that occurs on addition of the compatibilizer is due mainly to reduced interfacial tension, which retards the dispersed-phase coalescence.¹⁸

For higher TS loadings of 40%, a maximum modulus value which corresponds to 70% of that of pure LDPE is obtained with a compatibilizer content of 15% (based on TS). Further addition of compatibilizer does not show any further improvement in the relative tensile modulus. With still higher, that is, 50% TS loading, the modulus increases steadily with the compatibilizer content to 20% (based on TS), beyond which there is no significant improvement. The improvement in the modulus even for such high TS loadings indicates that the EVOH compatibilizer containing both the polyethylene chain as well as hydroxyl groups improves the adhesion between the nonpolar LDPE and polar TS.

The nonlinear regression equation obtained by factorial analysis of the experimental relative modulus (RYM) data (see Table I for values of the coefficients) is represented by

$$\text{RYM} = a_1 + b_1(\text{TS}) + c_1(\text{TS})^3 + d_1(C)(\text{TS}) + e_1(C) \quad (3)$$

Elongation at break

The effect of the EVOH copolymer as a compatibilizer for LDPE/TS blends on the relative elongation at break is shown in Figure 5. The elongation at

break for uncompatibilized blends decreases drastically with increase in the TS loading and decreases to nearly 12% of that of neat LDPE for 50% loading. This is due to poor adhesion between the nonpolar hydrophobic LDPE and polar hydrophilic TS. An addition of 10% (based on TS) compatibilizer to the blend produces a sharp increase in the relative elongation at break for all loadings of TS. At a higher compatibilizer level, the elongation at break increases although not remarkably. A relative elongation at break greater than 0.85 is obtained with 15% (based on TS) compatibilizer at all TS levels. The hydroxyl groups in the vinyl alcohol part of the EVOH compatibilizes efficiently with the dispersed TS particles. This is in agreement with similar observations on TS/EVOH blends,¹⁷ which were found to have high elongation properties even at high (50%) TS loading. The nonlinear regression equation obtained by factorial analysis of the relative elongation at break (REB) data is represented by

$$\text{REB} = a_1 + b_1(\text{TS}) + c_1(\text{TS})^2 + d_1(\text{TS})^3 + e_1(C) + f_1(C)^2 + g_1(\text{TS})(C) \quad (4)$$

The values of the coefficients, that is, a_1 to g_1 , are given in Table I.

Blend morphology

SEM photographs of thin films of the blend specimens etched by soaking overnight in water at 80°C are shown in Figure 6(a–f). The photographs are shown for minimum (20%) and maximum (50%) TS loading in our study. For lower TS loading (20%), there is a good dispersion of TS in LDPE, as can be seen from Figure 6(a), even without the compatibilizer. The addition of 10% (based on TS) compatibilizer to the blend causes improved adhesion [Fig. 6(b)], as revealed by its smooth surface. Increasing the compatibilizer further to 25% (based on TS) [Fig. 6(c)] does not, however, lead to better adhesion and the morphology remains similar to that in Figure 6(b). The improvement in adhesion between the two phases is due to the reduced interfacial tension, leading to a finer dispersion of TS particles in the LDPE matrix.

With increase of the TS loading to 50% [Fig. 6(d)], the poor adhesion between LDPE and TS becomes more evident. Thus, the micrograph reveals a loose matrix with an irregular domain size when no compatibilizer was added to the blend. However, increasing the TS loading is important from the standpoint of increased biodegradability. At the same time, the blend should have good mechanical properties. The addition of the compatibilizer (15% based on TS) to the blend causes the TS particles to be finely dispersed

and interlocked with the LDPE matrix [Fig. 6(e)]. An increase in the compatibilizer content to 25% (based on TS) produces a finer dispersion [Fig. 6(f)].

Figure 7 shows SEM photographs of the tensile fractured surface of blends containing 25 and 15% (based on TS) compatibilizer with different starch loadings. Similarly, Figure 7(a)–(c) are for blends with 20, 30, and 40% TS loading and 25% (based on TS) compatibilizer. Figure 7(a) shows the tensile fractured surface for 20% TS loading with 25% (based on TS) compatibilizer. The photograph shows a fibrous fractured surface with highly stretched regions, indicating that the material failed by voiding and general yielding, leading to ductile fracture. Figure 7(b) shows the tensile fractured surface of the blend with 30% TS loading. The micrograph reveals a ductile failure that is characteristic of a mode A-type of fracture.¹⁹ In this, the TS particles debonded from the LDPE matrix cause voids around the particles. It appears that the ligament bundles underwent plastic deformation and were pulled out by a tearing mechanism. The SEM micrograph shown in Figure 7(c) indicates a mixed mode of ductile and brittle fracture, suggesting that cavitation as well as plastic deformation has taken place during fracture.

Figure 7(d–f) shows the tensile fractured surfaces of blends with 30, 40, and 50% TS loading and 15% (based on TS) compatibilizer. A blend with 30% TS loading and compatibilizer [Fig. 7(d)] shows a large plastic deformation prior to ductile failure. Figure 7(e) shows an SEM micrograph of the tensile fractured surface of the blend with 40% TS loading. The micrograph shows extensive fibrillation, indicating that shear deformation has taken place. In this, the TS particles act as stress concentrators during the tensile fracture process. As shear deformation dissipates a large amount of energy, the blend shows a high elongation at break (Fig. 5). For still higher TS loading of 50% [Fig. 7(f)], the figure shows fibrillation, leading to ductile failure. This is typical of mode A-type ductile failure as discussed earlier for 7(b).

Figure 8(a–f) shows the impact fractured surface of blend specimens containing 20, 40, and 50% TS loading. Figure 8(a,b) shows the fractured surfaces of blends with 20% TS loading. For a lower TS loading of 20%, the fracture occurs mainly by matrix yielding even without the compatibilizer, as is evident from Figure 8(a). The addition of 15% (based on TS) compatibilizer [Fig. 8(b)] to this blend results in ductile failure characterized by both crazing and plastic deformation. The improved adhesion between the two phases leading to ductile fracture may be attributed to the effective compatibilization by EVOH. This is also reflected by the high relative impact strength values, showing the impact strength almost at par with that of neat LDPE.

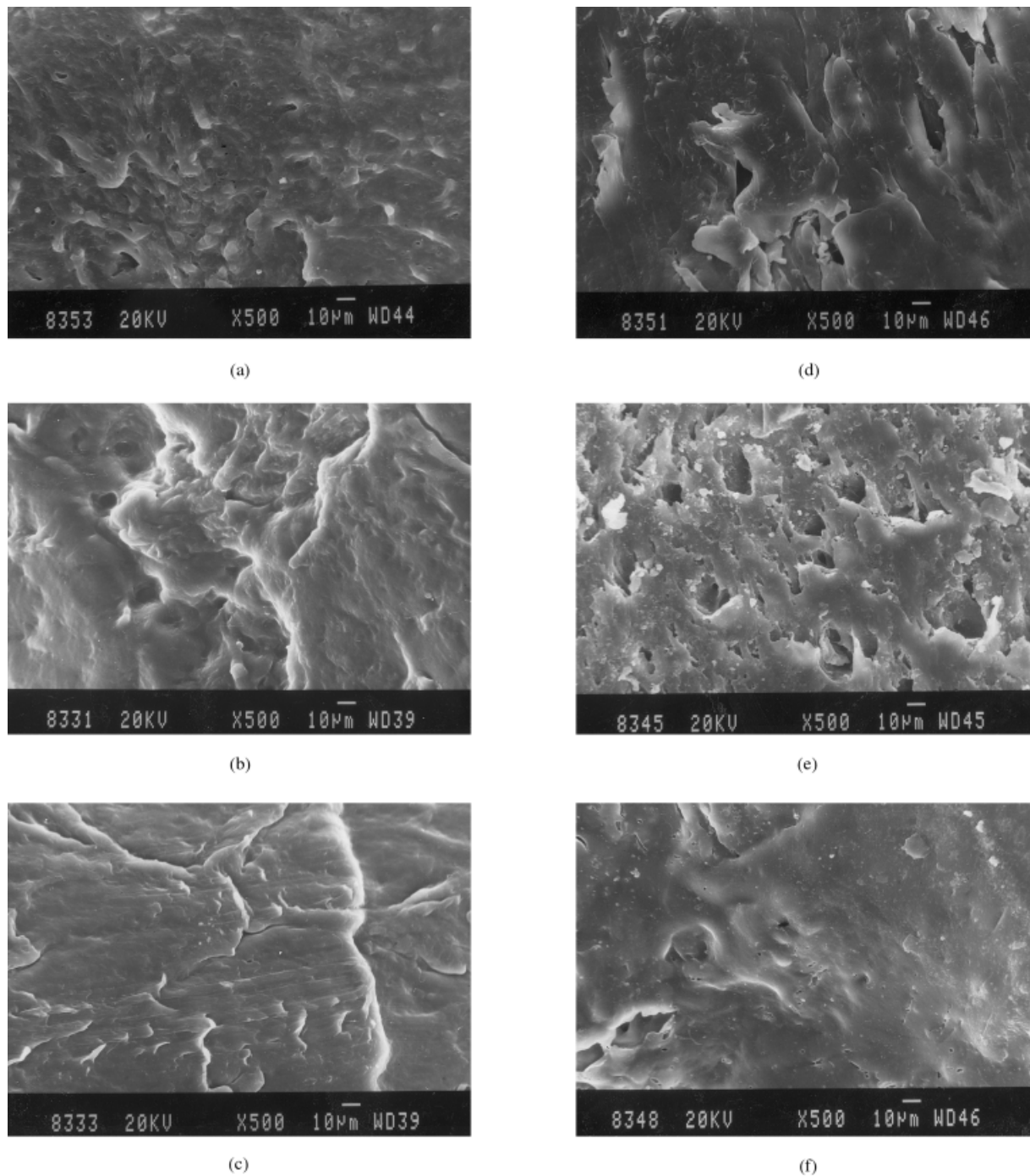


Figure 6 SEM micrographs showing morphology of etched blend specimens: (a) blend containing 20% TS and no compatibilizer; (b) blend containing 20% TS and 10% compatibilizer; (c) blend containing 20% TS and 25% compatibilizer; (d) blend containing 50% TS and no compatibilizer; (e) blend containing 50% TS and 15% compatibilizer; (f) blend containing 50% TS and 25% compatibilizer. All percentages are given on the basis of TS in the blend.

Figure 8(c,d) shows the impact fractured SEM micrographs with 40% TS loading. Figure 8(c) shows a brittle fractured surface when no compatibilizer is added to the blend. This is due to poor adhesion between the phases in the blend containing higher amounts of dispersed TS particles. With the addition of 15% (based on TS) compatibilizer,

the fractured surface [Fig. 8(d)] shows large plastic deformation along with flushing out of TS particles due to debonding of TS from the matrix. This resistance to fracture imparts a high relative impact strength to the blend that is characteristic of ductile failure. The ductile failure observed on addition of the compatibilizer may be attributed to improved

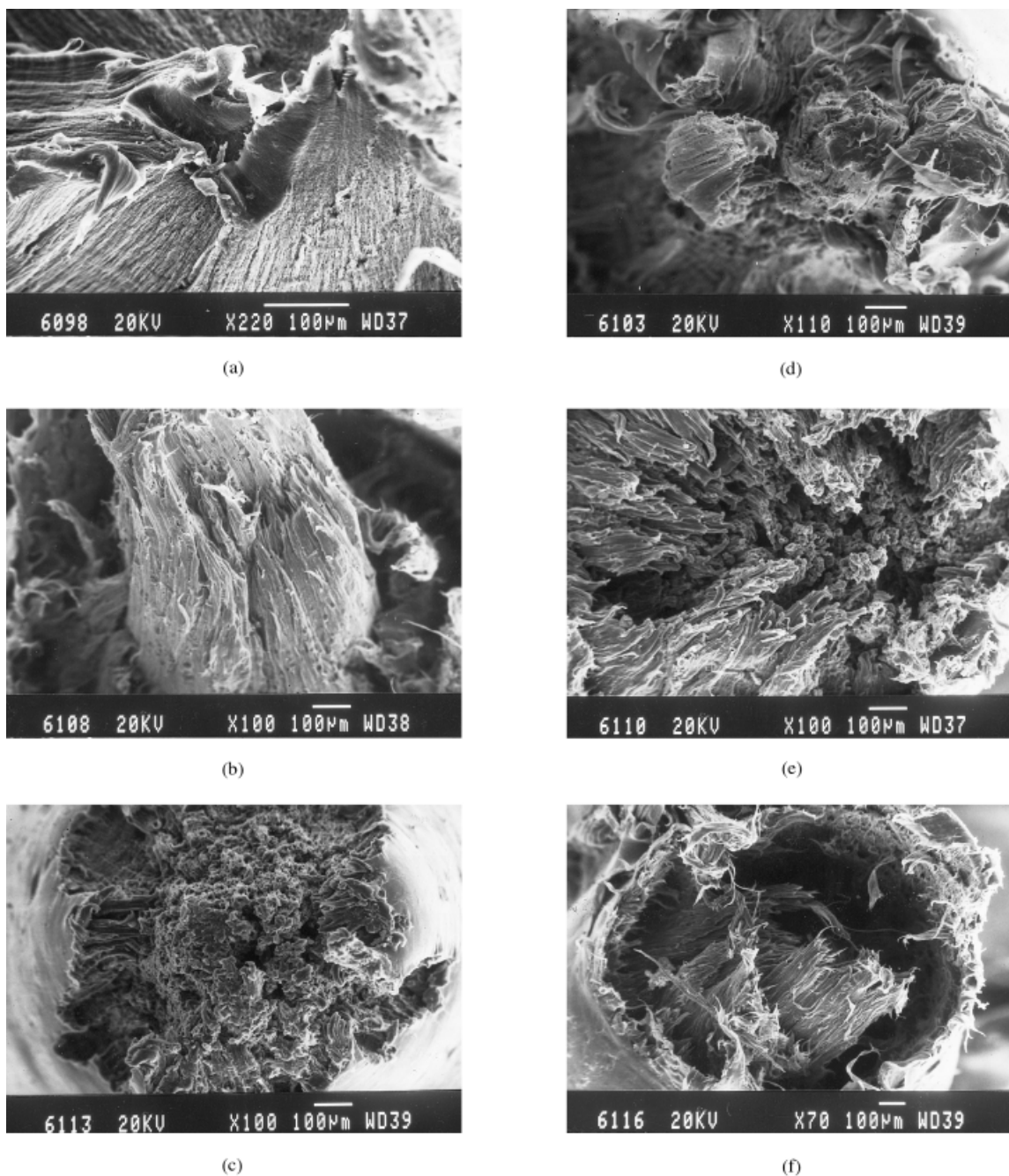


Figure 7 SEM photographs showing tensile fractured blend specimens: (a) blend containing 20% TS and 25% compatibilizer; (b) blend containing 30% TS and 25% compatibilizer; (c) blend containing 40% TS and 25% compatibilizer; (d) blend containing 30% TS and 15% compatibilizer; (e) blend containing 40% TS and 15% compatibilizer; (f) blend containing 50% TS and 15% compatibilizer. All percentages are given on the basis of TS in the blend.

interfacial adhesion caused by strong interactions of the two immiscible phases with the EVOH compatibilizer. This also accounts for the high impact strength values obtained.

Figure 8(e-f) shows SEM photographs of impact fractured surfaces containing 50% TS loading. The blend containing no compatibilizer shows brittle fracture owing to very poor adhesion between LDPE and TS, as is evident from Figure 8(e). Figure 8(f) is for a

blend containing 15% (based on TS) compatibilizer, which indicates the occurrence of slight plastic deformation prior to quasi-brittle fracture.

CONCLUSIONS

Blends of LDPE and TS compatibilized with the EVOH copolymer were molded into dumbbell speci-

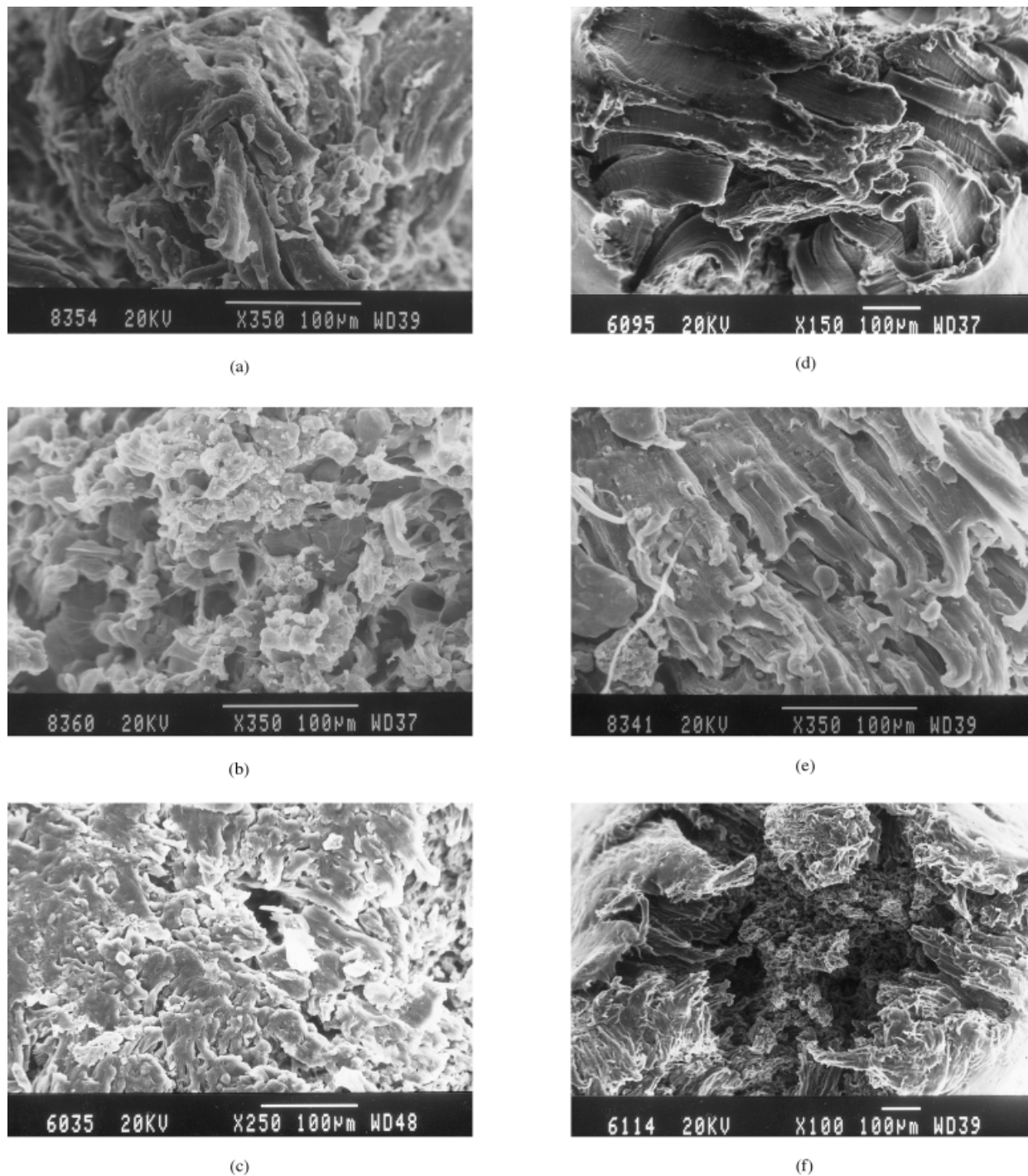


Figure 8 SEM photographs showing impact fractured blend specimens: (a) blend containing 20% TS and no compatibilizer; (b) blend containing 20% TS and 15% compatibilizer; (c) blend containing 40% TS and no compatibilizer; (d) blend containing 40% TS and 15% compatibilizer; (e) blend containing 50% TS and no compatibilizer; (f) blend containing 50% TS and 15% compatibilizer. All percentages are given on the basis of TS in the blend.

mens to study their mechanical properties. While the impact strength of the uncompatibilized blends decreases with increase in the TS loading, the compatibilized blends show a significant improvement in impact strength, nearly reaching the value obtained for neat LDPE. The modulus and tensile strength values

also increase on addition of EVOH. High values of elongation at break can be obtained by compatibilizer addition even at high TS loadings of 40 and 50%. The blend morphology of the water-etched surface reveals a finer dispersion of TS in LDPE for compatibilized blends, while the fracture morphology shows fibrilla-

tion and debonding of TS from the matrix, leading to ductile failure even for these high TS loadings of 40 and 50%, thereby leading to better mechanical properties.

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