

Effect of Electron Beam Irradiation on Mechanical Properties of High Density Polyethylene and Its Blends with Sericite-Tridymite-Cristobalite

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ABSTRACT: Some oxygen containing groups (mainly the C=O group) are formed on the molecular chain of high density polyethylene (HDPE) during electron beam irradiation in air. The affinity between HDPE and sericite-tridymite-cristobalite (STC), the dispersion of STC in the HDPE matrix, and the mechanical properties of the HDPE/STC blend are improved quite a lot by the introduction of polar groups. Compared with HDPE, the tensile and impact strength of electron beam irradiated HDPE (30 kGy)/STC (60/40) are increased to 29.0 MPa and 518 J/m, respectively, from 24.5 MPa and 215 J/m; the tensile and impact strength of irradiated HDPE (30 kGy)/STC (50/50) are 31.1 MPa and 424 J/m, respectively. The Ceast impact test showed that the increase of impact strength was mainly due to the strong interfacial adhesion between irradiated HDPE and STC, thus preventing the spreading of cracks over wide areas. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 243–249, 2000

Key words: electron beam irradiation; high density polyethylene; sericite-tridymite-cristobalite

INTRODUCTION

Polyolefines make up over 35% of all plastics produced in the world; polyethylene (PE) and polypropylene (PP) are the only high volume polyolefines. For the purposes of increasing its stiffness at room temperature, as well as at static state, and increasing its toughness at low temperature and a high strain rate, we studied the effect of electron beam irradiation on the mechanical properties of high density PE (HDPE) filled with sericite-tridymite-cristobalite [STC, a kind of naturally born flaky sericite, which contains about 70% $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ and 30% fibroillary sil-

ica]. We hoped to gain an innovative route to simultaneously increase the stiffness and toughness of polyolefine-based materials.

Polyolefine is hydrophobic polymer. Efforts have to be made to enhance its compatibility with its reinforcers, which are hydrophilic. Through electron beam irradiation in air, some oxygen-containing groups (mainly the carbonyl group) can be introduced on the molecular chain of HDPE,^{1–8} and the interface compatibility and mechanical properties of its blend with STC can be improved. The crux of the matter is to avoid crosslinking reaction and an excessive degradation of HDPE during irradiation. Optimal control of the dose and dose rate are important; otherwise, the strength of the irradiated materials will be dampened or will cause trouble in processing because of the presence of gelled material.

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Figure 1 FTIR spectra of electron beam irradiated HDPE at (a) 0, (b) 20, (c) 40, (d) 60, (e) 80, and (f) 100 kGy.

EXPERIMENTAL

Materials

The materials used were HDPE-5000S powder, with a melt index (MI) of 0.8 g/10 min and a density of 0.943 g/mL (China) and STC with an average particle size of 1.6 μm and a specific gravity of 2.7 (China).

Irradiation of HDPE

Irradiation was performed in air at ambient temperature (about 298 K) with a JJ-2 static electron

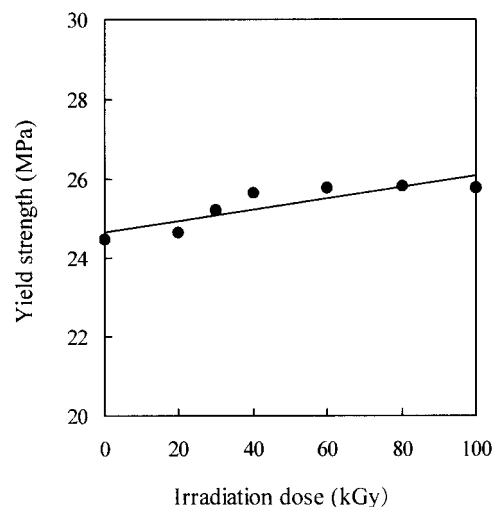


Figure 2 The yield strength of HDPE vs. the irradiation dose.

accelerator at a voltage of 1.75 MeV and a current of 20 μA . The conveyor on which the HDPE powder was placed was reciprocated at a speed of 2.38 cm/min. The irradiation dose per passage of the conveyor under the electron beam was 10 kGy.

Sample Preparation and Mechanical Properties Testing

The HDPE (or electron beam irradiated HDPE) and STC were blended in a twin roller at $145 \pm 2^\circ\text{C}$ for a period of 10 min; then they were molded into 1 and 4 mm thick sheets, respectively. The mechanical tests were performed according to GB 1040-92 and GB 1843-80.

FTIR Measurement

The spectra were recorded on a Nicolet-560 FTIR spectrometer.

Table I Molecular Weight and Its Distribution, Contact Angle, and Gel Content of Electron Beam Irradiated HDPE

Dose (kGy)	$\bar{M}_w (\times 10^{-4})$	$\bar{M}_n (\times 10^{-4})$	\bar{M}_w/\bar{M}_n	Contact Angle	Gel (%)
0	10.61	2.85	3.73	82°	0
20	6.18	2.13	2.89	76°	0
40	5.88	1.95	3.02	70°	0
60	5.10	1.78	2.83	68°	0
100	5.10	1.58	3.23	62°	0

The dose rate was 360 kGy/h.

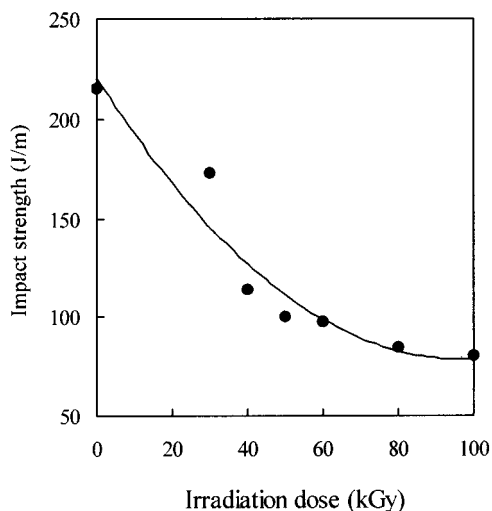


Figure 3 The impact strength of HDPE vs. the irradiation dose.

Contact Angle Measurement

The HDPE was compression molded into a 100 μm thick film; the contact angle was measured with an Erma G-1 contact angle tester.

Ceast Impact Test

The test was conducted on Ceast instrumental impact tester (Italy) according to GB 1843-80.

Scanning Electron Microscopy (SEM)

The fractured surfaces of the specimens after being frozen with liquid nitrogen and the impact

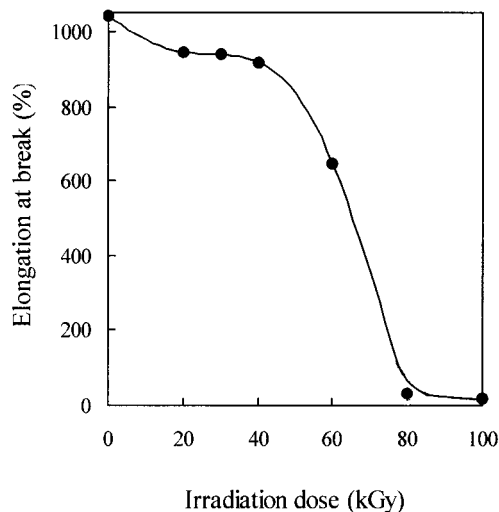


Figure 4 The elongation at break of HDPE vs. the irradiation dose.

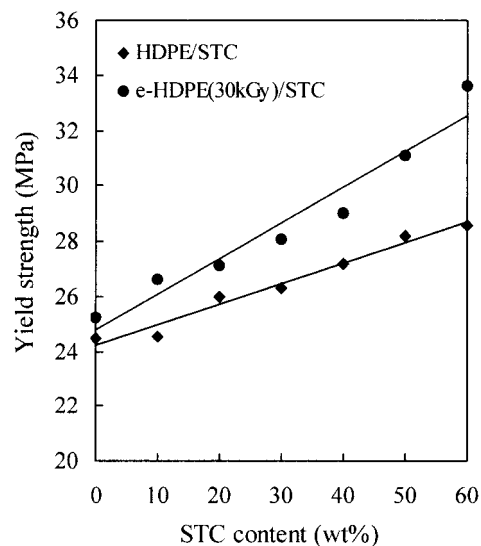


Figure 5 The yield strength of the HDPE/STC blend vs. the STC content.

fractured surfaces were observed through an X-650 scanning electron microanalyzer.

RESULTS AND DISCUSSION

Effect of Electron Beam Irradiation on HDPE

As shown in Figure 1, the HDPE is oxidized during electron beam irradiation in air. Oxygen-containing groups (mainly carbonyl groups, situated

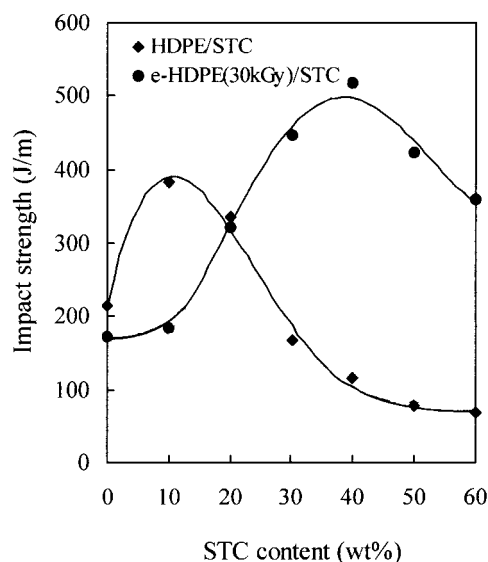


Figure 6 The impact strength of the HDPE/STC blend vs. the STC content.

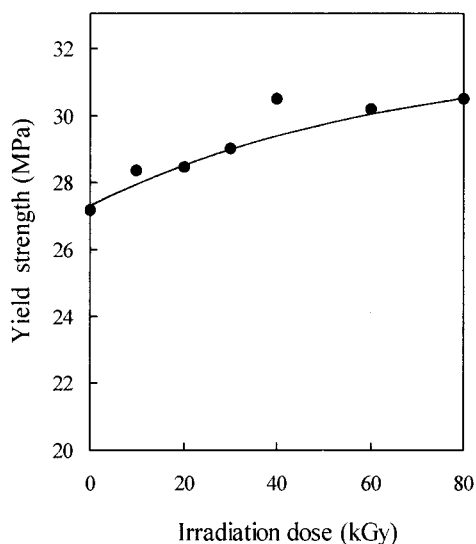


Figure 7 The yield strength of the HDPE/STC blend vs. the irradiation dose.

at 1727 cm^{-1}) are introduced on the molecular chain of HDPE, and its contact angle with water becomes smaller (Table I). During irradiation, the $-\text{CH}=\text{CH}-$ (*trans*) group (situated at 960 cm^{-1}) also appears in the HDPE chain. Irradiation causes the degradation of HDPE: the molecular weight is decreased with an increase in the dose of irradiation (Table I).

The yield strength of HDPE increases (Fig. 2) with the irradiation dose. Its impact strength (Fig. 3) and elongation at break (Fig. 4) decrease

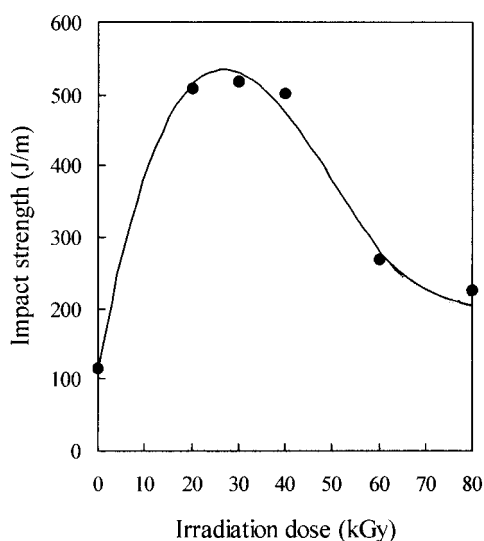


Figure 8 The impact strength of the HDPE/STC blend vs. the irradiation dose.

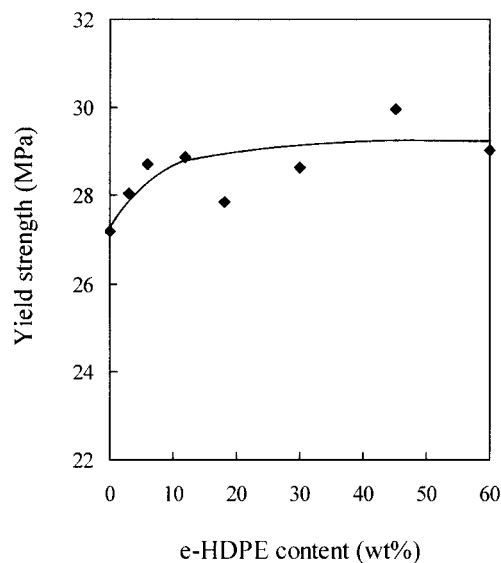


Figure 9 The yield strength of the e-HDPE (30 kGy)/HDPE/STC (40%) blend vs. the e-HDPE content.

with the irradiation dose because of excessive degradation during irradiation; the molecular weight of the irradiated sample is too low to stand against the high strain rate. The optimal irradiation dose in this case is 30 kGy.

Mechanical Properties of Electron Beam Irradiated HDPE (e-HDPE)/STC Blend

As shown in Figure 5, the yield strength of electron beam irradiated HDPE (e-HDPE) (30 kGy)/STC is

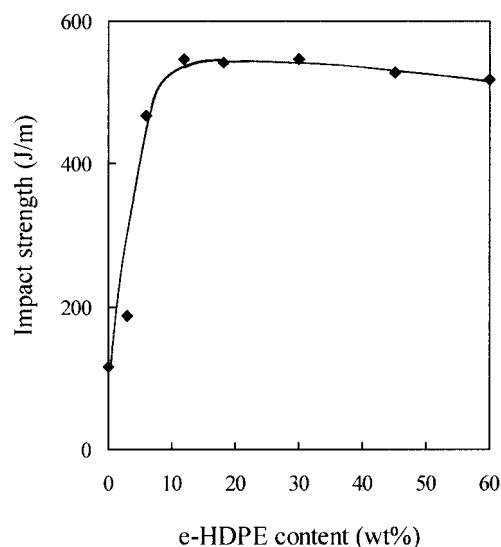


Figure 10 The impact strength of the e-HDPE (30 kGy)/HDPE/STC (40%) blend vs. the e-HDPE content.

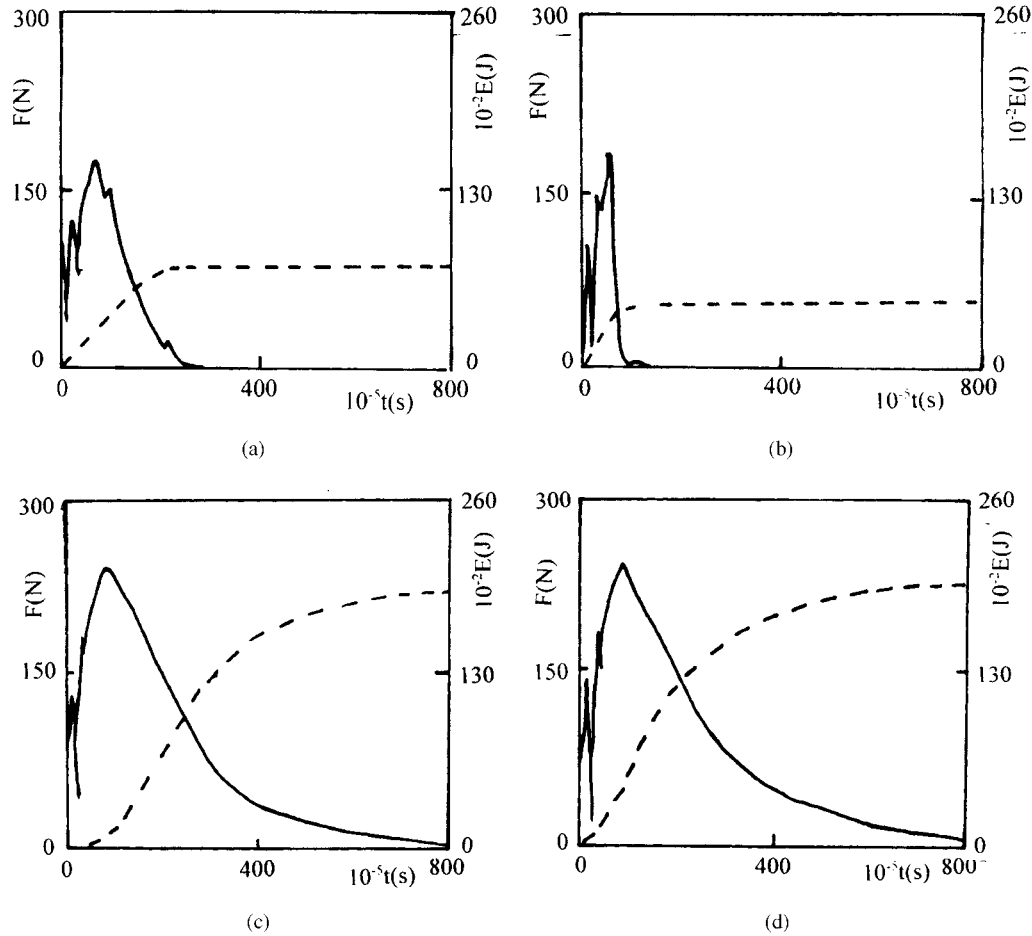


Figure 11 The impact force and the total energy of cracking vs. the breaking time in the Ceast impact test for (a) HDPE, (b) HDPE/STC 60/40, (c) e-HDPE (30 kGy)/STC 60/40, and (d) e-HDPE (30 kGy)/HDPE/STC 12/48/40.

higher than that of HDPE/STC with the same STC content. Compared with the HDPE/STC blend, the impact strength of the e-HDPE (30 kGy)/STC blend is greatly increased (Fig. 6) and reaches a maximum value when the STC content is 40%.

Figures 7 and 8 show the irradiation dose effect on the yield strength and impact strength of the

e-HDPE/STC blend. The yield strength of the e-HDPE/STC blend increases with the dose, and the impact strength of the blend reaches its maximum value when the irradiation dose is 30 kGy.

As shown in Figure 9, the yield strength of the e-HDPE (30 kGy)/HDPE/STC blend is improved with the increase of the e-HDPE content in the

Table II Characteristic Values of Specimen during Ceast Impact Test

Sample	X (m) (10^{-3})	t (s) (10^{-5})	F_{\max} (N)	E (J)	E_i (J)	E_p (J)
HDPE	10.07	300.	203.2	0.8592	0.3189	0.5403
HDPE/STC (60/40)	4.40	128.6	219.5	0.4645	0.3297	0.1348
e-HDPE (30 kGy)/STC (60/40)	25.18	>800	263.4	2.073	0.4708	1.6022
e-HDPE (30 kGy)/HDPE/STC (12/48/40)	24.90	>800	261.4	2.1932	0.3977	1.7953

Normalized data. X , pendulum displacement; t , breaking time; F_{\max} , maximum impact force; E , total energy of cracking; E_i , energy associated with initial crack; E_p , energy associated with crack propagation.

Table III Impact Properties of Specimen in Ceast Impact Test

	S (J/m)	S_i (J/m)	S_p (J/m)
HDPE	215	80	135
HDPE/STC (60/40)	116	82	34
e-HDPE (30 kGy)/STC (60/40)	518	118	400
e-HDPE (30 kGy)/HDPE/STC (12/48/40)	548	100	448

S , impact strength; S_i , impact cracking strength; S_p , impact crack propagation strength.

blend. The impact strength of the blend reaches its maximum when the e-HDPE (30 kGy) content in the blend amounts to 18% (Fig. 10).

Impact Course Analysis

Ceast instrumental impact tester was used for analyzing the toughening mechanism of the e-HDPE (30 kGy)/STC blend. The HDPE/STC blend is a brittle material [Fig. 11(b)]; it tends to crack at its limit of elastic deformation, followed by a rapid rupture, then a sudden drop of antiforce to zero. For the e-HDPE (30 kGy)/STC blend [Fig. 11(c)], the peak of the impact force curve $F(t)$ is broadened and the energy integration curve reaches its limit slowly, indicating that more energy is absorbed during fracturing, cracks propagate more slowly, and the material becomes

tougher. The e-HDPE (30 kGy)/HDPE/STC blend [Fig. 11(d)] behaves like the e-HDPE/STC blend during the course of impact.

As shown in Table II, the impact force at the peak, F_{\max} , represents the highest loading that the specimen can sustain; t is the breaking time; E is the total energy of cracking; and E_i and E_p ($E_p = E - E_i$) are tentatively taken as the measures of energy associated with crack initiation and propagation, respectively. The more brittle the material, the less the energy absorbed during failing; the corresponding parameters such as pendulum displacement X , breaking time t , and E_i and E_p behave like E .

From E , E_i , and E_p we can calculate the impact strength S , the impact crack initiating strength S_i , and the impact crack propagating strength S_p : $S = E/b$, $S_i = E_i/b$, and $S_p = E_p/b$, where b is the specimen thickness. The figures listed in Table III are calculated values. The increase of S and S_p clearly shows that owing to irradiation the interfacial adhesion between HDPE and STC gets improved, the spread of cracks over wide areas is prevented, and the impact strength becomes higher.

SEM Analysis

The dispersion of STC particles in the matrix could be seen from the SEM of the liquid nitrogen frozen, fractured surface of the specimen. STC particles are unevenly dispersed in the HDPE/STC blend [Fig.

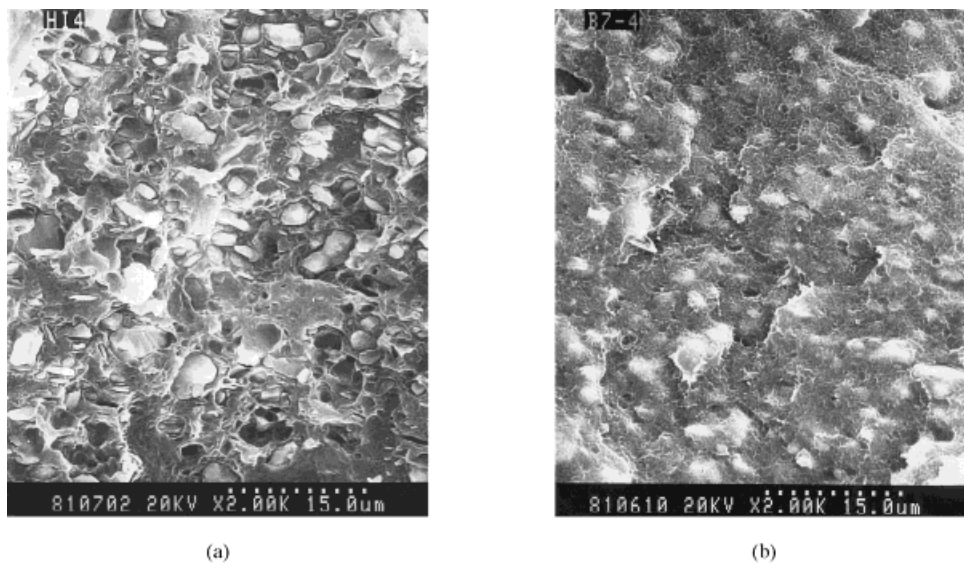


Figure 12 SEM of liquid nitrogen frozen, fractured surface of specimen (original magnification $\times 2000$) for (a) HDPE/STC 60/40 and (b) e-HDPE (30 kGy)/STC 60/40.

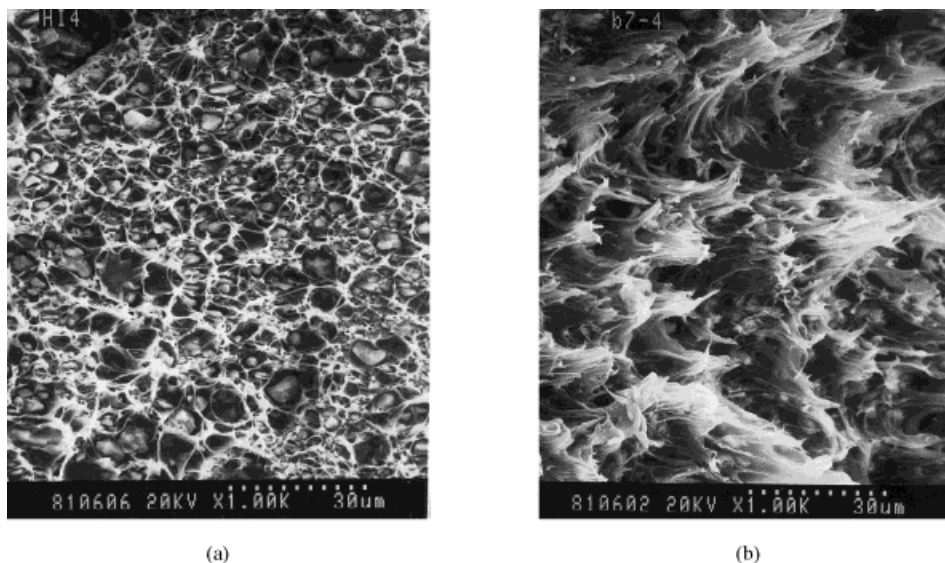


Figure 13 SEM of the fractured surface of the specimen after impact testing (original magnification $\times 1000$) for (a) HDPE/STC 60/40 and (b) e-HDPE (30 kGy)/STC 60/40.

12(a)]. In the e-HDPE (30 kGy)/STC blend, all STC particles are wrapped with e-HDPE; none are exposed on the surface [Fig. 12(b)].

As shown in Figure 13(a), the STC particles are exposed on the surface, showing a weak adhesion between the STC and the matrix. The interfacial adhesion is improved [Fig. 13(b)] in the e-HDPE (30 kGy)/STC blend.

REFERENCES

1. Singh, A.; Sjlverman, J. *Radiation Processing of Polymers*; Hanser: Munich, 1991; p 222.
2. Ivanov, V. S. *Radiation Chemistry of Polymers*; VSP: Utrecht, The Netherlands, 1992; p 191.
3. Clough, R. L.; Shalaby, S. W. *Radiation Effect on Polymers*, ACS Symposium Series 475; American Chemical Society: Washington, DC, 1991; p 473.
4. Carlsson, D. J.; Chmela, S.; Lacoste, J. *Macromolecules* 1990, 23, 4934.
5. Spadaro, G.; Valenza, A.; Acierno, D.; Galderaro, E. *Proceedings of The Ninth Annual Meeting of the Polymer Processing Society*, Manchester, UK, April 5–8, 1993; p 283.
6. Tidjani, A.; Watanabe, Y. *J Polym Sci Part A Polym Chem* 1995, 33, 1455.
7. Lacoste, J.; Carlsson, D. J.; Falicki, S.; Wiles, D. M. *Polym Degrad Stabil* 1991, 34, 309.
8. Xu, W.; Liu, P.; Luo, L. *Polym Mater Sci Eng (China)* 1997, 13, 101.