Effect of Interfacial Interaction on the Mechanical Properties of Electron Beam Irradiated HDPE/STC Blend

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ABSTRACT: Some oxygen-containing groups (mainly C═O group) are introduced on the molecular chain of HDPE during electron beam irradiation in air. The affinity between HDPE and sericite–tridymite–cristobabite (STC), the dispersion of STC in HDPE matrix are improved owing to the polar groups introduced. By treating STC with amino-containing silane coupling agent, the interfacial adhesion between irradiated HDPE (e-HDPE) and treated STC (t-STC) is further improved, the mechanical properties of e-HDPE/t-STC blend are improved quite a lot. The experimental results show that due to the improvement of interfacial interaction, the interfacial phase can transmit the stress subjected to the HDPE matrix and make the matrix absorb energy by plastic yield or deformation; the impact strength of e-HDPE/t-STC blend is thus improved. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 814–820, 2002; DOI 10.1002/app.10345

Key words: electron beam irradiation; polyethylene (PE); blends; interfaces

INTRODUCTION

Stiffness and toughness are the important mechanical properties for the application of polyolefine. How to improve the stiffness and toughness of polyolefine in the meantime has become an interesting topic in polymer science. Elasticity toughening usually worsens the modulus, stiffness, and heat distortion temperature (HDT) significantly. In recently years, inorganic fillers are widely used in polymer blends to increase modulus and stiffness. However, the application of inorganic filler often causes the toughness, especially the notched impact strength decrease.

The hydrophobic polyolefine is weak in interfacial adhesion with hydrophilic inorganic filler. To improve the mechanical properties of HDPE filled with sericite–tridymite–cristobalite (STC, a kind of naturally born flaky sericite, contains about 70% $KAl_2(AlSi_3O_{10})(OH)_2$, 30% fibroillary silica), some approaches have to be made for enhancing the interfacial interaction.

Some oxygen-containing groups (mainly carbonyl group) could be introduced on the molecular chain of HDPE[1–6] through electron beam irradiation in air, the interfacial interaction and mechanical properties of electron beam irradiated HDPE (e-HDPE)/STC blend are thereby improved greatly.

EXPERIMENTAL

Materials

Materials used were HDPE-5000S powder, with a melt index (MI) of 0.8 g/10 min and density of

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0.943 g/cm^3, STC with a average particle size of 1.6 μm and specific gravity of 2.7, silane coupling agents A-1100 [$H_2N(CH_2)_3Si(OC_2H_5)_3$], A-151 [$CH_2{=}CHSi(OC_2H_5)_3$], A-187 [$CH_2\text{—}\underset{\diagdown\,O\,\diagup}{CH}\text{—}CH_2\text{—}O(CH_2)_3Si(OCH_3)_3$] and A-174[$CH_2{=}\underset{\displaystyle CH_3}{\overset{\displaystyle \|\,O}{C\text{—}C}}\text{—}(CH_2)_3Si(OCH_3)_3$].

Irradiation of HDPE

It was performed in air at ambient temperature (about 298 K) by a JJ-2 static electron accelerator at a voltage of 1.75 Mev and current of 20 μA. The conveyer on which the HDPE powder was placed was reciprocated at a speed of (2.38 cm/min). Irradiation dose per passage of the conveyer under the electron beam is 10 kGy.

Treating of STC Powder

STC powder and silane coupling agent were mixed in a certain ratio by a high-speed blender.

Sample Preparation and Mechanical Properties Testing

HDPE (or electron beam irradiated HDPE) and STC (or treated STC) were blended in a twin roller at 145 ± 2°C for a period of 10 min, then molded to sheet of 1 mm and 4 mm thick, respectively. The mechanical tests were performed according to GB 1040-92 and GB 1843-80.

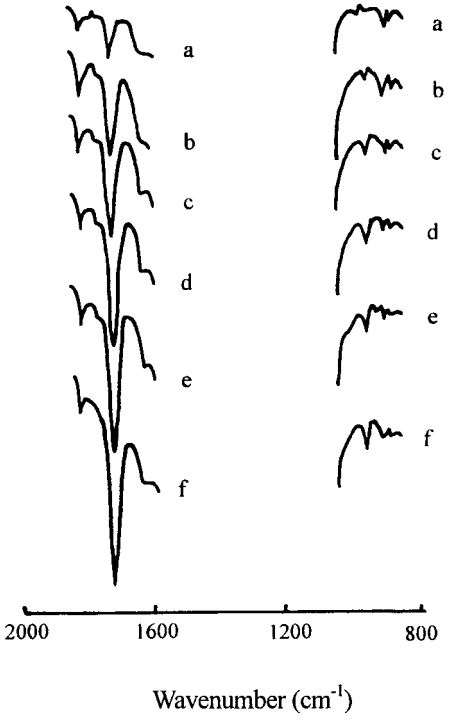


Figure 1 FTIR spectra of electron beam irradiated HDPE. (a) 0kGy, (b) 20kGy, (c) 40kGy, (d) 60kGy, (e) 80kGy, (f) 100kGy; dose rate: 360kGy/h.

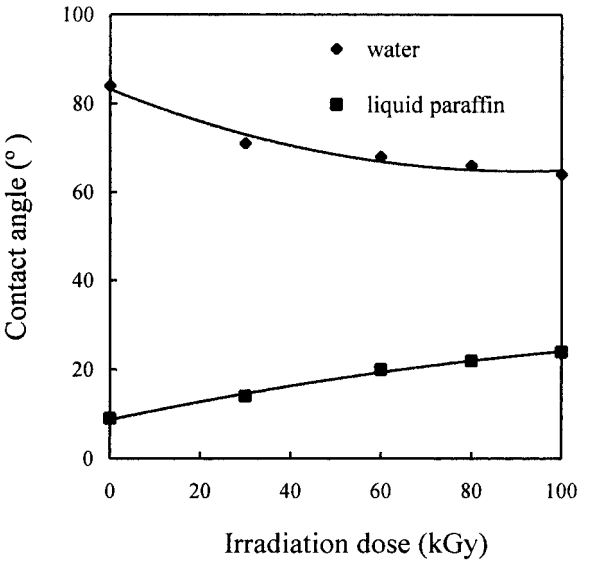


Figure 2 Contact angle of electron beam-irradiated HDPE vs. irradiation dose.

FTIR Measurement

HDPE was molded to film of 100 μm thick, the spectra were recorded on Nicolet-560 FTIR spectrometer.

Contact Angle Measurement

HDPE was molded to film of 100 μm thick, then measured with Erma G-1 contact angle tester.

Particle Size Analysis

The particle size and its distribution of size were measured with SALDZ2001 Laser Grainsize Analyzer.

Table I Chemical Composition of Sericite–Tridymite–Cristobalite

Component	Content by Weight	Component	Content by Weight
SiO_2	70.69%	Al_2O_3	16.24%
Fe_2O_3	3.11%	ZnO	2.37%
K_2O	6.07%	MgO	0.16%
CaO	1.22%	TiO_2	0.14%

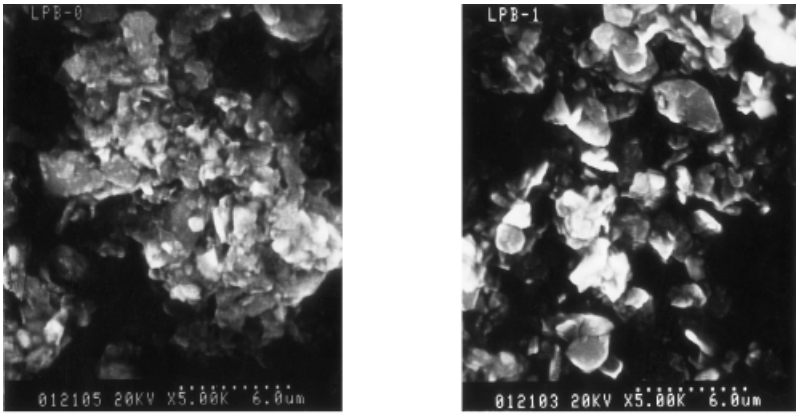


Figure 3 Morphology of STC particles (×5000).

Scanning Electron Microscopy (SEM)

The fractured surfaced of specimens after being frozen with liquid nitrogen and the impact fractured surfaces were observed through X-650 Scanning Electron Microanalyzer.

RESULTS AND DISCUSSION

Effect of Electron Beam Irradiation on the Hydrophilicity of HDPE

HDPE is hydrophobic polymer, through electron beam irradiation in air, oxygen-containing groups (mainly carbonyl groups, situated at 1727 cm^{-1}) are introduced on the molecular chain of HDPE (Fig. 1). With the increase of irradiation dose, the contact angle of HDPE with water becomes smaller, and that with liquid paraffin increases (Fig. 2), indicating the increase of polarity of HDPE. With the increase of irradiation dose, the molecular weight of HDPE is decreased, its yield strength increases, and the impact strength decreases.[6]

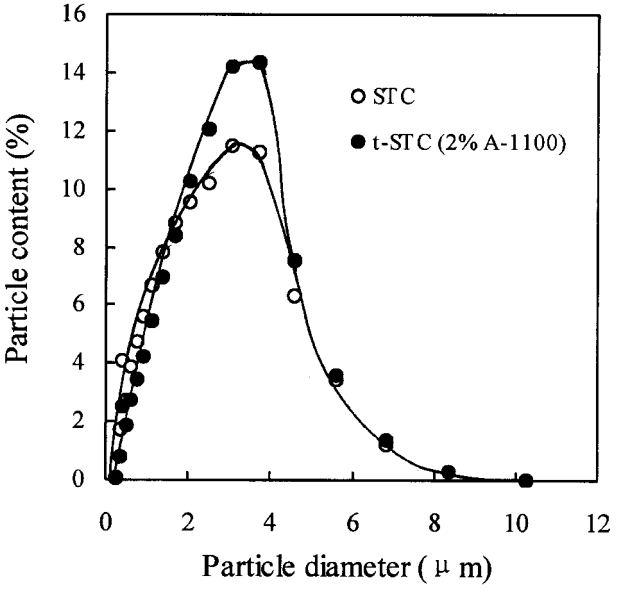


Figure 4 Particle size distribution of STC.

The Chemical Composition and Properties of Sericite–Tridymite–Cristobalite (STC)

The chemical composition of STC is listed in Table I. STC have the advantages of weather and chemical corrosion resistance and the high heat stability. Figure 3 is the scanning electron morphology of STC particles, the STC particles

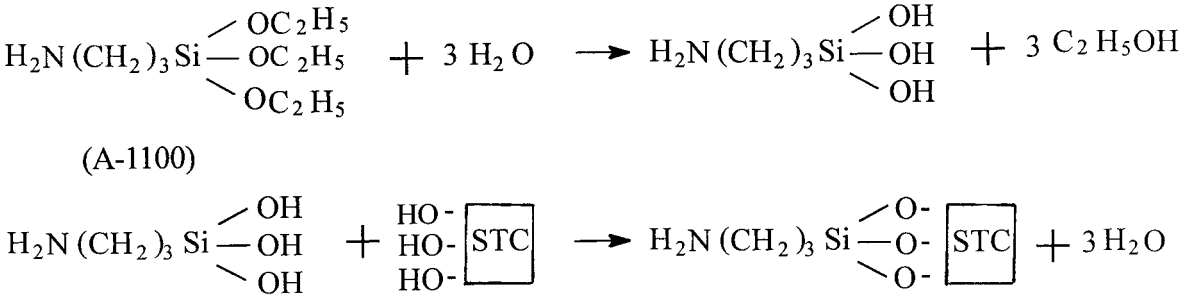
Table II Mechanical Properties of HDPE/STC Blend

Sample	Yield Strength (MPa)	Impact Strength (J/m)
HDPE	24.5	215
HDPE/STC (60/40)	22.6	39
e-HDPE(30kGy)/STC (60/40)	27.5	105
HDPE/t-STC (2% A-1100) [60/40]	27.2	116
e-HDPE(30kGy)/t-STC (2% A-1100) [60/40]	29.0	518

Table III Mechanical Properties of e-HDPE (30 kGy)/STC (60/40)Blend Containing Different Kind of Silane Coupling Agent

Silane Coupling Agent	Molecular Formula	Yield Strength (MPa)	Impact Strength (J/m)
—	—	27.5	105
A-1100	$H_2N(CH_2)_3Si(OC_2H_5)_3$	29.0	518
A-151	$CH_2{=}CHSi(OC_2H_5)_3$	27.0	194
A-187	$CH_2(O)CH{-}CH_2{-}O(CH_2)_3Si(OCH_3)_3$	25.8	96
A-174	$CH_2{=}C(CH_3)C(=O)O(CH_2)_3Si(OCH_2)_3$	26.8	74

agglomerate, in case STC is treated with a 2% silane coupling agent A-1100, the dimension of agglomeration particles turns small, and the particle size distribution becomes narrower (Fig. 4). The reaction of A-1100 with STC is below:



After treating with A-1100, some amino groups are introduced on the surface of STC particles.

The Interfacial Interaction of Electron Beam Irradiated HDPE/STC Blend

The Mechanical Properties of Electron Beam-Irradiated HDPE/STC Blend

Compared with the HDPE/STC blend, the yield and impact strength of electron beam-irradiated HDPE (e-HDPE) (30 kGy)/STC blend are increased to 27.5 MPa and 105 J/m from 22.6 MPa and 39 J/m, respectively; in case the treated STC is used, the yield and impact strength of HDPE/STC (treat with 2% A-1100) blend are 27.2 MPa and 116 J/m. Through the electron beam irradiation and STC treating with A-1100, the yield and impact strength of the e-HDPE (30 kGy)/STC (treat with 2% A-1100) blend are increased to 29.0 MPa and 518 J/m, respectively, the impact strength is 2.4 times of that of HDPE, the toughening effect is very evident (Table II).

To analyze the interfacial interaction of the e-HDPE/t-STC blend, four kinds of silane coupling agents containing different functional groups were used for the surface modification of STC. The data listed in Table III show that the blends of e-HDPE and STC treated with different silane coupling agent differ greatly in their mechanical properties. The low polar functional groups of the A-151, A-187, A-174 could not inter-

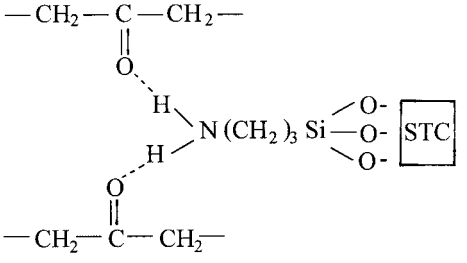


Figure 5 The schematic diagram of the interaction between e-HDPE and STC treated with A-1100.

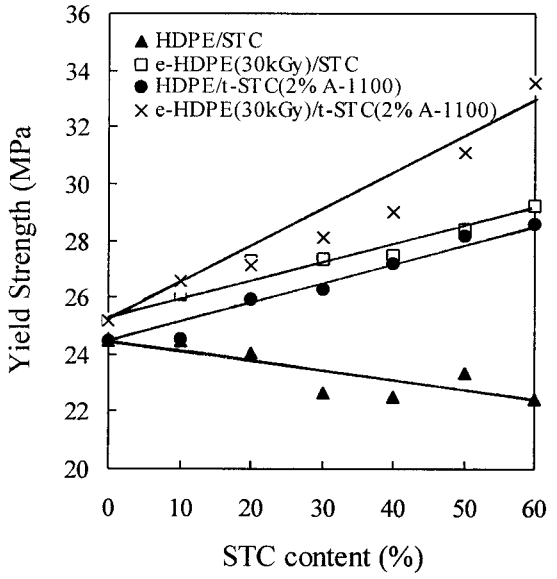


Figure 6 Yield strength of HDPE/STC vs. STC content.

act with the carboxyl groups on the molecular chains of e-HDPE, thereby the mechanical properties decrease; for the coupling agent A-1100, the polar amino groups could interact with the carbonyl groups on the e-HDPE molecular chains (Fig. 5), the interfacial interaction is strengthened and the mechanical properties are thus improved greatly.

Due to the strengthening of interfacial interaction, the yield strength of e-HDPE (30 kGy)/t-STC

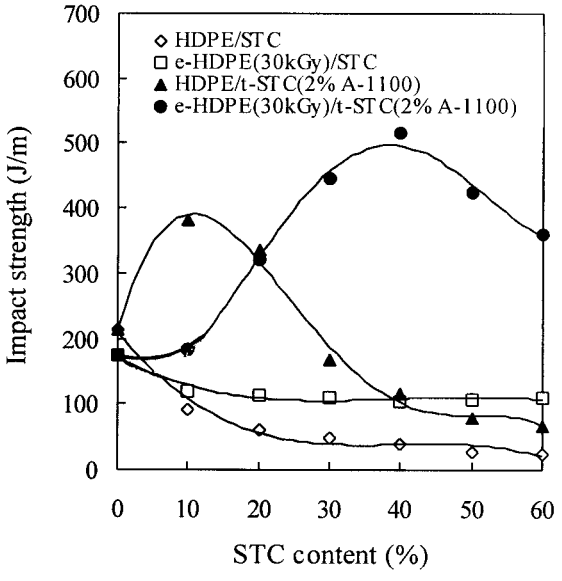


Figure 7 Impact strength of HDPE/STC vs. STC content.

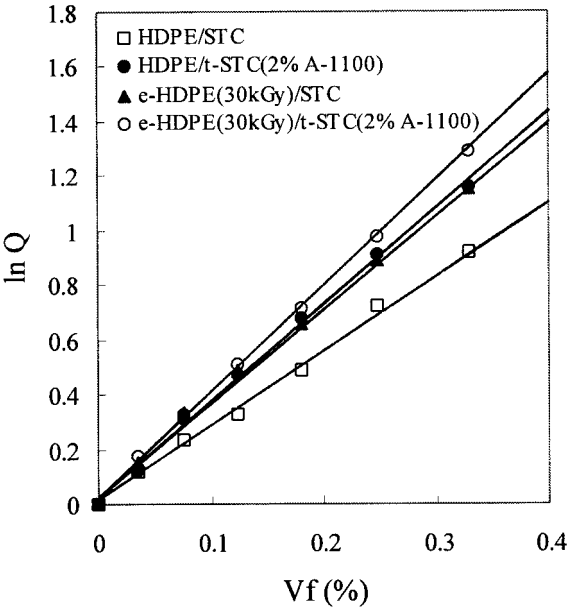


Figure 8 In Q vs. volume fraction of STC.

(2% A-1100) is higher than that of the HDPE/STC and e-HDPE/STC blend with the same STC content (Fig. 6), and the impact strength of the blend is greatly increased quite a lot, reaches a maximum value of 518 J/m when the t-STC content is 40% (Fig. 7).

The Interfacial Interaction of the e-HDPE/t-STC Blend

To quantitatively character the effect of interfacial adhesion on the mechanical properties of the blend, the interfacial interaction parameter β was introduced in this article. Turczanyi has proposed a one-parameter equation to calculate the interfacial interaction between the matrix and fillers with different surface treatments[7,8]:

$$\sigma_{yc} = [(1 - V_f)/(1 + 2.5V_f)]\sigma_{ym}\exp(\beta V_f),$$

where, σ_{yc} is the yield strength of the blend; σ_{ym} is the yield strength of the matrix, V_f is the filler volume fraction; β is the interfacial interaction parameter. β is a semiempirical parameter, $\beta = (1 + k\gamma A_f \rho_f)\ln(\sigma_{yi}/\sigma_{ym})$, where, k is semiempirical constant, γ is the filler surface free energy, ρ_f and A_f are the density and specific surface area of the filler, and σ_{yi} is the yield stress of the matrix immobilized by the filler.

By introducing a relative yield strength Q : $Q = \sigma_{yc}/\sigma_{ym}[(1 + 2.5V_f)/(1 - V_f)]$, and plotting ln

Table IV β Values of HDPE/STC Blend

Blend	β-Value
HDPE/STC	2.8
e-HDPE(30kGy)/STC	3.6
HDPE/t-STC (2% A-1100)	3.6
e-HDPE(30kGy)/t-STC (2% A-1100)	4.0

Q vs. V_f, we could obtain the linear dependences (Fig. 8). Slopes of these plots determined the interfacial interaction parameters β (Table IV).

The β values of HDPE/STC, e-HDPE(30 kGy)/STC, HDPE/t-STC(2%A-1100), and e-HDPE (30 kGy)/t-STC (2% A-1100) blend are 2.8, 3.6, 3.6, and 4.0, respectively. Due to the interaction of the polar amino groups of A-1100 with e-HDPE molecules, the interfacial interaction of the e-HDPE (30 kGy)/t-STC (2% A-1100) blend becomes stronger, the mechanical properties are thus improved greatly.

SEM Analysis

The adhesion between e-HDPE and STC particles could be seen from the SEM of the liquid nitrogen frozen fractured surface of the specimen. For the e-HDPE (30 kGy)/t-STC (2% A-1100) blend, all t-STC particles are wrapped with e-HDPE; none are exposed on the surface (Fig. 9), showing a stronger interfacial adhesion between t-STC and e-HDPE matrix.

As shown in Figure 10, the fractured surface is full of bumps and holes, a lot of fibrils are left on the fractured surface, indicating that during impact the interfacial phase could transmit external stress to the HDPE matrix, and the matrix absorb energy through a plastic yield or deformation; the impact strength of e-HDPE/t-STC blend is thus improved.

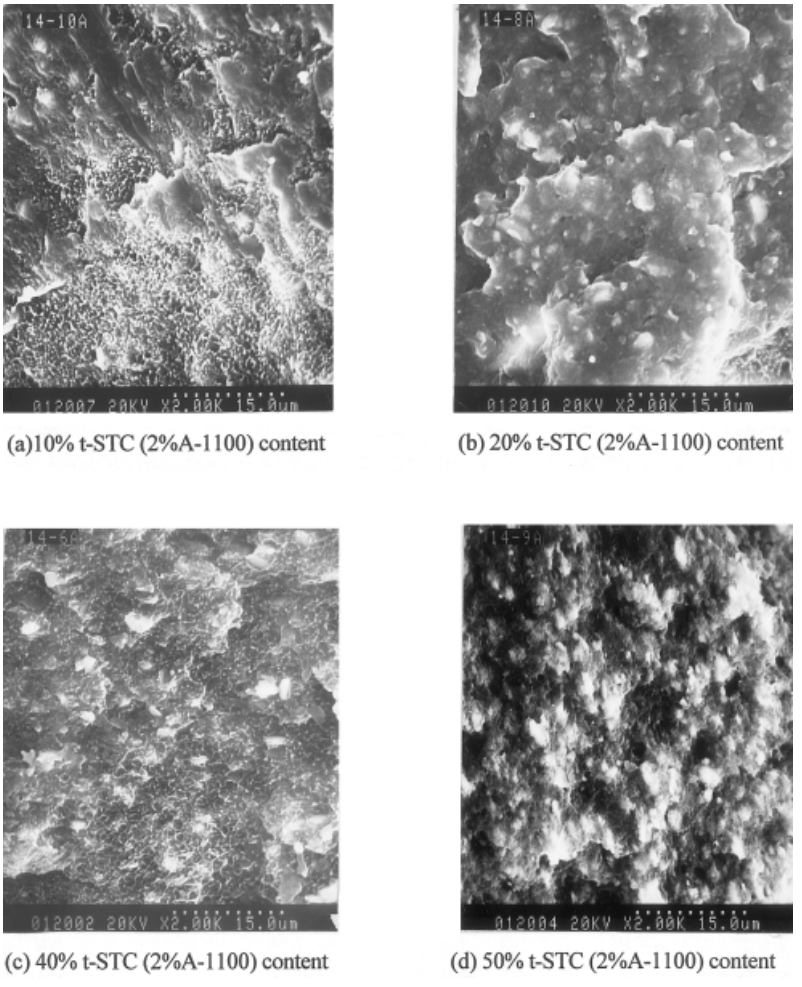


Figure 9 SEM of liquid nitrogen frozen fractured surface of specimen (×2000).

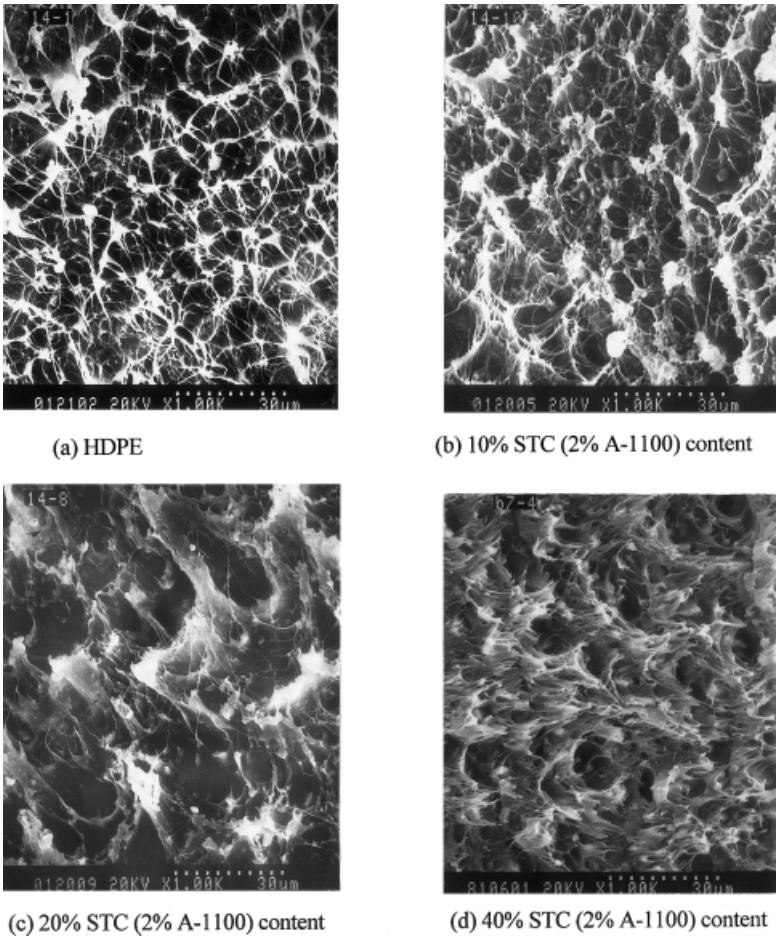


Figure 10 SEM of fractured surface of specimen after impact testing (×1000).

CONCLUSIONS

1. Through electron beam irradiation, oxygen-containing groups (mainly carbonyl groups) are introduced on the molecular chain of HDPE; the polarity of HDPE is thus increased.
2. By treating STC with the silane coupling agent A-1100, some amino groups are introduced on the surface of STC particles, which could react with the carbonyl groups on the e-HDPE molecular chains, and the interfacial interaction is further strengthened and the mechanical properties of the blend are thus improved markedly.

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