

Radiation Preparation of Ultrafine Carboxylated Styrene–Butadiene Rubber Powders and Application for Nylon 6 as an Impact Modifier

Jing Peng,¹ Xiaohong Zhang,² Jinliang Qiao,² Genshuan Wei¹

¹Institute of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, People's Republic of China

²SINOPEC Beijing Research Institute of Chemical Industry, Beijing, People's Republic of China

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ABSTRACT: Ultrafine carboxylated styrene–butadiene rubber(CSBR) powders were prepared by using gamma irradiation and following spray-drying method. The influences of dose rate, absorbed dose, and sensitizer content on the crosslinking density of CSBR latices were studied in detail. Then the ultrafine CSBR powders were used to toughen nylon 6. The toughness and thermal properties of nylon 6/CSBR blends were measured by using notched Izod impact test and differential scanning calorimetry and thermogravimetry, respectively. Results showed that the crosslinking density of CSBR increased with increasing of dose and sensitizer content, and it is independent on dose rate. The notched Izod impact strength of nylon 6 under room temperature increased after incorporation of irradiation

crosslinked CSBR powders with appropriate crosslinking density. The morphology of higher impact nylon 6/CSBR blends indicated that the finer dispersion existed with dispersed particles of 150-nm diameter. Fracture morphology of nylon 6/CSBR blend suggested that the shear yielding in matrix is the primary toughening mechanism for nylon 6/CSBR blends. The crystallinity of nylon 6/CSBR blends decreased slightly compared with pure nylon 6, whereas the addition of CSBR powders had little influence on the thermal stability of nylon 6. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3040–3046, 2002

Key words: irradiation; crosslinking; nylon

INTRODUCTION

Nylon is a very attractive class of engineering polymers, and has been used widely in numerous applications because of its excellent tensile properties, chemical and abrasion resistance, wear resistance, and high melting point. Nevertheless, nylon, especially nylon 6, is known to be very notch-sensitive and brittle at low temperature.¹ Adding some thermoplastic elastomers or rubbers is a commonly employed practice to obtain new materials with good impact properties.^{2–7} The tougher usually used is a maleated ethylene propylene rubber (EPR-g-MAH) or a maleated ethylene propylene diene rubber (EPDM-g-MAH). Recently, Ou^{8,9} used maleated poly(ethylene-octane) (POE-g-MAH) to modify nylon 6, and obtained the super-tough nylon 6. However, it should be noted that most of maleated elastomers are prepared by melt grafting in an extruder or mixer, due to the high volatility and toxicity of MAH monomer; the working environment is very harmful to workers' health. So we

should choose the monomer with no toxicity and little pollution for the environment to modify the polyolefin elastomers.

Carboxylated styrene–butadiene rubber (CSBR) latex has been used as adhesive in the carpet industry, and has low cost. Few of them are used to modify thermoplastics. Because the chemical structure of CSBR has the carboxyl group that can react with the amine end group of nylon 6 during the melt blending, it is expected that CSBR has good miscibility with nylon 6, and thus can modify the property of nylon 6. In this article, ultrafine CSBR rubber powders were prepared, and the toughness, morphology, and thermal stability of nylon 6/CSBR blends were investigated. On the technical side, this work provided a new method to improve the toughness of thermoplastics with gamma irradiation tailor-made ultrafine crosslinked rubber powders with different crosslinking densities.

EXPERIMENTAL

Materials

Carboxylated styrene–butadiene rubber latex (type XSBR-541), was provided by YanShan petrochemical Co., China. 2-Ethyl hexyl acrylate (2-EHA) was served

Correspondence to: G. S. Wei (gswei@pku.edu.cn).

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as crosslinking sensitizer. Nylon 6(UBE 1013B), with an inherent viscosity of 2.7, was supplied by the UBE Co., Japan. Toluene was used as received. Nylon 6 pellets were dried at 100°C in a vacuum oven for 24 h prior to blending.

Preparation of ultrafine CSBR powders

First, the sensitizer with a certain content was added into the CSBR latex and stirred for 1 h, then kept for more than 10 h under room temperature. The CSBR latex was irradiated by gamma rays from a ^{60}Co source. The ultrafine powders were made by spray drying the irradiated CSBR latex. The latex particles range in size from 0.1 to 0.2 μm .

Measurement of swelling ratio and calculation of crosslinking density

Latex films were obtained by drying irradiation crosslinked and unirradiated CSBR latex that were poured onto glass plates. Equilibrium swelling was obtained by immersing the sample in toluene for 24 h under 30°C. The excess solvent was wiped off immediately by filter papers before the weighing the samples. Then the volume swelling ratio (Q_v) was calculated by the following equation:

$$Q_v = \frac{(W_2 - W_1)/\rho_s}{W_1/\rho_r} \quad (1)$$

where W_1 is the initial weight of gel, W_2 is the final weight of gel after swelling, ρ_s , ρ_r is the density of toluene and rubber, respectively. The crosslinking density of latices was calculated from the following relations.¹⁰

$$\Phi_r = 1/(Q_v + 1) \quad (2)$$

$$M_c = -\rho_r V_1 (\Phi_r^{1/3} - \Phi_r/2) / \{\ln(1 - \Phi_r) + \Phi_r + \mu \Phi_r^2\} \quad (3)$$

$$V_c = \rho_r N / M_c \quad (4)$$

where Φ_r is the volume fraction of rubber in gel samples, M_c is the average molecular weight per crosslinked units of the rubber ($\text{g} \cdot \text{mol}^{-1}$), V_1 is the molar volume of solvent ($\text{cm}^3 \cdot \text{mol}^{-1}$), and μ is the Flory-Huggins interaction parameter between the solvent and polymer. V_c is the crosslinking density or the number of crosslinks (cm^{-3}), N is Avogadro's number.

Blend preparation

The blends were prepared by compounding nylon 6 with radiation crosslinked CSBR powders on a

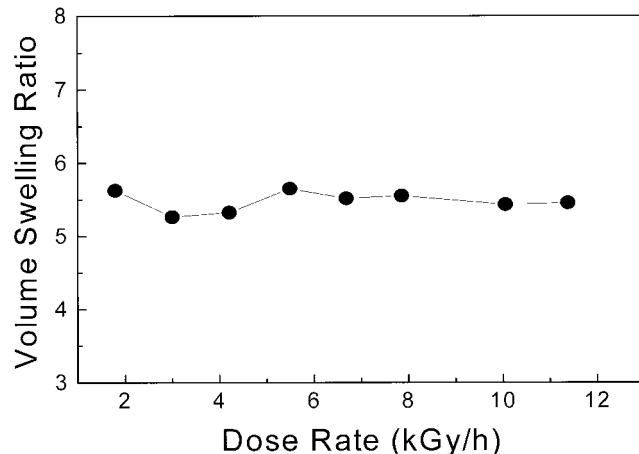


Figure 1 Effect of the dose rate on the swelling ratio of the CSBR latices (25 kGy, 3% 2-EHA).

SJSH-30 twin-screw extruder (Nanjing machinery industry, China). The blends were injected on a NC-150 injection-molding machine to samples for mechanical strength tests.

Material characterization

Notched Izod impact strength was measured according to ASTM D256 at 23°C. Morphology of undeformed impact specimens and deformation zones were studied by means of a Hitachi-800 transmission electron microscope (TEM) at an accelerating voltage of 200 kV using ultrathin sections cryogenically microtomed at -60°C. The rubber phase was stained by vapors of 2% OsO₄ aqueous solution for 40 min to distinguish the rubber phase. The impact fracture surface of nylon 6 and its blends were sputtered with a layer of gold and observed with a Hitachi S-530 scanning electron microscope (SEM). The melting temperature T_m and crystallization temperature T_c of nylon 6/CSBR blends were measured by using a Dupont 1090 differential scanning calorimetry (DSC) with the following procedure: the samples were heated up to 240°C and kept at this temperature for 10 min. Thereafter, the samples were cooled to room temperature at 10°C/min and the T_c was recorded, then the samples were heated at 10°C/min, the T_m , and the apparent enthalpies of melting, ΔH^* were obtained from the maximum and the area, respectively, of the melting peaks. The whole thermal scanning was carried out in nitrogen. The crystallinity of the nylon 6 $X_c(\text{Ny})$ and of the overall blend $X_c(\text{blend})$ was calculated by means of the following relations

$$X_c(\text{Ny}) = \Delta H^*(\text{Ny}) / \Delta H^0(\text{Ny}) \quad (5)$$

$$X_c(\text{blend}) = \Delta H^*(\text{blend}) / \Delta H^0(\text{Ny}) \quad (6)$$

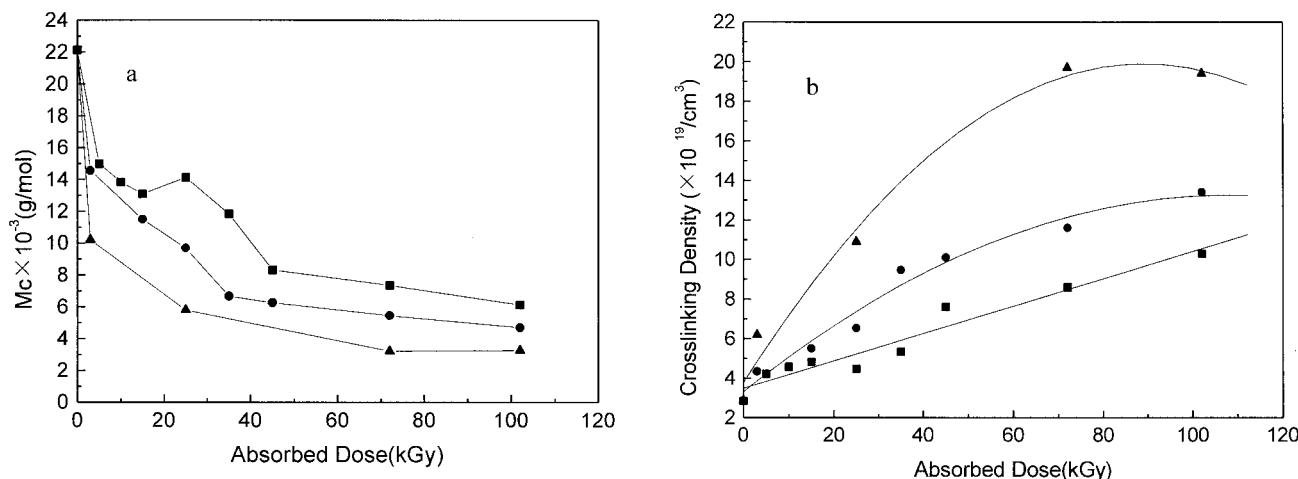


Figure 2 Relationship between the absorbed dose and M_c (a) and crosslinking density (b) of CSBR latices (3 kGy/h): (■) 0% 2-EHA; (●) 3% 2-EHA; (▲) 6% 2-EHA.

where $\Delta H^*(\text{Ny})$ and ΔH^* (blend) are the apparent enthalpy of melting per gram of nylon and its blend, respectively; $\Delta H^0(\text{Ny})$ is the heat of fusion per gram of 100% crystalline nylon ($\Delta H^0(\text{Ny}) = 189 \text{ J g}^{-1}$).¹¹

The thermal stability of CSBR and nylon 6/CSBR blends was studied on a Shimadzu TGA-50. The samples were heated at 10°C/min over the range of 50–500°C under nitrogen.

RESULTS AND DISCUSSION

It is well known that the toughness of many engineering thermoplastics can be improved by incorporation of a low modulus rubber. When the rubber is highly dispersed, the rubbery phase acts as an effective stress concentrator, and enhances crazing and shear yielding in the matrix. Due to absorption of large amounts of energy in these processes, the materials can exhibit superior resistance to crack propagation under impact conditions. Our experimental results showed that unirradiated CSBR latex could not be made into ultrafine rubber powders; only the irradiated latex under certain conditions can be used to form ultrafine rubber powders with diameter in 150 nm. Moreover, when the crosslinking density of rubber reaches a higher value, it is easy to prepare ultrafine powders. Additionally, the shear modulus of rubber particles relates to the crosslinking density. Steenbrick¹² used the network elasticity theory for Gaussian chains to estimate the shear modulus of the rubber particles. Accordingly, the relation between mean molecular weight per crosslinked units M_c and shear modulus G is given by following equation:

$$G = nRT = 4 \rho_r RT / M_c \quad (7)$$

where n is network density ($\text{mol} \cdot \text{m}^{-3}$), R is the universal gas constant ($\text{J mol}^{-1}\text{K}^{-1}$), and T is the ab-

solute temperature (K). It can be noted that the G value is proportional to the crosslinking density. Because the crosslinking density is related to irradiation parameters such as dose rate, absorbed dose, and sensitizer content, it is very necessary to study the relationship between the shear modulus of rubber and toughness of nylon 6/CSBR blends to optimize irradiation conditions.

Crosslinking property of CSBR latices

We studied the crosslinking property of irradiated CSBR latex by measuring the swelling ratio. The effect of dose rate on the swelling ratio is shown in Figure 1. During the dose rate range of 1.0–12 kGy/h, no marked effect is observed on the swelling ratio under 25 kGy dose. It can be concluded that the dose rate has a small effect on the crosslinking density of CSBR particles. Figure 2(a) and 2(b) show the effect of absorbed dose on the average molecular weight per crosslinked units (M_c) and crosslinking density (V_e), respectively. It can be seen that M_c decreased with the increase of absorbed dose, V_e increased with increasing of the absorbed dose. Due to the increase of the absorbed dose, the energy of the latex obtained is increased, which could directly produce some free

TABLE I
Effect of 2-EHA Content on the Crosslinking Density of CSBR Latices (25 kGy)

Concentration of 2-EHA (%)	Q_v	M_c (g/mol)	$v_e \times 10^{-19} (\text{cm}^{-3})$
0	8.52	15803.4	3.99
1	6.69	10426.8	6.06
3	6.41	9713.7	6.51
5	5.53	7551.1	8.37
6	4.73	5796.5	10.9

TABLE II
Effect of Absorbed Dose of CSBR on Notched Izod Impact Strength of Nylon 6/CSBR (95/5) Blends (3% 2-EHA)

Absorbed dose (kGy)	Crosslinking density ($10^{19}/\text{cm}^3$)	Shear modulus G of rubber (MPa) ^a	Notched Izod impact strength (J/m)
Pure nylon 6	—	—	79.1
15	5.50	0.22	77.9
25	6.51	0.27	104
72	11.6	0.47	90.3

^a Calculated values.

radicals in the polymer chain, and active intermediates from the radiolysis of the water; as a consequence, the crosslinking reaction is promoted. Similarly, the effect of a sensitizer content on the M_c and V_e is the same as that of the absorbed dose. Results are presented in Table I.

Toughness of nylon 6/CSBR blend

The 5% radiation crosslinked CSBR powders were added into the nylon 6 by melt mixing. The effect of absorbed dose on notched Izod impact strength is shown in Table II. It can be seen that the notched Izod impact strength increased with increasing the absorbed dose, and reached a maximum value at 25 kGy; with continuing to increase the dose, the impact strength dropped. Comparing the impact strength of pure nylon 6, the addition of 5% radiation-crosslinked CSBR powders with shear modulus of 0.27 MPa, at 25 kGy is very useful to improve the notched impact strength of nylon 6. Similarly, as shown in Table III, with the increase of the sensitizer content, the notched Izod impact strength of the blends was enhanced under a 25 kGy dose. However, at 72 kGy, the increase of the 2-EHA content is harmful to the impact strength, which may be attributed to the degradation of rubber under a higher dose and excessive stiffness of the rubber particles (with shear modulus of 0.80 MPa). Therefore, in the studied dose range, the rubber powders irradiated at 3% sensitizer content and 25 kGy dose has the best modification for the toughness of nylon 6.

Morphology of nylon 6/CSBR blends

The morphology of undeformed nylon 6/CSBR (95/5) blends was studied by TEM. As indicated in Figure 3, the particles of CSBR in nylon 6 matrix appear as uniform and darken spheres of a 150 nm diameter, which is close to the particle size of CSBR latex. Moreover, the rubber particle sizes of nylon 6/CSBR are nearly constant, which means that neither a further reduction nor aggregation of the particles has taken place during the dilution step and the injection molding process. Borggreve¹³ obtained similar results and explained that when there is sufficient interfacial adhesion between the dispersion and the matrix phase, the coalescence in melt blending of two polymers is prevented.

The stress whitening of the fracture surface of pure nylon 6 and nylon 6/CSBR (95/5) with the best-notched Izod impact strength was viewed by means of the scanning electron microscope (SEM; Fig. 4). As observed in the fracture surface of nylon 6 toughened with POE-g-MAH,⁹ the fracture surface of the pure nylon 6 exhibits plenty of feather like markings that are typical of a fractograph for brittle broken polymer as shown in Figure 4(a) and (b). The addition of 5% (wt %) CSBR changed the fracture morphology of nylon 6. Figure 4(c) displays some parabola markings, which are produced by the intersection of the main crack front, with secondary cracks propagating radically from the flaws on different planes. The higher magnification of the fracture surface of the nylon 6/CSBR blend is shown in Figure 4(d). It can be seen

TABLE III
Effect of 2-EHA Content on Notched Izod Impact Strength of Nylon 6/CSBR 95/5) Blends

Absorbed dose (kGy)	2-EHA content (%)	Crosslinking density ($10^{19}/\text{cm}^3$)	Shear modulus G of rubber (MPa) ^a	Notched Izod impact strength (J/m)
Pure nylon 6	0	—	—	79.1
25	0	3.99	0.16	94.0
25	3	6.51	0.27	104
72	3	11.6	0.47	90.3
72	6	19.7	0.80	72.9

^a Calculated values.

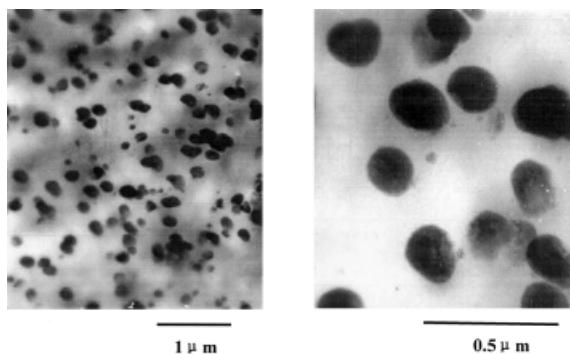


Figure 3 TEM photographs of the undeformed nylon 6/CSBR blend.

that some voids exist, and matrix shear yielding is observed. Because of these voids and shear yielding, a large amount of plastic deformation of the matrix resulted; therefore, the notched Izod impact strength of nylon 6 was improved.

The stress-whitened zone of nylon 6/CSBR impact specimens under 23°C was also studied by TEM (Fig.

5). TEM photographs show a number of elongated rubber particle with a length/diameter ratio of 8 and the orientation angle of particles is ~ 60° to the direction of the impact. Because the ultrathin sections were cut at 0–2 μm from the fracture surface, no crazes and cavities were observed, a similar case was shown for polyvinyl chloride (PVC) toughened with butadiene-based (MBS) modifier particles.¹⁴ It reported that no cavitation was detected and only high particle elongation was observed. Also, the rubber particle we used is ~ 150 nm in diameter, where it is not easy to initiate the cavitation in the rubbers.⁴ Although, we did not observe the cavitated rubber by TEM, further studies on cavitation of rubber particles in nylon 6/CSBR blends will be carried out. In the present work, the strongly deformed rubber particles suggest that the shear yielding is the primary toughening mechanism of nylon 6 modified with radiation-prepared ultrafine CSBR powders.

Thermal behavior

The melting temperature T_m of nylon 6 and its blend is reported in Table IV, as a function of crosslinking

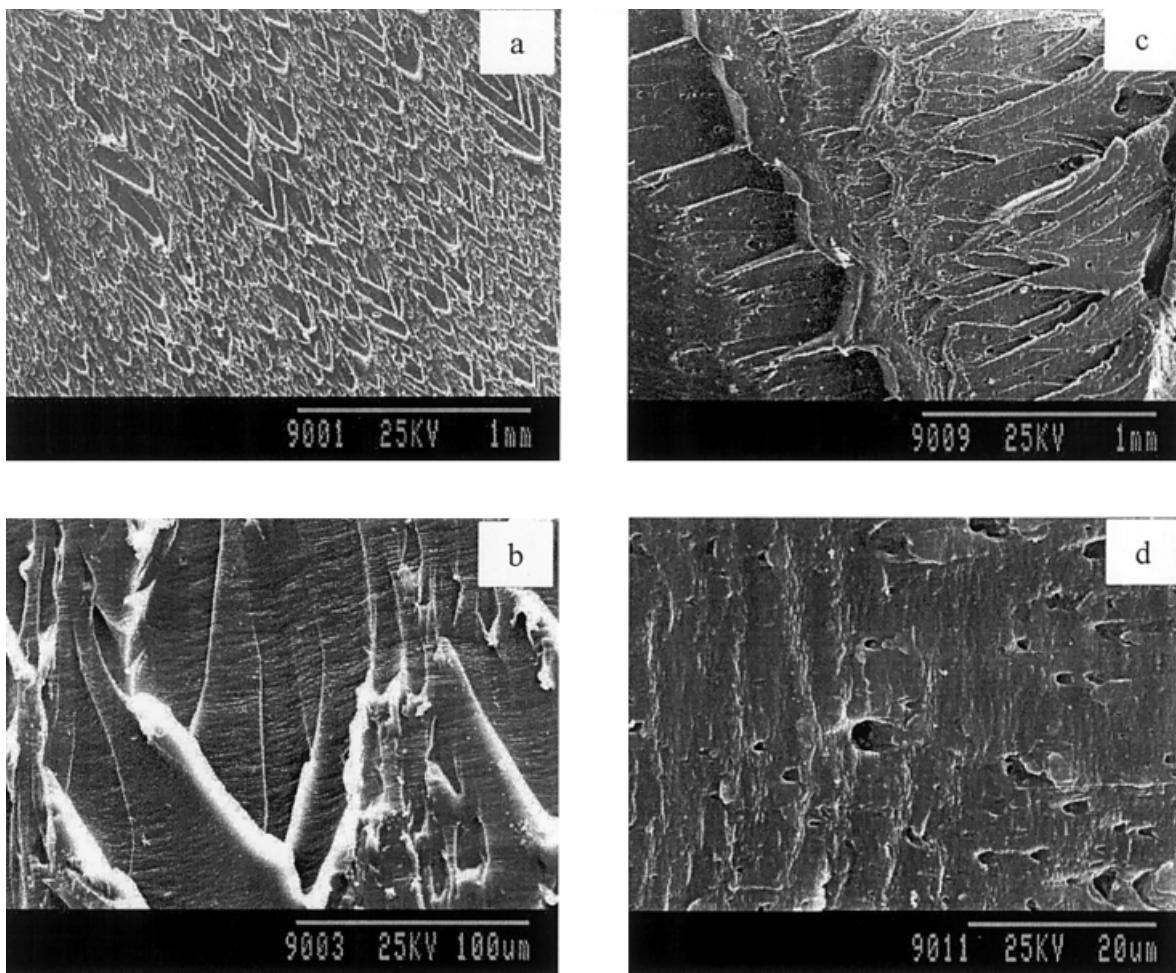


Figure 4 SEM study on the fracture surface in the stress-whitened region of pure nylon 6 (a,b) and the nylon 6/CSBR (95/5) blend with a higher impact strength (c,d).

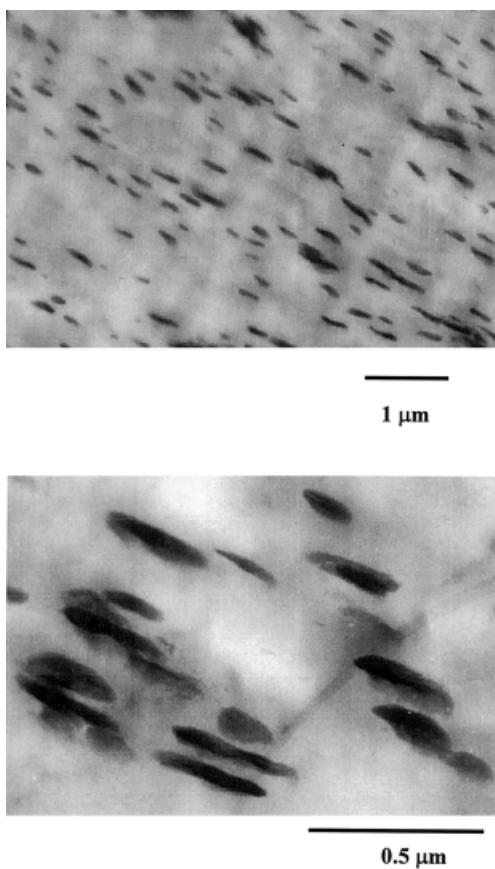


Figure 5 TEM photographs of a stress-whitening zone near the fracture surface of the nylon 6/CSBR blend with a higher impact strength.

density of CSBR. It indicates that both the addition of rubber powders and the variation of crosslinking density do not affect the thermal behavior of nylon 6. It is same with the results of Martuscelli;¹⁵ he reported that the T_m of the blends is almost independent of composition and chemical structure of the rubber. The T_c and crystallinity (x_c) of the nylon 6/CSBR blends and that of nylon 6 are also presented in Table IV. It shows that the addition of radiation crosslinked CSBR powders caused a small change of T_c and a slight decrease in x_c of the blends.

The thermal stability was studied by using thermogravimetry (TGA). Results are reported in Table V. The thermal stability of the blend under nitrogen was

TABLE V
TG Analysis Data of Nylon 6/CSBR (95/5) as a Function of V_e of CSBR Powders

$V_e(10^{19} \text{ cm}^3)$	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_{on} (°C)	T_{dmax} (°C)
Nylon 6	394.7	446.4	416.1	456.6
5.50	389.1	442.5	397.8	451.9
6.51	389.9	443.3	412.4	451.9
11.6	388.8	442.3	416.5	451.0

$T_{5\%}$, decomposition temperature at 5 wt % weight loss; $T_{50\%}$, decomposition temperature at 50 wt % weight loss; T_{on} , onset decomposition temperature; T_{dmax} , decomposition temperature with maximal degradation speed.

improved slightly with increasing of the crosslinking density of the CSBR powders. Compared with pure nylon 6, a small decrease in degradation temperature was observed after incorporation of the CSBR powders; nevertheless, the radiation crosslinked CSBR powders do not significantly affect the thermal stability of nylon 6.

CONCLUSIONS

The crosslinking density of irradiated CSBR latices is dependent on the absorbed dose and sensitizer content and independent on the dose rate. With the increase of absorbed dose and sensitizer content, M_c decreases and crosslinking density increases. The radiation-prepared ultrafine CSBR powders with appropriate crosslinking density can be used to modify the toughness of nylon 6; in the studied dose range, the rubber powders prepared at the 25 kGy dose and 3% 2-EHA can most effectively improve the notched Izod impact strength of nylon 6. The morphology of the undeformed sample exhibits the well dispersed rubber phase with a diameter of 150 nm. SEM photographs of the impact fracture surface of pure nylon 6 and its blends show certain characteristic features formed during the notched Izod impact process. Voids and shear yielding was observed in higher impact nylon 6/CSBR blends. Also, TEM photographs confirm the existence of shear yielding near the fracture surface in the stress-whitened zone. Due to these voids of rubber particles and shear yielding, the blends show a higher notched Izod impact strength. The addition of radiation-crosslinked CSBR powders slightly

TABLE IV
DSC Analysis of Nylon 6/CSBR (95/5) Blends and Pure Nylon

Samples	V_e ($10^{19}/\text{cm}^3$)	T_m (°C)	T_c (°C)	ΔH_f (J/g)	ΔH_c (J/g)	x_c (%)
Pure nylon 6	—	216.7	191.0	27.5	30.3	14.6
15 kGy, 3% 2-EHA	5.50	215.7	190.8	21.2	25.3	11.2
25 kGy, 3% 2-EHA	6.51	219.2	191.3	24.6	32.0	13.0
72 kGy, 3% 2-EHA	11.6	214.9	191.1	26.9	31.7	14.2
72 kGy, 6% 2-EHA	19.7	214.9	190.9	23.4	26.6	12.4

decreases the crystallinity of the nylon phase in its blends. However, almost no change in the T_m and degradation temperature was observed. Thus, the nylon 6 modified by radiation-crosslinked CSBR powders has good thermal stability. Because the radiation processing does not produce toxic byproducts and is beneficial for the environment, it can be expected that the preparation of rubber powders as a toughening agent for thermoplastics by using the radiation processing method has a deeply potential application in the future.

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