Chinese Journal of Polymer Science Vol. 20, No. 2, (2002), 93–98

Chinese Journal of Polymer Science

Rapid Communication

SPECIAL EFFECT OF ULTRA-FINE RUBBER PARTICLES ON PLASTIC TOUGHENING*

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Abstract According to the present theories of plastic toughening, it is impossible to enhance the toughness, stiffness and/or heat resistance of plastics simultaneously by using rubber. A series of novel nano-rubber particles (UFPR) were introduced, which were prepared through irradiating common rubber lattices and spray drying them. Epoxies toughened with UFPR showed a much better toughening effect than those with CTBN, and the heat resistance of epoxy was unexpectedly elevated. For polypropylene toughening, UFPR can improve the toughness, stiffness and heat resistance of PP simultaneously. These special toughening effects overcome the deficiencies in rubber toughening technology and are worth further investigating.

Keywords Powdered rubber, Nano-particles, Toughening, Polypropylene, Epoxy resin

The theories and technologies concerning plastic toughening with rubber have been studied comprehensively[1–12]. They indicate that the toughness of plastics could be improved by incorporation of rubber, but unfortunately the stiffness and heat resistance decrease to some extent at the same time. Moreover, it is impossible to enhance simultaneously the toughness, stiffness and/or heat resistance of plastics. However, the appearance of nano technology has made it possible to increase the toughness, stiffness and/or heat resistance of plastics simultaneously. Nano-inorganic materials in either lamellar form[13] or spherical form[14, 15] were able to improve the stiffness and heat resistance of plastics greatly, and enhance the toughness slightly. Thus it is worthwhile investigating whether the stiffness and heat resistance of plastics will be improved, when the toughness of plastics is evidently enhanced using nano-rubber as the toughening agent. The results of this work indicate that nano-rubber can improve the toughness, stiffness and/or heat resistance of many plastics simultaneously.

A series of nano-rubber particles (we call it ultra-fine full-vulcanized powdered rubber, UFPR) were prepared by the method[16] schematically shown in Fig. 1. The raw material for producing UFPR was common rubber latex, with or without premixing with cross-linking agent, which was then irradiated with γ ray or electron beam to change the latex particle from linear or slightly cross-linked to highly cross-linked structure. The UFPR was finally prepared by spray drying the highly cross-linked rubber latex. Since the UFPR has a highly cross-linked structure, it is non-sticky and can be used both in plastic toughening and in fully cured thermoplastic elastomer. As used in plastic toughening, the UFPR can greatly improve the toughness of many plastics, and at the same time it can keep the stiffness and/or heat resistance of plastics not only from lowering but also from increasing substantially.

* This work was financially supported by the Special Funds for Major State Basic Research Projects of China (No. G1999064800).
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Received October 25, 2001; Revised November 21, 2001; Accepted November 23, 2001

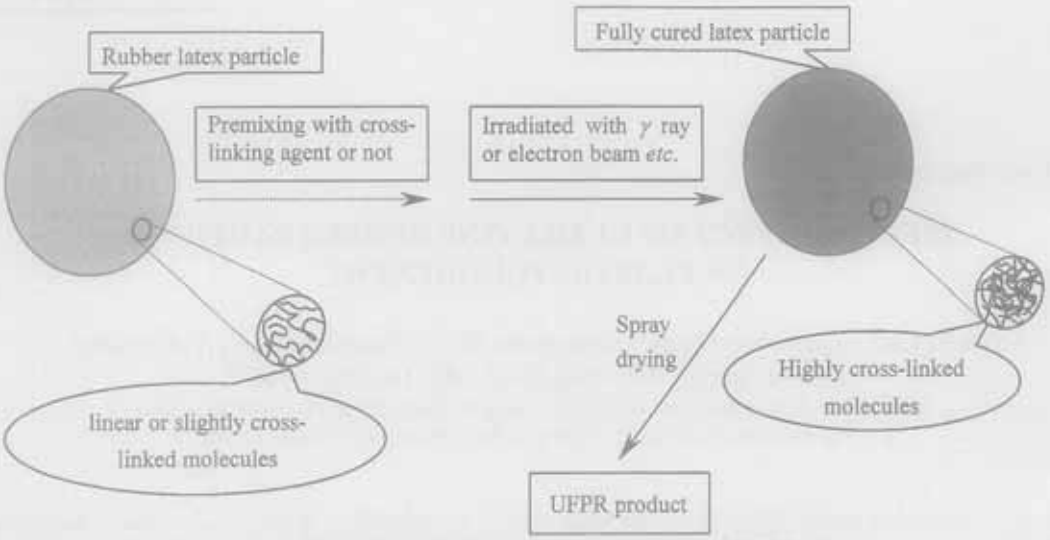

Fig. 1 Schematic diagram of the preparation of UFPR

Epoxy resins, the most widely used and studied thermosetting materials, are extensively employed as structural materials and adhesives in the aerospace and electronics industries for their high strength, high elastic modulus, and good heat and solvent resistance. Neat epoxy resins, however, have very low crack growth resistance and are one of the most brittle polymeric materials. Therefore, they need to be toughened in order to achieve a broad range of applications. Research concerning the toughening of epoxies[17–20] employs carboxyl-terminated butadiene acrylonitrile (CTBN) liquid rubber as the typical toughening agent. Some other rubber particles such as core-shell type rubber particles are also extensively used in toughening epoxy to investigate the toughening mechanism[21, 22]. However, the heat resistance of epoxies deteriorates through toughening.

Table 1. Mechanical and physical properties of different epoxy samples[a]

Sample	Izod impact strength (kJ/m^2)	Flexural strength (MPa)	Flexural modulus (GPa)	Heat distortion temperature(℃)	T_g (℃)[b]	
					DSC[c]	DMA[d]
A	11.4	102	3.18	113.2	110.8	142.0
B	22.3	81.4	2.76	114.4	118.3	150.0
C	15.9	86.6	2.66	107.6	107.1	—
Test standard	Chinese standard 1843	Chinese standard 9341	Chinese standard 9341	Chinese standard 1634	—	—

[a] A: neat epoxy; B: epoxy toughened with carboxylic nitrile-butadiene UFPR; C: epoxy toughened with CTBN (CTBN: M_η = 1586 g/mol, AN content = 27%)
The rubber contents in the toughened samples were all 12 phr based on uncured epoxy.
[b] The T_g values were determined by both DSC and DMA.
[c] PE-7 thermal analysis system was used, the heating rate was 20 K/min.
[d] The DMA determination was performed on a Rheometric Scientific DMTA-V apparatus at 1 Hz at a heating rate of 10 K/min in single bending mode. The T_g value determined using DMA method is the peak temperature of tanδ (see Fig. 2).

We used carboxylic nitrile-butadiene UFPR (average particle size 90 nm) to toughen epoxy resin, and its toughening effect was compared with that of CTBN (Table 1). Curing procedure: The curing agent (methyl tetrahydrophenylanhydride) and epoxy (diglycidyl ether of bisphenol A, epoxy value is 0.44 mol/100 g) containing premixed CTBN rubber or UFPR are mixed together; the UFPR was premixed with epoxy by a three-roll grinder. The mixture was stirred at 90℃ for 15 min and then the accelerator (triethanolamine) was added. After degassing, the mixture was cast in a preheated mould and cured at 130℃ for 1 h then at 110℃ for 16 h to

get the cured epoxy resin.

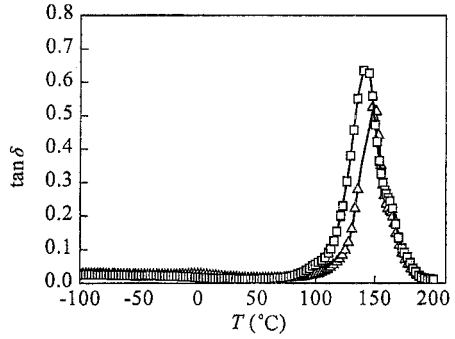

Fig. 2 Dynamic mechanical analysis (DMA) temperature scan of epoxy samples
Neat epoxy (□), epoxy toughened with carboxylic nitrile-butadiene UFPR (△)

As shown in Table 1, the UFPR has a much better toughening effect than CTBN. To our surprise, the epoxy resin toughened by UFPR has better heat resistance than neat epoxy. The heat distortion temperature (HDT) of UFPR toughened epoxy is 1.2℃ higher than that of neat epoxy, while the HDT of epoxy toughened with CTBN drops 5.6℃ as compared with neat epoxy. Through comparison of the glass transition temperature, T_g, of some samples (Table 1) determined by DSC and DMTA methods, it is indicated that the T_g of epoxy sample (sample B) increases after toughening with UFPR, but it decreases with the incorporation of CTBN (sample C). The microstructure of UFPR toughened sample is shown in Fig. 3, which reveals that UFPR particles are well dispersed in epoxy matrix on a nano scale; moreover, the distribution morphology looks like a "pseudo-network" structure[23–25]. According to the present theory of rubber toughening plastics, rubber particles with particle size under 100 nm will have little effect on toughening epoxy[26]. The UFPR with particle size of 90 nm, however, displays this special toughening effect, the reason for which needs to be further investigated.

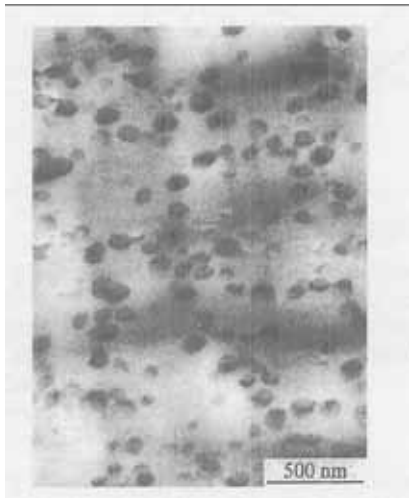

Fig. 3 TEM micrograph of epoxy resin toughened with carboxylic nitrile-butadiene UFPR

Besides epoxy toughening, the special toughening effect of UFPR was also found in other plastics. As we all know, polypropylene is a widely used general-purpose plastic and it needs to be toughened with rubber in many application fields. Usually the stiffness and heat resistance of PP will drop after toughening with rubber. In this paper polybutadiene UFPR was used to toughen PP, and some special results were again found. As shown in Fig. 4, the toughness, stiffness and heat resistance of PP are improved simultaneously by the incorporation of a small

amount of UFPR. The changing tendencies of flexural strength, flexural modulus and HDT are consistent with each other, which rise gradually and then fall down. Through the analysis of crystallization of samples using the DSC method, it was found that the crystallization temperature and the crystallization enthalpy of PP both increase after toughening (see Table 2). This increase is more obvious if the factor of UFPR mass content is deducted. These results indicate that UFPR has a toughening effect, and a nucleating effect as well. Work[27–29] concerning the nucleating effect of rubber on PP toughening has been reported. All these reports reveal that whereas blending rubber into PP may cause some nucleation effect, such as improving PP crystallization temperature and reducing the size of spherulites, it does not increase but on the contrary lower the crystallinity. Therefore it is believed that nano-scale UFPR has special toughening and nucleating effects, which improve both the crystallization temperature and crystallinity, thus not only the toughness but also the stiffness of PP can be improved and the heat resistance can be elevated.

Table 2. Thermal analysis results of crystallization of PP toughened by polybutadiene UFPR*

UFPR content (phr)	Crystallization temperature (℃)	ΔH (J/g)	$\Delta H'$ (J/g)
0	107.8	−87.6	−87.6
0.5	112.8	−89.2	−89.7
1	114.4	−89.3	−90.1
1.5	113.7	−91.3	−92.7
2	112.9	−87.3	−89.1

* Determined on PE-7 thermal analysis system, samples stayed at 190℃ for 5 min then started determination at cooling rate of 10 K/min. $\Delta H'$ is the value of ΔH with UFPR content deducted and can be calculated as $\Delta H' = \Delta H \cdot (1 + X/100)$, where X is UFPR content.

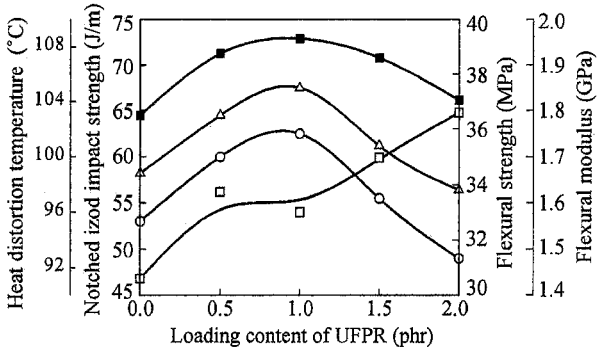

Fig. 4. Plot of mechanical properties of PP toughened by various contents of polybutadiene UFPR
(■) Heat distortion temperature; (□) Impact strength; (△) Flexural strength; (○) Flexural modulus

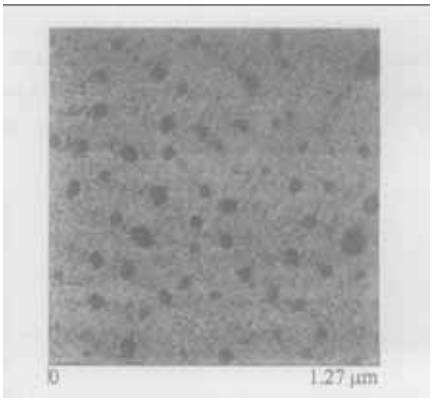

Fig. 5. AFM micrograph of toughened PP using sodium benzoate modified styrene-butadiene UFPR
The phase graph was obtained in tapping mode. The observation surface was obtained through slicing in liquid nitrogen.

By using the sodium benzoate modified styrene-butadiene UFPR in PP toughening, a more striking effect of improving both stiffness and toughness can be obtained. As illustrated in Table 3, the PP toughened with modified UFPR has higher toughness, stiffness and heat resistance than the neat PP. The atomic force microscope (AFM) micrograph (Fig. 5) of modified UFPR toughened PP sample clearly shows that the rubber particles with size 70 nm are dispersed uniformly in the PP matrix. The sodium benzoate modified UFPR has a strong effect on crystallization ability of PP toughened with it. As shown in Fig. 6, the crystallization temperature of PP sample toughened with modified UFPR is elevated compared with neat PP. The crystallization rate constant K at 124℃ of PP sample toughened with modified UFPR is approximately 150 times higher than that of neat PP. For the modified UFPR, it is inferred that the sodium benzoate may be located on the surface of UFPR on the nano scale

and this special structure should be closely related to the excellent crystallization properties and to the simultaneous improvements of stiffness, toughness and heat resistance of materials. Further investigations of these aspects are still in progress.

Table 3. Mechanical properties of PP toughened by modified styrene-butadiene UPFR*

Sample	Tensile strength (MPa)	Notched Izod impact strength (J/m)	Flexural strength (MPa)	Flexural modulus (GPa)	Heat distortion temperature (℃)
Neat PP	34.9	99.7	34.3	1.49	113.6
1 wt% UFPR	36.6	105	37.2	1.62	124.8
2 wt% UFPR	37.0	265	38.0	1.65	126.8
5 wt% UFPR	35.7	479	35.9	1.58	122.5
Test standard	Chinese standard 1040	Chinese standard 1843	Chinese standard 9341	Chinese standard 9341	ASTM D648

* The styrene-butadiene UPFR was modified by spray drying the UFPR latex together with dissolved sodium benzoate (10 phr based on dry latex). The neat PP is isotactic PP (B-200) made by SINOPEC Luoyang PetroChem. China

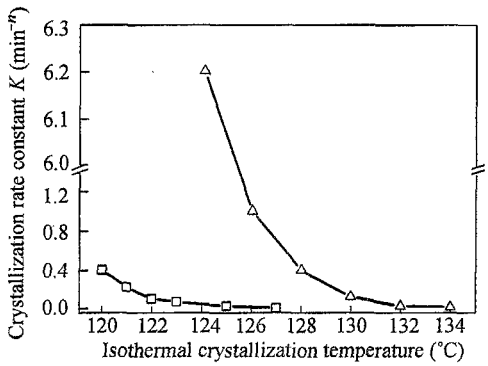

Fig. 6 Isothermal crystallization of neat PP (□), toughened PP with sodium benzoate modified styrene-butadiene UFPR (△)

In our research on toughening polyethylene terephthalate, polybutylene terephthalate and polycarbonate by using UFPR, it was also found that toughness, stiffness and heat resistance can be increased simultaneously. The reason is not very clear at present. In a word, nano-rubber particles such as UFPR do have some special effects on plastic toughening. These special toughening effects can supplement the ideas of traditional elastomer toughening technology and are worth further investigating.

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