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Ultrafine full-vulcanized powdered rubbers/PVC compounds with higher toughness and higher heat resistance

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Abstract

A new type of rigid PVC compound with higher toughness and higher heat resistance was prepared by using a new type of PVC modifier, ultrafine full-vulcanized powdered rubber (UFPR). The UFPRs used in this paper were butadiene nitrile UFPR-1 (NBR-UFPR-1) with particle size of about 150 nm and butadiene nitrile UFPR-2 (NBR-UFPR-2) with particle size of about 90 nm. Dynamic mechanical thermal analysis (DMTA) showed that glass transition temperature (T_g) of PVC in compounds increased from 77.52 °C of neat PVC to 82.37 and 85.67 °C, while the notched impact strengths increased from 3.1 kJ/m^2 of neat PVC to 5.2, 5.5 kJ/m^2, respectively. It can be found that both T_g and toughness of PVC have been improved simultaneously, and the smaller the particle size of NBR-UFPRs, the higher the T_g and the impact strength. The property could be attributed to larger interface and more interfacial interaction between NBR-UFPRs and PVC matrix. Transmission electron microscopy (TEM) showed that NBR-UFPRs could be well dispersed in PVC matrix.

Keywords: Rigid PVC/UFPR compounds; Toughening; Glass transition temperature

1. Introduction

Rigid PVC has been widely used in construction, transportation, and many other industries due to its high stiffness, flame retardancy, chemical resistance and low cost [1]. However, the disadvantages of rigid PVC, such as low notch impact strength and low heat resistance, have restricted its application.

Rubbers like NBR, acrylic rubber, chloride–butadiene rubber etc. can improve the toughness of PVC [2–4], but decrease its heat resistance. PVC toughened by NBR, commercialized by Advance Solvents and Chemical Corporation of USA 60 years ago, was the first toughened PVC compound [5]. Research results [6–12] had shown that PVC and NBR are fairly compatible, and the compatibility increased with the increase of acrylonitrile content (within the range 23–45%) in NBR. As a partly compatible system, there are two T_gs in PVC/NBR compounds, the lower one corresponding to NBR phase and the higher one corresponding to PVC phases [7–10]. Unfortunately, the T_g of PVC in PVC/NBR compounds is always lower than that in neat PVC, which means the toughness improvement of PVC toughened by NBR is always on the sacrifice of heat resistance. The rigid PVC's application has been markedly restricted because of this disadvantage, especially in the case of window profile. Therefore, it is very important and very difficult to improve both toughness and heat resistance of rigid PVC simultaneously by using NBR.

A new type of PVC/NBR compound with both higher toughness and higher T_g was introduced in this paper. The NBR used in this paper was a novel powdered NBR, ultrafine full-vulcanized powdered NBR (NBR-UFPR). The NBR-UFPR, prepared by combined technologies of irradiation and spray drying, had special microstructure, very high crosslinking degree on the surface of the NBR particles and moderate crosslinking degree in the inner parts [13,14].

2. Experimental section

2.1. Materials and sample preparation

Table 1 lists the materials used in this paper. Five per hundred parts of rubber (phr) TMPTA was added dropwise into

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Table 1
Materials used in this paper

Materials	Name	Manufacture
PVC	ws-1000s	Shanghai Chlor-Alkali Chemical Co. Ltd of China
NBR latex	DQ-248 (acrylonitrile content: 33%)	Eliokem Inc. of France
	DQ-6387 (acrylonitrile content: 33%)	Eliokem Inc. of France
Irradiation sensitives	Trimethylol propane tracrylate (TMPTA)	Beijing Dongfang Chemical Co.
Processing aid	ACR-401 (shell-core acrylate copolymer)	Suzhou Anli Chemical Co. Ltd of China
Heat stabilizer	Thermolite® 890 (octyltins)	Atofina Beijing Chemical Co. Ltd
Lubricant	PE wax	Beijing University of Chemical and Technology of China
	G60 (sebacic acid ester)	Shandong Zibo Agent Co. Ltd of China

DQ-248 and DQ-6387 NBR-latex during stirring. After stirring for 1 h, the two kinds of mixed NBR latices were irradiated with a ^{60}cobalt-source. Two types of NBR-UFPRs, NBR-UFPR-1 (abbreviated as P-248) and NBR-UFPR-2 (abbreviated as P-6387), were obtained after spray drying.

PVC (100 phr), NBR-UFPRs (8 phr), thermolite® 890 (5 phr), ACR-401 (1 phr), G60 (0.8 phr) and PE wax (0.3 phr) were firstly premixed in a high speed mixer with the mixing temperature in the range 70–110 °C. Then the cooled mixture was blended in an internal mixer (Brabender PLE 651) at 175 °C for 8 min at a speed of 45 rpm. The two samples, PVC/P-248 compound with 8 phr P-248 (PVC-1) and PVC/P-6387 compound with 8 phr P-6387 (PVC-2), were compressed into 4 and 2 mm thick sheets at 200 °C and 7 MPa for 6 min. The 4 mm thick samples were machined into notched impact specimens (GB/T 1843-1996, $80\times10\times4$ mm^3); the 2 mm thick samples were machined into dynamic mechanical thermal analysis specimens ($45\times6\times2$ mm^3) and tensile test specimens (GB/T 16421-1996, $75\times10\times2$ mm^3). The TEM specimens were also cut from the compressed sheets.

2.2. Experimental measurements

The notched impact strengths were measured at room temperature by using a CEAST impact machine according to GB/T 1843-1996. The tensile test was performed at room temperature according to GB/T 16421-1996. Dynamic mechanical thermal properties were tested in an American Rheometric Scientific DMTA V machine, and scans of temperature from −100 to 150 °C with a ramp rate of 5.0 °C/min in dual cantilever mode at a frequency of 1.0 Hz. Morphology of the PVC/UFPRs compounds was observed with a TEM, Philips Tecnai 20; ultrathin sections, about 50–100 nm thick, was microtomed at −80 °C before being stained with osmium tetroxide (OsO_4). Fracture surface morphology of notched impact specimen was observed on an environmental scanning electron microscope, Philips XL-30 ESEM, and the fracture surfaces were sputter-coated with a thin gold layer before observation.

3. Results and discussion

Fig. 1(a) and (b) are the log tan $\delta\sim$temperature curves of PVC, NBR-UFPRs and PVC/ NBR-UFPR compounds. There were two peaks that correspond to the T_gs of PVC and NBR-UFPR in log tan $\delta\sim$temperature curves of PVC/NBR-UFPR compounds. It was surprising to find that the T_gs of PVC in both samples of PVC-1 and PVC-2 were higher than that of neat PVC. This result was contrary to those of PVC compounds modified by conventional NBR rubber. For example, Zakrzewski [10] found that conventional NBR rubber reduced the T_gs of PVC from 74 to 62 and 42 °C corresponding to 10 and 30 phr NBR. Moreover, the T_g of PVC was 82.4 °C in the sample of PVC-1 in which the particle size of NBR-UFPR was about 150 nm, and 85.7 °C in PVC-2 in which the particle size of NBR-UFPR was 90 nm. It is interesting to know why the special rubber particle, NBR-UFPR, can increase the heat

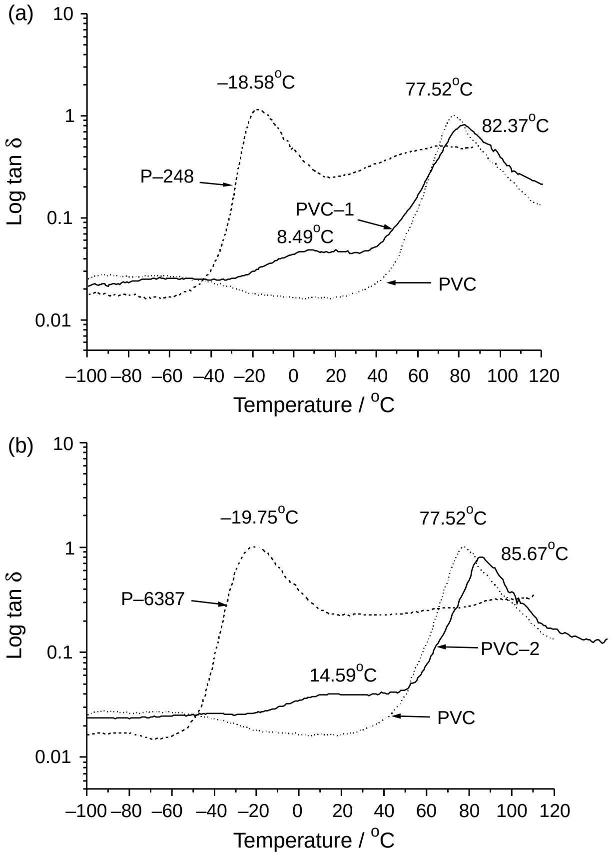

Fig. 1. Log tan δ curves of neat PVC, various NBR-UFPRs and PVC/UFPRs compounds at a function of temperature. (a) Neat PVC, P-248, and PVC-1; (b) neat PVC, P-6387, and PVC-2.

resistance and why the smaller the particle size of NBR-UFPR, the higher the T_g of PVC in PVC/NBR-UFPR compounds.

It had been found that good dispersion of NBR-UFPRs in PVC matrix ensure larger interface between NBR-UFPR and PVC matrix (Fig. 2). Therefore, there existed more interfacial interaction between NBR-UFPRs and PVC matrix in PVC/NBR-UFPR compounds. We had found that interface played a key role in heat resistance of plastic/UFPR compounds and large interface and strong interfacial interaction between UFPR and epoxy resin could increase the heat resistance of epoxy/UFPR composite [15]. Moreover, we found in this paper that PVC-2 with NBR particle size of 90 nm had higher T_g than PVC-1 with NBR particle size of 150 nm. Therefore, it is understandable that interface plays an important role in heat resistance of PVC/UFPR compounds and the larger interface between NBR-UFPRs and PVC matrix in PVC/UFPR compounds can increase the T_g of PVC.

NBR-UFPR was also in favor of the toughness of the PVC/UFPR compounds as shown in Table 2. Compared with neat PVC, the increment of impact strength of PVC-1 and PVC-2 are 67 and 77%, respectively. It was interesting

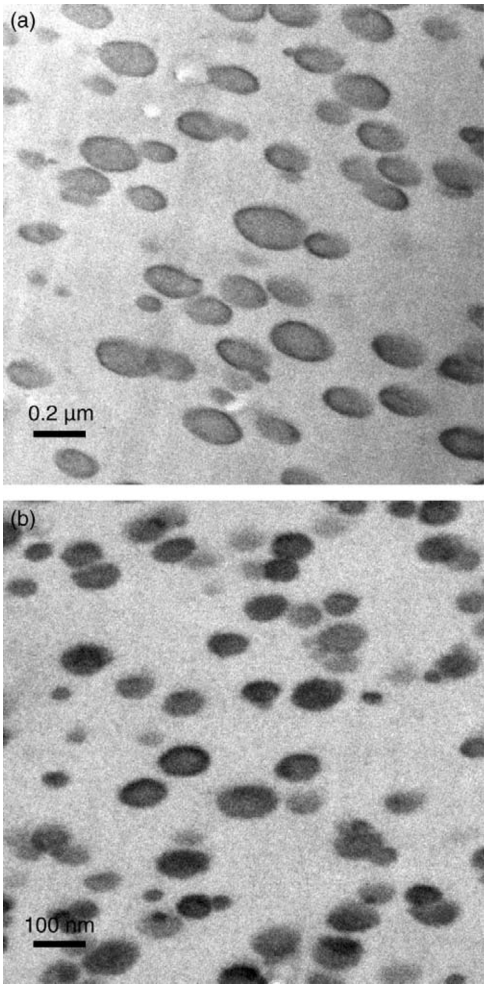

Fig. 2. TEM micrographs of PVC compounds modified with 8 phr NBR-UFPRs (stained with OsO_4). (a) PVC-1, (b) PVC-2.

Table 2
Mechanical properties of various PVC compounds modified with 8 phr NBR-UFPRs

PVC compounds (NBR-UFPR)	Neat PVC	PVC-1 (P-248)	PVC-2 (P-6387)
Notched impact strength (kJ/m^2)	3.1	5.2	5.5
Tensile strength (MPa)	41.7	43.1	44.2

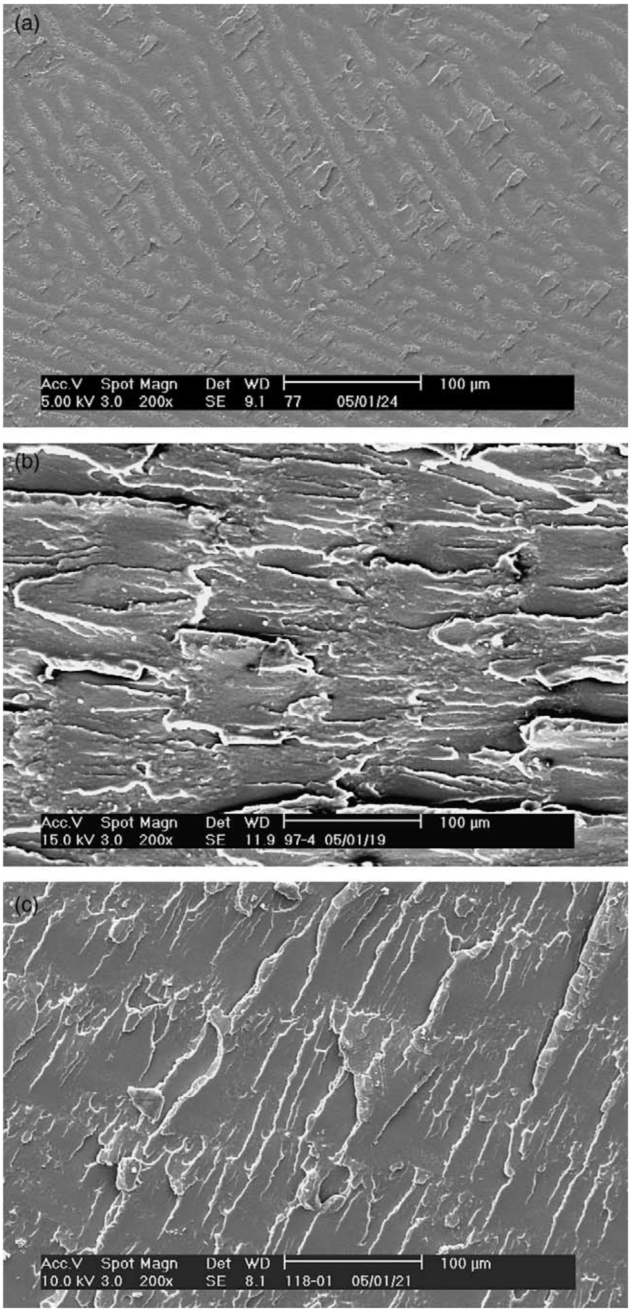

Fig. 3. SEM micrographs of the fracture surface of neat PVC and various PVC/UFPRs compounds (a) Neat PVC (×200), (b) PVC-1 (×200), (c) PVC-2 (×200).

to find that the increment caused by UFPR with particle size of 90 nm was 10% more than that by UFPR with particle size of 150 nm. Although the result is of the same view with Bucknall's opinion of rubber-toughened PVC that the optimum rubber particle size for PVC should be less than 100 nm [2], it is still difficult to understand that the impact strength of PVC-2 with smaller rubber particle size was higher than that of PVC-1.

It is well known that energy absorption mechanism of rubber particles consists of not only rubber cavitation, tearing, and debonding but also crazing and deformation of matrix caused by rubber particles [2,16–20]. PVC deformation could be probably the key factor for explaining the increased toughness of PVC compounds in this study. The probability that a craze meets a rubber particle and is extended by that rubber particle is bigger when the rubber particle size is smaller because the smaller the rubber particle, the shorter the distance between rubber particles when same amount of rubber is used in rubber-toughened plastics. The average ligaments (distance between rubber particles) of PVC-1 and PVC-2 were 136 and 78 nm in the PVC/NBR-UFPR compounds according to Wu [21]. Therefore, there should be more extended crazes and less cracks in PVC-2 than in PVC-1. The SEM micrographs of the fracture surfaces of PVC-1 and PVC-2 in Fig. 3 did show us that there were less large cracks in PVC-2 than in PVC-1.

It is also well known that the improvement of toughness comes at the cost of stiffness for most of plastic/rubber blends. However, the tensile strengths of PVC-1 and PVC-2 with improved toughness were also increased compared with that of neat PVC (Table 2). The results need to be studied further.

4. Conclusion

A new type of rigid PVC/NBR-UFPR compound has been successfully fabricated. The NBR-UFPRs could increase the toughness and heat resistance of rigid PVC simultaneously. Moreover, the smaller the particle size of NBR-UFPR, the higher the heat resistance and toughness of the PVC/UFPR compound. Images of TEM indicated that NBR-UFPRs were well dispersed in PVC matrix. The increased heat resistance had been attributed to larger interface between NBR-UFPRs and PVC matrix, whilst more craze extension had been used to explain the improved toughness. Further study is needed for understanding the reason that UFPR can increase the toughness and heat resistance of PVC at same time.

Acknowledgements

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Appendix A

The following equation derived by Wu [21] can be used to calculate the ligament thickness, τ (distance between two rubber particle surface)

$$\tau = D\left\{\left(\frac{\pi}{(6\phi_r)}\right)^{1/3} - 1\right\} \tag{A1}$$

where D is the average rubber particle size and ϕ_r is the rubber volume fraction. Thus, using D_1 (150 nm) of P-248 and D_2 (90 nm) of P-248, we can calculate the τ_1 (136 nm) of PVC-1 and τ_2 (78 nm) of PVC-2.

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