

Novel rigid poly(vinyl chloride) ternary nanocomposites containing ultrafine full-vulcanized powdered rubber and untreated nano-sized calcium carbonate

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Abstract

Novel rigid poly(vinyl chloride)/ultrafine full-vulcanized powdered rubber (UFPR)/untreated nano-sized calcium carbonate (UNCC) ternary nanocomposites were fabricated. TEM observation revealed that good dispersion of UNCC particles (about 40 nm) in the PVC matrix was achieved with the help of UFPR (about 150 nm). Interestingly, the PVC ternary nanocomposites excel corresponding PVC binary ones, as well as neat rigid PVC, in both heat resistance and toughness due to the synergistic effect of UNCC and NBR-UFPR.

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1. Introduction

Rigid PVC has been widely used in the construction, transportation and many other industries due to its high stiffness, flame retardancy and chemical resistance, as well as its low cost [1]. However, the disadvantages of rigid PVC, such as low notch impact strength and low heat resistance, have restricted its application. It is well known that nano-sized calcium carbonate (NCC) is an important and cheap nano-filler for the modification of polymers [2–14]. Many works [12–14] demonstrate that good dispersion of NCC in polymer matrix can significantly improve the polymer's mechanical properties, especially the stiffness. However, dispersion of untreated NCC (UNCC) particles in polymer matrix can be hardly achieved without agglomeration, which usually leads to the poor mechanical properties of the resultant composite [9–11]. Therefore, treatment on the surface of NCC with coating agents is required to improve its dispersion in polymer matrix [13,14]. However the high price of NCC with surface treatment is not acceptable to the industry.

In our previous work, we have developed a nitrile ultrafine full-vulcanized powdered rubber (NBR-UFPR), which can be well dispersed in the PVC matrix to increase the toughness and the heat resistance of rigid PVC simultaneously [15]. In this paper, we fabricated a new PVC/NBR-UFPR/UNCC ternary nanocomposite with the technologies of irradiation and spray drying. In the PVC ternary nanocomposite, UNCC particles can be well dispersed in the PVC matrix with the help of the easy dispersing NBR-UFPR. The synergistic effect of UNCC and NBR-UFPR on the improvement of heat resistance and toughness has been found.

2. Experimental section

2.1. Materials

Table 1 lists the experimental materials.

2.2. Fabrication

Fig. 1 illustrates the procedure used for the fabrication of PVC/NBR-UFPR/UNCC ternary nanocomposites. Firstly, the

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Table 1
Materials used for this paper

Materials	Purity	Manufacturer
PVC: ws-1000s	Industry product	Shanghai Chlor-Alkali Chemical Co. Ltd. of China
NBR latex: DQ-248 (acrylonitrile content: 33%)	Industry product	Eliokem Inc. of France
DQ-26 (acrylonitrile content: 26%)	Industry product	PetroChina Lanzhou Petrochemical Company
CaCO ₃ : Nano-sized CaCO ₃ slurry (47.3 wt.%)	Industry product	Beijing University of Chemical Technology
Irradiation sensitives: Trimethylol propane tracrlylate (TMPTA)	Industry product	Beijing Dongfang Chemical Co. Ltd.
Processing aid: ACR-401 (shell-core acrylate copolymer)	Industry product	Suzhou Anli Chemical Co. Ltd. of China
Heat stabilizer: Thermolite 890 (octyltins)	C.P.	Atofina Beijing Chemical Co. Ltd
Lubricant: PE wax	Industry product	Beijing University of Chemical Technology
G60 (sebacic acid ester)	Industry product	Shandong Zibo Agent Co. Ltd. of China

irradiated NBR latex (DQ-248) was prepared in accordance with the method stated in our previous paper [15]. Secondly, a mixture of irradiated NBR latex and UNCC slurry (10 wt.%) was prepared at a certain solid weight ratio (8/5 wt/wt). This was followed by spray drying, and thus a compounding powder of NBR-UFPR/UNCC (P-248/UNCC) was obtained. The PVC/P-248/UNCC ternary nanocomposites were fabricated by the conventional melt blending method in an internal mixer (Brabender PLE 651). PVC/P-248 binary composites were further prepared according to the method reported in our early work [15].

The PVC samples 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 × 10 × 4 mm³); the 2 mm thick samples were machined into tensile testing specimens (GB/T 16421-1996, 75 × 10 × 2 mm³) and dynamics mechanical thermal analysis specimens (45 × 6 × 2 mm³). Transmission electron microscopy (TEM) specimens were also cut from the compressed sheets.

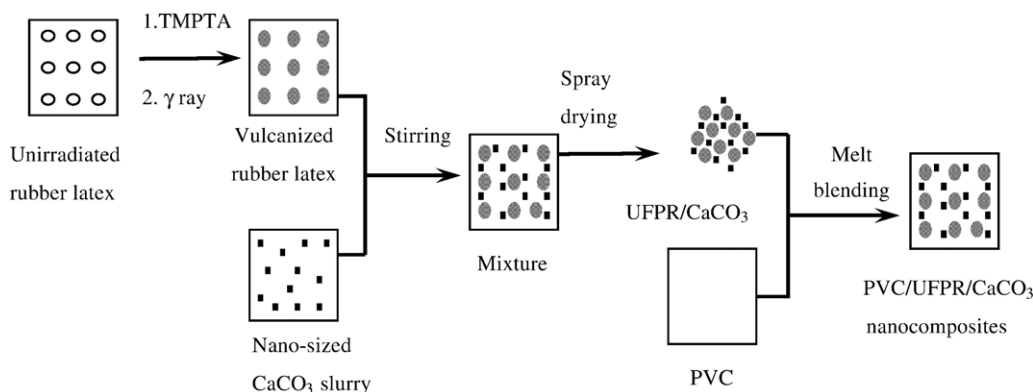


Fig. 1. Schematic diagram of the fabrication procedure of the PVC/NBR-UFPR/UNCC ternary nanocomposites.

2.3. Testing and characterization

Notched impact strengths were measured at room temperature by using a CEAST impact machine according to GB/T 1843-1996, which is equivalent to ISO 180:1993. The tensile test was performed at room temperature according to GB/T 16421-1996, which is equivalent to ISO 527-2:1993. Dynamic mechanical thermal properties were tested in an American Rheometric Scientific DMTA V machine, and scans of temperature were 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. The morphology of the PVC composites was observed using a transmission electron microscope (TEM, Philips Tecnai 20). Ultrathin sections, about 50–100 nm thick, were microtomed at –80 °C before being stained with osmium tetroxide (OsO₄).

3. Results and discussion

3.1. Morphology of PVC/NBR-UFPR/UNCC ternary nanocomposites

Fig. 2 shows the TEM images of the PVC/P-248/UNCC ternary nanocomposites. It can be seen that most of the NBR-UFPR and UNCC particles (with cubic shape and average size of 40 nm) are separately dispersed in the PVC matrix. As is well known, the UNCC particles can separate in the UNCC slurry during stirring, after mixing with irradiated NBR latex and spray drying, and the separated UNCC particles could be partitioned by NBR-UFPRs in a compound powder of NBR-UFPR/UNCC. As we have reported before, the NBR-UFPR can be easily dispersed in the PVC matrix due to its good miscibility with PVC and its special microstructure, higher crosslinking degree on the surface than in the interior [15]. Therefore, with the help of good dispersion of NBR-UFPR in the PVC matrix, the separated UNCC particles in the compounding powder NBR-UFPR/UNCC could be easily dispersed in the PVC matrix during the melting process.

3.2. The heat resistance of PVC composites

Fig. 3 illustrates $\tan\delta$ vs. temperature curves for neat PVC and PVC composites. Compared to neat PVC, both PVC/P-248 binary composites and PVC/P-248/UNCC ternary nanocomposites showed higher T_g , and the increments were 4 and 10 °C, respectively. We have found that a larger interface and interfacial interaction between UFPRs and the plastic matrix led to increased T_g [15–17]. It is worth noting

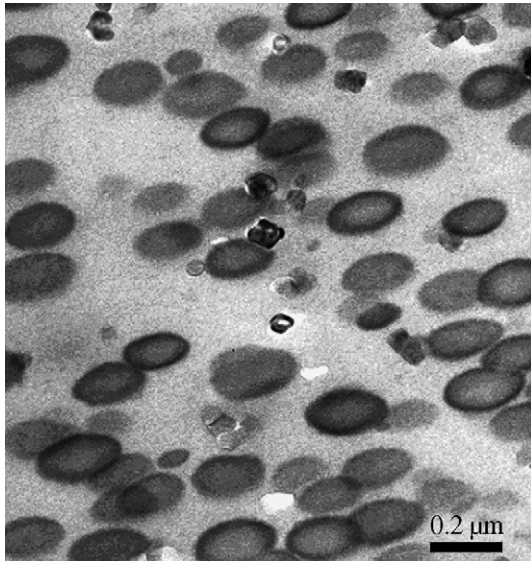


Fig. 2. TEM micrographs of rigid PVC/P-248/UNCC ternary nanocomposites (100/8/5, wt/wt/wt), stained with OsO_4 ; black spheres were the NBR-UFPRs (P-248), and the smaller cube particles were the UNCC particles.

that the PVC/P-248/UNCC ternary composites had an even higher T_g (the increment is 6 °C) than the PVC/P-248 binary one due to the addition of 5 phr UNCC. It is not difficult to understand the reason why the separated UNCCs can further increase the heat resistance of PVC, because the separately dispersed UNCCs can restrict the segmental mobility of PVC molecules along with NBR-UFPRs.

3.3. The toughness of PVC composites

Some mechanical properties of neat PVC and the PVC composites are listed in Table 2. Compared to neat PVC, both PVC/P-248 binary composites and PVC/P-248/UNCC ternary composites have higher impact strength and longer elongation at break, while without deterioration in tensile strength. However, the PVC/UNCC binary composites have lower impact strength and shorter elongation at break than neat PVC. The results show that both NBR-UFPR and NBR-UFPR/UNCC could increase the toughness of rigid PVC, and the

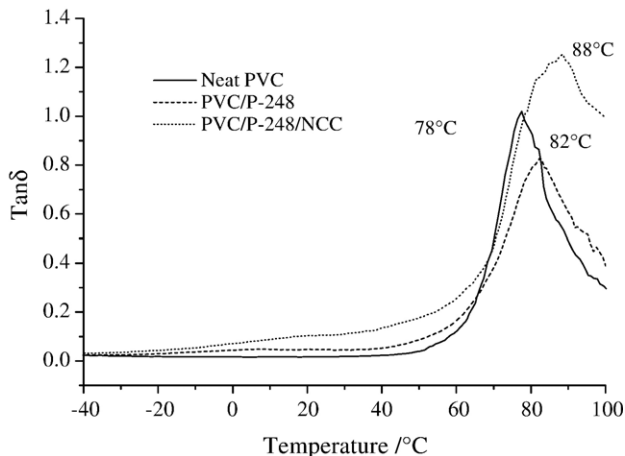


Fig. 3. $\text{Tan}\delta$ curves of neat PVC, PVC/P-248 binary composites (100/8, wt/wt) and PVC/P-248/UNCC ternary nanocomposites (100/8/5, wt/wt/wt) at a function of temperature.

Table 2
Mechanical properties of various PVC composites

PVC composites	Notched impact strength (kJ/m^2)	Tensile strength (MPa)	Elongation at break (%)
Neat PVC	3.1	41.7	165
PVC/UNCC=100/5	3.0	40.8	20
PVC/P-248=100/8	4.1	43.1	208
PVC/P-248/UNCC=100/8/5	5.5	41.0	206

increment caused by NBR-UFPR/UNCC was higher than that by NBR-UFPRs, which indicates that the dispersed UNCCs in the PVC/NBR-UFPR/UNCC ternary composites could further increase the toughness of PVC, while the same kind of UNCCs decreased the toughness of PVC/UNCC binary composites because of the serious aggregation of UNCCs in the PVC matrix. Why did the dispersed UNCCs increase the toughness and elongation of PVC when used together with NBR-UFPRs?

It is known that crazing and shear band is the main deformation mechanism to explain the increased toughness of rigid PVC composites [18–25]. We have discussed that NBR-UFPR can initiate crazing in PVC/NBR-UFPR binary composites, and the good dispersion and small size of NBR-UFPR particles are also in favor of the extension and termination of crazing, which can prevent crazing from developing into cracks [15]. Due to the addition of dispersed UNCC particles, the inter-particle distances (ligament thickness of PVC matrix) in the PVC/NBR-UFPR/UNCC ternary nanocomposites should be much shorter than that in PVC/NBR-UFPR binary ones. The probability of crazing being terminated by NBR-UFPR and UNCC particles is bigger than that in the PVC/NBR-UFPR binary composites. Therefore, the possibility of crazing developing into cracks and leading to PVC fracture would become smaller in the PVC/NBR-UFPR/UNCC ternary nanocomposites. It seems that NBR-UFPRs and the dispersed UNCC particles have a synergistic toughening effect on rigid PVC.

To confirm the above presumption that the dispersed UNCC particles could help terminate crazing, we also fabricated another PVC/NBR-UFPR/UNCC ternary composite, where the particle size of NBR-UFPR (P-26, with lower acrylonitrile content than that of P-248) was about 90 nm, smaller than that of P-248. The two PVC ternary composites had different increments of impact strength over the two related PVC binary composites even they had the same amount of UNCC. The increment of PVC/P-248/UNCC is 34%, while that of PVC/P-26/

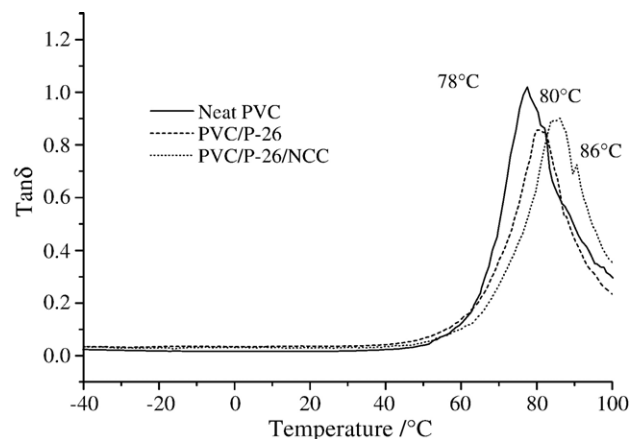


Fig. 4. $\text{Tan}\delta$ curves of neat PVC, PVC/P-26 binary composites (100/8, wt/wt) and PVC/P-26/UNCC ternary nanocomposites (100/8/5, wt/wt/wt) at a function of temperature.

UNCC is 16% (from 6.3 kJ/m² to 7.8 kJ/m²). Bucknall reported that larger rubber particles are more efficient in initiating crazes than smaller ones when toughening a glassy polymer [18]; therefore, P-248 of larger particle size (150 nm) can initiate more crazing than P-26 of smaller particle size (90 nm). As a crazing terminator, the dispersed UNCC particles can play a more important role in PVC/P-248/UNCC ternary composites than in PVC/P-26/UNCC ternary composites. On the other hand, T_g of the PVC/P-26/UNCC ternary nanocomposite is also 6 °C higher than that of the corresponding PVC binary one (see Fig. 4), the same as in the case of the PVC/P-248/UNCC ternary composites due to the addition of the same amount of dispersed UNCC.

4. Conclusion

Novel PVC ternary nanocomposites have been successfully fabricated with NBR-UFPR and untreated nano-sized calcium carbonate (UNCC). Both NBR-UFPR and UNCC were dispersed separately in the PVC matrix. The PVC ternary nanocomposites had higher T_g than both PVC/NBR-UFPR binary ones and neat PVC, which can be explained as a result of more restriction of dispersed UNCC particles and NBR-UFPR particles on the segmental mobility of the PVC molecules. At the same time, the impact strength of PVC ternary composites also increased due to the synergistic toughening effect of NBR-UFPR and UNCC. Further study is needed for understanding the reasons why the compound powder of NBR-UFPR/UNCCs can increase the toughness and the heat resistance of PVC ternary composites simultaneously.

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