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Influence of the diameter of $CaCO_3$ particles on the mechanical and rheological properties of PVC composites

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Abstract PVC composites filled with $CaCO_3$ particles with different diameter (about 40, 80, 500, 25000 nm) were prepared by using a single-screw extruder. The mechanical and rheological properties of the composites were investigated. The results showed that while the diameter of $CaCO_3$ nanoparticles was smaller, the mechanical properties of composites were higher. By adding 40-nm $CaCO_3$ nanoparticles into the PVC matrix, the single-notched impact strength of the nanocomposite at room temperature reached 82.4 kJ/m^2, which was 3.5 times that of the PVC matrix without $CaCO_3$ (23.3 kJ/m^2) and 4.6 times that of the PVC blend filled with micro-$CaCO_3$ (17.9 kJ/m^2). The tensile and flexural properties of nanocomposites were also prior to those of the composites with 500-nm and 25-μm $CaCO_3$ particles. The $CaCO_3$ particles could make the rheological property of PVC composites worse. Moreover, the effect of mass ratio of nano-$CaCO_3$ and micro-$CaCO_3$ on the properties of PVC door and window profile in industry was studied. When the mass ratio was 2.5/9, the profile could obtain good mechanical properties.

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Introduction

Polyvinyl chloride (PVC) is now one of the most commonly used general-purpose plastic materials in the world. However PVC is too hard, brittle, and stiff, which makes it unsuitable for harsh applications. Polymer blending is widely used as a method for improving the toughness of PVC. Conventionally, plastic can be toughened by rubber particles, and the mineral fillers only reduce the cost of plastic. Notched impact strength of the plastics increases significantly when the rubber particles are present, however, the rigidity of plastics decreases remarkably. Now as a development in the preparation of nanoparticles and the surface modification of inorganic particles, the incorporation of inorganic particulate fillers with plastic has been proved to be an effective way for the improvement of the mechanical properties, in particular the toughness of polymers [1–5]. At the same time the rigidity of polymer does not decrease.

$CaCO_3$ has been one of the most commonly used inorganic fillers in plastics. Considerable research efforts in recent years have been directed toward the $CaCO_3$/polymer nanocomposites [6–12], but few publications concerning the effect of the diameter of $CaCO_3$ particles on the properties of polymeric blends have been reported. In this paper, the properties of PVC composites filled with $CaCO_3$ particles with different diameters were studied.

Experimental

PVC (polymerization degree: 1,000–1,100) was supplied by NO.2 Chemical Factory of Beijing, China. Chlorinated

Polyethylene (CPE) with 35% weight content of chloride was produced by Weifang Chemical Factory, China. Acrylamide (ACR-401) was obtained from JiLin Chemical Industry Corporation SuZhou Anli Chemical Plant, China. Stabilizer (QHL-2000, main ingredients: $3PbO \cdot PbSO_4 \cdot H_2O$ and $2PbO \cdot PbHSO_3 \cdot 1/2H_2O$) was provided by North China Plastic Assistant Factory in BaoDing, China. Ultrafine particles of $CaCO_3$ with 40-nm average diameter were synthesized in the novel rotating packed bed by means of high gravity from Mengxi Advanced Materials Co. Ltd in inner Mongolia province, China. The 80-nm and 25-μm $CaCO_3$ particles were obtained from Taiwan Plastics Company and Beijing Ultrafine Powder Co. Ltd, respectively. The spindle-type $CaCO_3$ particles of about 500 nm were prepared in our laboratory as reported previously [13]. The surface agent of 40-nm and 500-nm $CaCO_3$ was also a fatty acid. The 80-nm and 25-μm fillers produced in industry were also modified and fit for PVC matrix.

The treated $CaCO_3$ particles, CPE, PVC, ACR, and the stabilizer were mixed in a high-speed stirring facility and then were put into a single-screw extrusion. The screw speed was 40 rpm, and the processing temperatures were 165, 175, 185, and 183. Samples of about 10 mm*4 mm dimensions were prepared through the single-screw extrusion. The contents of materials in PVC composites are shown in Table 1.

TEM analysis of the $CaCO_3$ particles was carried out on a Hitachi H-800 apparatus (Osaka, Japan). Impact strength of the PVC composite was measured by Charpy pendulum impact testing machines according to the international standard ISO 179. Tensile and flexural properties were obtained from an Instron universal testing machine (Instron 1185, Instron Company, England). The rheological property was recorded at 180 °C by a Brabender machine (PLV2151, country), and the revolving speed of the screw was 10 rpm/min.

The industrial experiment was performed in Tianjin Zhongcai Plastic Co. Ltd. The mixed materials, in which micro-sized $CaCO_3$ was taken partly by nano-sized $CaCO_3$, were put into a cone-shaped twin-extruder screw extrusion and then extruded into a PVC profile to make an 80-type window. The temperatures of the extruder were 160–260 °C and the speed was 1.92 m/min. The test specimens were taken from the 80-type window directly. The National Research & Analysis Centre of Chemical Building Materials presented the testing results.

Table 1 Composition of the PVC composites

Materials	PVC	CPE	ACR	Stabilizer
Content (phr)	100	8	4	4

Results and discussion

The microstructures of $CaCO_3$ particles with different diameters are shown in Fig. 1.

The impact strength of the unfilled PVC and PVC/$CaCO_3$ composites was measured at a room temperature of 23 °C and low temperature of −20 °C. The results are shown in Table 2. It can be seen that with the decrease in the diameter of $CaCO_3$, the impact strength of the composites improved remarkably. At room temperature, When the diameter of $CaCO_3$ particles was 40 nm, the notched impact strength of the PVC/$CaCO_3$ nanocomposite reached 82.4 kJ/m^2, which was 3.5 times that of the PVC blend without $CaCO_3$ (23.3 kJ/m^2) and 4.6 times that of the PVC blend with micro-$CaCO_3$ (17.9 kJ/m^2). At the low temperature, when the diameter of $CaCO_3$ particles reduced from 25 μm to 40 nm, the notched impact strength of PVC composites increased from 4.5 to 12.8 kJ/m^2, which exhibited the same change as that at room temperature. Clearly, nano-sized $CaCO_3$ had an effective toughening effect on the PVC system. And with the addition of micro-sized $CaCO_3$, the impact strength had a little reduction. When the nanoparticles were welldispersed in the polymer matrix, at the stress concentration sites, they could initiate and terminate a large number of the crazing (silver streak) not the crack in impact testing. At the same time, they caused the polymer matrix to create shear yielding, which could also improve the toughness of the composites.

Table 3 gives the tensile property and flexural property to the PVC matrix without $CaCO_3$ and PVC/$CaCO_3$ composites. The tensile strength decreased gradually with the diameter of $CaCO_3$ from 40 nm to 25 μm. Compared with the unfilled PVC composite, the tensile strength increased by 6% (from 41.3 MPa to 43.6 MPa) in the 40-nm $CaCO_3$ particles and decreased by 8% (from 41.3 MPa to 37.8 MPa) in the 25-μm $CaCO_3$ particles. At the same time, without $CaCO_3$ particles, the flexural modulus of the PVC composite was 2230 MPa. The flexural modulus of the composite with 40-nm $CaCO_3$ particles was 2318 MPa. $CaCO_3$ nanoparticles increased 4% in flexural modulus. When the diameter of particles increased from 80 nm to 25 μm, the modulus of plastics had little change and was close to that of the unfilled PVC blend.

Figure 2 shows the effect of $CaCO_3$ nanoparticles and microparticles on the rheological behavior of composites. Both nano-$CaCO_3$ and micro-$CaCO_3$ containing PVC blends showed higher torque than that of unfilled PVC blend. Comparing the nano-$CaCO_3$ to micro-$CaCO_3$-filled systems, the former exhibited higher equilibrium torque, because of its huge specific surface area. The melt viscosity of blend increased with nano-$CaCO_3$ loading. To improve the rheological behavior of nanocomposites, some flow modifying agents should be added.

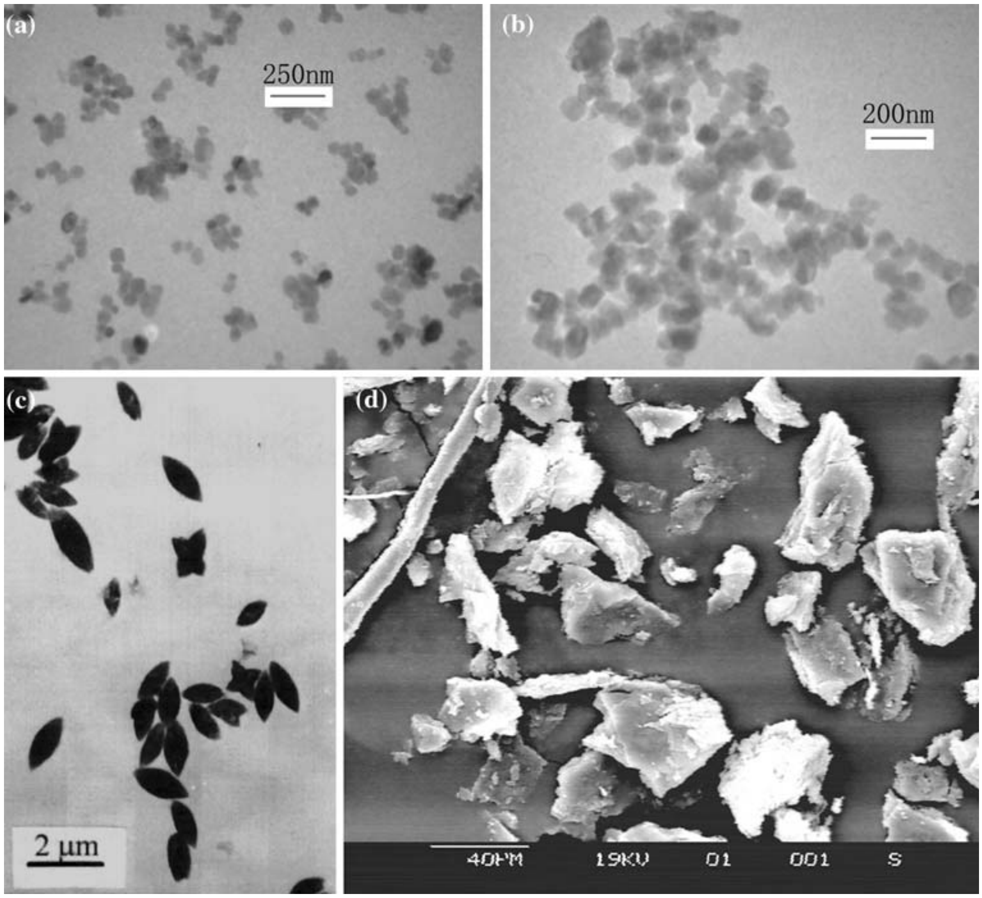

Fig. 1 TEM micrographs of the $CaCO_3$ particles. The diameter of $CaCO_3$ particles is (**a**) 40 nm (**b**) 80 nm (**c**) 500 nm (**d**) 25,000 nm

Table 2 Impact strength of composites

Main composition (wt PHR)		Diameter of $CaCO_3$ (nm)	Single-notched impact strength (kJ/m^2)	
PVC	$CaCO_3$		23 °C	−20 °C
100	0	–	23.3 ± 2.2	5.5 ± 0.9
100	8	40	82.4 ± 8.3	12.8 ± 1.9
100	8	80	51.1 ± 15.9	9.4 ± 2.0
100	8	500	28.8 ± 5.9	6.8 ± 0.7
100	8	25000	17.9 ± 4.1	4.5 ± 0.6

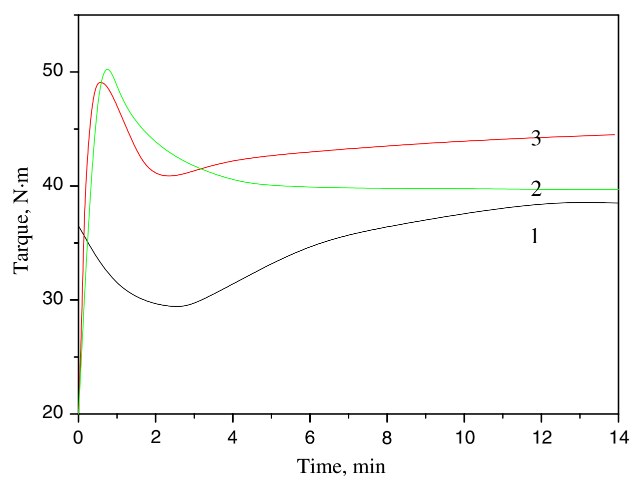

Fig. 2 The rheological property of blends 1-unfilled PVC; 2-PVC filled with micro-$CaCO_3$; 3-PVC filled with nano-$CaCO_3$

To investigate the effect of $CaCO_3$ nanoparticles and microparticles on the mechanical properties of the PVC door and window profiles produced in the industrial line, the properties of profiles with $CaCO_3$ nanoparticles and microparticles together were tested. Table 4 displays the mechanical properties of the plastic profiles produced in Tianjin Zhongcai Plastic Co. Ltd. Clearly, the nano-$CaCO_3$ particles toughen PVC blend significantly. When the content of nano-$CaCO_3$ was 2.5 gram per hundred resin (phr), the impact strength at room and low temperatures increased by 28% and 15%, respectively. The flexural property of the profiles also improved with the addition of nano-$CaCO_3$. However, due to the presence of micro-$CaCO_3$, the profile could get good mechanical properties with just a small

Table 3 Tensile property and flexural property of blends

Main composition (wt PHR)		Diameter of $CaCO_3$ (nm)	Tensile strength (MPa)	Elongation at break (%)	Flexural modulus (MPa)
PVC	$CaCO_3$				
100	0	–	41.3 ± 1.1	111 ± 7	2,230 ± 21
100	8	40	43.6 ± 1.8	127 ± 13	2,318 ± 29
100	8	80	42.7 ± 1.0	97 ± 5	2,229 ± 18
100	8	500	39.7 ± 1.2	100 ± 10	2,256 ± 12
100	8	25,000	37.8 ± 0.4	52 ± 3	2,183 ± 50

Table 4 Mechanical properties of the PVC plastic profiles produced in industry

Samples	1	2	3	4
Micro-$CaCO_3$/Nano-$CaCO_3$, mass ratio	0/9	1.5/10	2.5/9	3.5/8
Twin-notched impact strength (23 ± 2 °C), kJ/m^2	61.1	68.6	78.5	55.0
Twin-notched impact strength (−18 °C ± 1 °C) , kJ/m^2	74.6	78.3	85.9	–
Tensile yield strength, MPa	41.7	38.7	41.5	40.6
Elongation at break, %	160	168	161	166
Flexural modulus, MPa	2,190	2,200	2,740	–

quantity of nano-$CaCO_3$. Moreover, when comparing laboratory and industry experiments, the properties of plastic profile could not be improved as much as those of the samples made in laboratory because of the difference of extruder machine, composition of materials, processing conditions, testing specimen between industry experiment and laboratory experiment. In industry experiment, we must add micro-$CaCO_3$ to the PVC system, to cut costs. And the test samples were cut from the door-window profiles. The thickness of those was about 2 mm, which was smaller than those of laboratory experiment. So the impact strength-testing specimens were twin-notched specimens. All these contributed to the results that the properties of the nanocomposites in industry could not be improved as much as those of the samples in laboratory.

Conclusion

The properties of PVC composites filled with $CaCO_3$ particles with different diameters were investigated. By adding 40-nm $CaCO_3$ particles into the PVC matrix, the notched impact strength of the PVC composite at room temperature reached 82.4 kJ/m^2, which was 3.5 times that of the PVC matrix without $CaCO_3$ and 4.6 times that of the PVC blend filled with micro-$CaCO_3$. When the diameter of $CaCO_3$ particles was smaller, more silver streak could be initiated and terminated under the external force because of the huge interface between particles and matrix and higher mechanical properties of composites. The tensile and flexural properties of nanocomposites were also studied prior to that of composites with 500-nm or 25-μm $CaCO_3$ particles. The melt viscosity of the blend increased with nano-$CaCO_3$ loading because of its huge specific surface area. So to improve the rheological behavior of the system filled with nanoparticles, some flow modifying agents should be added. Moreover, the effect of mass ratio of nano-$CaCO_3$ and micro-$CaCO_3$ on the properties of PVC door and window profiles in industry was studied. Nanoparticles could increase the impact strength and modulus of plastic profile simultaneously. But the mechanical properties could not be improved as much as those of the samples made in laboratory because of the difference of extruder machine, composition of materials, processing conditions, the dimension and the shape of the testing samples between industry experiment and laboratory experiment.

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