Nanocomposites of Poly(vinyl chloride) and Nanometric Calcium Carbonate Particles: Effects of Chlorinated Polyethylene on Mechanical Properties, Morphology, and Rheology

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ABSTRACT: Nanocomposites of poly(vinyl chloride) (PVC) and nano-calcium carbonate ($CaCO_3$) particles were prepared via melt blending, and chlorinated polyethylene (CPE) as an interfacial modifier was also introduced into the nanocomposites through preparing CPE/nano-$CaCO_3$ master batch. The mechanical properties, morphology, and rheology were studied. A moderate toughening effect was observed for PVC/nano-$CaCO_3$ binary nanocomposites. The elongation at break and Young's modulus also increased with increasing the nano-$CaCO_3$ concentration. Transmission electron microscopy (TEM) study demonstrated that the nano-$CaCO_3$ particles were dispersed in a PVC matrix uniformly, and a few nanoparticles agglomeration was found. The toughening effect of the nano-$CaCO_3$ particles on PVC could be attributed to the cavitation of the matrix, which consumed tremendous fracture energy. The notched Izod impact strength achieved a significant improvement by incorporating CPE into the nanocomposites, and obtained the high value of 745 J/m. Morphology investigation indicated that the nano-$CaCO_3$ particles in the PVC matrix was encapsulated with a CPE layer through preparing the CPE/nano-$CaCO_3$ master batch. The evaluation of rheological properties revealed that the introduction of nano-$CaCO_3$ particles into PVC resulted in a remarkable increase in the melt viscosity. However, the viscosity decreased with addition of CPE, especially at high shear rates; thus, the processability of the ternary nanocomposites was improved. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2714–2723, 2004

Key words: nanocomposites; poly(vinyl chloride) (PVC); morphology; toughness

INTRODUCTION

Polymer composites represent an important class of engineering materials. The incorporation of inorganic fillers into thermoplastics has been widely practiced in industry to extend them and to improve certain properties. One primary purpose of adding inorganic fillers to polymers is cost reduction.[1,2] The use of fillers has been also a common practice to enhance the mechanical properties of thermoplastics, such as heat distortion temperature, hardness, toughness, dimension stability, stiffness, and mold shrinkage.[3,4] The effects of filler on the mechanical and other properties of the composites depend strongly on filler origin, particle shape and size, aggregate size, the fraction of filler, surface characteristics, and degree of dispersion.[5,6] Most of the studies revealed that addition of rigid, inorganic fillers to polymers generally resulted in a significant decrease of toughness compared to neat polymers. There are, however, several studies demonstrating an increase in toughness with rigid particulate fillers in certain composite systems such as, for example, filled polypropylene (PP) and filled polyethylene (PE).[7–10] An impressive increase of impact strength was reported by the literature for PE filled with calcium carbonate ($CaCO_3$) particles.[11,12]

In the recent decade, organic–inorganic nanocomposites have attracted great interest to scientists, because nanocomposites have emerged as a very efficient strategy to upgrade properties of synthetic polymers to the point where performances exceed largely the ones of conventional composites.[13–16] Nanocomposites could dramatically induce an improvement in mechanical and electrical properties, heat resistance, radiation resistance, and other properties as a result of the nanometric scale dispersion of the filler in the matrix.[17] One of the most promising composite systems would be polymer–clay nanocomposites based on organic polymers and inorganic clay minerals consisting of silicate layers.[18–20] A typical example is the nylon 6-montmrillonaite nanocomposites wherein 1-nm thick silicated layers of the clay minerals exfoliated and homogeneously dispersed at the nanometer level.[21] The nylon 6-montmrillonaite nanocomposites exhibited various superior properties such as high
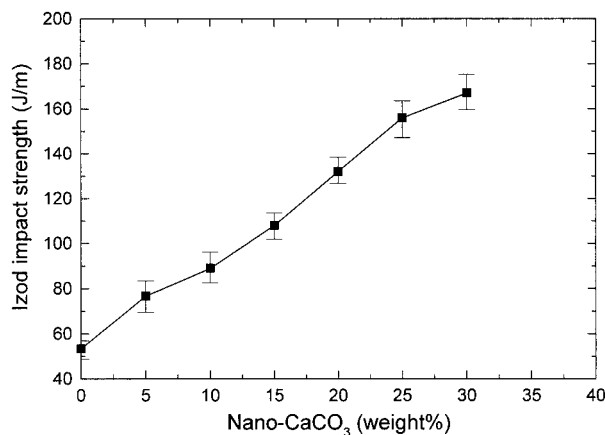
Figure 1 Notched Izod impact strength of PVC/nano-CaCO$_3$ nanocomposites vs. nano-CaCO$_3$ content.

strength, high modulus, high heat resistance, and low gas permeability compared to neat resin.[22,23] The other polymer–clay nanocomposites such as polyimide,[24] epoxy resins,[25] polystyrene,[26] polycaprolactone,[27] acrylic polymers,[28] polyurethane,[29] and poly(ethylene terephathalate)[30] were reported successively.

Other nanoparticles such as nanometric CaCO$_3$, SiO$_2$, TiO$_2$, and ZnO particles have been used to prepare nanocomposites.[31–35] CaCO$_3$ has been one of the most commonly used inorganic fillers for thermoplastics, such as poly(vinyl chloride) (PVC) and PP. The most commercially available CaCO$_3$ fillers possess the particle size varying from 1 to 50 μm.[36] The results of numerous studies have indicated that the improvement in the mechanical properties of micron-sized CaCO$_3$-filled composites is found to be minimum.[37] One of the key factors may be imputed to the poor filler–polymer interaction.[38] Many efforts have been devoted to surface-treated CaCO$_3$ filler to increase the interaction between the polymer and filler. The effects of surface modification on mechanical properties have been positive.[39] The use of nano-CaCO$_3$ particles may bring new insights in the study of polymer–inorganic nanocomposites.[40,41] In addition, the mechanical properties of nano-CaCO$_3$–filled composites, which may be very different from those of the micron-sized CaCO$_3$-filled composites, are rarely studied.[42]

The goal of the present study was to investigate the probability of toughening of PVC filled with nano-CaCO$_3$ particles. For this purpose, a kind of nanometric CaCO$_3$ particles was employed as a filler to prepare nanocomposites with PVC and chlorinated polyethylene (CPE) via a melt mixing, and the mechanical properties, morphology, and rheology were investigated. The correlation between the mechanical properties and morphology of nanocomposites was established. The toughening mechanisms were also proposed.

EXPERIMENTAL

Materials

A suspension PVC (S1000) employed in this study was purchased from Qilu Petrochemical Corp., Shandong Province, China. It has a number-average molecular weight of 62,500. CPE (CPE 3615), with a chlorine content of 36 wt %, was commercially obtained from Dow Chemical Co., USA. A nano-CaCO$_3$ filler with an average particle diameter of 40 nm was supplied by Nano-Tech Science & Technology Company, Beijing, China. The filler was surface treated with a coupling agent of the titanate type by the manufacturer. The treatment method is described as follows: the required volume of the titanate-type coupling agent was diluted with an equal amount of toluene, and a 1 : 1 solution was formed. The diluted solution was slowly sprayed, for 10-min periods, on the nano-CaCO$_3$ filler contained in a rotating mixer of the Sigma type. The rotation direction of the mixer was changed every 5 min to ensure distribution of the coupling agents in the nano-CaCO$_3$ filler. The additives, such as a lead complex thermal stabilizer, calcium stearate, and external wax, were provided by Haolong Chemical Co, Tianjin, China.

Preparation of nanocomposites

The PVC compounds were formulated with 3 phr heat stabilizer, 3 phr of calcium stearate lubricant, and 0.5 phr external wax lubricant, as well as various content of nano-CaCO$_3$ particles. The formulations were dry mixed in a high-speed rotating mixer for 20 min. For preparation of PVC/nano-CaCO$_3$ composites, the prepowders were melt blended via a laboratory two-roll mill under the experimental condition of 50 rpm and 175°C for 10 min. For preparation of PVC/CPE/nano-
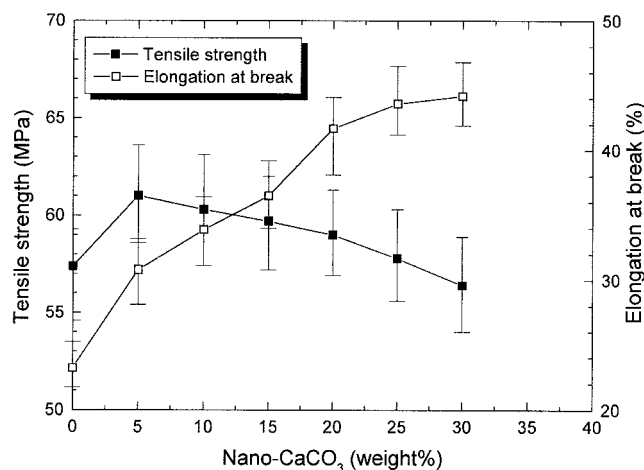

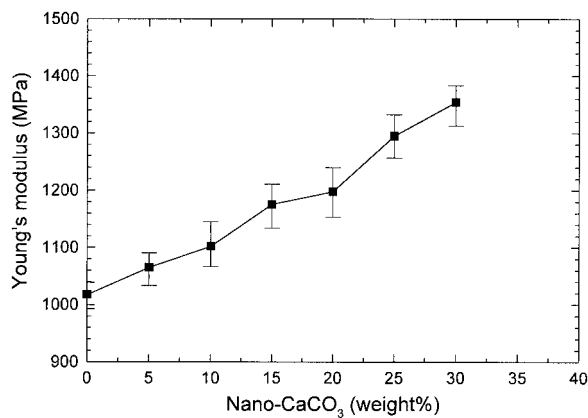**Figure 2** Tensile strength and elongation at break of PVC/nano-CaCO$_3$ nanocomposites vs. nano-CaCO$_3$ content.

Figure 3 Young's modulus of PVC/nano-CaCO₃ nanocomposites vs. nano-CaCO₃ content.

Figure 4 Notched Izod impact strength of PVC/CPE/nano-CaCO₃ nanocomposites vs. nano-CaCO₃ content.

CaCO₃ composites, CPE/nano-CaCO₃ master batches were first prepared via melt mixing in a two-roll mill at 130°C for 10 min. Then the prepowders of PVC and master batches at various proportions were melt blended via a laboratory two-roll mill under the experimental condition of 50 rpm and 175°C for 10 min. All of milled sheets were cooled to room temperature and then fragmentized into powder through a crusher.

Measurement of mechanical properties

The impact and tensile test bars were prepared via injection molding using a reciprocating screw-injection machine (CJ150NC-2). The barrel temperature was 180°C, and the mold temperature was 60°C. Notched Izod impact strength was measured with a SUMITOMO impact tester according to the standard of ASTM D256 at room temperature. The thickness of the Izod impact specimens was 1/8 inch, and the impact energy was 4 J. The tensile properties were determined with an Instron universal testing machine (Model: 1185) using a 5000 Newton load transducer according to the standard of ASTM D-638. All the tests were done at room temperature, and five measurements were carried out for each data point.

Transmission electron microscopy

Morphology was determined by transmission electron microscopy (TEM). To prepare the nanoparticle sample for TEM examination, the nano-CaCO₃ particles were dispersed in ethanol in an ultrasonic bath for 10 min. All of nanocomposites samples were cryogenically microtomed from Izod impact bars perpendicular to the flow direction using a diamond knife. The PVC/CPE/nano-CaCO₃ nanocomposites samples were stained with ruthenium tetroxide (RuO₄), but PVC/nano-CaCO₃ nanocomposites were directly ob-
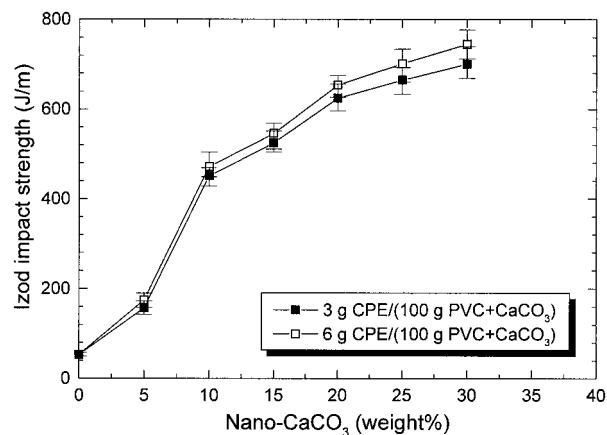
served without dyeing. An Hitachi H-800 transmission electron microscope was used to view and photograph these samples that were only of an order of nanometer in thickness.

Scanning electron microscopy

A scanning electron microscope (Cambridge S250) was employed to study and record the fracture surface of all the blending samples. The fractured specimen surfaces were coated with a thin layer (10–20 nm) of gold palladium. The coating was carried out by placing the specimen in a high vacuum evaporator and vaporizing the metal held in a heated tungsten basket. Scanning electron microscopy (SEM) observations were performed only on the fractured surface of all the blends.

Rheology measurements

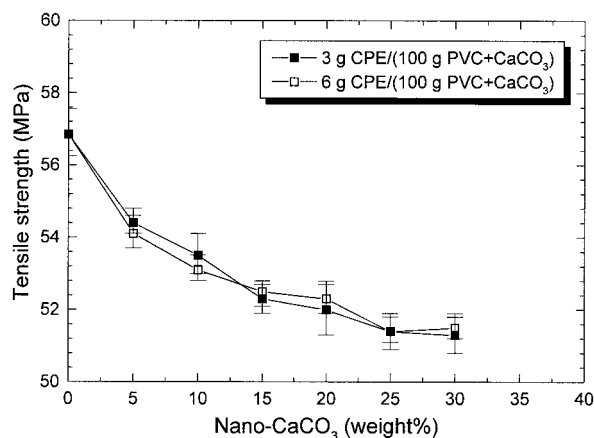The apparent viscosity at various shear rates was determined using a capillary rheometer (Caprograph-1B,

Figure 5 Tensile strength of PVC/CPE/nano-CaCO₃ nanocomposites vs. nano-CaCO₃ content.
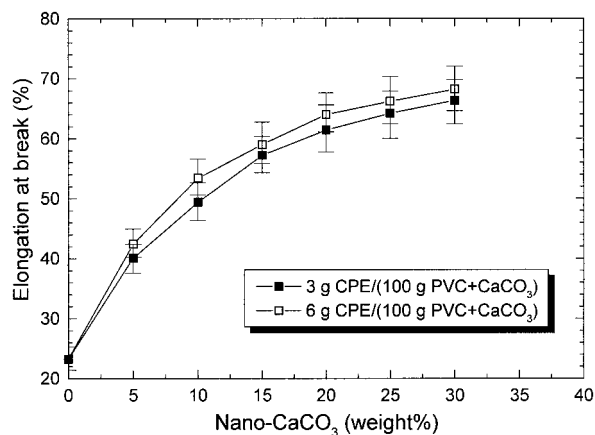
Figure 6 Elongation at break of PVC/CPE/nano-CaCO₃ nanocomposites vs. nano-CaCO₃ content.

Toyoseiki Manufacture Company) with a capillary diameter of 1.262 mm and an L/D ratio of 60.51. The measurements were carried out at 180°C under a shear rate ranging from 1 to 10^5 s^{-1}.

RESULTS AND DISCUSSION

Mechanical properties of PVC/nano-CaCO₃ nanocomposites

Figure 1 presents the notched Izod impact strength of PVC/nano-CaCO₃ nanocomposites at various weight ratios, which indicated that the nano-CaCO₃ particles had a remarkable toughening effect on PVC. The impact strength of pure PVC was 53.4 J/m, and it increased slightly to 76.5 J/m for the PVC/nano-CaCO₃ nanocomposites at a weight ratio of 95/5. Predictably, the impact strength increased gradually with increasing the nano-CaCO₃ particles content. The toughness of PVC was improved by a factor of 3 with addition of 30 wt % nano-CaCO₃ particles. Although extensive
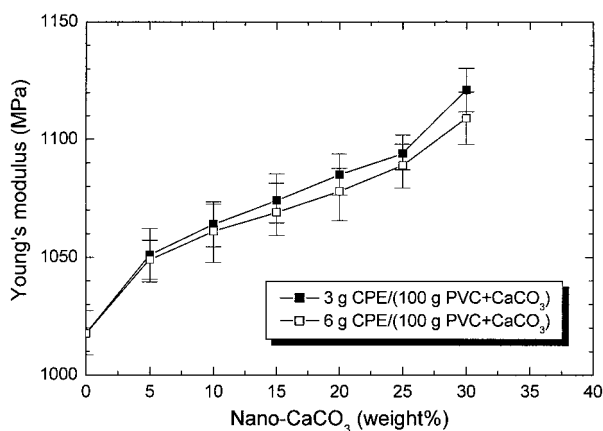

Figure 7 Young's modulus of PVC/CPE/nano-CaCO₃ nanocomposites vs. nano-CaCO₃ content.
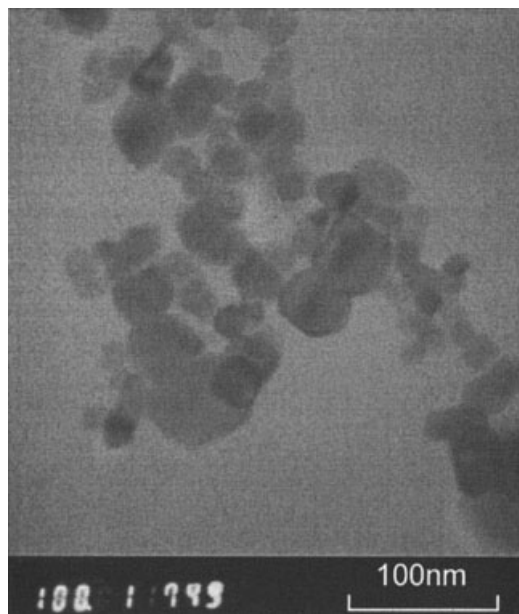

Figure 8 TEM micrograph of the nano-CaCO₃ particles.

literatures reported that microsized CaCO₃ fillers had a positive effect on toughness of PVC,[3,4] the improvement in Izod impact strength was moderate. It is obvious that the toughening efficiency of nano-CaCO₃ particles on PVC is much higher than that of normal microsized CaCO₃ fillers. The toughening of PVC by microsized CaCO₃ particles could be explained by the crack front bowing mechanism.[43,44] For the toughening polymer system using inorganic particles, the rigid particles can resist the propagation of the crack, so the primary crack has to bend between the neighboring particles. However, the size of nano-CaCO₃ particles used in this study is of the order of 40 nm or less; the applicability of the bowing mechanism is questionable, because such small-sized rigid particles may not be able to resist the propagation of the crack. Obviously, the toughening effect of nano-CaCO₃ particles on PVC could be contributed to a new mechanism that was indeed observed for a number of nanocomposites. According to this mechanism,[42] the nano-CaCO₃ particles could act as stress concentration sites, which could promote cavitation at the particle–PVC matrix boundaries during loading. The cavitation could release the plastic constraints and trigger mass plastic deformation of the matrix, leading to much improved toughness.

The tensile strength and elongation at break of PVC/nano-CaCO₃ nanocomposites at various weight ratios are presented in Figure 2. The PVC/nano-CaCO₃ nanocomposites, at a weight ratio of 95/5, exhibited a slightly higher tensile strength than that of pure PVC, which revealed that the nano-CaCO₃ particles gave a strength enhancement on the PVC matrix like the normal microsized CaCO₃ filler.[3] However, a
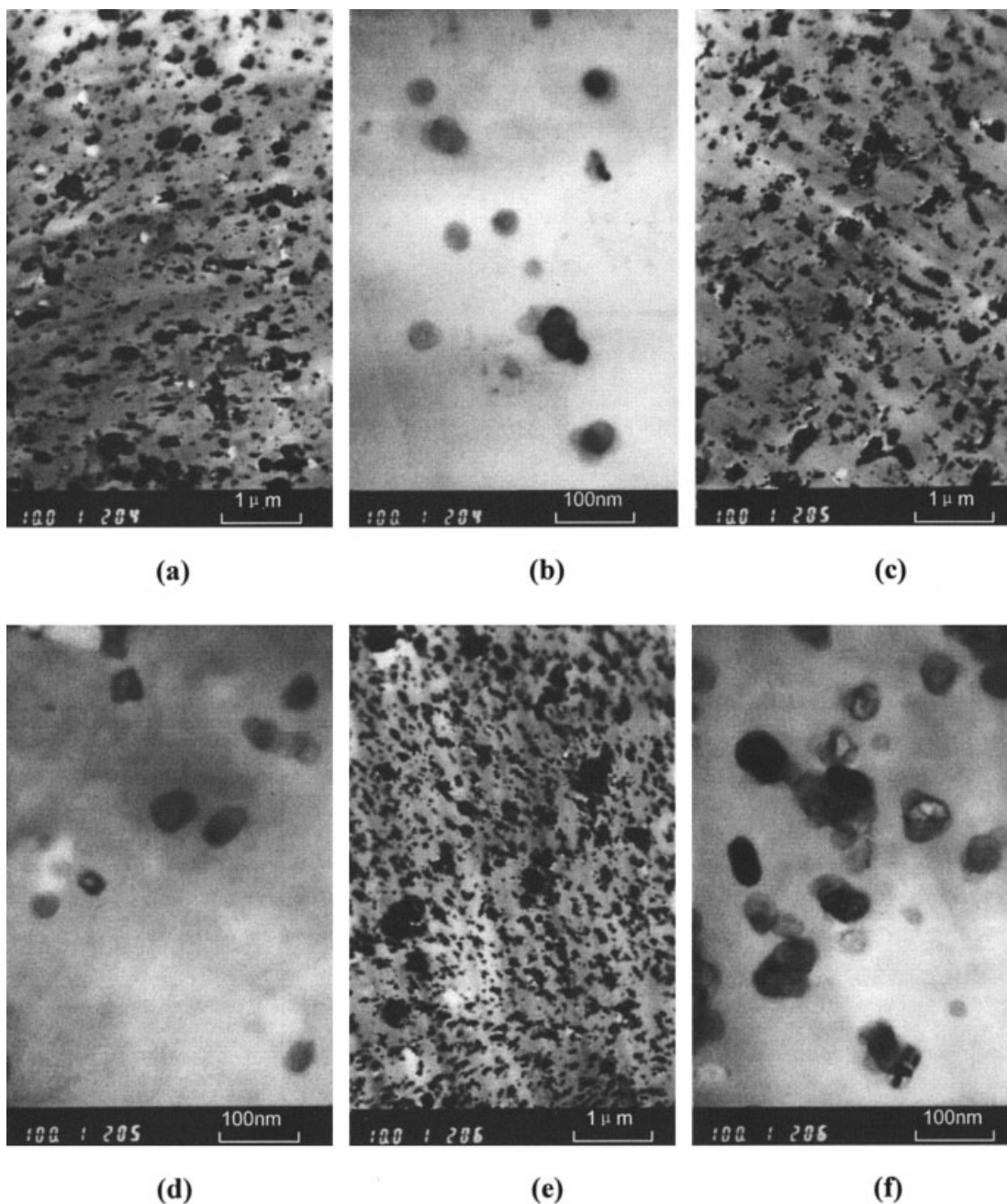
Figure 9 TEM micrographs of the PVC/nano-CaCO$_3$ nanocomposites at a weight ratio of: (a, b) 95/5, (c, d) 90/10, (e, f) 80/20.

further increase in the nano-CaCO$_3$ particle contents resulted in a decrease in the tensile strength. This may be a result of the poor filler–polymer interaction. On the other hand, the elongation at break kept a continuous increase with increasing the nano-CaCO$_3$ content. This could be explained by the increasing the deformation of the matrix caused by the energy dissipating in toughening. It could also be found, as shown in Figure 3, that Young's modulus of PVC/nano-CaCO$_3$ nanocomposites gave higher performance with increasing the nano-CaCO$_3$ content, which could

be attributable to the improvement of rigidity of nanocomposites due to introduction of a rigid filler into the PVC matrix.

Effects of CPE on mechanical properties of nanocomposites

The effect of CPE contents on notched Izod impact strength of PVC/CPE/nano-CaCO$_3$ nanocomposites against the nano-CaCO$_3$ content is showed in Figure 4. Comparing the binary nanocomposites with ternary
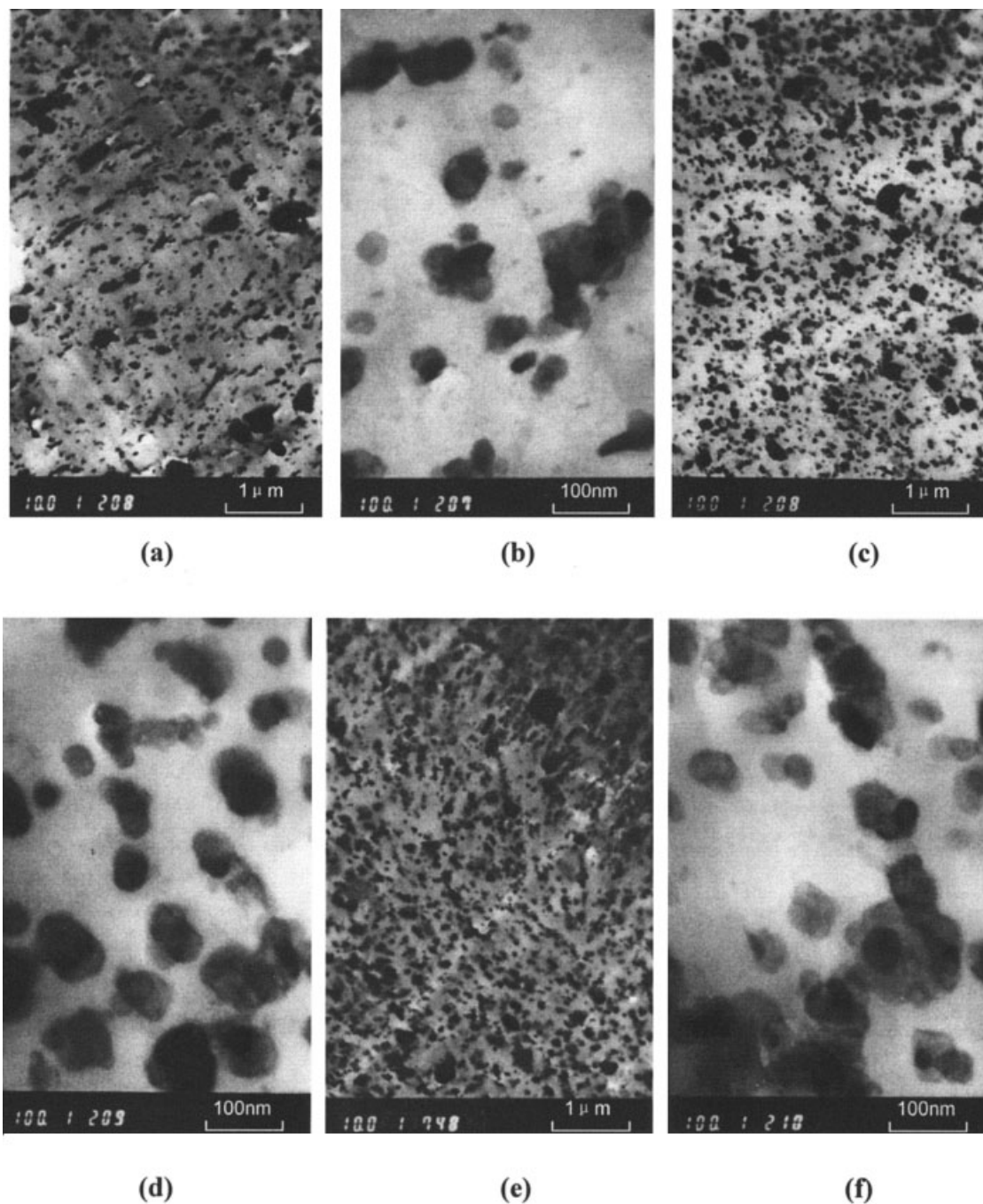
Figure 10 TEM micrographs of the PVC/CPE/nano-CaCO₃ nanocomposites stained with RuO₄ at a weight ratio of: (a, b) 95/3/5, (c, d) 90/3/10, (e, f) 80/3/20.

nanocomposites in the same PVC/nano-CaCO₃ proportion, the Izod impact strength of ternary nanocomposites are much higher than that of the binary one. At the same time, the greater the CPE content, the higher the Izod impact strength. The remarkable improvement in impact strength shows how important the effect of CPE is on the nanocomposites. It is well known that CPE is a good impact modifier for PVC, and a toughening effect for the PVC/CPE system can be observed only when the CPE content is higher that

15 wt %. In the beginning of this study, we prepared the ternary nanocomposites by directory melt mixing of PVC with nano-CaCO₃ and CPE in the two-roll mill; however, we could not find a significant increasing in impact strength for ternary nanocomposites compared with the binary nanocomposites. In succession, we first prepared a CPE/nano-CaCO₃ master batch, and then we melt mixed PVC with the CPE/nano-CaCO₃ master batch. As a result, the ternary nanocomposites gave an excellent tough performance in all cases. It is
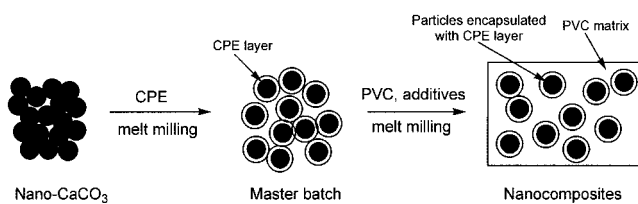
Figure 11 Scheme of the processing for PVC/CPE/nano-CaCO$_3$ nanocomposites.

simply acceptable that this significant increase in toughness was caused by a synergetic effect of CPE and nano-CaCO$_3$. But the effect of the processing methods on the toughness gives information about the difference of toughening mechanism between nano-CaCO$_3$ and CPE/nano-CaCO$_3$, which will be discussed in the following section.

The effect of CPE content on tensile properties of PVC/CPE/nano-CaCO$_3$ nanocomposites has also been studied by tensile testing, as reported in Figures 5 to 7. The tensile strength and Young's modulus of the ternary nanocomposites are lower compared to pure PVC, as a result of introduction of CPE, which, as a flexible polymer, would soften the composite materials.[45] However, the decrease in tensile strength for the ternary nanocomposites is continuous and slight, compared to the strongly negative influence of nano-CaCO$_3$ for binary nanocomposites. Apparently, CPE is naturally miscible with PVC. The nano-CaCO$_3$ particles are surface modified with CPE by preparing the CPE/nano-CaCO$_3$ master batch, which functions to strengthen the interaction between PVC and nano-CaCO$_3$. As a result, the mechanical properties could be enhanced partially. The same reason could be explained for the increase in elongation at break and Young's modulus with increasing the nano-CaCO$_3$ content.

Morphology

The TEM micrograph of the nano-CaCO$_3$ particles, as shown in Figure 8, demonstrates that nanoparticles have a high spherical structure and rough surface, and some aggregates can be seen. Because of the aggregate nature of these nanoparticles, it is difficult to determine the primary particle size precisely. The primary particle size was determined by measuring the sizes of some randomly chosen particles from the TEM micrograph. An approximate particle size ranging from 30 to 50 nm was evaluated.

Figure 9 shows the TEM micrographs of PVC/nano-CaCO$_3$ nanocomposites. The dark nano-CaCO$_3$ particles could be clearly observed in a light background without staining samples. It is well known that the dispersion of filler in the polymer matrix can have a

significant effect on the mechanical properties of the composites. When using nano-CaCO$_3$ particles as a filler, because the nanoparticles have a strong tendency to agglomerate, homogeneous dispersion of them in PVC is a difficult job. From the TEM micrographs of binary nanocomposites, one could find that most nano-CaCO$_3$ was dispersed as primary particles while some nanoparticles aggregated. The individual nano-CaCO$_3$ particles could also be observed clearly from the magnified TEM micrographs. However, more aggregates were found for the binary nanocomposites with a high nano-CaCO$_3$ content. This is reasonable, considering that at high nano-CaCO$_3$ concentration, the interparticle distance is small, and hence, flocculation of these nanoparticles can occur after the mixing is stopped. Due to appropriate processing conditions and surface treatment for nano-CaCO$_3$ used in this study, a relatively good dispersion was achieved. Consequently, the improvement in toughness of PVC/nano-CaCO$_3$ nanocomposites was obtained.

We also observed the morphology of PVC/CPE/nano-CaCO$_3$ nanocomposites directly by TEM using same the sampling method, but we could see a complete same morphology with that of PVC/nano-CaCO$_3$ binary ones. However, when the TEM samples of ternary nanocomposites were stained with RuO$_4$, the dark particles could be observed clearly in the light background, as shown in Figure 10. Comparing the TEM micrographs of ternary nanocomposites with those of binary ones, the dispersions of the particles in PVC matrix for both are quite similar. However, the individual particle size of ternary nanocomposites is slightly larger than that of binary ones from the TEM micrographs. Based on the above experimental results,
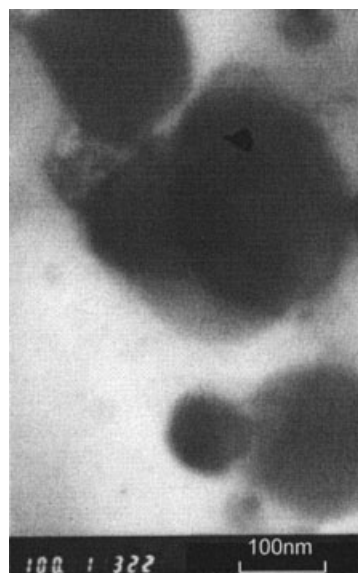

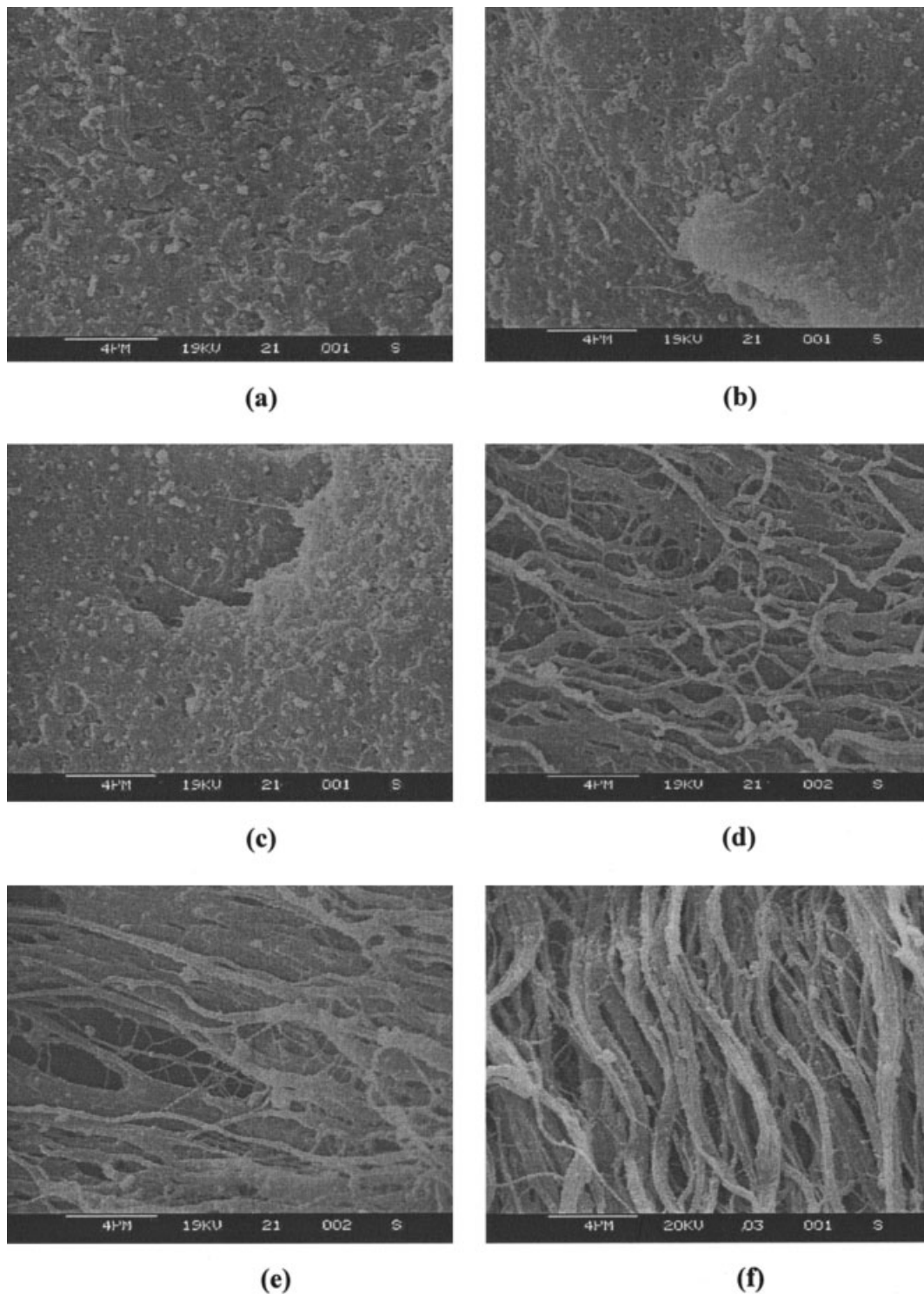**Figure 12** TEM micrograph of the PVC/CPE blend stained with RuO$_4$ at a weight ratio of 97/3.

Figure 13 SEM micrographs of the PVC/nano-CaCO₃ nanocomposites at a weight ratio of: (a) 95/5, (b) 90/10, (c) 80/20; and the PVC/CPE/nano-CaCO₃ nanocomposites at a weight ratio of: (d) 95/3/5, (e) 90/3/10, (f) 80/3/20.

it could be concluded that all nano-CaCO₃ particles were encapsulated with a CPE layer through preparation of the CPE/nano-CaCO₃ master batch. When we prepared the ternary nanocomposites through melt mixing the PVC and master batch, the CPE layer was not broken down during the processing of the PVC and master batch. Finally, in the PVC matrix, the nano-CaCO₃ particles act as "core-shell" particles with an elastomeric shell and rigid core, which is schematically illustrated in Figure 11. Obviously, differerent from the rigid particle toughening mechanism for PVC/nano-CaCO₃ nanocomposites, the toughening

effect for ternary nanocomposites can be attributable to a rubber-toughening mechanism, because the nano-CaCO$_3$ particles encapsulated with the CPE layer play a role of elastomer particles in the matrix. This mechanism is in good agreement with the observed notched Izod impact strength of ternary nanocomposites. To verify the above conclusion, we also observed the TEM micrograph of the PVC/CPE blend at a weight ratio of 97/3 stained with RuO$_4$, as shown in Figure 12. It was found that the CPE domain had a particle size ranging from 100 to 200 nm, which was much larger than the particles observed in the TEM micrographs of ternary nanocomposites. This result confirmed the fact that the nano-CaCO$_3$ particles were encapsulated with the CPE layer.

Fracture surfaces

Figure 13 shows SEM micrographs of the impact fractured surface of PVC/nano-CaCO$_3$ binary and PVC/CPE/nano-CaCO$_3$ ternary nanocomposites, which demonstrated the completely different fracture behaviors. From Figure 13(a)—(c), which is based on the binary nanocomposites, one can find that the fracture surface is smooth and featureless. It is observed that better particle dispersion in the matrix tend to form smaller agglomerates. However, it is also observed that massive plastic deformation on the fracture surface of binary composites is accompanied by a large number of voids, which was clearly caused by matrix cavitation due to the addition of the nano-CaCO$_3$ particles.

On the other hand, as demonstrated in Figure 13(d)–(f), the fracture surface of the ternary nanocomposites had a highly plastic deformation exhibiting high-impact energy. This extensive plastic deformation of the matrix was accompanied by the crack propagation. A characteristic feature of the fracture surface of the ternary nanocomposites is the formation of thread-like striations perpendicular to the direction of the crack propagation. These striations are associated with heavily plastically deformed fibrils of the PVC matrix. Such typical morphology was observed easily in rubber-modified plastics systems where their origin was explained fully.[46–49] Through investigating the fracture surface of both nanocomposites, it is noteworthy that the toughening mechanism of the ternary nanocomposites is quite different from that for binary composites. This result is in support of the above conclusion from the TEM observation.

Rheological properties

The apparent viscosities of pure PVC, and PVC/nano-CaCO$_3$ and PVC/CPE/nano-CaCO$_3$ nanocomposites measured in the capillary rheometer at 180°C, are shown in Figure 14. The PVC/nano-CaCO$_3$ binary
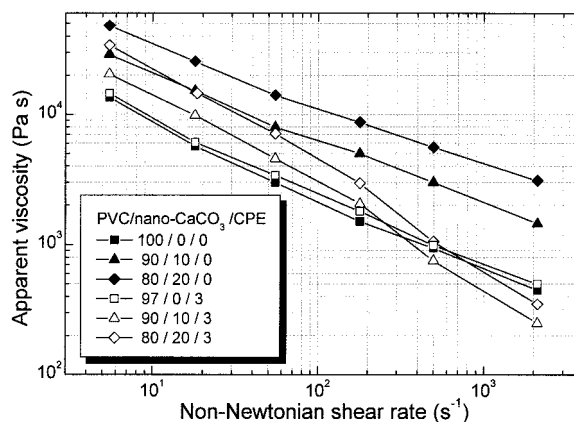

Figure 14 Plots of apparent viscosity vs. non-Newtonian shear rate for the PVC/nano-CaCO$_3$ binary and PVC/CPE/nano-CaCO$_3$ ternary nanocomposites and PVC/CPE blend.

nanocomposites had a much higher viscosity than pure PVC in all rangeS of the shear rates carried out in this experiment. The greater the content of nano-CaCO$_3$, the higher the viscosity. It is obvious that the introduction of a rigid filler into PVC reduced the flow ability of PVC, and hindered the disentanglement of the molecular chains of PVC. The increase in melt viscosities of binary composites is due to these two effects.

When CPE was introduced to PVC/nano-CaCO$_3$ binary nanocomposites, the viscosity of ternary nanocomposites was lower than that of the binary ones in the same PVC/nano-CaCO$_3$ proportion. Due to the encapsulation of nano-CaCO$_3$ by CPE, the viscosity of ternary nanocomposites was principally influenced by CPE. CPE can improve the plasticizing ability of PVC, and consequently, improve the flow ability and decrease the melt viscosity.[50] It could also be found that the viscosity of ternary nanocomposites was higher than pure PVC at low shear rates but lower than pure PVC at high shear rates. The molecular chains of CPE are more flexible than that of PVC, so they are entangled in the melt. This entanglement severely impedes the flow of the melt at low shear rates, and consequently, the viscosity becomes higher. However, the disentangling effect is much greater than entangling one at high shear rates, because the repulsion between the PVC chains and the CPE ones arises from more flexible chains of CPE than that of PVC. As a result, PVC/CPE/nano-CaCO$_3$ ternary nanocomposites showed lower viscosities than pure PVC at high shear rates.

CONCLUSION

Nanocomposites of PVC and nano-CaCO$_3$ were prepared via a melt blending. A moderate toughening effect was achieved for the nanocomposites, and the

elongation at break and Young's modulus also increased. The TEM study demonstrated that the nano-CaCO$_3$ particles were dispersed in the PVC matrix uniformly and a few nanoparticles agglomeration was found. The toughening effect of the nano-CaCO$_3$ particles on PVC could be attributed to the cavitation of the matrix, which consumed tremendous fracture energy. The notched Izod impact strength of nanocomposites could be improved remarkable by the incorporation of CPE. The TEM study indicated that the nano-CaCO$_3$ particles in the PVC matrix was encapsulated with a CPE layer through preparing the nano-CaCO$_3$/PVC master batch. Such a high toughening effect for PVC/CPE/nano-CaCO$_3$ nanocomposites was attributable to a typical rubber–plastics-toughening mechanism.

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