

Effects of the Reinforcement and Toughening of Acrylate Resin/CaCO₃ Nanoparticles on Rigid Poly(vinyl chloride)

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ABSTRACT: Novel composite particles based on nanoscale calcium carbonate (nano-CaCO₃) as the core and polyacrylates as the shell were first synthesized by *in situ* encapsulating emulsion polymerization in the presence of the fresh slush pulp of calcium carbonate (CaCO₃) nanoparticles. Subsequently, these modified nanoparticles were compounded with rigid poly(vinyl chloride) (RPVC) to prepare RPVC/CaCO₃ nanocomposites. At the same time, the effects of the reinforcement and toughening of these modified nanoparticles on RPVC were investigated, and the synergistic effect of modified nanoparticles with chlorinated polyethylene (CPE) was also studied. The results showed that in the presence of nano-CaCO₃ particles, the *in situ* emulsion polymerization of acrylates was carried out smoothly, and polyacrylates suc-

cessfully encapsulated on the surface of nano-CaCO₃ to prepare the modified nanoparticles, breaking down nano-CaCO₃ particle agglomerates, improving their dispersion in the matrix, and also increasing the particle–matrix interfacial adhesion. Thus, the effects of the reinforcement and toughening of these modified nanoparticles on RPVC were very significant, and the cooperative effect of the nanoparticles with CPE occurred in the united modification system. Scanning electron microscopy analyses indicated that large-fiber drawing and network morphologies coexisted in the system of joint modification of nanoparticles with CPE. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3940–3949, 2007

Key words: poly(vinyl chloride); nanoparticles; modification

INTRODUCTION

As is well known, poly(vinyl chloride) (PVC) is one of the most versatile thermoplastic resins used today, and a considerable number of cost-efficient compounds have been developed from PVC with good processability and high impact resistance in pipes, outdoor furniture, and building materials.^{1–4} In general, the basic resin used to manufacture outdoor construction is rigid poly(vinyl chloride) (RPVC), and this kind of PVC resin is relatively brittle and notch sensitive. To meet using requirements, RPVC must be modified to improve its mechanical properties, in particular, its toughness,⁵ and some elastomers, such as chlorinated polyethylene (CPE), ethylene–vinyl acetate copolymer, and nitrile–butadiene rubber, have been used for this purpose.^{6,7} However, with these

modifications, there are many negative effects on PVC's other properties, including its tensile and flexural properties and hardness. To overcome these defects, some new toughening mechanisms and methods have been developed by many researchers. In the early 1980s, Kurauchi and Ohta⁸ put forward a new toughening method in which materials could be toughened by rigid modifiers, which may be divided into two basic groups.⁹ The one involves a rigid organic modifier added to RPVC to improve its mechanical properties, particularly, its toughness. Some scholars have researched the synthesis of core–shell type modifiers, such as methyl methacrylate–butadiene–styrene copolymer (MMA) and acrylate resin (ACR), and their modified effects on RPVC.^{10–17} Another method involves rigid inorganic modifiers.¹⁸ Compounding PVC with inorganic fillers is a convenient and efficient method. It is well known that the particle size, structure, and surface characteristics of the modifier are the three main factors that effect or determine its modified ability. Some studies have focused on improving the compatibility of inorganic modifiers with a matrix resin.^{19–21}

As for inorganic particles, calcium carbonate (CaCO₃) has been used as inorganic filler for many years. However, the modified ability of CaCO₃ is poor

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because of its big size and low surface activity. So, surface treatment is essential,²² which involves the simple addition of a type of phosphate coupling agent and graft polymerization of vinyl monomers onto CaCO₃ by a mechanochemical method or by irradiation of γ rays.^{23–25} Although many attempts have been made to increase the compatibility between the CaCO₃ particle surface and polymers, the results have shown that this was not sufficient to meet commercial requirements.

Recently, after the development of inorganic particle micropowder technology and particle surface treatment technology,^{26,27} nanoscale particles have been very useful in the reinforcement and toughening of some plastics;^{28–36} these can not only increase the toughness of materials but also maintain their tensile strength, flexural strength and modulus, Vicat softening temperature, and hardness in higher levels.

Although composite systems composed of inorganic nanoparticle and organic polymers are widely being studied and are becoming the most applied potential systems,^{37–44} because of the strongly agglomerating tendency of nanoparticles, the homogeneous dispersion of nanoparticles in a polymer matrix is still a major problem.

Since Hergeth et al.⁴⁵ first applied an emulsion polymerization process to encapsulate inorganic particles by a polymer layer, *in situ* polymerization has become a common method for the preparation of nanoparticle-filled composites with good dispersion.^{46–49} In this article, a composite particle with nanoscale calcium carbonate (nano-CaCO₃) as the core and with polyacrylate as the shell was synthesized by *in situ* emulsion polymerization, and then, the effects of the reinforcement and toughening of this kind of nanoparticle on RPVC and the synergistic effect of the modified nanoparticles with CPE were studied.

EXPERIMENTAL

Materials

Butyl acrylate (BA), MMA, and acrylic acid (AA; commercial grade, Beijing Dongfang Chemical Plant, Beijing, China) were washed with aqueous sodium hydroxide to remove inhibitor. Sodium dodecyl sulfate (SDS; analytical-reagent grade) was from Beijing Donghuan United Chemical Plant. Potassium persulfate (K₂S₂O₈; analytical-reagent grade) was from Beijing Chemical Plant. The protecting colloid (a commercial-grade polycarboxylate derivative) was from Beijing Dongfang Chemical Plant. The nano-CaCO₃ powders with average primary particle sizes of 20–60 nm were supplied courtesy of Beijing University of Chemical Technology (Beijing, China).⁵⁰ The crosslinking agent (a commercial-grade ester derivative) was from American Sartomer Co. (Exton, PA). Aluminum

sulfate was analytically pure grade. Distilled deionized water was used in all of the polymerizations.

PVC (S-1000) with a *K* value of 65–70 was obtained from Qilu Petrol Chemical Corp. (Zibo, China). The composite stabilizer (XFW-02) was obtained from Nanjing Concorde Chemical Co., Ltd. (Nanjing, China). CaCO₃ (AH-I) was produced by Shijiazhuang Chunlan Chemical Co., Ltd. (Shijiazhuang, China). Titanium dioxide (TiO₂; RCL-666) was produced by American Meilian Inorganic Chemical Co., Ltd. (Ashtabula, OH). The ACR processing additive (K125P) and ACR impact modifier (KM355P) were supplied by Kureha Chemicals Industry Co., Ltd. (Tokyo, Japan). CPE (135A) with a chlorine content of 36% was produced by Weifang Chemical Factory (Weifang, China).

In situ encapsulating emulsion polymerization of monomers onto nano-CaCO₃ powders

All components were purged under N₂ for 10 min. Unless indicated, polymerizations were conducted in two steps. First, the fresh slush pulp of nano-CaCO₃ was ultrasonically dispersed in aqueous water. The ingredients (SDS as the emulsifier, BA as the monomer, and AA as the functional monomer and protecting colloid) were added to the reactor vessel, heated, and stirred continuously until the reaction temperature was reached. Then, an aqueous solution of K₂S₂O₈ as the initiator (preheated to the reaction temperature) was added to start the encapsulating polymerization reaction by poly(butyl acrylate) (PBA). This polymerization had ultrasonic wave conditions at 75°C. After 3 h, the second reaction, the seeded emulsion polymerization of MMA onto the previous particles, was subsequently performed with a dropped method. The sample was precipitated by an Al₂(SO₄)₃ solution, purified by washing with warm distilled deionized water, and then dried *in vacuo*. The recipe included 750 mL of H₂O, 100 mL of BA, 125 mL of MMA, 50 g of nano-CaCO₃, 4 g of SDS, 1.75 g of K₂S₂O₈, 22.5 g of the protecting colloid, 2.0 g of AA, and 0.75 g of the crosslinking agent.

Preparation of ACR/CaCO₃-nanoparticle-filled PVC nanocomposites

PVC resin, the composite stabilizer, CaCO₃, TiO₂, the ACR processing additive, the ACR impact modifier, CPE, the nanoparticle rigid impact modifier, and other additives were weighed and poured into a high-speed mixer. All of the ingredients were mixed. When the temperature was up to 120°C, the composite mixtures were discharged into a cooling mixer. After they were cooled down to 40°C, the previous mixtures were plasticized in a two-roll mill at 180°C for 10 min and then discharged into a sheet shape. The sheets were piled up and laminated onto a plate at a temperature of 175°C, and the pressure was



Figure 1 TEM micrograph of CaCO₃ nanoparticles.

maintained at 12 MPa for 10 min. Care was taken at this stage to ensure precise timing to eliminate any difference in thermal histories.

Characterization

The particle size and morphology of the unmodified and modified nano-CaCO₃ particles were observed by transmission electron microscopy (TEM; Hitachi Co., Tokyo, Japan) with a 2% aqueous solution before the encapsulating emulsion breakage. Specimens were collected on mesh copper TEM grids and were subsequently dried with filter paper and examined by the H-600A transmission electron microscope.

The composing structure of the ACR/CaCO₃ nanoparticles was characterized by thermogravimetric analysis (TGA; 7 series, PerkinElmer Co., Wellesley, MA) at a rate of 20°C/min under a nitrogen atmosphere, electron spectroscopy for chemical analysis (ESCA; 220i-XL, VG Co., London, UK), and differential scanning calorimetry (DSC; 2100 General V4.1c, DuPont Co., Wilmington, OE) at a 10°C/min heating rate under a nitrogen atmosphere.

Notched Izod impact strength was performed with a pendulum-type tester according to ASTM D 256. The tensile strength and elongation at break were performed with an electronic universal tester (model CSS-1101, Changchun Tester Research Institute, Changchun, China) according to ASTM D 638 type I at a crosshead speed of 50 mm/min. The flexural strength and modulus were measured according to ASTM D 790. The Vicat softening temperature was tested according to ASTM D 1525. The fracture surface morphology was observed by scanning electron microscopy (SEM; S-530, Hitachi Co.). Rockwell hardness testing was con-

ducted with a high-quality Rockwell-type hardness tester (model DXL-6, Matsuzawa SEIKI Co., Ltd., Tokyo).

RESULTS AND DISCUSSION

ACR/CaCO₃ nanoparticle characterization

Heterogeneous latices of nano-CaCO₃ as the core and acrylates as the shell polymers were designed and successfully prepared via a two-stage *in situ* encapsulating emulsion polymerization for impact modification on RPVC. The latices were characterized by TEM.

Figure 1 shows the TEM image of unmodified CaCO₃ particles. Most of the CaCO₃ particles agglomerated, which made it difficult to obtain the single particle shape and size. So, dispersion processing was essential. After dispersion, the primary average particle size was 20–60 nm, as shown in Figure 2. Figure 3 shows the TEM micrograph of nano-CaCO₃ latex particles encapsulated by ACR. Clearly, particles were composed of two different parts, in which the core is black and the shell is light in the micrograph, which indicated that nano-CaCO₃ was encapsulated by the polymers as expected, and the average particle size of the ACR/CaCO₃ nanoparticles was about 70–90 nm. It is well known that nanoparticles, because of the weak force that stacks them together, can be easily separated in a solvent under vigorous stirring or an ultrasonic environment. During polymerization, ACR could enter the gaps and empty space between the primary particles under a stirring and an ultrasonic environment together. So, polymerization could be initiated by the diffusion of an initiator, and the heat released inside the gaps led to the breakdown of the nano-CaCO₃ particle agglomerates.

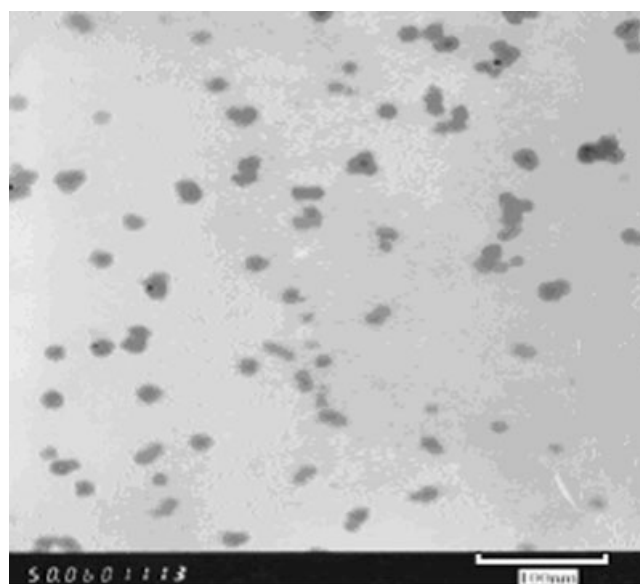


Figure 2 TEM micrograph of CaCO₃ nanoparticles after dispersion.

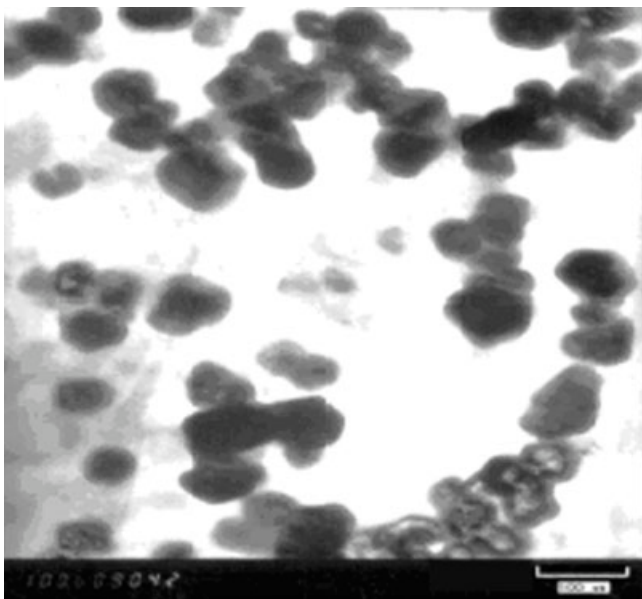


Figure 3 TEM micrograph of ACR/CaCO₃ nanoparticles.

In this study, the composing structure of the multi-phase nanoparticles were characterized by testing methods such as TGA (Fig. 4), ESCA (Fig. 5), and DSC (Fig. 6). Figure 4 shows three decomposing temperatures (250.21, 379.61, and 710.24°C) and the remaining content of 19.2% at above 600°C. These results indicate that this kind of ACR/CaCO₃ nanoparticle was made up of three components: PBA, poly(methyl methacrylate) (PMMA), and CaCO₃. As shown in Figure 5, there was no CaCO₃ on the surface of this kind of nanoparticle, which indicated that the nano-CaCO₃ particles were entirely encapsulated by the polymers. To further clarify the composing structure of this sort of nanoparticle, DSC was also conducted. Figure 6 gives the following results: the first glass-transition temperature (T_{g1}) was about -40°C, the second glass-transition temperature (T_{g2}) was about 60°C, and the third glass-transition temperature (T_{g3}) was about

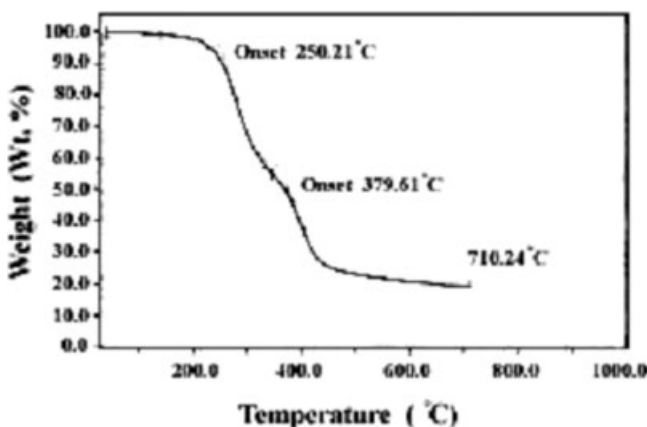


Figure 4 TGA spectra of ACR/CaCO₃ nanoparticles.

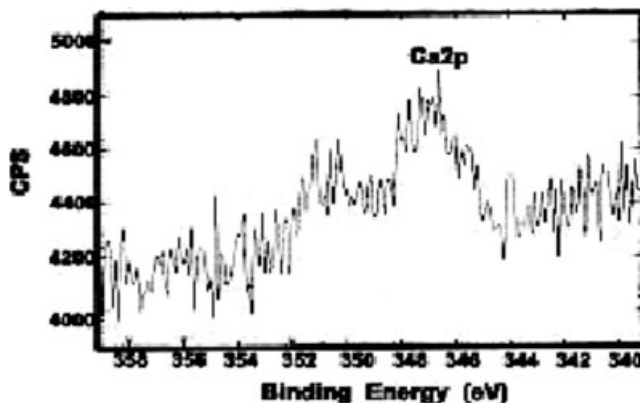


Figure 5 ESCA spectra of ACR/CaCO₃ nanoparticles.

120°C. It is clear that the value of T_{g1} was near the glass-transition temperature of PBA and the value of T_{g2} was not near the glass-transition temperature of PMMA. The results demonstrate that the polymer components of the nanoparticles were composed of two different polymers. The value of T_{g1} indicated that the autopolymerization of a great majority of BA took place on the surface of the nano-CaCO₃ powders. In this study, a crosslinking agent with two double bond was introduced to the rubbery layer, so in this layer, a crosslinking reaction between BA and crosslinking agent partly took place, which directly led to a value of T_{g1} that was higher than that of PBA. A certain degree of crosslinking structure could initiate a lot of crazes and shear belts to absorb a lot of energy during the impact course. The value of T_{g2} indicated that the copolymerization of a part of BA with MMA occurred, and an interpenetrating polymer network (IPN) structure with the main content of PMMA developed in the transition encapsulating layer. The value of T_{g3} indicated that the autopolymerization of MMA took place in the outer layer as the shell.

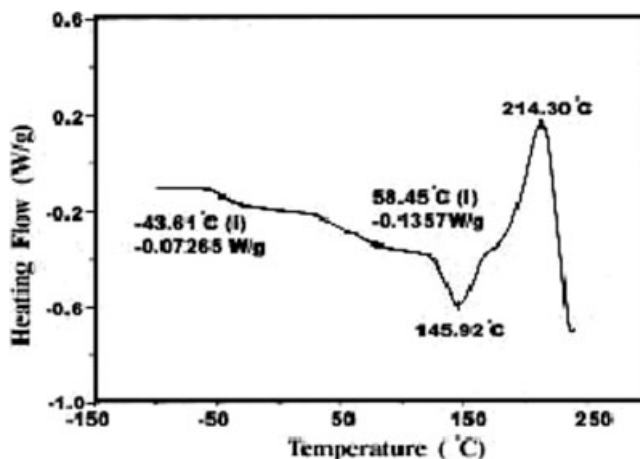


Figure 6 DSC spectra of ACR/CaCO₃ nanoparticles.

Above all, the core-shell structure nanoparticles as an impact modifier were achieved in our laboratory; there were three layered parts composed of nano-CaCO₃ as the core, PBA as the middle layer containing the IPN structure of PBA with PMMA as a transition layer, and PMMA as the shell.

Mechanical properties of the PVC/ACR/CaCO₃ nanocomposites

PVC is a kind of important thermoplastic, and its output is only less than that of polyethylene and ranks the second position in the world. However, its toughness is poor and cannot meet using requirements. Until now, the method used most to improve PVC toughness has been to mix PVC with elastomers, such as CPE, PMMA-butadiene-styrene copolymer, and ACR;^{6,11} these toughening theories have been proposed for some years. For comparison of the toughening effects between the ACR/CaCO₃ nanoparticles and these commercial materials on RPVC, the experimental recipes and corresponding results are summarized in Table I.

In Table I, the effects of different concentrations of ACR/CaCO₃ nanoparticle modifiers with fixed values for other components on RPVC are investigated as recipe 1, recipe 2, and recipe 3. This kind of ACR/CaCO₃ nanoparticle as a modifier with increasing nanoparticle contents from a minimum to 8 phr added to RPVC evidently improved the performance of the matrix; particularly, the Charpy impact strength could increase up to 87.4 and 83.0% with 6 phr nanoparticle modifier content at room temperature and a lower temperature, respectively. When the nanoparticle content was 8 phr, the modification on RPVC progressively decreased, most probably due to these nanoparticles' rigid filler (RF) properties. The theory of a RF reinforcing RPVC supposed that the reinforcement

improvement had a maximum value as the RF loading increased that differed from the reinforcement mechanism with elastomer.⁵¹ Further evidence is given in following SEM images.

As shown in Table I, the effect of the ACR/CaCO₃ nanoparticle modifier (recipe 2) was similar to that of KM355P (recipe 5) on RPVC, and the values of impact strength mixed by these two modifiers at low temperature (−20°C) were all almost twice as high than that of pure RPVC. Meanwhile, the RPVC/ACR/CaCO₃ nanocomposite had a higher modulus, strength, and Vicat softening temperature than pure RPVC. These reflect the advantage in the reinforcement and toughening of the nanocomposite. However, the toughening effects on RPVC of both KM355P (recipe 5) and the nanocomposite (recipe 2) were inferior to that of CPE (recipe 4).

Synergistic reinforcement and toughening of nanocomposites with CPE

Although the toughening effect with the content of single CPE added by 9 phr (recipe 4) on RPVC was very good, the other properties of the composite, such as strength, rigidity, and Vicat softening temperature, obviously decreased. According to the rigid particle toughening theory, the matrix can obtain perfect impact strength under the condition that it should have a certain toughness.¹⁸ So, it is necessary to improve the toughness of a matrix resin before the nanoparticles are filled. In this study, the synergistic modification effects of the nanoparticles with CPE were investigated with mass ratios of CPE to the nanoparticles of 5 : 3, 4.5 : 3, 4 : 4, and 2 : 5, and these results are given in Figures 7–12.

As shown in Figures 7–12, the synergistic effect of nanoparticles with CPE on the toughening of RPVC was very significant. Particularly, the toughening

TABLE I
Formulation and Properties of the Samples

	Recipe 1	Recipe 2	Recipe 3	Recipe 4	Recipe 5
Materials					
PVC	100	100	100	100	100
Composite stabilizer	5	5	5	5	5
TiO ₂	4	4	4	4	4
CaCO ₃	6	6	6	6	6
Nanocomposite modifier		6	8		
CPE				9	
KM355P					6
Properties					
Tensile strength (MPa)	60.3	71.4	56.0	48.9	64.2
Elongation at break (%)	30.5	73.8	70.1	80.0	72.5
Flexural strength (MPa)	85.9	86.6	85.7	70.1	74.9
Flexural modulus (MPa)	2563	2496	2826	1760	2460
Impact strength for the double-notched sample (kJ/m ²)					
Room temperature	6.80	15.4	13.3	78.0	22.1
−20°C	3.30	6.69	5.44	15.8	7.95
Vicat softening temperature (°C)	96.5	96.0	97.0	90.0	96.0

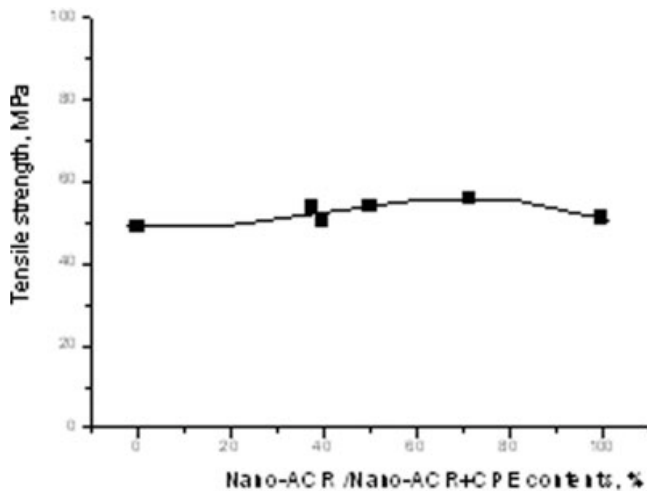


Figure 7 Variation of the tensile strength of the nanocomposites with nanoparticle loading.

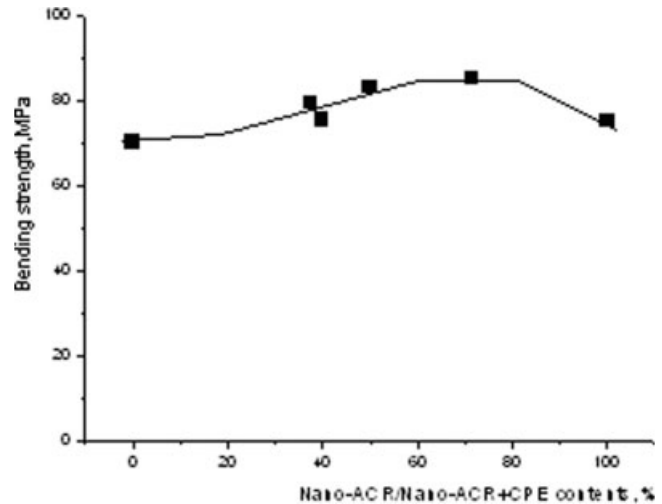


Figure 9 Variation of the bending strength of the nanocomposites with nanoparticle loading.

effects of the nanoparticles with CPE on RPVC (16.9 kJ/m^2) at -20°C was five times greater than that of pure RPVC (3.3 kJ/m^2) when the mass ratio of CPE (4 phr added) to the nanocomposite was 1 : 1; at the same time, the toughness of the former at a low temperature (16.9 kJ/m^2) was better than that of the system modified by single CPE (15.8 kJ/m^2 , 9 phr CPE added). Generally, RPVC modified only by CPE could obtain a brittle-ductile transition when the amount of CPE was up to 10–20 phr. When the content of CPE was lower, its toughness was very small, near to that of pure RPVC (6.8 kJ/m^2 at room temperature). So the toughness value (51.8 kJ/m^2 at room temperature) of RPVC modified by both 4 phr CPE and 4 phr nanoparticles was even higher than the sum of the value of about 3.3 kJ/m^2 (modified only by 4 phr CPE) and the value below 15.4 kJ/m^2 (modified only by 6 phr nanoparticles). At the same

time, surprisingly, the system of the nanocomposite with CPE also had better effects of reinforcement on RPVC, including in the modulus, strength, rigidity, and Vicat softening temperature, than that of the single-CPE system. This means that the network of the nanocomposite together with rubber achieved a synergistic effect, and the addition of this kind of nanoparticle in PVC blends led to a shift to an earlier brittle-ductile transition with a comparatively lower loading of nanoparticles or CPE.

Fracture mechanism

One can see from the previous results that the effects of the reinforcement and toughening of the nanoparticle rigid impact modifier with CPE on RPVC were better than that of the system modified by CPE or KM355P only, particularly at a low temperature. At

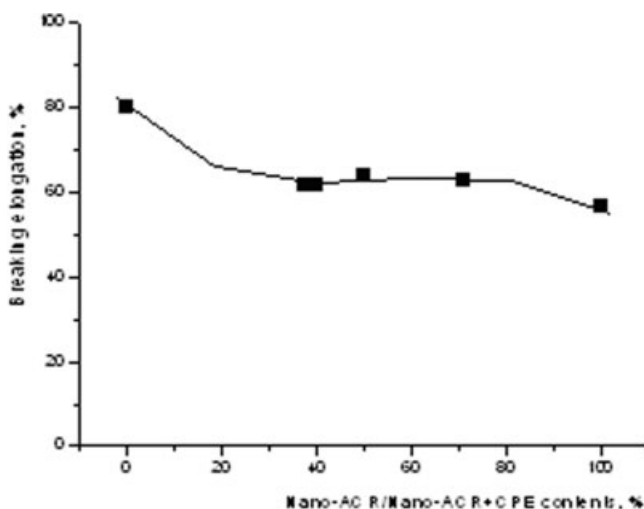


Figure 8 Variation of the elongation at break of the nanocomposites with nanoparticle loading.

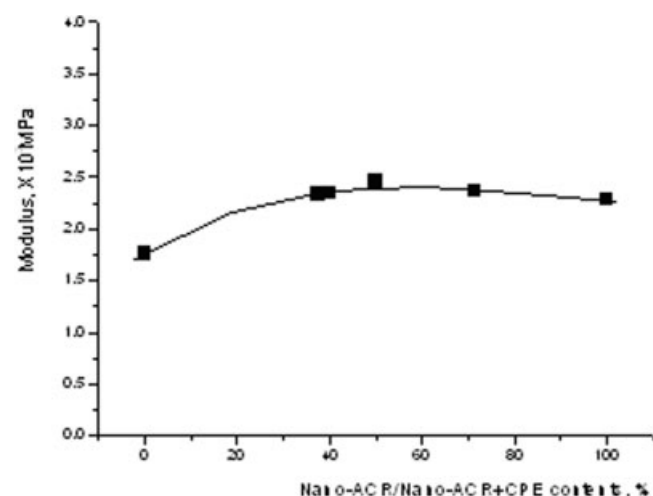


Figure 10 Variation of the modulus of the nanocomposites with nanoparticle loading.

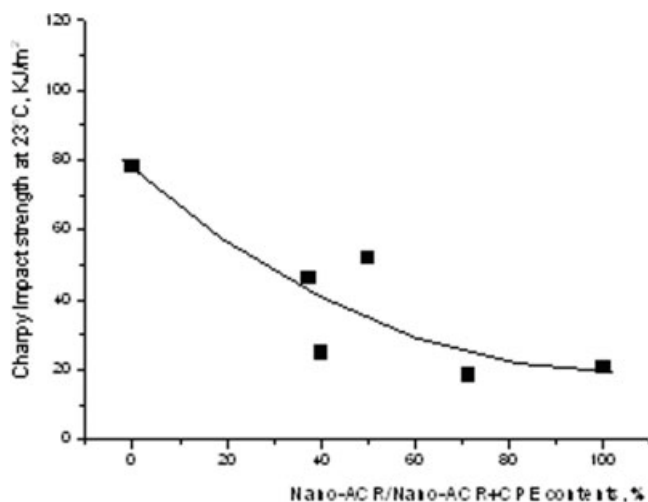


Figure 11 Variation of the Charpy notched impact strength of the nanocomposites at 23°C with nanoparticle loading.

the same time, this indicates that it was necessary for the matrix resin to have moderate toughness to obtain the point of brittle–ductile transition for the reinforcement and toughening system by the rigid modifier, which met the results put forward by former researchers.^{9,52} The toughness of the RPVC resin was improved by the rigid nanoparticles, and only when the rigid nanoparticles and CPE were used simultaneously was the point of brittle–ductile transition reached and the effect of toughening of rigid nanoparticle most remarkable.

The morphologies of the impact fracture surfaces at a low temperature (−20°C) were observed by SEM, as shown in Figure 13–17 with a magnification of 6000× and in Figure 18 with a magnification of

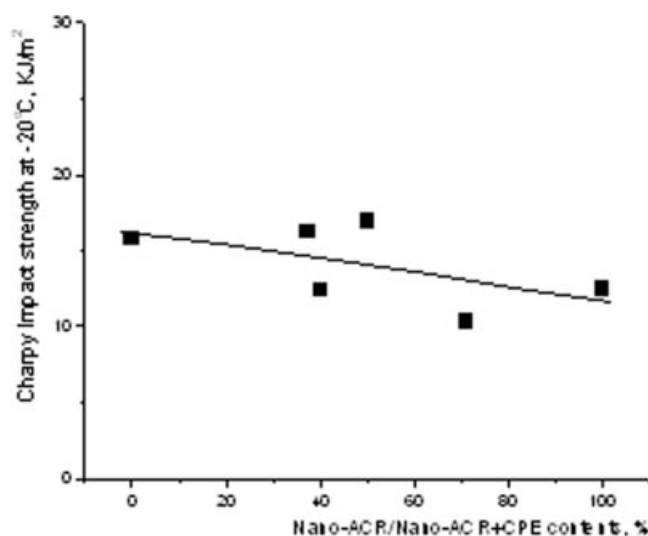


Figure 12 Variation of the Charpy notched impact strength of the nanocomposites at −20°C with nanoparticle loading.

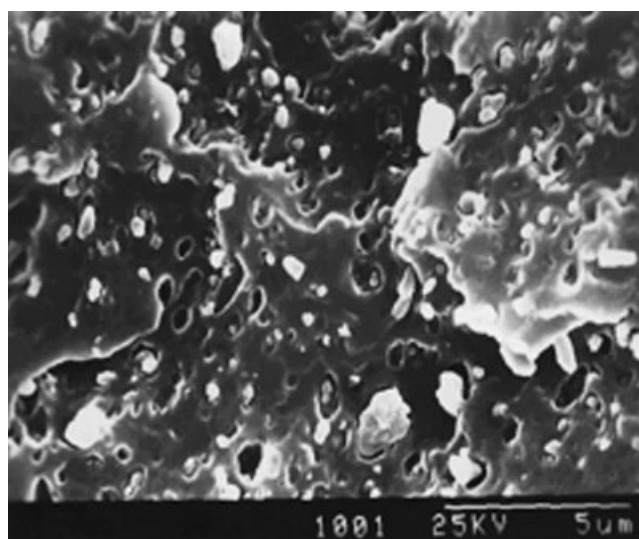


Figure 13 SEM photograph of the impact fractured pure RPVC.

600×. As shown in these figures, clearly, the impact strength of the blends was strongly dependent on the blend morphology. There were obviously different morphologies for the fracture surfaces between the system toughened by the elastomer as CPE and the system modified by the rigid modifier. Similar to the tensile behavior, the morphology of the pure RPVC was smooth and exhibited brittle failure, as shown in Figure 13. The morphology of the system toughened by CPE, as shown in Figure 14, had a sea-island structure; the interface was obscure, and cavitations of soft rubber particles in the polymer blends were seen. Stress whitening in rubber-toughened blends is attributed to rubber cavitation,⁵³

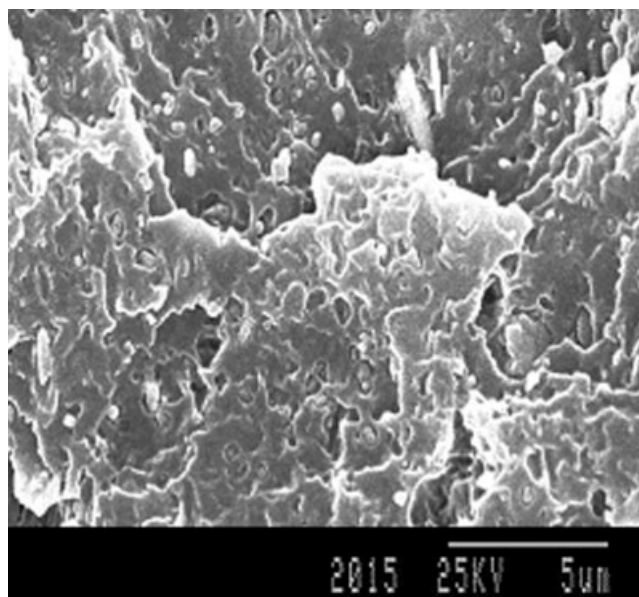


Figure 14 SEM photograph of RPVC modified by CPE.

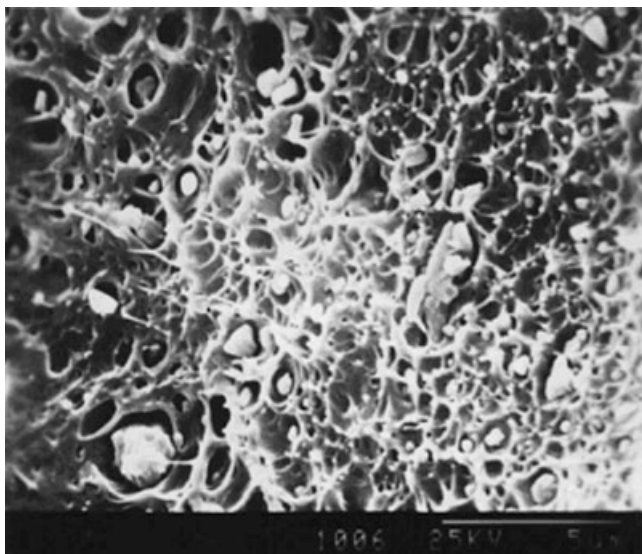


Figure 15 SEM photograph of RPVC modified by KM355P.

which indicates that this system should have had a higher impact strength. As shown in Figure 15, the system toughened by ACR was not entirely the same as the system of CPE, and its morphology of fracture surface seemed like a honeycomb. Figure 16 shows that the fracture surface of the system modified by nanoparticles was similar to that of ACR. Similarly, stress whitening was seen in both the PVC/ACR-modified system and the PVC/nanoparticle-modified system when stretched, which could be regarded as cold stretching, which should have had a certain impact strength. As shown in Figures 17 and 18, with different magnifications, we observed that a kind of large-fiber drawing and network morphologies occurred on the fracture surface

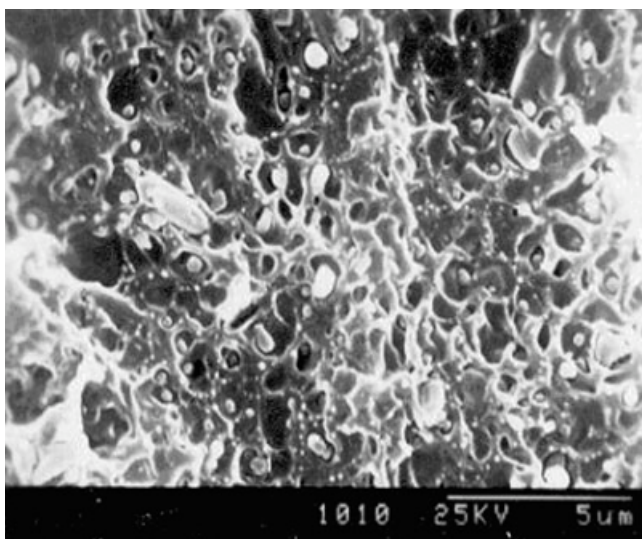


Figure 16 SEM photograph of RPVC modified by the nanoparticles.

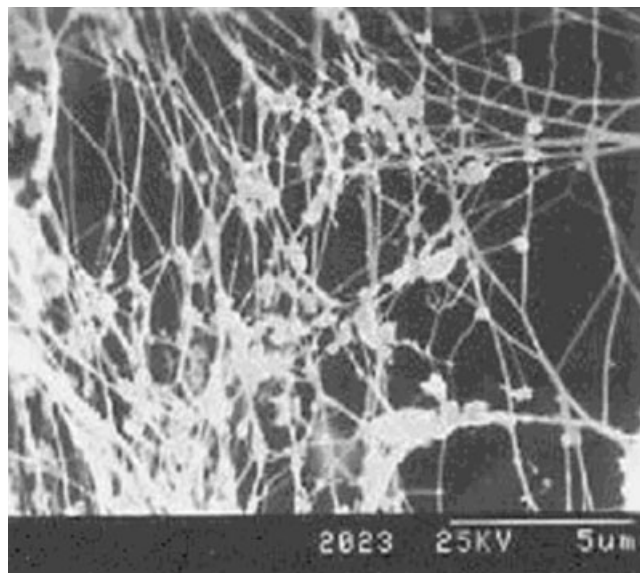


Figure 17 SEM photograph of RPVC modified by the nanoparticles with CPE (6000 \times).

of the matrix modified by nanoparticles together with CPE. Meanwhile, severe deformation and shearing yield existed on the PVC matrix; particularly, the adhesion between the core and shell was so strong that it was not destroyed during the blending process, and large-fiber drawing and a reticulate structure occurred around the particles. This indicated that there were triaxial stresses, which were locally elevated at the nanoparticles and acted as stress concentrations, and there was good interfacial bonding between the nanoparticles and PVC matrix because of the large interfacial area of nanoparticles and better compatibilization of the PMMA shell on the surface of nanoparticles with PVC arising from the similar polarity of these two materials and the entanglement of molecular chains between PMMA and PVC. As is known, better compatibilization can enhance the nanoparticles' dispersion in PVC matrix and promote a more homogeneous debonding/voiding and matrix drawing mechanism. Furthermore, the special structure of the ACR/CaCO₃ nanoparticles could also lead to a very higher impact strength. In general, it was difficult for nanoparticles to be uniformly distributed in the PVC matrix due to its hydrophilic properties. For this reason, a serious interfacial defect structures took place in the interface boundary between the matrix and inorganic particles, which led to lower mechanical properties. In this study, both the special treatment on nano-CaCO₃ carried out to deduce this kind of serious imperfection and the introduction of organic components on the surface of nanoparticles to improve compatibilization between inorganic particles and matrix were carried out. As is well known, the surface of nano-CaCO₃ contains an —OH group,

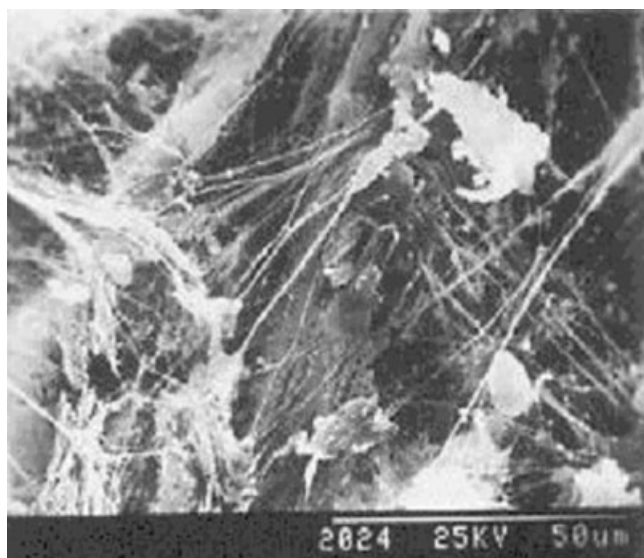


Figure 18 SEM photograph of RPVC modified by the nanoparticles with CPE (600 \times).

so the condensation between the —OH group on the surface of nanoparticles and the functional monomer with bifunctionality can occur, and this functional monomer acts as bridge group to join completely different materials such as nano-CaCO₃ and PBA to enhance the bonding force and deduce the imperfection. As mentioned before, the PBA layer had partly crosslinking structure through the crosslinking agent introduced and the IPN structure, which was a typical toughening structure, which existed in the encapsulated organic layer. These structures as stress concentrations were useful for absorbing more energy during stretching. The comparatively strong interaction between every different component of the nanoparticles made the nanoparticles as stress concentrations not subjected to deformation and even crack under external force, and as Figure 17 and 18 show, the nanoparticles may have acted as physical and chemical crosslinking points in the PVC matrix to enhance one or more properties of the plastic by blending. At the same time, the rigid shell inducing cold drawing and the elastic polymer (PBA) as a middle layer could absorb a very large amount of energy during stretching. It is this kind of large-fiber drawing morphology and reticular deformation that can absorb a large amount of energy to make this system have a very high impact strength.

CONCLUSIONS

In situ emulsion polymerization of acrylate monomers onto original nano-CaCO₃ particles was first carried out, and the novel nanoparticles, of which the core was nano-CaCO₃ particles and the shell was polyacry-

late, were synthesized. Subsequently, the effects of the reinforcement and toughening of these nanoparticles on RPVC were studied. The results indicate that these sort of nanoparticles could reinforce and toughen RPVC. However, the effect of nanoparticles on toughening was not better than that of CPE at a normal temperature. The reinforcement and toughening effect of the nanoparticles united with CPE on RPVC were better than those of only CPE or ACR, and the effect of toughening was remarkable at a low temperature (–20°C). The SEM photographs of the fracture surface showed that large-fiber-drawing structures were formed when the nanoparticles and CPE were used as comodifiers, and this structure achieved a real brittle-ductile transition.

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