

Effect of Surface Modifiers and Surface Modification Methods on Properties of Acrylonitrile–Butadiene–Styrene/Poly(methyl methacrylate)/Nano-Calcium Carbonate Composites

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ABSTRACT: Nano-calcium carbonate (nano-CaCO₃) was used in this article to fill acrylonitrile–butadiene–styrene (ABS)/poly(methyl methacrylate) (PMMA), which is often used in rapid heat cycle molding process (RHCM). To achieve better adhesion between nano-CaCO₃ and ABS/PMMA, nano-CaCO₃ particles were modified by using titanate coupling agent, aluminum–titanium compound coupling agent, and stearic acid. Dry and solution methods were both utilized in the surface modification process. ABS/PMMA/nano-CaCO₃ composites were prepared in a corotating twin screw extruder. Influence of surface modifiers and surface modification methods on mechanical and flow properties of composites was analyzed. The results showed that collaborative use of aluminum–titanium compound coupling agent and stearic acid for nano-CaCO₃ surface modification is optimal in ABS/PMMA/nano-CaCO₃ composites. Coupling agent can increase the melt flow index (MFI) and tensile yield strength of ABS/PMMA/nano-CaCO₃ composites. The Izod impact strength of composites increases with the addition of titanate coupling agent up to 1 wt %, thereafter the Izod impact strength shows a decrease. The interfacial adhesion between nano-CaCO₃ and ABS/PMMA is stronger by using solution method. But the dispersion uniformity of nano-CaCO₃ modified by solution method is worse. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Blending of polymers is an economic way to obtain improved comprehensive properties. In the past decades, blend systems based on acrylonitrile–butadiene–styrene (ABS) were widely studied.^{1–8} Recently, ABS/poly(methyl methacrylate) (PMMA) has attracted much attention owing to its good mechanical, optical, processing properties, and relatively low cost. In addition, ABS/PMMA is quite suitable for rapid heat cycle molding process (RHCM) process, which is raised in recent years. Products made in RHCM process can be put into practical use without painting. This process has a broad development prospect due to its environmental protection and low cost. However, little research has been carried out on ABS/PMMA blends.^{9–13} To enhance properties and/or lower costs of ABS/PMMA, incorporation of inorganic particles is a promising approach. Nano-

calcium carbonate (nano-CaCO₃) is one of important inorganic fillers for resins modification. Our team has done some work about ABS/PMMA/nano-CaCO₃ blends.¹⁴ But there are still many problems to be solved.

The adhesion between nano-CaCO₃ particles and ABS/PMMA is worse because nano-CaCO₃ particles are hydrophilic while polymer matrix (ABS/PMMA) is hydrophobic. Thus, the surface modification of nano-CaCO₃ particles becomes a hot topic in nano-CaCO₃ particles modified plastics. A lot of research about surface modification of CaCO₃ has been carried out in depth. Zhang et al.¹⁵ found the dispersion quality of CaCO₃ was improved and Izod impact strength was increased significantly by the addition of a nonionic modifier (polyoxyethylene nonylphenol). Maurizio et al.¹⁶ grafted poly(butylacrylate) chains onto CaCO₃ to modify CaCO₃ from hydrophilic to hydrophobic. Sun

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et al.¹⁷ used titanate coupling agent and sodium stearate as modifiers to treat CaCO₃ particles. Zhang and Pan¹⁸ also used coupling agent as modifier and studied the relationship between the interfacial stress and mechanical properties of high-density polyethylene. Most of the studies mentioned earlier focused on polypropylene/CaCO₃ composites. A little research about ABS/nano-CaCO₃ was conducted.^{19–23} Liang and coworkers^{19–21} studied the rheological and mechanical properties of ABS/CaCO₃ blends; the research results showed both of tensile strength and impact strength decreased with the increase of CaCO₃ content. Lam and coworkers²² studied the mechanical properties of ABS with nano-sized and micron-sized CaCO₃. The results revealed that nano-sized fillers were superior to micron-sized counterparts. But the influence of two types of fillers on mechanical properties of ABS was consistent. Chen and coworker²³ prepared nano-CaCO₃ composite particles and researched the effect of nano-CaCO₃ on mechanical properties of ABS. ABS/PMMA blend is similar to ABS. However, the morphology of ABS/PMMA blend is more complex than that of ABS. By now, there was little work on ABS/PMMA/nano-CaCO₃ blends.²⁴

Study on the influence of nano-CaCO₃ particles modification on properties of ABS/PMMA/nano-CaCO₃ system has a great significance. In this work, various modifiers and different modification methods were utilized for modification of nano-CaCO₃. The influence of modifiers and modification methods on various properties of ABS/PMMA/nano-CaCO₃ composites was explored in this article.

EXPERIMENTAL

Materials

ABS resin (0215A) and PMMA resin (CM207) were purchased from Jilin Petrochemical and Taiwan Chimei, respectively. Nano-CaCO₃ without any treatment and nano-CaCO₃ modified with stearic acid were obtained from Hangzhou Wanjing New Material. The mean diameters of the two kinds of nano-CaCO₃ particles are both approximately 100 nm. The isopropyl tri (dioctyl pyrophosphate acyl-oxy) titanate coupling agent (HW-201) and aluminum–titanium compound coupling agent (HW-133) were provided by Hangzhou Feidian Chemical. The stearic acid was provided by Tianjin Fuchen chemical reagent factory. The molecular structures of titanate coupling agent, aluminum–titanium compound coupling agent and stearic acid are shown in Figure 1. To describe simply, modified nano-CaCO₃ was denoted as CC–X, where X represents the surface modifier. Nano-CaCO₃ without any treatment is named as CC–N; nano-CaCO₃ modified with stearic acid is named as CC–SA.

Sample Preparation

Surface Modification for Nano-CaCO₃ Particles

Dry Method. CC–N particles were dried in an air circulating oven at 120°C for about 4 h. Titanate coupling agent was dissolved in ethanol (1/1, w/w). The diluent titanate coupling agent was divided into three parts. One part of coupling agent and CC–N particles were put into a type 6202 high-speed grinder (Beijing Xingshilihe Technology) for stirring. The other two parts of coupling agent were put into the grinder successively during the stirring. The total stirring time is ~ 30 min. Finally, the treated CaCO₃ particles were dried in an air circulating oven at 120°C for ~ 4 h to remove the ethanol. Nano-

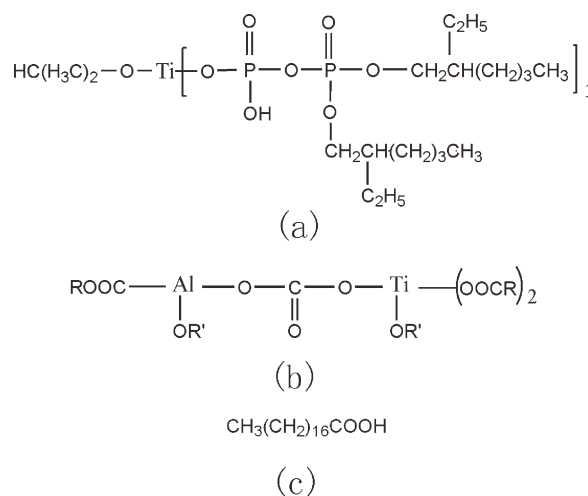


Figure 1. Molecular structures of (a) titanate coupling agent; (b) aluminum–titanium compound coupling agent; and (c) stearic acid.

CaCO₃ modified with titanate coupling agent by dry method is named as CC–TiD.

Aluminum–titanium compound coupling agent is waxy solid. To make the mixture more uniform, aluminum–titanium compound coupling agent was cut into small pieces. Then, the coupling agent was divided into three parts. One part of coupling agent and CC–N particles were put into a type 6202 high-speed grinder for stirring. The other two parts of coupling agent were put into the grinder successively during the stirring. The total stirring time is ~ 30 min. Nano-CaCO₃ modified with aluminum–titanium compound coupling agent is named as CC–AlTi.

Aluminum–titanium compound coupling agent was cut into small pieces and divided into three parts. One part of coupling agent and CC–N particles were put into a type 6202 high-speed grinder for stirring. The other two parts of coupling agent were put into the grinder successively during the stirring. After mixing for 25 min, stearic acid was added into the mixture. Materials in the grinder continued mixing for another 5 min. Here, nano-CaCO₃ modified with aluminum–titanium compound coupling agent and stearic acid is designated as CC–AlTiSA.

Solution Method. In order to investigate the effect of surface modification method on properties of composites, solution method was also used for the surface modification of nano-CaCO₃. Titanate coupling agent was chosen as modifier here. Titanate coupling agent was dissolved in isopropyl alcohol to form a solution. The solution was kept in an ultrasonic bath for ~ 5 min. Then CC–N particles were put into the solution. The slurry of nano-CaCO₃ continued to be kept in an ultrasonic bath for another 30 min. Finally, the isopropyl alcohol was removed by distillation. The treated nano-CaCO₃ was dried in an air circulating oven at 120°C for ~ 4 h and milled in a mortar to obtain the final product. This kind of nano-CaCO₃ is named as CC–TiS.

Preparation of ABS/PMMA/Nano-CaCO₃ Composites. All of the materials were pre-dried in an air circulating oven at 80°C for 12 h to remove all the moisture. ABS, PMMA, and nano-

Table I. The Compositions of ABS/PMMA/Nano-CaCO₃ Composites

Number	ABS/PMMA (wt %)	Nano-CaCO ₃ code	Content of coupling agent (with respect to nano-CaCO ₃ , wt %)	Content of nano-CaCO ₃ (wt %)
1	80/20	-	-	-
2	80/20	CC-N	-	2
3	80/20	CC-N	-	4
4	80/20	CC-N	-	6
5	80/20	CC-SA	-	2
6	80/20	CC-SA	-	4
7	80/20	CC-SA	-	6
8	80/20	CC-TiD	1	2
9	80/20	CC-TiD	1	4
10	80/20	CC-TiD	1	6
11	80/20	CC-AltI	1	2
12	80/20	CC-AltI	1	4
13	80/20	CC-AltI	1	6
14	80/20	CC-AltISA	1/0.5	2
15	80/20	CC-AltISA	1/0.5	4
16	80/20	CC-AltISA	1/0.5	6
17	80/20	CC-TiS	0.5	4
18	80/20	CC-TiS	1	4
19	80/20	CC-TiS	2	4
20	80/20	CC-TiD	0.5	4
21	80/20	CC-TiD	2	4

CaCO₃ were put into a co-rotating twin screw extruder with a screw diameter of 21 mm and length to diameter ratio of 36 for blending. Temperature profile of 205°C–225°C–235°C–220°C–180°C was set from the hopper to the die. The feed rate was kept at 3.6 kg/hr and the screw speed was set at 120 rpm. The extruded pellets were put into the extruder for the second blending to improve the uniformity of the blends. Then, the pellets were dried once again in an air circulating oven at 80°C for 12 h. The test samples as per ASTM standard specifications^{25,26} were molded on a 68 tons injection molding machine. In the injection molding process, the mold temperature was ~ 45°C, the injection pressure was 6 MPa and the package pressure was 5.5 MPa. The mass ratio of ABS to PMMA is fixed at 80/20. The compositions of ABS/PMMA/nano-CaCO₃ are listed in Table I. For CC-AltISA particles, the first value of coupling agent content refers to the content of aluminum–titanium compound coupling agent, and the second value is the content of stearic acid.

Characterization

Mechanical properties such as tensile yield strength and Izod impact strength were measured. Tensile tests were carried out on a CMT 4204 20KN Electrical Testing Machine (maximum load: 20KN) at room temperature according to ASTM-D-638.²⁵ The crosshead speed was kept at 5 mm/min. The dimensions of all the specimens made for Izod impact strength test were

63.5 mm × 12.7 mm × 6.35 mm with a V-shape notch according to ASTM-D-256.²⁶ The tests were carried out on a XC-5.5D impact tester at room temperature. The melt flow behavior of the blends was characterized by melt flow index (MFI). The MFI testing was carried out in a XNR-400 MFI tester at 230°C and 3.8 kg.

The injection specimens were frozen in liquid nitrogen for ~ 2 h and then quickly fractured. The cryofractured surfaces of injection specimens were observed by a Hitachi SU-70 FESEM to evaluate the dispersion state of nano-CaCO₃ particles in ABS/PMMA matrix. Polymer specimens were coated with gold in an automatic sputter coater (E-1010 ion sputter) before the FESEM observations. The FESEM micrographs were analyzed by using Image Software Scion.

RESULTS AND DISCUSSION

Effect of Coupling Agent Types

Dispersion Quality. The FESEM micrographs of cryofractured surfaces of various ABS/PMMA/nano-CaCO₃ composites are presented in Figure 2. The contents of nano-CaCO₃ are all fixed at 4 wt %. And the contents of surface modifiers with respect to nano-CaCO₃ are all fixed at 1 wt %. Figure 3 illustrates the diameter distribution of nano-CaCO₃ in various composites. From the histogram, it can be found that there are more than 8% nano-CaCO₃ particles with diameters over 300 nm in CC-N composites. And only 26% nano-CaCO₃ particles with diameters less than 200 nm can be found in CC-N composites. The diameters of various nano-CaCO₃ particles are shown in Table II. It is clearly noticed that the mean diameter of CC-N particles is largest among the six types of particles. These entire phenomena indicate that the agglomeration of CC-N particles is serious and the dispersion quality of CC-N particles is worst among the six kinds of nanoparticles. The frequency of nano-CaCO₃ particles with diameters of 100–200 nm gradually increases from Figure 3(a–e). It is implied that more and more nano-CaCO₃ particles are broken into smaller particles from Figure 3(a–e). The mean diameter of nano-CaCO₃ particles becomes smaller and smaller from Figure 3(a–e) as shown in Table II. The mean diameter of CC-AltISA particles is smallest in the five kinds of particles. This means the dispersion quality of CC-AltISA particles is best. In addition, collaborative use of stearic acid and aluminum–titanium compound coupling agent for nano-CaCO₃ is slightly better than aluminum–titanium compound coupling agent alone. And the coupling effect of titanate coupling agent is worse than that of aluminum–titanium compound coupling agent. As the modifier for the surface modification of nano-CaCO₃, both titanate coupling agent and aluminum–titanium compound coupling agent are better than stearic acid.

Although both CC-TiD and CC-TiS particles are treated by titanate coupling agent, the modification method is different. The dispersion quality of CC-TiD and CC-TiS particles are illustrated in Figure 3(c,f). From the FESEM micrographs, it can be seen that the dispersion quality of CC-TiD particles is better than that of CC-TiS particles. The mean diameter of CC-TiD particles is smaller than that of CC-TiS particles as shown in Table II. This is mainly because some CC-TiS particles bond

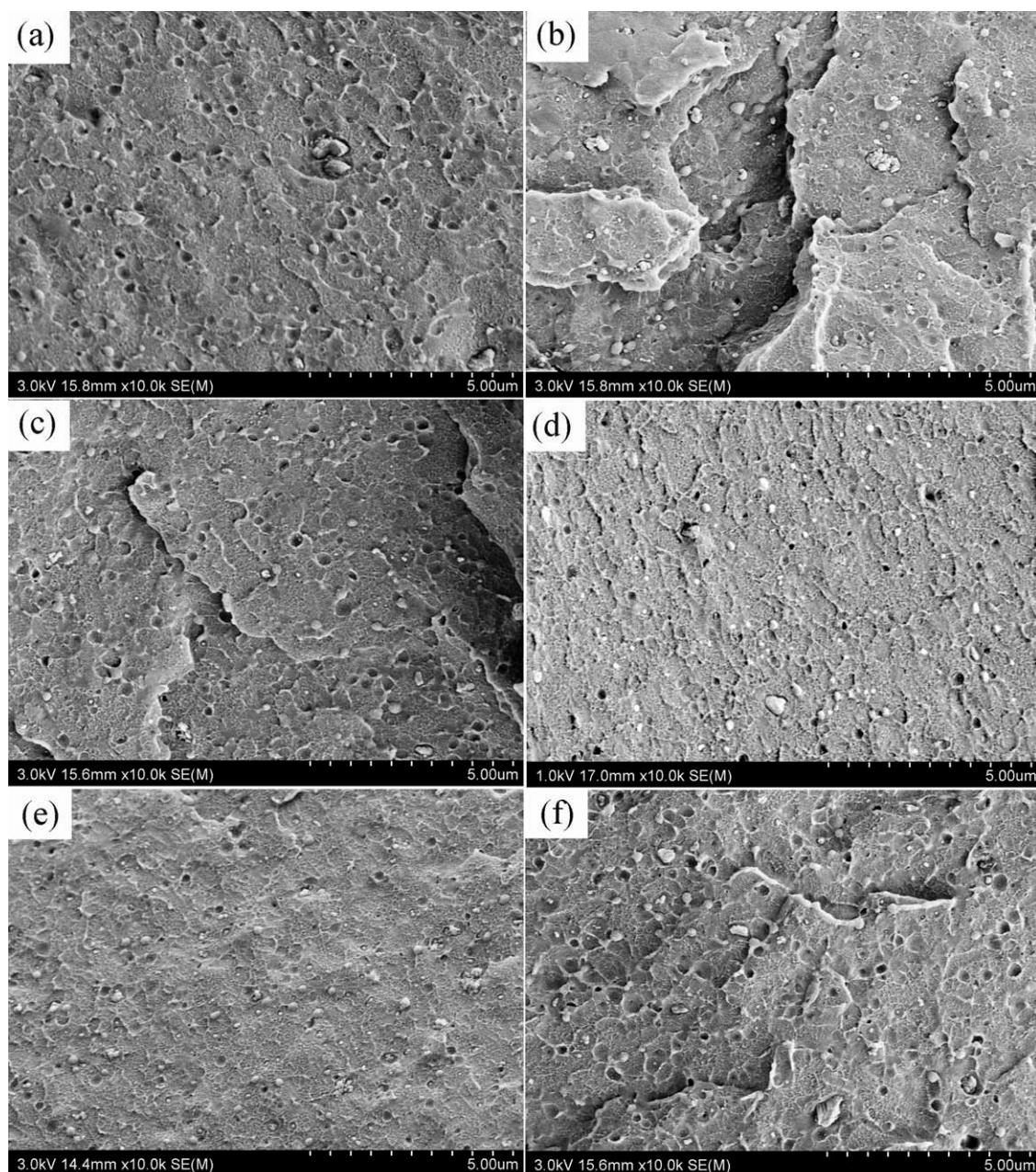


Figure 2. FESEM micrographs of cryofractured surfaces of various composites. (a) CC-N composites; (b) CC-SA composites; (c) CC-TiD composites; (d) CC-ALTi composites; (e) CC-ALTiSA composites; and (f) CC-TiS composites.

together in solution method. And the treated CC-TiS particles were not milled to nanoscale. Therefore, CC-TiS particles can not disperse well in polymer matrix.

Mechanical Properties. Figure 4 shows the effect of nano- CaCO_3 content on the tensile yield strength of composites. When an external force is imposed on the composites, nano- CaCO_3 particles are apt to debond from polymer matrix. The debonding of smaller particles becomes more difficult than larger particles in particulate-filled polymers.²⁷ This means smaller particles can absorb more energy than larger particles can before the fracture of composites. Therefore, less energy is

absorbed by composites when the size of particle is larger. Namely, the larger the nano- CaCO_3 particle is the smaller the tensile yield strength of ABS/PMMA/nano- CaCO_3 composites is. The tensile yield strength of CC-N composites is lowest among the five kinds of composites because the mean diameter of CC-N particles is largest as discussed in the previous paragraph. All of the modifiers used in this study can improve the interfacial adhesion and thus increase the tensile yield strength of ABS/PMMA/nano- CaCO_3 composites.

Coupling agent can prevent the agglomeration of inorganic particles and build a bridge between inorganic particles and

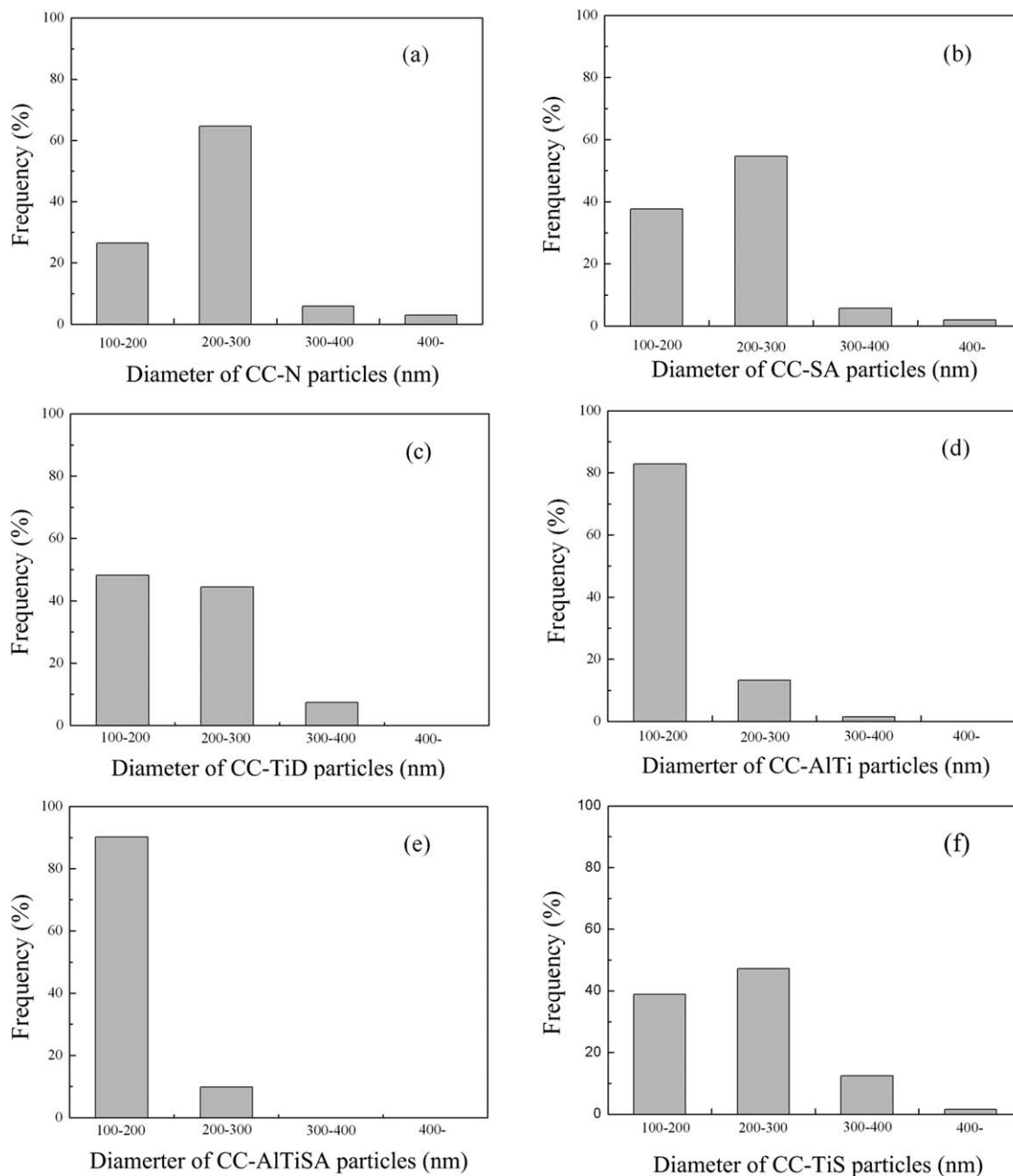


Figure 3. Diameter distribution of nano-CaCO₃ in various composites.

Table II. The Nano-CaCO₃ Particles Sizes in Composites

Nanoparticles	Mean diameter (nm)	Largest diameter (nm)
CC-N	243.8	596
CC-SA	234.5	616
CC-TiD	183.9	334
CC-AlTi	162.3	448
CC-AlTiSA	155.3	283
CC-TiS	231.9	589

polymer matrix. So, coupling agent can improve the tensile yield strength of composites. At the same time, it also has a plasticizing effect and can decrease the tensile yield strength of ABS/PMMA/nano-CaCO₃ composites. However, stearic acid as a fatty acid has no plasticizing effect on ABS/PMMA/nano-CaCO₃ composites. Thereby, tensile yield strength of CC-SA composites is higher than that of CC-AlTi and CC-TiD composites considering these two factors. However, CC-AlTiSA composites combine the advantage of aluminum-titanium compound coupling agent and stearic acid. So, the tensile yield strength of CC-AlTiSA composites is highest here. When nano-CaCO₃ content is 6 wt %, the tensile yield strength of CC-

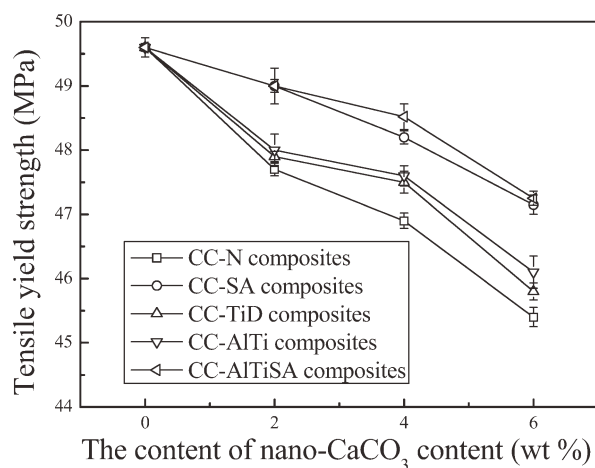


Figure 4. The effect of nano-CaCO₃ content on the tensile yield strength of composites.

ALTiSA composites is higher than CC-N composites by 4%. However, the tensile yield strength of all the five kinds of composites decreases by adding nano-CaCO₃.

Izod impact strength is one of the most important parameters to evaluate the toughness of composites. From Figure 5, it can be seen that Izod impact strength decreases with the increase of nano-CaCO₃ content for the five kinds of composites. Dispersion quality of inorganic particles plays a crucial role in toughening efficiency.¹⁵ All of the modifiers used can decrease the surface energy of inorganic particles and then prevent the agglomeration of nano-CaCO₃ particles. The dispersion quality has been discussed in earlier section. It can be found that the Izod impact strength of CC-ALTiSA composites is highest as the dispersion uniformity of CC-ALTiSA particles is best. And the Izod impact strength of CC-N composites is lowest as the dispersion uniformity of CC-N particles is worst. The dispersion quality of nano-CaCO₃ particles influences the Izod impact strength of ABS/PMMA/nano-CaCO₃ composites greatly. The Izod impact strength is closely related to the dispersion quality of nano-CaCO₃.

Interfacial Adhesion. Interfacial adhesion between fillers and polymer matrix is one of the most important factors which influence the properties of polymer composites, especially the tensile yield strength. The interfacial layer can not transfer stress in case of weak interaction between filler and polymer matrix.²⁸

The load is endured only by the polymer matrix if the adhesion between filler particles and polymer matrix is zero. The effective load-bearing cross-section can be expressed as $(1 - \varphi)/(1 + 2.5\varphi)$, where φ is the filler volume fraction. So, the tensile yield strength of the composites can be described as²⁹:

$$\sigma_{yc} = \frac{1 - \varphi}{1 + 2.5\varphi} \sigma_{yp} \exp(B\varphi) \quad (1)$$

where σ_{yc} is the tensile yield strength of the composites, σ_{yp} the tensile yield strength of polymer matrix, and B a constant char-

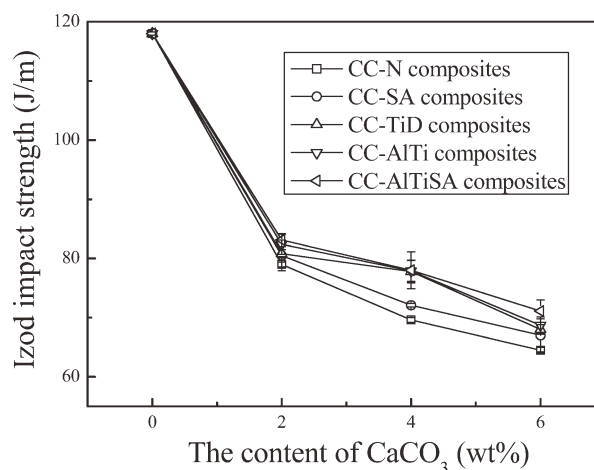


Figure 5. The effect of nano-CaCO₃ content on the Izod impact strength of composites.

acterizing the interfacial interaction between fillers and polymer matrix. Equation (1) can be rewritten as:

$$\ln\left(\frac{\sigma_{yc}(1 + 2.5\varphi)}{1 - \varphi}\right) - \ln \sigma_{yp} = B\varphi \quad (2)$$

To explore the effect of different surface modifiers on the surface adhesion between nano-CaCO₃ particles and polymer matrix, $\left\{ \ln\left(\frac{\sigma_{yc}(1 + 2.5\varphi)}{1 - \varphi}\right) - \ln \sigma_{yp} \right\}$ was plotted against φ . And the slope of the line gives the parameter B , which is illustrated in Table III. The larger the B is, the stronger the interfacial adhesion is. It can be found that the interfacial adhesion between CC-ALTiSA particles and polymer matrix is strongest, and the interfacial adhesion between CC-N particles and polymer matrix is weakest.

Furthermore, Liang proposed a concept of debonding angle.^{28,30} The relationship between tensile yield strength of composites and debonding angle can be described by the following equation:

$$\sigma_{yc} = \sigma_{yp}(1 - 1.21\sin^2\theta\varphi^{2/3}) \quad (3)$$

where σ_{yc} is the tensile yield strength of composites, σ_{yp} the tensile yield strength of polymer matrix, θ the debonding angle, and φ the filler volume fraction. θ represents the interfacial interaction between fillers and polymer matrix. θ should be zero when the interfacial adhesion is very good and 90° when there is no interfacial adhesion.¹⁷ The smaller

Table III. The Value B and Debonding Angle θ of Composites Filled with Various Nano-CaCO₃

Composites	B	θ (degrees)
CC-N composites	0.33	69.8
CC-SA composites	1.35	57.6
CC-TiD composites	0.37	63.2
CC-ALTi composites	0.61	58.1
CC-ALTiSA composites	1.51	54.7

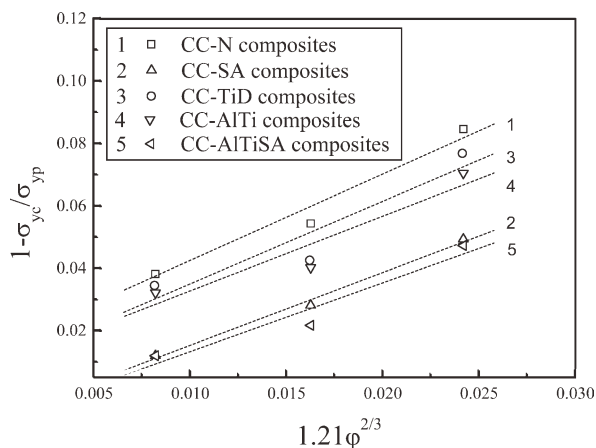


Figure 6. Plots of $(1 - \sigma_{yc}/\sigma_{yp})$ against $1.21\phi^{2/3}$.

the θ is, the stronger the interfacial adhesion is. $(1 - \sigma_{yc}/\sigma_{yp})$ was plotted against with $1.21\phi^{2/3}$ as shown in Figure 6. The slope of the line gives $\sin^2\theta$. And the slope of line is obtained by using least square method. The calculated θ of different composites is shown in Table III. It can also be found that the interfacial adhesion between CC-AltISA particles and polymer matrix is strongest, and the interfacial adhesion between CC-N particles and polymer matrix is weakest.

Effect of Coupling Agent Content

Melt Flow Behavior. In this section, titanate coupling agent was chosen as modifier for surface modification of nano- CaCO_3 . The effect of surface modification methods on properties of composites was analyzed. Nano- CaCO_3 particles were treated using titanate coupling agent by dry and solution method respectively. Figure 7 illustrates the effect of titanate coupling agent on MFI of nano- CaCO_3 (4 wt %) filled ABS/PMMA composites. It can be found that the MFI increases with the increase of coupling agent content for the two kinds of composites. Higher MFI indicates better molecular motion between polymer chains. The plasticizing action induced by titanate coupling agent might be the reason for this phenomenon. Plasticizing action can make the sliding of the molecular chain segments much easier. Therefore, the MFI is increased by adding titanate coupling agent. In addition, it can also be demonstrated that the MFI of CC-TiS composites is higher than that of CC-TiD composites. This is because in solution method, titanate coupling agent can form a uniform interfacial layer and improve the MFI of composites more effectively.

Mechanical Properties. Figure 8 shows the effect of coupling agent content on the tensile yield strength of nano- CaCO_3 (4 wt %) filled ABS/PMMA composites. The tensile yield strength increases with the increase of coupling agent content for the two kinds of composites. The coupling agent which is a bridge between the inorganic particles and resin matrix can enhance the interfacial adhesion. Thereby, the interfacial layer can transfer stress more sufficiently. So, the tensile yield strength increases with the increase of coupling agent content.

Figure 8 also reveals that the tensile yield strength of CC-TiS composites is slightly higher than that of CC-TiD composites

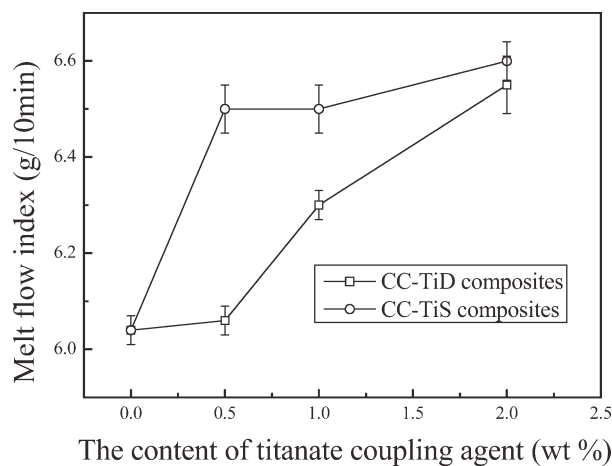


Figure 7. The effect of titanate coupling agent content (with respect to nano- CaCO_3) on MFI of nano- CaCO_3 (4 wt %) filled ABS/PMMA.

when the content of nano- CaCO_3 is less than 2 wt %. This is presumably because the coupling agent can react more sufficiently with hydroxyl groups on the surface of nano- CaCO_3 in solution method than in dry method. So, the interfacial adhesion of CC-TiS composites is stronger than that of CC-TiD composites. Interfacial adhesion has obvious influence on tensile yield strength.¹⁹ Thus, CC-TiS composites' tensile yield strength is higher than CC-TiD composites when the content of nano- CaCO_3 is less than 2 wt %. However, when the content of nano- CaCO_3 is 2 wt %, the content of coupling agent is large enough to react with hydroxyl groups on the surface of nano- CaCO_3 sufficiently. So, coupling agent can react sufficiently with nano- CaCO_3 both in dry and solution method. Thus, the tensile yield strengths of CC-TiS and CC-TiD composites are almost the same when the content of nano- CaCO_3 is 2 wt %.

Figure 9 depicts that the influence of titanate coupling agent on the Izod impact strength of nano- CaCO_3 (4 wt %) filled ABS/PMMA composites. The Izod impact strength of both CC-TiD

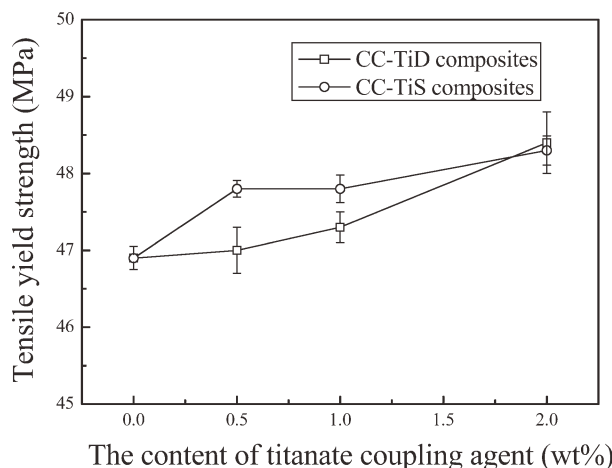


Figure 8. The effect of titanate coupling agent content (with respect to nano- CaCO_3) on the tensile yield strength of nano- CaCO_3 (4 wt %) filled ABS/PMMA.

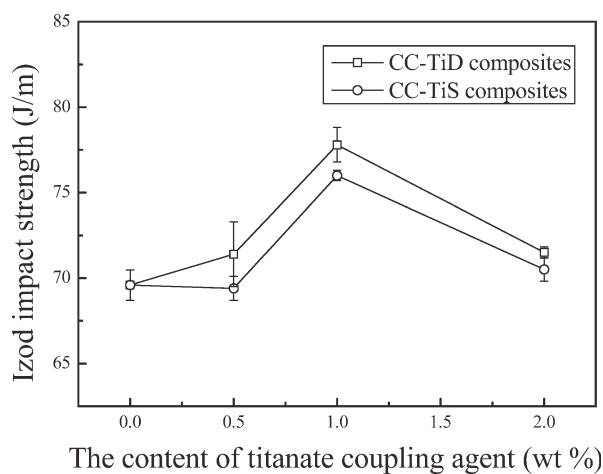


Figure 9. The effect of titanate coupling agent content (with respect to nano- CaCO_3) on the Izod impact strength of nano- CaCO_3 (4 wt %) filled ABS/PMMA.

and CC-TiS composites increases with the addition of titanate coupling agent up to 1 wt %, thereafter the Izod impact strength begins to decrease with increasing titanate coupling agent. The optimal content of titanate coupling agent content is 1 wt %. The coupling agent can change the inorganic particles from hydrophilic to hydrophobic and improve the dispersion uniformity of nano- CaCO_3 particles. The dispersion quality of inorganic particles plays a crucial role in toughening efficiency. So, the Izod impact strength increases first with the increase of coupling agent content. However, multilayer of coupling agent is formed on the surface of inorganic particles as the content of coupling agent continues to increase.³¹ And this phenomenon can increase agglomeration. So, the dispersion uniformity will be decreased. Thus, the Izod impact strength begins to decrease with excess content of coupling agent.

Besides, the Izod impact strength of CC-TiD composites is higher than that of CC-TiS composites. As discussed in "Dispersion quality" section, the diameters of CC-TiD particles are smaller than that of CC-TiS particles after surface modification. This means the dispersion quality of CC-TiD particles is better than that of CC-TiS particles. Dispersion quality of nano- CaCO_3 particles played a crucial role in toughening efficiency.¹⁵ Thus, the Izod impact strength of CC-TiD composites is higher than that of CC-TiS composites.

CONCLUSION

Titanate coupling agent, aluminum-titanium compound coupling agent and stearic acid can improve the interfacial adhesion between nano- CaCO_3 particles and ABS/PMMA matrix. And they can improve the dispersion quality of nano- CaCO_3 particles in ABS/PMMA matrix. However, coupling agent also has a plasticizing action. Considering the mechanical properties of ABS/PMMA/nano- CaCO_3 composites, collaborative use of aluminum-titanium compound coupling agent and stearic acid is best for surface modification of nano- CaCO_3 particles. And CC-AlTiSA composites are found to give the best combination of properties in this study.

Titanate coupling agent can increase the MFI and tensile yield strength of ABS/PMMA/nano- CaCO_3 composites. The Izod impact strength of composites increases first and then decreases as the titanate coupling agent increases. The optimal content of titanate coupling agent content for nano- CaCO_3 surface modification is 1 wt %. The MFI and tensile yield strength of ABS/PMMA/nano- CaCO_3 composites is much higher when nano- CaCO_3 is treated using solution method. However, solution method is worse than dry method considering Izod impact strength of ABS/PMMA/nano- CaCO_3 .

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