

A Study on the Interfacial Adhesion Strength of Different Types of Calcium Carbonate Filled Poly(vinyl chloride) Composites

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Keywords: Calcium Carbonate, Polyvinyl-chloride, Composite, Mechanical Properties, Adhesion Strength

Abstract. The Polyvinyl-chloride (PVC) composites filled with micro-Calcium Carbonate (CaCO_3), submicro- CaCO_3 , nano- CaCO_3 and nano-coating micron CaCO_3 powder were prepared by the method of melt blending process. The tensile properties of the PVC/ CaCO_3 composites were tested at the room temperature. The interfacial adhesion strength between the CaCO_3 particle and the PVC matrix was measured. The results showed that the tensile properties of the PVC/ CaCO_3 composites were better than those of the pure PVC in the most conditions; the mechanical properties of the surface treated CaCO_3 filled PVC composites were better than the ones of the non-surface treated CaCO_3 filled PVC composites. The mechanical properties of the PVC composites filled with nano-coating micron heavy CaCO_3 were better than the ones of the he PVC composites filled with heavy CaCO_3 ; among the four types of CaCO_3 , the mechanical properties of the PVC composites filled common light CaCO_3 and ultra-fine light CaCO_3 were relatively better; as the interfacial interaction strength, the strength between the ultra-fine light CaCO_3 and the PVC matrix was maximum, the one between the common light CaCO_3 and the PVC matrix was minimum, the strength between the nano-coating micron heavy CaCO_3 and the matrix was bigger than that between the micron heavy CaCO_3 and the matrix, the strength between the CaCO_3 after being treated and the matrix was increased.

Introduction

Polyvinyl chloride (PVC) is one of the earliest industrialized production of the plastic varieties, which is widely used in automobiles, home appliances, medical, aviation industry because of excellent mechanical property, corrosion resistance, flame retardant properties, cheap price, and abundant sources of raw materials[1][2]. Its production is less than that of the polyethylene (PE) only, and is the second general plastics in the world. While, the hardness and the impact strength of PVC is not good, it is sensitive to notch, its toughness is low, and the tensile properties cannot meet product requirements. So, its application is limited.

Calcium Carbonate (CaCO_3) is one of the inorganic fillers widely used in the processing of PVC composites. It can not only reduce the amount of resin and the cost, but also can improve the strength, toughness [3] [4], hardness, elastic modulus [5], size stability of the products, etc. While, the bad interfacial compatibility between the CaCO_3 particle and PVC matrix may results that the tensile strength, impact strength and compressive strength of the PVC/ CaCO_3 composites decreases[6] and the processing performance becomes worse. Therefore, the CaCO_3 surface modification to improve the interfacial adhesion between the particle and the matrix was payed attention widely in recent years[7]. Generally speaking, the interfacial adhesion strength between the modified CaCO_3 powder and PVC matrix is much larger than that of the non-modified CaCO_3 powder and PVC matrix, and the mechanical properties of composite materials is improved; the interfacial adhesion strength between the micro CaCO_3 powder and PVC matrix is lower, the mechanical properties of the composite materials is also not well, the interfacial adhesion strength between the sub-micro CaCO_3 powder and PVC matrix is improved slightly, and the mechanical properties of the composite material is also improved slightly, the interfacial adhesion strength between the nano-meter CaCO_3 powder and PVC matrix is the best due to the tunnel effect and

surface effect of nano-meter powder, so mechanical properties of the composite material is the best one. But, the nano-meter CaCO_3 particles can't easily dispersed uniformly in the PVC matrix during the processing of the composite materials, because the nano-meter CaCO_3 particles are easily aggregative. That results two negative hands. On one hand, the filling amount of nano-meter CaCO_3 powder in PVC is limited, so the production cost cannot be reduced effectively. On the other hand, even if the filler content is low, the local agglomeration cannot be avoided, so, the mechanical properties of the composites cannot be improved ideally. To solve the problems, the researchers tried to mix nano-meter CaCO_3 with the micro CaCO_3 powder and filled them into the PVC matrix to disperse the nano-meter CaCO_3 particle. But, the results were not idea. In recent years, some references reported a new kind product called the micro and nano-meter CaCO_3 composite particle was prepared by generating nano-meter CaCO_3 particles on the surface of the micro CaCO_3 by chemical reaction, and payed attention widely.

The objectives in this study are to prepare PVC composites filled with four kind of CaCO_3 powder and measure the their tensile properties, including tensile strength, elongation at break, tensile elastic modulus, at the room temperature, to investigate effects of the different kinds of the CaCO_3 powder on the tensile properties of the PVC/ CaCO_3 composites. What is more, the interfacial adhesion strength between the CaCO_3 particle and the PVC matrix will be calculated and analyzed.

Experiment

Raw Materials. The common light calcium carbonate(P- CaCO_3) was prepared by the Powder Engineering Labatory of Tsinghua University. Heavy calcium carbonate (G- CaCO_3), with particle size 5000 mesh, was prepared by the Powder Engineering Labatory of Tsinghua University, whose mineral was supplied by Jiangxi Xinyu Henghui Mineral Co. Ltd... Micro and nano-meter CaCO_3 composite particle (MG- CaCO_3), with particle size 5000 mesh, was prepared by the Powder Engineering Labatory of Tsinghua University. Superfine ground calcium carbonate (N- CaCO_3), with the settling volume 2.71g/ml, was prepared by the Powder Engineering Labatory of Tsinghua University. γ -Aminopropyl triethoxysilane, with trademark KH550, was supplied by Nanjing Jingwei Chemical Industry Co. Ltd.; PVC, with trademark SG-5 and k value 70, was supplied by Shanghai Chlor-alkali Chemical Industry Co. Ltd.

Apparatus. Electronic balance, with trademark SL-N, was produced by Shanghai Minqiao Precision Scientific Instruments Co. Ltd.; High speed mixing machine, with trademark SHR-10A, was manufactured by Zhangjiagang City Yatong Machinery Co. Ltd...Co-rotating twin screw extruder, with trademark TSE-35A, was manufactured by Nanjing Ruiya Polymer Equipment Co., Ltd...Vacuum oven, with trademark ZK0258, was produced by Shanghai Experiment Instrument Factory Co. Ltd... Numerical control full-automatic injection molding machine, with trademark CJ80NC, was manufactured by Zhendei Plastics Machinery Co. Ltd... Desk universal material testing machines, with trademark 5566, was manufactured by the Instron Co. Ltd...

Preparation. The four different kinds of CaCO_3 powder were first blended with PVC in a high-speed mixer. The filler volume fractions of P- CaCO_3 , G- CaCO_3 , and MG- CaCO_3 were 50% respectively, and that of the N- CaCO_3 was 5%. Then, the PP/ CaCO_3 blends were extruded in the molten state of the resin by means of the co-rotating twin-screw extruder under temperatures from 170 to 185°C; the screw rotation was 30 rpm, and the screw length-to-diameter ratio was 40/35.6; the die temperature is 180°C. The feeding of the raw materials was done in the forced mode, and the feeding rate was the screw rotation of 25 rpm. Then, the extrudate was granulated to produce the PVC/ CaCO_3 composites. These granular composites were dried for 5 h at 90°C in Vacuum oven. Finally, the specimens for tensile testing were molded with a plastics injection machine under temperatures ranging from 190 to 205°C, with the injection pressure varied from 6 to 8MPa, a holding time of 14s, and a cooling time of 26s.

Tensile Property Measurements. The tensile properties of the PP/ CaCO_3 composites were measured at room temperature by means of the desk universal materials testing machine. The tests were conducted according to ASTM D 638-91, and the cross-head speed was 50 mm/min.

Results and Discussion

The Tensile Properties of PVC/CaCO₃ Composite. The tensile properties are the basic properties of the plastic and important characteristics for the utilization of materials. The tensile properties of the PVC/CaCO₃ composites are shown in Table 1, 2, 3, and 4.

Table 1 the tensile properties of the PVC/P-CaCO₃ composites

Materials	Tensile property	σ / MPa	δ / %	E / MPa
Pure PVC		37.07	3.98	2568.94
PVC/CaCO ₃ composite filled with modified P-CaCO ₃		36.49	3.38	1659.97
PVC/CaCO ₃ composite filled with non-modified P-CaCO ₃		39.69	4.45	3536.27

Table 2 the tensile properties of the PVC/G-CaCO₃ composites

Materials	Tensile property	σ / MPa	δ / %	E/ MPa
Pure PVC		37.07	3.98	2568.94
PVC/CaCO ₃ composite filled with modified G-CaCO ₃		39.23	2.53	2882.11
PVC/CaCO ₃ composite filled with non-modified G-CaCO ₃		39.71	5.18	3494.77

Table 3 the tensile property of the PVC/NG-CaCO₃ composites

Materials	Tensile property	σ / MPa	δ / %	E/ MPa
Pure PVC		37.07	3.98	2568.94
PVC/CaCO ₃ composite filled with modified NG-CaCO ₃		39.71	2.48	3741.20
PVC/CaCO ₃ composite filled with non-modified NG-CaCO ₃		40.16	2.32	3786.59

Table 4 the tensile properties of the PVC/N-CaCO₃ composites

Materials	Tensile property	σ / Pa	δ / %	E/ MPa
Pure PVC		37.07	3.98	2568.94
PVC/CaCO ₃ composite filled with modified N-CaCO ₃		39.84	3.25	2156.21
PVC/CaCO ₃ composite filled with non-modified N-CaCO ₃		41.09	11.72	2818.73

One can see by comparing Table 1, 2, 3 and 4 that the tensile properties of the PVC/CaCO₃ composite filled with modified CaCO₃ is better than that filled with non-modified CaCO₃. For the PVC/P-CaCO₃ composite, the σ and E of PVC/P-CaCO₃ composite filled with modified P-CaCO₃ increase 8.77% and 113.03% compared with PVC/P-CaCO₃ composite filled with non-modified P-CaCO₃, respectively. The δ of PVC/N-CaCO₃ composite filled with modified N-CaCO₃ increases 3.61 times compared with the PVC/N-CaCO₃ composite filled with non-modified N-CaCO₃. This illustrated that the CaCO₃ surface treated with the silane coupling agent was beneficial or improving the interfacial adhesion and resulted in an enhancement of the tensile properties of the PVC/CaCO₃ composites. It is the reason that the silane coupling agent might have made the chemical reaction with the CaCO₃ surface and PVC matrix to improve the compatibility between the filler and matrix, respectively. Consequently, the dispersion of CaCO₃ in the PVC matrix and the interfacial adhesion between them were improved correspondingly; this resulted in an increase in the tensile properties. Under the modification conditions, σ and δ of the PVC/N-CaCO₃ composite are largest; the PVC/P-CaCO₃ has the largest E among the four different PVC/CaCO₃ composites. Contrastive analyzing the tensile properties of the PVC/G-CaCO₃ and PVC/NG-CaCO₃ composites (as the Table 2 and 3 shows), we can find that the σ and E of the PVC/NG-CaCO₃ composite are larger than those of the PVC/G-CaCO₃ composite. This is the reason that there are sharp edges and corners on the surface of the G-CaCO₃ particle, when mixing in the resin matrix, the sharp edges and corners are not benefit for formation of a good interface layer, and produce

stress concentration effect inside the material easily, thus affecting the mechanical properties of the composite; when the nano-meter CaCO_3 particles generating on the surface the micro CaCO_3 particle , sharp edges and corners on the surface of the G- CaCO_3 particle are reduced or eliminated, which is benefit to the improve the interfacial bond strength, so as to improve the material mechanical properties to some degree.

Interfacial Adhesion Strength Of PVC/ CaCO_3 composite. Turcsanyi and Pukanszky [8] supposed that interfacial adhesion strength is one of important parameters affecting the mechanical properties of the plastic composites, and proposed the interfacial interaction parameter (B) to characterize the interfacial adhesion strength between the surface of the filler particle and the polymer matrix, as the Eq.1 shows:

$$B = \frac{1}{\phi_f} \ln \left[\frac{\sigma_c (1 + 2.5\phi_f)}{\sigma_m (1 - \phi_f)} \right] \quad (1)$$

Where ϕ_f is volume fraction of the inorganic filler, σ_c is tensile strength of the composite, MPa; σ_m is the tensile yield strength of the resin, MPa; B is the interfacial interaction parameter, if the interfacial adhesion strength is strong, $B > 3$, and the σ_c increases with the increasing of ϕ_f . It can be seen from Eq.1 that the B has no physical meaning, but it reflects the interface characteristics and depends on the filler volume of the inorganic and the tensile yield strength; the larger the B is, the stronger the interfacial adhesion strength between particle and the matrix.

One can use the calculating program reported in the references[9] [10] to calculate the interfacial reaction parameter of the PVC/ CaCO_3 composites, the results are shown in Table 5.

From Table 5, we can see that most B values of the PVC/ CaCO_3 composites are larger than 3, and the B of the PVC/N- CaCO_3 composite is maximum among the four different PVC/ CaCO_3 composites; the B of PVC/ CaCO_3 composites filled with modified CaCO_3 is larger than the one of the PVC/ CaCO_3 composites filled with non-modified CaCO_3 , for example, the B of the PVC/ CaCO_3 composite filled with modified N- CaCO_3 increases 12.86% compared with non-modified N- CaCO_3 filled PVC/ CaCO_3 composite. That is to say, all of the interfacial adhesion strength between the CaCO_3 particle PVC matrix is strong and increase after modified by CaCO_3 particles. If comparing the B values of the PVC/G- CaCO_3 and PVC/NG- CaCO_3 composites, we can find that the B value of the PVC/NG- CaCO_3 composites are larger than those of the PVC/G- CaCO_3 composites, that is, the interfacial adhesion strength between the NG- CaCO_3 particle and PVC matrix are larger than the one between the G- CaCO_3 particle and PVC matrix.

The interfacial morphology between the inorganic particle and the polymer matrix is one of the facts affecting the tensile strength and elastic module of the polymer composites. To improve the interfacial morphology, especially enhance the interfacial adhesion strength, can increase the tensile properties of the polymer composites.[11] Comparative analysis of the data in Table 1,2,3,4 and 5, we know that the larger the B is, the stronger the interfacial adhesion strength is, and the better the tensile properties is.

Table 5 the interfacial interaction strength of the PVC/ CaCO_3 composites

Materials	PVC/P- CaCO_3	PVC/G- CaCO_3	PVC/NG- CaCO_3	PVC/N- CaCO_3
Modification or not	no	yes	no	yes
B	2.98	3.14	3.12	3.15

Conclusion

After modification, the tensile properties of PVC/ CaCO_3 composites was improved, the PVC/P- CaCO_3 composite has the maximum growth rate in tensile strength and tensile elastic module, the PVC/P- CaCO_3 composite has the maximum growth rate in elongation at break.Under the same modification conditions, the PVC/N- CaCO_3 had the maximum tensile strength and elongation at break, the PVC/P- CaCO_3 composite had the maximum tensile elastic module. The interfacial adhesion strength between the CaCO_3 particle and PVC matrix increased, and the tensile

properties of the PVC/CaCO₃ composites were improved. The interfacial adhesion strength of the PVC/NG-CaCO₃ composite was larger than that of PVC/G-CaCO₃ composite.

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