تاثیر نانوذرات کربنات کلسیم روی خواص مکانیکی PVC و مخلوط ABS/PVC

PVC پلیمری است که به خاطر خواص ویژه نظیر پایین بودن قیمت و عدم اشتعال پذیری به طور وسیعی در صنعت مورد استفاده قرار می گیرد. ولی مشکلاتی مانند نقطه نرم شدگی و چقرمگی پایین PVC کاربرد آن را در صنایع تا حدودی محدود کرده است. کربنات کلسیم به عنوان یک رنگدانه و پر کننده به PVC اضافه می شود. در این مقاله اثر نانوذرات کربنات کلسیم روی خواص مکانیکی پلیمر مورد بررسی قرار می گیرد. در صورتی که پرکننده به صورت نانوذرات استفاده شود باعث کاهش تجمع پرکننده در یک قسمت خاص و افزایش بر همکنش بین پرکننده و ماتریکس پلیمر می شود. نانوذرات کربنات کلسیم یکی از معمولترین پرکننده ها در مقیاس نانوبه شکل کروی است که برای تهیه نانوکامپوزیت استفاده می شود.

از PVC خالص و ترکیب PVC/ABS که به اختصار 338 \BLENDEX نامیده می شود در این مقاله استفاده می شود. مشاهدات میکروسکوپ الکترونی نشان داد که نانو ذرات کربنات کلسیم به طور یکنواخت تری در PVC و PVC مقود. مشاهدات میکروسکوپ الکترونی نشان داد که نانو ذرات کربنات کلسیم به طور یکنواخت تری در PVC و PVC مقود. مثاهدات میکروسکوپ الکترونی نشان داد که نانو ذرات کربنات کلسیم به طور یکنواخت تری در pVC و 338 \SLENDEX بعضی از خصوصیات مکانیکی مانند مقاومت به ضربه، مدول خمشی، دمای نرم شدن PVC و 338 \BLENDEX پس از افزودن 51–0 (phr) نانوذرات کربنات کلسیم افزایش پیدا کرد. اما خواص کششی هر دو نوع پلیمر تغییرات مختلفی را در حضور نانو ذرات کلسیم نشان داد. خواص کششی و ازدیاد طول در نقطه پارگی در PVC با افزودن نانوذرات کربنات کلسیم افزایش پیدا می کند در حالیکه این خواص در قوای پارگی در BLENDEX با افزودن نانوذرات کربنات کلسیم افزایش پیدا می کند در حالیکه این خواص در قده پارگی در BLENDEX با افزودن تانوذرات کلسیم کاهش پیدا می کند. افزایش نانوذرات کربنات کلسیم با با فزودن کاری با افزودن خوای کششی در علول در نقطه پارگی در PVC با افزودن نانوذرات کربنات کلسیم افزایش پیدا می کند در حالیکه این خواص در عوای نانوذرات کربنات کلسیم افزایش پیدا می کند در حالیکه این خواص در علول در نقطه پارگی در BLENDEX با افزودن نانوذرات کلسیم کاهش پیدا می کند. افزایش نانوذرات کربنات کلسیم باعث افزایش مدول کششی و افزایش دمای انتقال شیشه ای (Tg) در PVC و 338 \Stendex

(ABS با PVC سازگاری خوبی دارد و به عنوان اصلاح کننده ضربه در ترکیب با PVC مورد استفاده قرار می گیرد.)



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Effect of nano-CaCO₃ on mechanical properties of PVC and PVC/Blendex blend

Material Properties

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Abstract

The effects of nanoscale calcium carbonate (nano-CaCO₃) particles on the mechanical properties of different ductile polymer matrices were investigated. Polyvinyl chloride (PVC) and PVC/Blendex (BLENDEX[®] 338) blend were used as the matrix in this study. The nano-CaCO₃ particles were observed to be dispersed uniformly on the nanoscale in both PVC and PVC/Blendex blend by means of transmission electron microscopy. The impact strength, flexural modulus and Vicat softening temperature of PVC and PVC/Blendex blend were significantly enhanced after addition of 0–15 phr nano-CaCO₃, but the tensile properties of the two matrices showed different changes in the presence of nano-CaCO₃. The yield strength and elongation at break of PVC could be increased by the addition of nano-CaCO₃ while those of PVC/Blendex were decreased. Dynamic mechanical thermal analysis showed that the addition of nano-CaCO₃ led to an increase in storage modulus and glass transition temperature for both PVC and PVC/Blendex blend. © 2003 Elsevier Ltd. All rights reserved.

Keywords: Polyvinyl chloride; Calcium carbonate; Blendex; Mechanical properties

1. Introduction

Developing nanocomposites based upon polymers and nanoscale fillers has been an attractive approach to achieving good properties. Various nanoscale fillers, including montmorillonite [1], silica [2], calcium carbonate [3–5] and aluminum oxide [6], have been reported to enhance mechanical and thermal properties of polymers, such as toughness, stiffness and heat resistance.

It is well known that surface modification of nanoscale fillers play an important role in the preparation of nanocomposites. Nanoscale fillers are usually organically modified in order to reduce the filler aggregation and enhance the interaction between the filler and polymer matrix, hence acquiring good dispersion of the filler in the polymer matrix. In addition, the properties of nanocomposites are greatly dependent on the filler's aspect

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ratio, surface area and interactions between the filler and polymer matrix. For example, layered silicates and fibers exhibit good reinforcing effects on many polymeric matrixes due to their large aspect ratio, but this kind of filler with a high aspect ratio does not obviously improve the toughness, and sometimes even decreases it [7]. In contrast, spherical mineral nanoparticles are quite different. Their low aspect ratio but large surface area could result in a strong interfacial interaction between filler and polymer matrix. These particles were reported to be able to greatly increase strength, modulus, as well as toughness [3–6].

Nano-CaCO₃ is one of the most common spherical nanoscale fillers used in preparation of nanocomposites. A study on polypropylene (PP)/nano-CaCO₃ composites [3] revealed the dramatic toughening effect of nano-CaCO₃ on PP, but the yield strength of PP was slightly decreased, because of the nucleating effect of nano-CaCO₃. In another research [4], the glass transition and melting temperature of polyethylene terephthalate were considerably increased after nano-CaCO₃ was intro-

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duced. Both the studies found that organically treated nano-CaCO₃ was a good nucleating agent for semicrystalline polymers. Regarding noncrystalline polymers, only research focused on polymethyl methacrylate/nano-CaCO₃ composites' abrasion properties has been reported [6].

Polyvinyl chloride (PVC), as a commodity plastic, has been widely used in industrial fields for many years, due to its good properties, such as nonflammability, low-cost and formulating versatility. However, its low toughness and heat-softening temperature limit its application. In the past, a variety of PVC blends with other resins were developed to broaden PVC application. Among these blends, PVC/acrylonitrile butadiene styrene terpolymer (ABS) blend has been intensively studied [8,9]. ABS was reported to be compatible with PVC and had a good toughening effect on PVC. A modified ABS resin, BLENDEX[®] 338, was used to obtain PVC blends in this study. BLENDEX[®] 338 was produced by GE Specialty Chemicals Corporation and used as an impact modifier for PVC.

In recent years, nanocomposites based on PVC have attracted increasing attention. PVC/montmorillonite [1] and PVC/cellulose whisk [10,11] nanocomposites have been studied. The effect of finely powdered CaCO₃ on the impact resistance of PVC has also been researched [12], but few publications concerning the effect of nano-CaCO₃ on the mechanical properties of PVC or PVC blends have been reported.

In this paper, the morphology and mechanical properties of PVC/nano-CaCO₃ composites were studied. To evaluate the modification effects of nano-CaCO₃ on different ductile polymer matrices, the PVC/Blendex blend were used for comparison. Dynamic mechanical properties of nano-CaCO₃ filled PVC and PVC/Blendex blend are also discussed.

2. Experimental

2.1. Materials and sample preparation

Suspension PVC (WS-800, $\overline{DP} = 800$) was produced by Shanghai Chlor-Alkali Chemical Co., Ltd., China. Blendex (BLENDEX[®] 338), copolymerized with butadiene (70 wt%), styrene and acrylonitrile, was produced by GE Specialty Chemicals Co., USA. Nano-CaCO₃ (SP-200, surface-modified with stearic acid), was produced by Shanghai Perfection Nanometre New Material Co., Ltd., China. The organic tin stabilizer and stearic acid were industry grade products.

PVC 100 phr, organic tin stabilizer 5 phr and stearic acid 0.3 phr were premixed together in a high-speed mixer for 8 min to give the PVC compound. Nano-CaCO₃ was dried at 80 °C for 24 h in a vacuum oven. The PVC compound and nano-CaCO₃ were melt mixed

with a two-roll mixer at 170 °C for 10 min to give binary composites. The PVC compound, nano-CaCO₃, and Blendex 20 phr were mixed in the same way to give ternary composites. The composites thus prepared were molded into sheets of 1 and 3 mm in thickness by compression-molding at 180 °C and 20 MPa for 10 min, followed by cooling to room temperature at 10 MPa.

2.2. Characterization

Nano-CaCO₃ was dispersed in ethanol in an ultrasonic bath for 10 min. A drop of solution thus obtained was dripped onto a 200-mesh copper grid and air-dried for transmission electron microscopy (TEM) observation. The composites were ultrathin-sectioned using a microtome equipped with a diamond cutter. The sections (about 100 nm) were mounted on copper grids for TEM observation. In order to observe the Blendex dispersion in the ternary composites, the ternary composites were marinated on OsO_4 solution for 24 h prior to sectioning. The TEM observation was performed with a JEM-1200EX apparatus running at an acceleration voltage of 80 kV.

Notched Izod impact tests were performed at room temperature using an impact tester from RAY-RAN Co., UK, according to ASTM D256. The impact-fractured surfaces of composites were observed by scanning electron microscopy (SEM) with a HITACHI-S-2150 apparatus. The surfaces were covered with gold prior to observation. Tensile tests were performed at a crosshead speed of 10 mm/min using an Instron tensile tester according to ASTM D638M, and the flexure tests were performed using an Instron tensile tester according to ISO 178. Vicat softening temperatures (VSTs) were measured under a load of 5 kg using a VST test from RAY-RAN Co., UK. Dynamic mechanical thermal analysis (DMTA) was performed on a Rheometric Scientific DMTA IV in tension mode at 1 Hz. The heating rate was 3 °C/min.

3. Results and discussion

3.1. Morphology observation

Fig. 1 presents the TEM micrographs of nano-CaCO₃, PVC/nano-CaCO₃ binary composites and PVC/Blendex/nano-CaCO₃ ternary composites. As shown in Fig. 1(a), most of the nano-CaCO₃ particles have a diameter 30–45 nm, and these particles tend to aggregate together. Fig. 1(b) reveals the nanoscale dispersion of CaCO₃ in PVC matrix when the content of nano-CaCO₃ is 10 phr. Some aggregates are found when the content of nano-CaCO₃ is increased to 15 phr, as shown in Fig. 1(c). It can be observed from Fig. 1(d) and (e) that nano-CaCO₃ is well dispersed in the ternary composites, and Blendex is homogenously dispersed in



Fig. 1. TEM photographs of nano-CaCO₃ and the composites: (a) nano-CaCO₃ particles, (b) PVC/nano-CaCO₃ (10 phr), (c) PVC/nano-CaCO₃ (15 phr), (d) and (e) PVC/Blendex/nano-CaCO₃ (10 phr).

the matrix, indicating good compatibility of Blendex and PVC.

3.2. Notched impact strength

The impact strengths of the composites are presented in Fig. 2. It can be seen that PVC/Blendex blend exhibits much better impact performance than PVC, and the impact strength of PVC/nano-CaCO₃ binary composites and PVC/Blendex/nano-CaCO₃ ternary composites can be increased simultaneously in a broad range of nano-CaCO₃ content. For example, the impact strength of the binary composites reaches the maximum value of 39 J/M when 15 phr nano-CaCO₃ is introduced, about 30% higher than that of pure PVC (30 J/M), while the maximum impact strength of the ternary composites is 819 J/M, which is about 81% higher than that of PVC/Blendex blend (453 J/M). This result suggests a much better toughening effect of nano-CaCO₃ on PVC/Blendex matrix than that on PVC matrix.

The SEM micrographs of the impact-fractured surfaces of the composites are shown in Fig. 3. As seen in



Fig. 2. Notched impact strength of the composites as a function of nano-CaCO₃ content.

(a)



(b)



(c)



Fig. 3. SEM photographs of the composites: (a) PVC/Blendex, (b) $PVC/Blendex/nano-CaCO_3$ (10 phr), (c) $PVC/nano-CaCO_3$ (10 phr).

Fig. 3(b), cavities can be found on the fracture surface of the ternary composites, some of which are occupied by CaCO₃ particles. These cavities are much larger than the particles, suggesting cavitation happens during the samples being impacted. Since no cavity is observed on the fracture surface of PVC/Blendex blend, as shown in Fig. 3(a), the presence of CaCO₃ particles must be responsible for the cavitation. This cavitation could absorb large amounts of energy, leading to the improvement of the composites' impact strength. Chan [4] also found cavitation on the fracture surface of PP/nano-CaCO₃ composites. As shown in Fig. 3(c), few cavities can be observed on the fracture surface of PVC/nano-CaCO₃ binary composites. This indicates that the toughening effect of nano-CaCO₃ on pure PVC is restricted to the mechanical coupling between the filler and polymer matrix, and no cavitation is involved.

3.3. Tensile properties

Figs. 4 and 5 represent the yield strength and elongation at break of PVC/nano-CaCO₃ binary composites and PVC/Blendex/nano-CaCO₃ ternary composites, respectively. The yield strength of the ternary composites is slightly decreased with the increase of nano-CaCO₃ content, while that of the binary composites can be increased when the nano-CaCO₃ is below 10 phr. An interesting phenomenon is that the elongation at break of the binary composites can be greatly increased when a low content of nano-CaCO₃ is introduced. That is quite different from many other composites based on spherical nanoscale fillers, which exhibit either decreased or not changed elongation at break with the addition of fillers. It also can be seen from Fig. 4 that the elongation at break of the ternary composites is decreased in general.



Fig. 4. Yield strength of the composites as a function of nano-CaCO₃ content.



Fig. 5. Elongation at break of the composites as a function of nano-CaCO₃ content.

3.4. Flexural modulus

As shown in Fig. 6, the flexural moduli of PVC/nano- $CaCO_3$ binary composites and PVC/Blendex/nano- $CaCO_3$ ternary composites increase simultaneously with the increase of nano- $CaCO_3$ content independent of the filler dispersion state. Classically, composites based on spherical mineral fillers and polymer matrix exhibit increased elastic moduli with the increase of the filler concentration [3,4], due to the rigidity of fillers and the strong interaction between the filler and polymer matrix.

3.5. Vicat softening temperature

The VSTs of PVC/nano-CaCO₃ binary composites and PVC/Blendex/nano-CaCO₃ ternary composites are

shown in Fig. 7. It can be seen that the addition of nano- $CaCO_3$ leads to increase in VST due to the rigidity of nano- $CaCO_3$ particles. The VSTs of the ternary composites increase with the nano- $CaCO_3$ content increase, while the VST vs. nano- $CaCO_3$ content curve of binary composites reaches its peak when 15 phr of nano- $CaCO_3$ is added. It can be concluded from this result that, besides the inherent properties of polymer matrix, the dispersion state of fillers also affects the VSTs of composites.

3.6. Dynamic mechanical properties

The DMTA spectra of composites are shown in Fig. 8. Glass transition temperature (T_g) is determined as the temperature at the maximum of loss factor (tan δ), and



Fig. 7. Vicat softening temperature of the composites as a function of nano-CaCO₃ content.



Fig. 6. Flexural modulus of the composites as a function of nano-CaCO₃ content.



Fig. 8. DMTA spectra of the composites: (a) PVC/nano-CaCO₃, (b) PVC/Blendex/nano-CaCO₃.

Table 1

Glass transition temperature of the composites as a function of nano-CaCO₃ content

Property	Sample	Nano-CaCO ₃ content (phr)		
		0	10	15
<i>T</i> _g (°C)	PVC/nano-CaCO ₃ PVC/Blendex/nano- CaCO ₃	62.5 65.8	63.9 67.7	64.1 68.0

summarized in Table 1. Due to the compatibility of Blendex and PVC, the curve of tan δ vs. temperature of PVC/Blendex blend exhibits only one relaxation peak that is attributed to the glass transition of the blend. Also,

it can be seen that, whether in the binary composite or the ternary composites, the presence of nano-CaCO₃ leads to a higher storage modulus (E') throughout the whole temperature range investigated and a slight shift of relaxation peak to high temperature. No obvious different effects of nano-CaCO₃ on the dynamic mechanical properties of PVC matrix and PVC/Blendex matrix could be observed.

4. Conclusion

composites PVC/nano-CaCO₃ binary and PVC/Blendex/nano-CaCO₃ ternary composites were prepared by melt mixing. Nano-CaCO₃ can be well dispersed in both the composites, when the nano-CaCO₃ content is below 10 phr. Nano-CaCO₃ had a much better toughening effect on PVC/Blendex matrix than that on PVC matrix. The yield strength and elongation at break of pure PVC can be increased by the addition of nano-CaCO₃, while those of PVC/Blendex blend were decreased. The flexural modulus and Vicat softening temperature of PVC and PVC/Blendex blend can be increased simultaneously by the presence of nano-CaCO₃, and higher storage moduli and glass transition temperatures can also be achieved for the two kinds of composites.

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