Mechanical properties of PVC/nano-$CaCO_3$ composites

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Impact strength is one of the most important mechanical properties of materials. Blends of polymer materials with rubbers have been widely investigated [1]. However, it lessens the tensile strength, modulus, resistance to heat, and processing behavior of materials. Addition of inorganic fillers improves the thermal stability and cost of materials, while decreases yield stress and impact strength. According to this, the newly developed nanoparticle modified polymer composites would be competitive candidates for improving the mechanical properties of polymers overall [2]. This nanoconcept has been mostly focused on thermoplastic and thermosetting polymers, including epoxys, polyamides, polypropylene, and polyesters [3, 4]. Relatively little attention has been paid to poly(vinyl chloride) materials. Poly(vinyl chloride) (PVC), as one of the most widely used polymers, has wide applications such as electrical insulators, plastics moldings, and building materials. When conventional toughening modifiers such as CPE, ACR, and NBR are replaced with nanoparticles such as $CaCO_3$, the fracture behavior is expected to be changed.

A homogeneous dispersion of nanoparticles in the polymer matrix is the key to the strengthening and toughening effect of nanoparticles [5]. In the present work, we investigate the mechanical properties of PVC-based nanocomposites filled with titanate treated nano-calcium carbonates ($CaCO_3$).

Poly(vinyl chloride) (WS-1000S) used in this work was supplied by Shanghai Chlor-Alkali Chemical Co Ltd. Untreated nanoparticles of $CaCO_3$(SP-200) were obtained from Shanghai Perfection Nanometre New Material Co Ltd with a median diameter 20–100 nm.

Nanoparticles were treated with coupling agent of organic titanate (JN-114, supplied by ChangZhou JiNai Chemical) by wet-grinding method in our lab. The PVC powder was dry-blended with various additives and nano-$CaCO_3$using a high-speed mixer for 10 min. The mixture was then melt-mixed using a mixing roll at $175 \pm 5\,^{\circ}C$ for 10 min. The sheets about 4 mm thickness were prepared by compressing at $190\,^{\circ}C$ under a pressure of 14.5 MPa for 3 min and quenching to $40\,^{\circ}C$ by a cold press.

Tensile tests were carried out using a dumbbell specimen (GB1040 Type II specimens, 150 mm × 10 mm × 4 mm and a Shimadzu AG-10TA tensile tester with a crosshead speed of 5 mm/min. Impact tests were performed on the rectangular bars (GB1843, 63.5 mm × 10 mm × 4 mm). A single-edge 45 ° V-shaped notch (tip radius 0.25 mm, depth 2 mm) was milled in the bars. The dispersion of nanoparticles in the matrix was analyzed by scanning electron microscopy (JSM-6360LV, Jeol).

The SEM micrographs of PVC/$CaCO_3$ nanocomposites are shown in Fig. 1. Fig. 1a shows that untreated nano-$CaCO_3$ particles agglomerate. The particle–particle interactions of the untreated nanoparticles are too high for dispersion. The size of $CaCO_3$ agglomerates at this filler loading is approximately 200–500 nm. It is also observed that the interface between $CaCO_3$ particles and the matrix is clear, which suggests that the interfacial adhesion between the two phases is poor and particles debonded from the matrix under the force loading. In contrast, titanate treated nano-$CaCO_3$ particles dispersed well in the PVC matrix. The particle size is about 100 nm. The interparticle distance is lower than that between aggregates observed in Fig. 1a at the same filler concentration. Moreover, the interfacial adhesion between treated particles and the matrix is improved obviously due to the bridge link of coupling agent.

The tensile strength is plotted as a function of particle content in Fig. 2. It is clearly demonstrated that the tensile strength is increased only when 5 phr treated $CaCO_3$ is added. With a rise in filler content, the strength of PVC/$CaCO_3$ composite decreases. At the same filler content, the decrease in tensile strength of treated-particle filled PVC is lower than that of untreated-particle filled PVC. This is due to the improved interfacial adhesion between treated $CaCO_3$ particles and the PVC matrix, which is shown in Fig. 1. With 15 phr treated $CaCO_3$, the tensile strength drops to 49.5 MPa, which is a lowering of 3% compared to the neat PVC.

Fig. 3 illustrates the variation in the impact strength of the composites as a function of $CaCO_3$ content. The fracture energy is increased considerably when treated $CaCO_3$ is incorporated into the PVC matrix. The impact strength is increased by a factor of 4 by adding 20 phr treated $CaCO_3$ particles. At the same time, the composites with untreated $CaCO_3$ showed that the impact strength increased from 4.8 to 12.5 kJ/m^2 by adding 15 phr $CaCO_3$, which is an increase of 160%, then decreased to 11.6 kJ/m^2 by adding 20 phr $CaCO_3$.

Wu *et al.* [6] proposed that a critical matrix ligament thickness was found to be a key parameter for the

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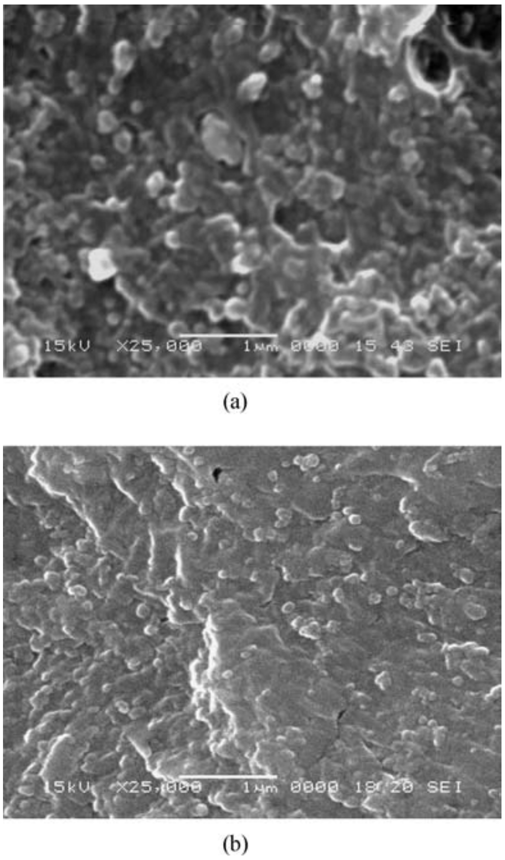

(a)

(b)

Figure 1 SEM images of PVC/nano-$CaCO_3$ composites with 5 phr of $CaCO_3$: (a) untreated $CaCO_3$ and (b) titanate treated $CaCO_3$.

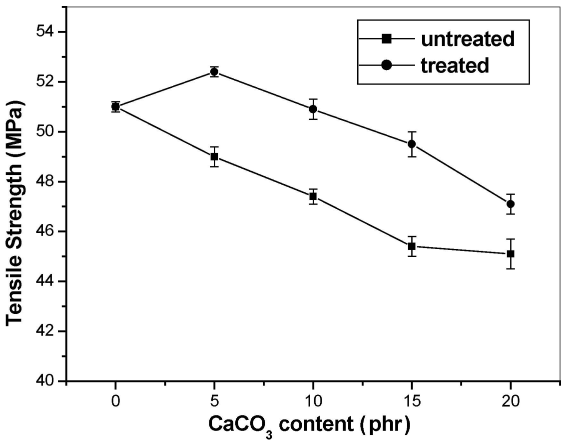

Figure 2 Tensile curves of PVC/nano-$CaCO_3$ composites.

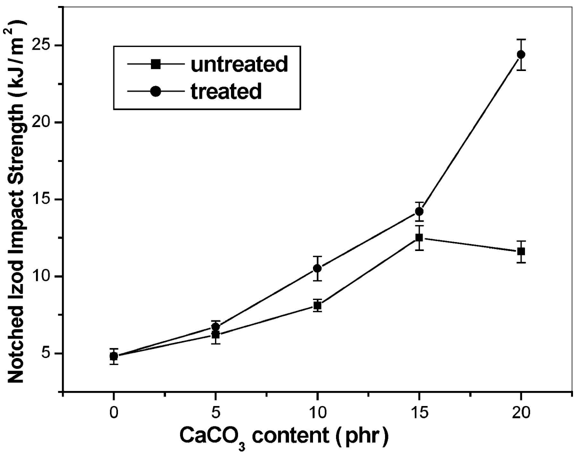

Figure 3 Impact curves of PVC/nano-$CaCO_3$ composites.

toughening effect. Thio *et al.* [5] observed that the impact behavior of 0.07 μm $CaCO_3$-filled nylon composites was compromised by the ubiquitous agglomeration of the particles. They pointed out that in addition to the critical interparticle distance, filler dispersion must be very regular to avoid creation of crack-initiating large agglomerates. Untreated $CaCO_3$-filled PVC samples were toughened less than the treated $CaCO_3$-filled ones, which is attributed to the presence of agglomerates due to poor dispersion.

The reinforcing and toughening of PVC with nanoparticles lead to a system with improved properties. The dispersion of the particles is critical in these composites. The titanate-treated $CaCO_3$ particles were found to give the best combination of properties. This is due to the improved interfacial adhesion and dispersion resulting from the surface treatment of the $CaCO_3$ particles.

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