Study on mechanical property of epoxy composite filled with nano-sized calcium carbonate particles

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Epoxy resin (EP) is used widely nowadays as a structural, adhesive and electronic material due to exhibiting high strength, high elastic modulus, high insulation etc. [1]. However, EP may show limitations, especially over-fragility in application, so other constituents have to be added to improve its performance. Methods of toughening EP has long been sought, and one of the most common methods is the incorporation into EP of a dispersed rubbery elastomer, which can enhance impact strenght of EP at the expense of weakening rigidity and heat-resistance of the matrix as well as raising cost [2]. Calcium carbonate is considered as a suitable substitute for rubbery elastomer in EP matrix because it demonstrates high rigidity and may overcome the shortcomings of rubbery elastomer if incorporated well into the EP matrix.

Traditionally, micron-sized calcium carbonate is added into polymers for the purpose of reducing formulation cost of the polymer-based composites. Nevertheless, micron-sized calcium carbonate may have negative impact on the mechnical performance of polymers. It was reported that mechanical properties of polymers could be otherwise improved by adding nano-sized fillers. Generally, mechanical behaviors of particulate-filled polymers, which have a very complex dependence on the interfacial bonding between the filler and the matrix, are influenced strongly by factors such as size, content and shape of the filler. Of these fillers, nano-sized calcium carbonate (nano-$CaCO_3$) particles have attracted considerable attention and play effective role in many composite systems [3]. This work reports an investigation of the influence of nano-$CaCO_3$ on the mechanical properties fo EP composite.

Nano-$CaCO_3$ employed in this experiment, with a cubic shape and an average diameter of 40 nm (Fig. 1), was synthesized by the reactive precipitation reaction method under high gravity environment. Detailed methodology and basic theory about the preparation of nano-$CaCO_3$ by this method can be found in the reference [4].

The dispersion degree of the filler in the matrix will significantly influence the properties of composite. However, it is very difficult to disperse nano-sized particles in a high viscous polymer matrix. Generl method is to introduce a high shearing force to the mixture in order to intermix the fillers with the matrix [5]. However, hydrophilic nano-$CaCO_3$ is not compatible to hydrophobic EP matrix and can not be uniformly distributed in EP. Appropriate surface modification is therefore needed to convert the hydrophilic surface of $CaCO_3$ to an hydrophobic surface. A coupling agent is selected in this work to graft heteropolar groups on nano-$CaCO_3$ and boost the miscibility of the filler with EP matrix.

Nano-$CaCO_3$ was modified with titanates coupling agent in a high-speed shear mixer which rotated at a speed of 24000 r/min for 10–15 min. Then bisphebnol A EP was mixed with the modified nano-$CaCO_3$ on a three-roll mill for several times. Curing agent was subsequently added at room temperature and the system was kept stirring till the curing agent was evenly mixed with EP. The mixture was afterwards cast in steel molds, followed by curing for 4 days at 25 °C to produce composite samples for the characterization of their mechanical performance. At least five samples were tested for each material studied.

Fig. 2 shows the effect of nano-$CaCO_3$ content on impact strength of EP composite. Experimental results indicate that impact strength of the composite increases with an increasing nano-$CaCO_3$ content in the range of less than 6 wt%, while impact strength of the composite declines when nano-$CaCO_3$ content is more than 6 wt%. This suggests that too many nano-$CaCO_3$ particles results in aggregation in the matrix nd degrades the toughness of EP composite whereas nano-$CaCO_3$ exhibits reinforcing capacities when added in small amounts. The optimum content of nano-$CaCO_3$ in EP is 6.0% by weight.

Table I lists the influence of nano-$CaCO_3$ on mechanical properties of EP composite. Sample **1** denotes the unfilled EP, sample **2** the composite filled with unmodified nano-$CaCO_3$ and sample **3** the composite filled with nano-$CaCO_3$ modified by titanates coupling agent. The content of the filler is 6.0% by weight in both sample **2** and **3**. Data in Table I demonstrates that the mechanical properties of EP are enhanced markedly by the addition of surface modified nano-$CaCO_3$ particles. Nano-$CaCO_3$, on using as a reinforcing material can improve the impact strength and stiffness of polymer matrix simultaneously, in contrast to elastomer particles, which only increase the impact strength of the composite. Improvements in impact toughness and tensile

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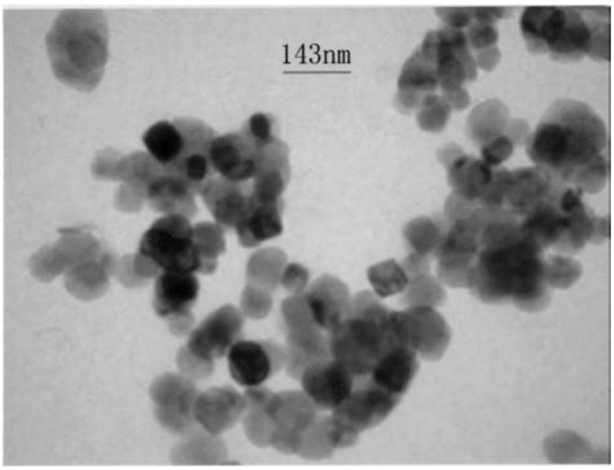


Figure 1 Transmission electron microscope (TEM) micrograph of nano-sized precipitated calcium carbonate synthesized by high gravity method.

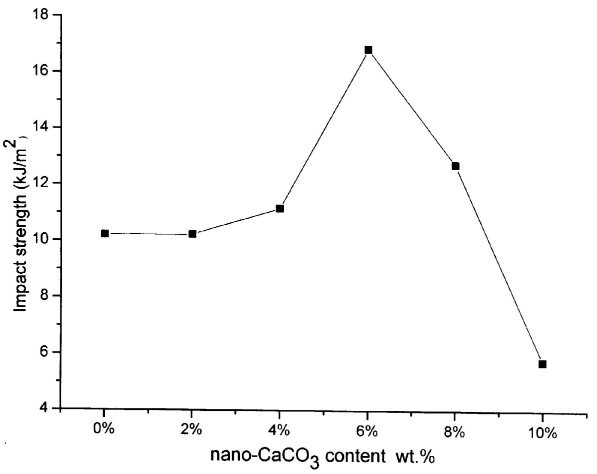


Figure 2 Impact strength of EP composite filled with nano-$CaCO_3$.

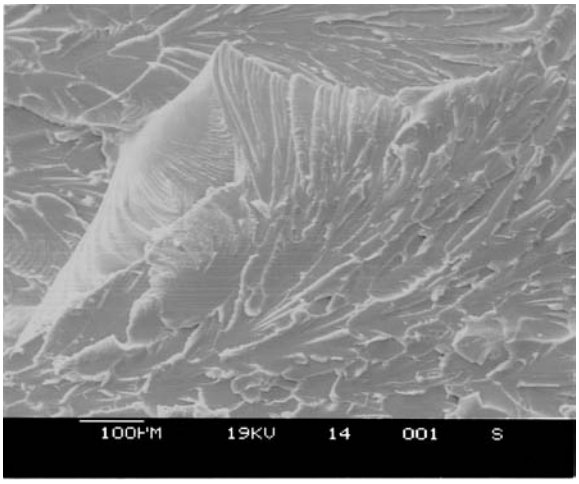
strength show that nano-$CaCO_3$ particles can be employed as a toughening constituent in EP but that surface modification of the filler is necessary.

Fig. 3 shows the scanning electron microscope (SEM) micrographs of the fracture surfaces of impact-loaded specimens. It is obvious that there is a rougher surface indicating a more complex crack path in (c) than in (a) and (b), which is consistent with nano-particles inducing cracking and increasing the energy for rupturing. There are many areas of nano-$CaCO_3$ agglomerates in (b), but none can be seen in (c). This indicates that nano-$CaCO_3$ after surface modification can disperse better than those without modification. Fig. 4 shows the dispersion state of nano-$CaCO_3$ in EP; after surface modification and mixing under high shearing force, filler particles are well dispersed in matrix.

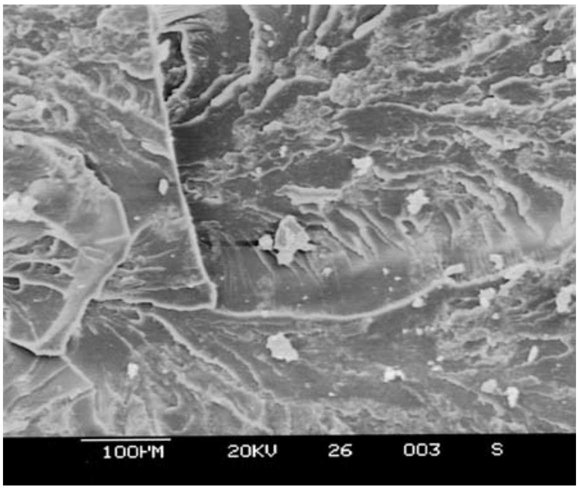
TABLE I Mechanical properties of EP and EP + nano-$CaCO_3$ composite

	σ_t (MPa)	E_t (MPa)	ε_t (%)	σ_b (MPa)	E_b (MPa)	A_k (kJ/m^2)
1	55.057	1374.3	3.9946	57.817	1509.3	10.2196
2	54.029	1461.4	4.5097	59.542	1974.7	10.9934
3	76.421	1648.7	6.3914	84.857	2307.4	16.8755

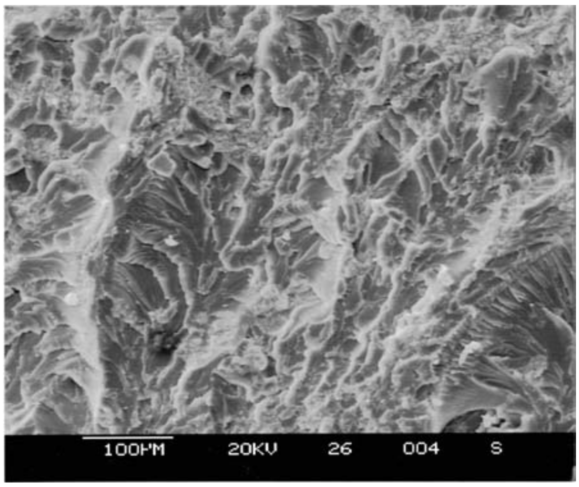
σ_t, tensile strength (MPa); E_t, tensile modulus (MPa); σ_b, bend strength (MPa); E_b, bending flexural modulus (MPa); A_k, impact toughness (kJ/m^2).



(a)



(b)



(c)

Figure 3 SEM micrographs of rupture surfaces of impact-loaded: (a) EP specimen without nano-$CaCO_3$; (b) EP specimen filled with unmodified nano-$CaCO_3$; (c) EP specimen filled with modified nano-$CaCO_3$.

In conclusion, this paper studied the mechanical properties of nano-$CaCO_3$ toughened EP composite, where nano-$CaCO_3$ used was cubic and had an average diameter of about 40 nm. Impact strength and flexural modulus of the composite improved remarkably when

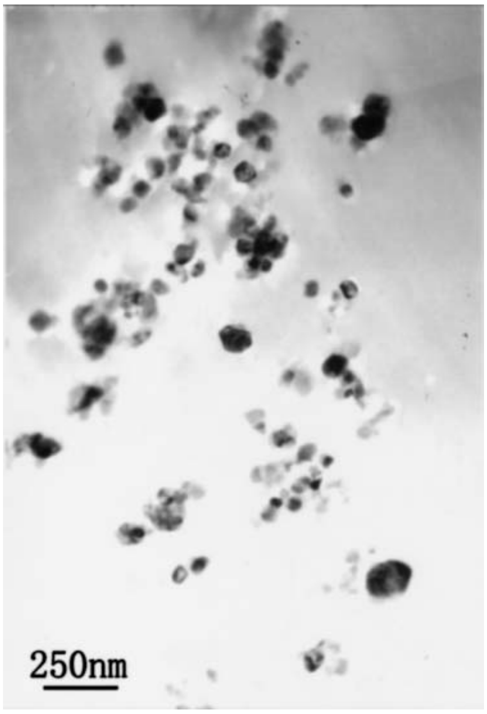


Figure 4 TEM micrographs of the composite.

6 wt% of nano-$CaCO_3$ was added. Surface treatment of nano-$CaCO_3$ by titanates coupling agent significantly improve the dispersibility of nano-$CaCO_3$ in such a high viscous matrix.

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