Preparation and Properties of Nano-CaCO$_3$/Acrylonitrile-Butadiene-Styrene Composites

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ABSTRACT: CaCO$_3$/acrylonitrile-butadiene-styrene (ABS) and CaCO$_3$/ethylene-vinyl acetate copolymer (EVA)/ABS nanocomposites were prepared by melting-blend with a single-screw extruder. Mechanical properties of the nanocomposites and the dispersion state of CaCO$_3$ particles in ABS matrix were investigated. The results showed that in CaCO$_3$/EVA/ABS nanocomposites, CaCO$_3$ nanoparticles could increase flexural modulus of the composites and maintain or increase their impact strength for a certain nano-CaCO$_3$ loading range. The tensile strength of the nanocomposites, however, was appreciably decreased by adding CaCO$_3$ nanoparticles. The microstructure of neat ABS, CaCO$_3$/ABS nanocomposites, and CaCO$_3$/EVA/ABS nanocomposites was observed by scanning electron microscopy. It can be found that CaCO$_3$ nanoparticles were well-dispersed in ABS matrix at nanoscale. The morphology of the fracture surfaces of the nanocomposites revealed that when CaCO$_3$/EVA/ABS nanocomposites were exposed to external force, nano-CaCO$_3$ particles initiated and terminated crazing (silver streak), which can absorb more impact energy than neat ABS. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3609–3614, 2008

Key words: nano-CaCO$_3$; EVA; acrylonitrile-butadiene-styrene; masterbatch; mechanical properties

INTRODUCTION

Micron-sized inorganic particle fillers demonstrated noticeable effect on improving properties and/or decreasing costs of polymer products. Young's modulus, hardness, heat distortion temperature, and thermal expansion usually improve to various extents, whereas impact strength and tensile strength deteriorate in polymer composites filled with micron-sized inorganic particles.[1–4] When particle fillers are in nanometer scale, due to the larger interfacial area between the particles and the surrounding polymer matrix, they are superior to the micron-sized counterparts in improving mechanical and thermal properties of thermoplastics. Nano-sized fillers could increase not only modulus and hardness of some polymers but also their tensile and/or impact strength at the same time.[5,6] Furthermore, compared with microparticles, nanoparticles could offer many unique properties such as transparency, surface smoothness, fire retardancy, and barrier property.[7–9]

CaCO$_3$/acrylonitrile-butadiene-styrene (ABS) composites have been a topic of great interest. Liang et al.

studied rheological properties of nano-CaCO$_3$/ABS composites such as shear viscosity, extension viscosity, and entry pressure dropped by capillary extrusion. It was found that there was a small "bearing effect" when the filler content was low.[10,11] Mechanical properties study revealed increase in tensile modulus but decrease in tensile and impact strengths by the addition of micron-sized CaCO$_3$ particles. In contrast, nano-CaCO$_3$ increased modulus of the composites whilst maintained or even increased its impact strength for a certain nano-CaCO$_3$ loading range. It can be concluded that CaCO$_3$ particle size and surface treatment have significant effect on the composite properties.[12]

In this article, to improve the dispersion of CaCO$_3$ nanoparticles in ABS matrix, two types of masterbatches, A-masterbatch and E-masterbatch, with different polymer and weight ratio between nano-CaCO$_3$ and the polymers were prepared. Particle dispersion and mechanical properties of nano-CaCO$_3$/ABS composites were studied.

EXPERIMENTAL

Materials

ABS, Chi Mei PA-747S, a copolymer of acrylonitrile (20–24%), butadiene (19–23%), and styrene (54–58%) was obtained from Chi Mei Corp. (Taiwan). This

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TABLE I
Content of ABS and A-Masterbatch in the Nanocomposites

Sample	ABS (PHR)	A-Masterbatch (PHR)
1	100	0
2	99	2
3	97	6
4	95	10
5	93	14

general-purpose grade ABS has a melt flow index (ASTM D1238) of 0.7 g/10 min at 200°C.

Ethylene-vinyl acetate (EVA)-14, a copolymer of vinyl acetate (14%) was obtained from Mitsui Chemistry Corp. (Japan). This general-purpose grade EVA has a melt flow index (ASTM D1238) of 4 g/10 min at 200°C.

The nano-sized precipitated $CaCO_3$ (cubic shape with an average primary particle size of 40 nm; prepared by our research center) was coated with stearic acid to increase the compatibility with the polymer matrix and was designed to be a reinforcing additive to improve the properties of plastic materials.

The preparation of masterbatches

To achieve a good dispersibility of nano-$CaCO_3$, masterbatches were first prepared. A-masterbatch was obtained by melt-mixing ABS with nano-$CaCO_3$ using a twin-screw extruder (PE-20, Keya Company, Nanjing, JiangSu, China). The temperatures of the extruder were set sequentially at 150, 175, 195, 190°C and the mixing weight ratio of neat ABS to nano-$CaCO_3$ was 1:1. E-masterbatch was obtained by melt-mixing EVA with nano-$CaCO_3$ using the above twin-screw extruder. The temperatures of the extruder were set sequentially at 120, 145, 175, 170°C and the mixing weight ratio of neat EVA to nano-$CaCO_3$ was 3 : 7.

The preparation of CaCO₃/ABS and CaCO₃/EVA/ABS nanocomposites

$CaCO_3$/ABS and $CaCO_3$/EVA/ABS nanocomposites samples were prepared by blending the above masterbatches with ABS in a single screw extruder (SJ-30, Beijing Plastic Engineering Co., China) with a temperature sequence of 160, 185, 205, 200°C. Table I and Table II show the mixing weight ratio of ABS to these masterbatches. As can be seen in Table II, extra EVA was supplemented to reach the same EVA content in different E-masterbatch/EVA/ABS nanocomposites.

Mechanical properties of the nanocomposites

The impact strength of the nanocomposites was measured by Charpy Pendulum Impact Testing

Machine (XJJ-5, Chengde Jinjian Testing Machine Company, Hebei, China) at room temperature. The tensile (testing speed: 50 mm/min) and flexural (testing speed: 10 mm/min) properties were recorded by Instron Universal Testing Machine (Instron 1185, Instron Company, England) at 20°C (293 K).

Microstructure of the fracture section of the composites

The microstructure of the fracture section of the composites was observed by scanning electron microscopy (SEM). The fracture surfaces were prepared by Instron Universal Testing Machine and coated with platinum/palladium. SEM images were obtained by Cambridge-S250MK3 (England).

Dispersibility of CaCO₃ nanoparticles in polymer matrix

The dispersion state of $CaCO_3$ nanoparticles in ABS matrix was examined by transmission electron microscopy (TEM). TEM specimens were obtained from nano-$CaCO_3$/ABS composites at -90°C using an ultra microtome (LKB-5, Switzerland) with a diamond knife. TEM images were obtained by Hitachi H-800 (Japan) with the acceleration voltage of 200 kV.

RESULTS AND DISCUSSION

Mechanical properties of CaCO₃/ABS and CaCO₃/EVA/ABS nanocomposites

The impact strength of neat ABS, EVA/ABS, $CaCO_3$/ABS nanocomposites with A-masterbatches and $CaCO_3$/EVA/ABS nanocomposites with E-masterbatches is presented in Figure 1. The content of EVA maintained 3 PHR in $CaCO_3$/EVA/ABS nanocomposites and EVA/ABS without $CaCO_3$. First, the impact strength of EVA/ABS is higher than that of neat ABS. Second, the toughness of the $CaCO_3$/EVA/ABS composites was improved when nano-$CaCO_3$ content increased. The impact strength of neat ABS was about 33.5 kJ/m^2 and at a nano-$CaCO_3$ content of 5 PHR, the impact strength of the $CaCO_3$/EVA/ABS compos-

TABLE II
Content of ABS, EVA, and E-Masterbatch in the Nanocomposites (EVA Content is Supplemented to Reach the Same EVA Content for all the Nanocomposites)

Sample	ABS (PHR)	EVA (PHR)	E-Masterbatch (PHR)
6	97	3	0
7	97	2.57	1.43
8	97	1.71	4.29
9	97	0.86	7.14
10	97	0	10

Figure 1 Effect of CaCO$_3$ content on impact strength of CaCO$_3$/ABS and CaCO$_3$/EVA/ABS nanocomposites.
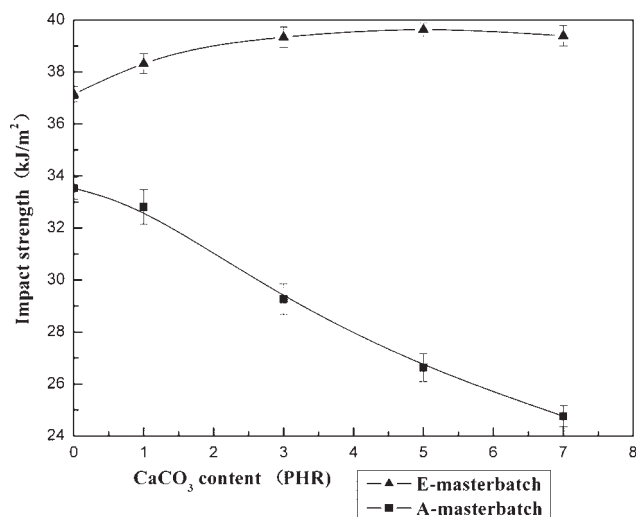

Figure 2 Effect of CaCO$_3$ content on tensile strength of CaCO$_3$/ABS and CaCO$_3$/EVA/ABS nanocomposites.

ite rose to a maximum of 39.6 kJ/m^2, which was 18% higher than that of neat ABS and higher than that of EVA/ABS. However, the impact strength slightly decreased with a further increase of nano-CaCO$_3$ content to 7 PHR (37.2 kJ/m^2).

By contrast, the impact strength of CaCO$_3$/ABS nanocomposites filled with A-masterbatch decreased significantly with the increase of nano-CaCO$_3$ content. As can be seen in Figure 1, when nano-CaCO$_3$ content reached 3 PHR (corresponding to 6 PHR of A-masterbatch) and 7 PHR (corresponding to 14 PHR of A-masterbatch), the impact strength of the nanocomposites dropped to 29.3 and 24.8 kJ/m^2, respectively.

Figure 2 shows the tensile properties of CaCO$_3$/ABS and CaCO$_3$/EVA/ABS nanocomposites. The tensile strength of the nanocomposites has decreased by adding either A-masterbatch or E-masterbatch. There are different mechanisms for the deterioration of the tensile performance in these two types of nanocomposites. In CaCO$_3$/ABS nanocomposites filled with A-masterbatch system, the weak interface combination between ABS and CaCO$_3$ nanoparticles is the main reason for the poor tensile strength. It can be seen from Figures 4(d) and 5(a) that most of the nanoparticles existed in aggregates and had a poor compatibility with the matrix. In CaCO$_3$/EVA/ABS composites filled with E-masterbatch system, CaCO$_3$ nanoparticles coated with EVA were well-dispersed in the matrix [Fig. 5(c,d)] since EVA has a good compatibility with ABS matrix [Fig. 4(e)]. Nevertheless, EVA is a flexible polymer itself and have a low tensile strength (the tensile strength of neat EVA-14 is 9 MPa), which contributed to the weak tensile strength of CaCO$_3$/EVA/ABS composites filled with E-masterbatch.
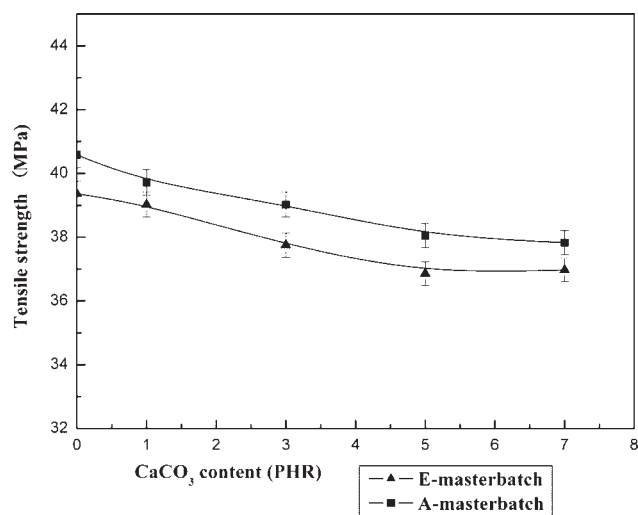
The flexural modulus of CaCO$_3$/ABS filled with A-masterbatch and CaCO$_3$/EVA/ABS filled with E-masterbatch was illustrated in Figure 3. As shown in Figure 3, A-masterbatch had a better modulus-enhancing effect than E-masterbatch. CaCO$_3$ nanoparticles were modified with stearic acid which can bond with ABS matrix, even if the bonding is very weak. In the course of testing, modulus was calculated in the linear elastic region of the composites where the strain was less than 1.5%. Because of this small strain, the stress in the composites was not high enough to break the bonding between the particles and ABS matrix. Therefore, the bending modulus of ABS composites increased by adding the rigid nanoparticles. However, CaCO$_3$ nanoparticles were wrapped with EVA and formed a core-shell
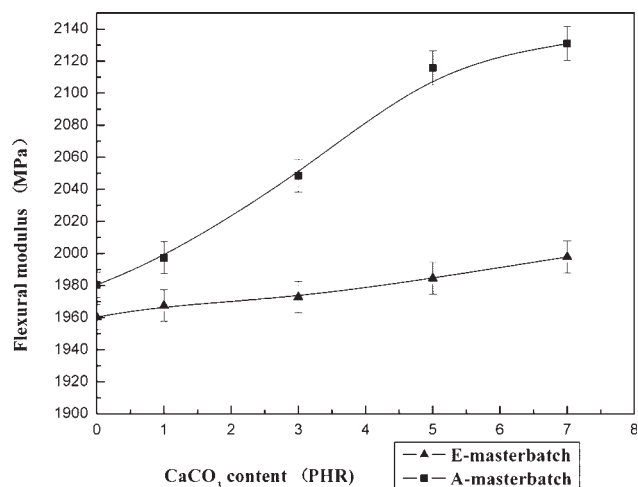

Figure 3 Effect of CaCO$_3$ content on flexural modulus of CaCO$_3$/ABS and CaCO$_3$/EVA/ABS nanocomposites.

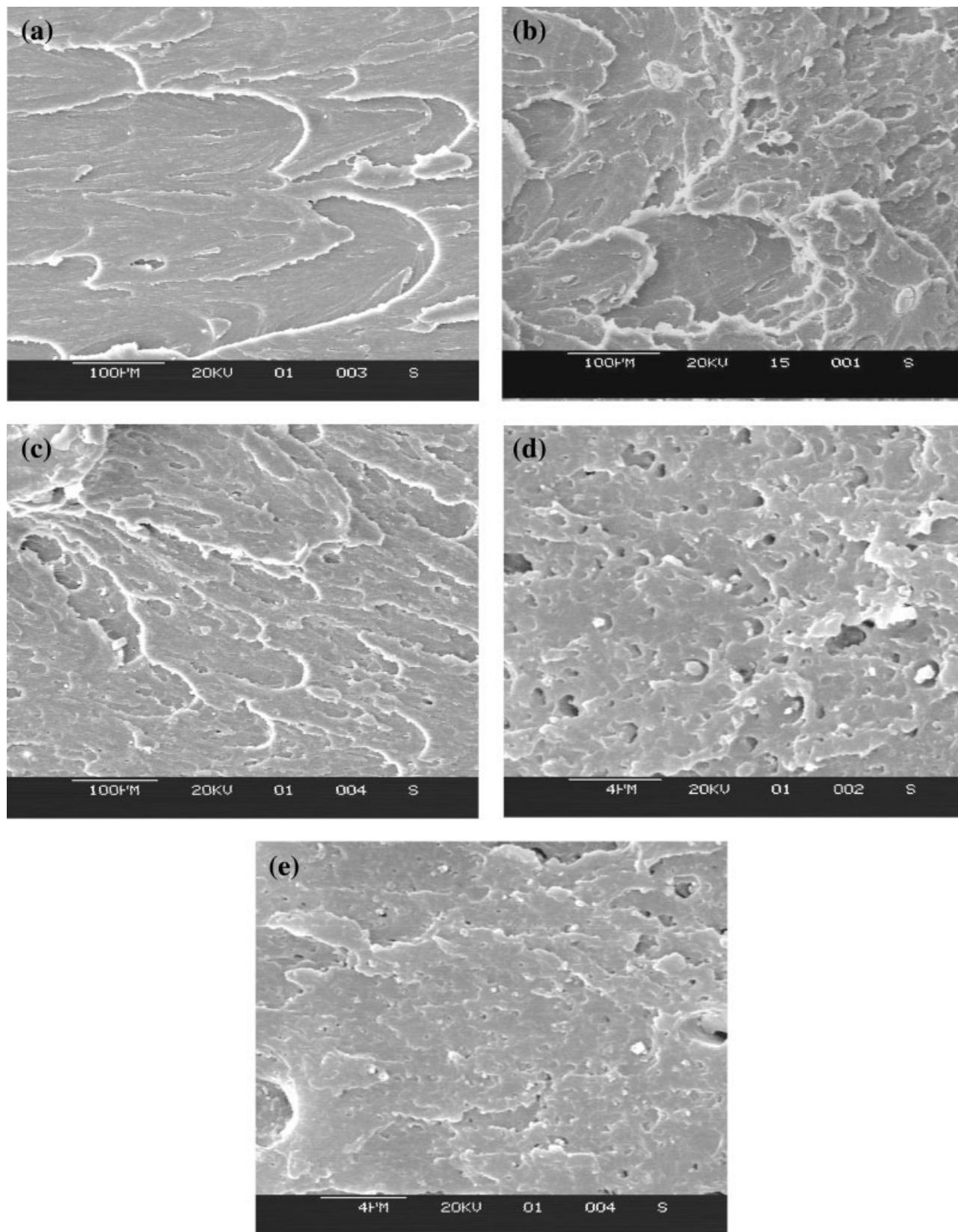**Figure 4** SEM images of neat ABS and nanocomposites: (a) neat ABS; (b, d) CaCO$_3$/ABS nanocomposites filled with A-masterbatch; (c, e) CaCO$_3$/EVA/ABS nanocomposites filled with E-masterbatch.
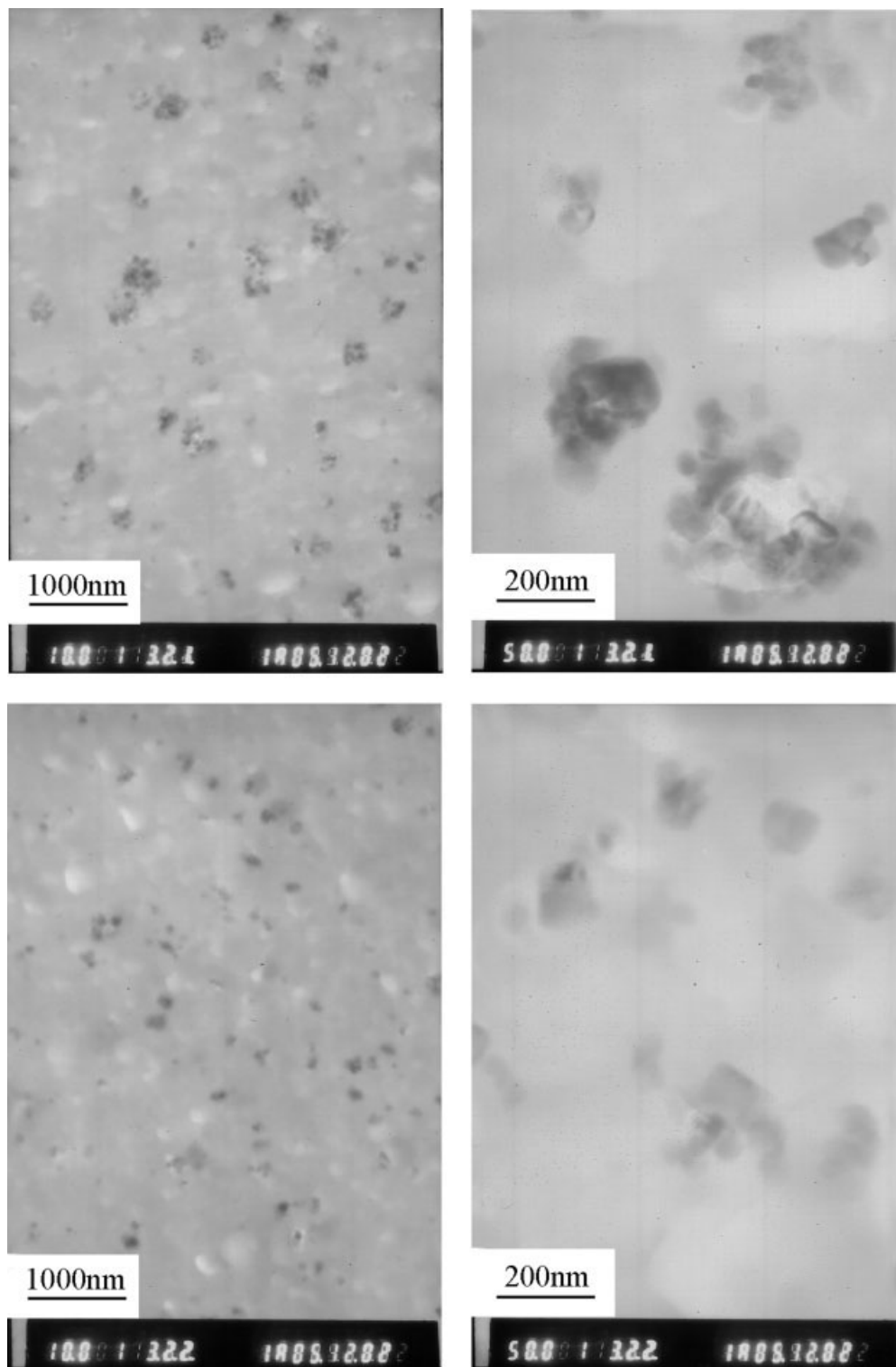
Figure 5 TEM images of nanocomposites: (a, b) CaCO$_3$/ABS nanocomposites filled with A-masterbatch; (c, d) CaCO$_3$/EVA/ABS nanocomposites filled with E-masterbatch.

structure in CaCO$_3$/EVA/ABS nanocomposites filled with E-masterbatch. Since the EVA shell was very soft, the resulting E-masterbatch had a poorer modulus-enhancing effect than A-masterbatch.

Microstructure of the fracture section of the composites

The fracture surfaces of neat ABS, CaCO$_3$/ABS, and CaCO$_3$/EVA/ABS nanocomposites are given in Fig-

ure 4 (SEM images). It is evident that the nanocomposites experienced extensive plastic deformation, leading to a ductile fracture. $CaCO_3$ nanoparticles, as stress concentration sites, initiated and terminated the crazing (silver streak) in impact testing. At the same time, they caused ABS chain to create shear yielding, which improved the toughness of the nanocomposites. However, if the agglomerates of $CaCO_3$ nanoparticles formed in the matrix [Fig. 5(a,b)], crazing was initiated and ulteriorly turned into the cracks [Fig. 4(d)], which decreased the impact strength of $CaCO_3$/ABS nanocomposites filled with A-masterbatch.

Figure 4(d,e) display the images of ABS blended with A-masterbatch and E-masterbatch, respectively. It can be observed that the dispersion state of $CaCO_3$ nanoparticles in $CaCO_3$/EVA/ABS nanocomposites was better than that in $CaCO_3$/ABS nanocomposites. The fracture surface image in Figure 4(d) shows that $CaCO_3$ nanoparticles or their agglomerates fell off from the matrix, indicating that the bonding between $CaCO_3$ nanoparticles and the matrix was very weak. It can also be found that the cavity in Figure 4(e) was much smaller than that in Figure 4(d), resulting from the fact that the interfacial bonding between EVA-modified nano-$CaCO_3$ and ABS is superior to that between unmodified nano-$CaCO_3$ and ABS.

Dispersibility of $CaCO_3$ nanoparticles in ABS matrix

It is difficult to disperse $CaCO_3$ nanoparticles well in thermoplastics since the surface of $CaCO_3$ nanoparticles has hydrophilic groups, and these nanoparticles have a strong tendency to agglomerate due to a small radius and a large surface energy. Therefore, nano-$CaCO_3$ surface should be modified to obtain a good dispersion in polymer matrix.

The dispersion state of the nano-$CaCO_3$ particles in ABS matrix is presented in Figure 5. Figure 5(a,c) is magnified 10k times and Figure 5(b,d) is magnified 50k times. The content of nano-$CaCO_3$ was 5 PHR.

Figure 5(a,b) indicates that most of $CaCO_3$ nanoparticles aggregated to a secondary particle size of several hundreds of nanometers in $CaCO_3$/ABS nanocomposites filled with A-masterbatch, while $CaCO_3$ nanoparticles were well-dispersed in $CaCO_3$/EVA/ABS nanocomposites filled with E-masterbatch, as shown in Figure 5(c,d), thanks to the modification effect of EVA.

Compared with Figure 5(b,d), the results show that E-masterbatch have a good interphase because

$CaCO_3$ nanoparticles wrapped with EVA and formed a core-shell structure. On the other hand, A-masterbatch has a normal interface because $CaCO_3$ nanoparticles are only modified with stearic acid.

CONCLUSIONS

Two types of masterbatches, A-masterbatch and E-masterbatch, were prepared using a twin-screw extruder. The $CaCO_3$/ABS nanocomposites filled with A-masterbatch and the $CaCO_3$/EVA/ABS nanocomposites filled with E-masterbatch were subsequently prepared by melting-blend with a single-screw extruder. With the E-masterbatch, $CaCO_3$ nanoparticles added to the thermoplastics can significantly increase bending modulus and impact strength of the nanocomposites simultaneously. It is found from TEM and SEM images that $CaCO_3$ nanoparticles were well-dispersed in ABS matrix at nanoscale and initiated much silver streak since EVA, as an interfacial modifier, enhanced the compatibility between the nanoparticles and the matrix in the $CaCO_3$/EVA/ABS nanocomposites. It is confirmed that, when added into ABS with a proper form of masterbatch, $CaCO_3$ nanoparticles can act as a new functional material to improve the toughness and modulus of the nanocomposites. This work also shows that $CaCO_3$/EVA/ABS nanocomposites can be prepared in ordinary machines, which provides a general approach for manufacturing polymer nanocomposites by direct melting-blend.

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