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High-shear processing induced homogenous dispersion of pristine multiwalled carbon nanotubes in a thermoplastic elastomer

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Abstract

We report a high-shear processing technology that allows the homogenous dispersion of unmodified multiwalled carbon nanotubes (UMWNTs) in a thermoplastic elastomer, poly(styrene-*b*-butadiene-*co*-butylene-*b*-styrene) (SBBS). We demonstrated that the dispersion of UMWNTs in a polymer matrix depends greatly on the shear stress exerted during melt processing. Mechanical tests showed that the tensile modulus, tensile strength and elasticity of the composites with fine nanotube dispersion processed at a high-shear rate are much higher than those of the composites processed at a low shear rate. The results indicated that high-shear processing is an effective method of improving the dispersion of unmodified carbon nanotubes in a polymer matrix.

Keywords: High-shear processing; Carbon nanotube; Nanocomposite

1. Introduction

Carbon nanotubes (CNTs) have been considered to be an ideal candidate for polymer reinforcement due to their excellent mechanical properties, high aspect ratio, and nanometer-scale diameter. Two methods have mainly been used to fabricate CNT/polymer composites over the past decade: physical mixing of CNTs with a polymer matrix in solution (solution blending) [1–6] or in melt state (melt blending) [7–10] and in situ polymerization by dispersing CNTs in monomers followed by the polymerization of the monomers [11–14]. These fabrication methods have overwhelmingly focused on improving the dispersion of CNTs in the polymeric matrix, as well as improving the interfacial interaction between the filler and the matrix [15]. Although solution blending can result in a fine dispersion of CNTs by applying high-power ultrasonication [3,16] or surfactants [17–19] and the prepared nanocomposites show markedly enhanced physical properties, this approach is limited to a small number of polymer systems and is not available for industrial scale processing. Melt blending is a more practical and attractive method of producing CNT/polymer composites by mixing CNTs with thermoplastic polymers in the melt state, followed by extrusion or injection molding to fabricate artifacts in the required form. However, the mechanical performance of CNT/polymer composites produced by melt blending is generally limited due to poor dispersion and weak interactions between CNTs and the surrounding matrix [20,21]. Numerous attempts have been made to improve the dispersion of CNTs in polymers in melt state. Focus has typically been on the surface modification and/or functionalization of CNTs in order to improve the compatibility between CNTs and polymer matrix [22–24]. However, pristine CNTs are greatly preferred for preparing CNT/polymer nanocomposites in industrial applications for both cost and environmental reasons.

The dispersion of fillers in a polymer matrix has been reported to be dependent upon the shear stresses exerted on the fillers during melt mixing [25,26]. The shear stress can overwhelm the electrostatic and van der Waals' interactions in the fillers and lead to the breakup of the filler agglomerates.

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This principle should also be applicable to CNT/polymer systems. We have recently developed a high-shear extruder, HSE3000mini. The extruder can reach a maximum screw rotation speed of 3000 rpm. The specially designed feedback-type screw was used to make the sample circulate in the extruder during melt mixing. The high-shear extruder has been successfully used to prepare a novel nano-dispersed polymer blend [27–29]. In this communication, unmodified multi-walled carbon nanotubes have been directly compounded with poly(styrene-*b*-butadiene-*co*-butylene-*b*-styrene) (SBBS) using the high-shear extruder. It is shown that a homogenous dispersion of pristine MWNTs in the SBBS matrix is obtained upon applying high shear on it. The physical properties of the prepared thermoplastic elastomer nanocomposites also depend strongly on the shear rate exerted during melt mixing.

2. Experimental section

2.1. Materials and sample preparation

The SBBS pellets used in this work are commercially available with the grade name of N503. The SBBS contained approximately 30% PS by weight with a mass-average molar mass of 40 000 g/mol. High purity MWNTs (about 95%) were purchased from CNT Co., Ltd. of Korea. The tube diameters were in the range 10–40 nm with lengths of 5–20 μm. SBBS composites containing 3 wt% MWNTs were prepared via a melt-compounding method using the high-shear extruder, HSE3000mini (Imoto, Co. Ltd., Japan). A feedback-type screw was used in this extruder. The *L/D* ratio of the screw was about 1.78. The rotation speed of the screw used in this study was set to be 300 rpm, 1000 rpm, and 2000 rpm and the processed composites were denoted CP300, CP1000, and CP2000, respectively. The melt compounding was carried out at 220 °C for 4 min using the extruder. The compounded samples were then extruded from a T-die. For the mechanical property measurements, all the extruded samples were hot-pressed at 220 °C to a sheet with a thickness of 500 μm, followed by quenching in ice water.

2.2. Structural characterization

The fracture surfaces of the melt-compounded samples were observed by scanning electron microscopy (SEM, Philips XL-20 SEM) at an accelerating voltage of 10 kV. The specimens were immersed in liquid nitrogen for 30 min and fractured. To check the dispersion of MWNTs in the matrix on a large scale, the composites were dissolved in toluene with a concentration of 5 wt%. A drop of solution was cast on a transparent glass slide and directly observed with an optical microscope (Olympus BX51) after the evaporation of the solvent. The thickness of the casting film is about 20 μm. Small-angle X-ray scattering (SAXS) patterns were obtained using microfocused Cu Kα radiation (45 kV, 60 mA) generated by an X-ray diffractometer (Rigaku Ultrax 4153A 172B) and an imaging plate detector. The exposure time was 4 h for each measurement.

Transmission electron microscopy (TEM) was performed using a Hitachi H7000 instrument operating at an accelerating voltage of 75 kV. The composite sample was ultramicrotomed at −120 °C to a section with a thickness of about 70 nm. The sections were then stained using osmium tetroxide (OsO_4) for 12 h.

2.3. Physical property measurements

Tensile tests were carried out according to the ASTM D 412-80 test method using dumb-bell-shaped samples punched out from the molded sheets. The tests were performed using a tensile testing machine, Tensilon UMT-300 (Orientec Co., Ltd.), at a crosshead speed of 50 mm/min at 20 °C and 50% relative humidity. The strain recovery test was performed as follows: after the preset strain (200% elongation) was attained, the crosshead was returned at the same speed as that when stretching until zero stress was reached.

3. Results and discussion

Fig. 1 shows SEM images of the fracture surfaces of the composites prepared under various screw rotation speeds. The bright parts in the images are the MWNTs as a result of their high conductivity. Many MWNT aggregates with sizes ranging from 5 to 50 μm are clearly observed in Fig. 1(a) and few bright dots are seen even under high magnification for CP300. This means that the MWNTs are not well dispersed in the SBBS matrix and most of the MWNTs are stacked together when processed at the screw rotation speed of 300 rpm. Note that the screw rotation speed of 300 rpm is even higher than that of conventional extruders and injection molding machines. The size of the CNT aggregates was significantly decreased to sub-μm scale upon increasing the screw rotation speed to 1000 rpm, as seen in Fig. 1(b). For CP2000, the MWNTs are homogenously distributed in the SBBS matrix without any aggregates. The typical diameter of the bright regions in the SEM image in Fig. 1(c) ranges from 20 to 50 nm, which is consistent with the diameter of a single carbon nanotube, indicating that most of the MWNTs are dispersed in the matrix as individual tubes. It is apparent that the dispersion of pristine MWNTs is greatly improved upon increasing the exerted shear rate and a homogenous dispersion is successfully achieved by using the screw rotation speed of 2000 rpm. It is considered that high screw rotation speed imparts high-shear stresses on the MWNT agglomerates, which may skew the stacks of carbon nanotubes and finally separate them into individual tubes. To check the effects of high screw rotation speed on the scission of CNTs during mixing, a high-magnification SEM measurement was performed, as shown in Fig. 1(d). It was observed that the CNTs maintained a relatively large aspect ratio even though the CNTs were partially embedded in the bulk matrix. Therefore, it is considered that the shortening of CNTs caused by a high-shear rate is not so serious. In addition, the fact that CNTs show a significant reinforcing role for the elastomer (see the following discussion)

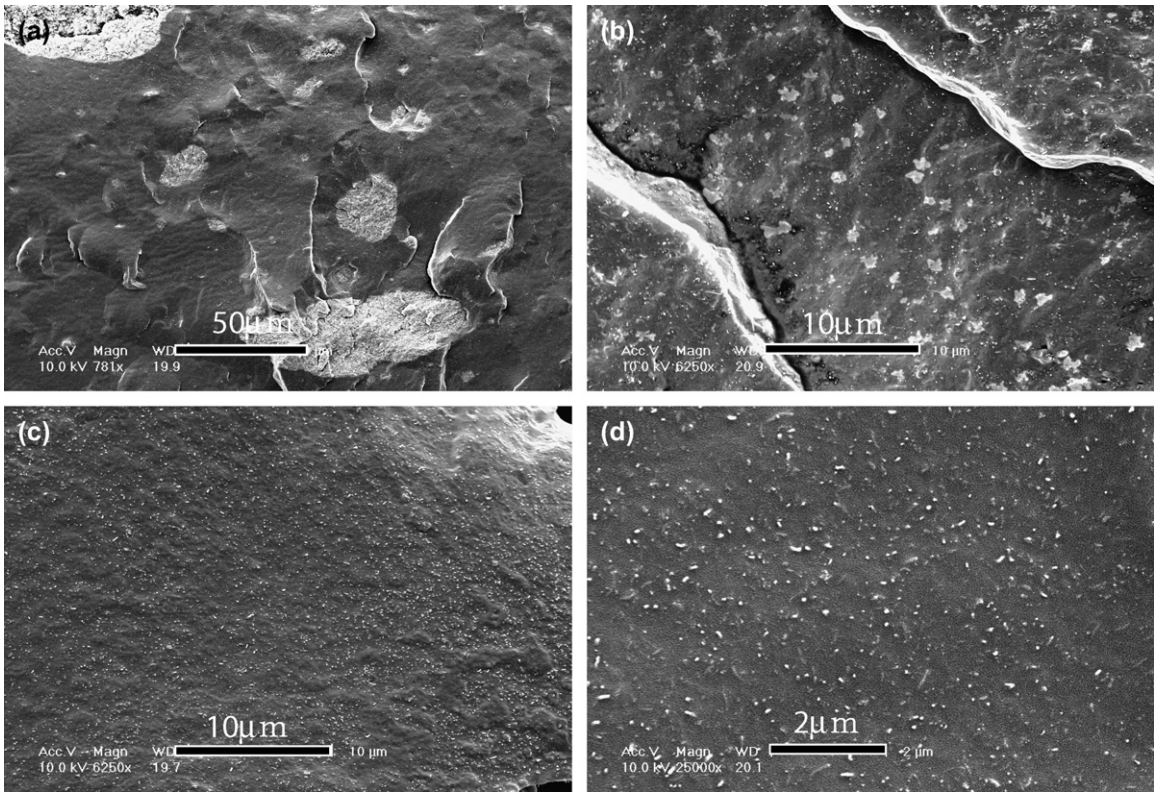

Fig. 1. SEM images for the fracture surface of the MWNT/SBBS composites (a) CP300, (b) CP1000, (c) CP2000 with low magnification, and (d) CP2000 with high magnification.

suggests that the shear rate used did not shorten the CNTs considerably.

The distribution of the nanotubes in the composites was further examined by optical microscopy (OM) to globally observe the dispersion of the nanotubes. Fig. 2 shows OM images of the film casting from a toluene solution of the composites prepared with the concentration of 5 wt%. The black particles are the MWNT agglomerates. An almost transparent film was obtained by casting the toluene solution of CP2000 and no big black particles were observed. In contrast, numerous MWNT particles were found for CP300, indicating the poor dispersion of MWNTs in this sample. Moreover, the toluene solution of CP2000 is very stable. The same OM image as in Fig. 2(c) was obtained after storing the solution for 2 weeks. The OM results are highly consistent with those obtained by SEM.

The neat SBBS used in this work forms a hexagonal-packed cylinder phase structure as a block copolymer with a 30 wt% polystyrene block [30]. It is expected that the homogenous dispersion of nanosized CNTs in the matrix can affect the phase structure of the matrix. Fig. 3 shows that Lorentz-corrected SAXS profiles for the neat SEBS, CP1000, and CP2000. Neat SBBS gives strong multiple scattering peaks with q ratios of $1 : \sqrt{3} : \sqrt{7} : \sqrt{9}$, indicating a typical hexagonal-packed cylinder microstructure. For the nanocomposites with well-dispersed MWNTs, only two scattering peaks are observed. This means that the long-ranged order of the SBBS cylinder structure was disrupted by the addition of MWNTs. On the other hand, it is seen that the strongest scattering peaks shift to a low angle direction upon increasing the screw rotation speed. The effects of the incorporation of nanotubes on the SBBS phase structure are directly observed using TEM, as shown in Fig. 4. The black dots are the dispersed CNTs. It is seen that SBBS forms a highly ordered phase structure in the region far from the CNTs, while only a disordered structure was observed in the region near the CNTs. Both the SAXS and TEM results indicate that the individual carbon nanotubes embedded in the matrix may disturb the phase structure of the matrix polymer. A detailed analysis of the phase structure will be reported in the near future.

Fig. 5 shows the strain–stress curves of the neat SBBS and the composites prepared at different shear rates. The modulus of the all composites is higher than that of the neat SBBS because of the strengthening effects of the inorganic filler. However, the strain–stress behaviors are different for the composites prepared under different shear rates even with the same MWNT loading contents. The modulus of CP2000 is almost the same as that of CP1000, but is higher than that of CP300. The better reinforcement effects of MWNTs in CP2000 than in CP300 are obviously due to the fine carbon nanotube dispersion in it. Moreover, the elongation at break of CP2000 is as high as 917%, which is also much larger than the value (628%) for CP300. The lower elongation at break for the low shear processed sample can again be attributed to the poor dispersion of MWNTs in the polymer matrix. The existence of MWNT aggregates (shown in Fig. 1(a)) may decrease the elongation of nanocomposites.

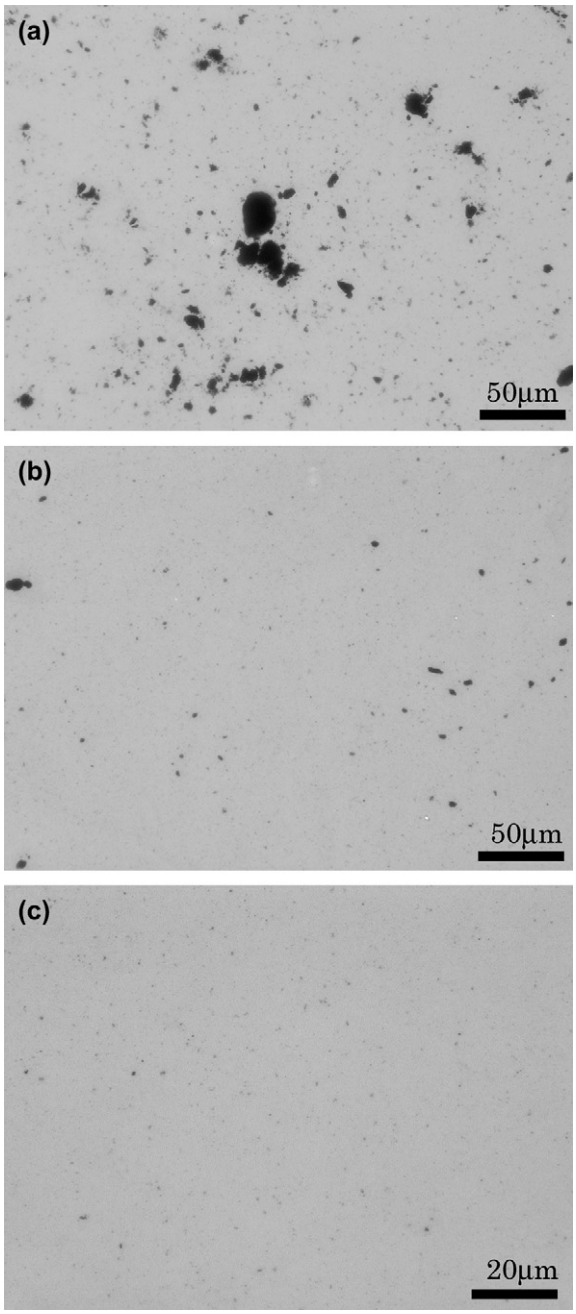

Fig. 2. Optical micrographs of the film casting from toluene solutions of MWNT/SBBS composites (a) CP300, (b) CP1000, and (c) CP2000.

Elasticity is very important for thermoplastic elastomer composites. Fig. 6 presents the stress–strain recovery behavior of the neat SBBS and the composites prepared at different shear rates. The neat SBBS shows excellent elastic recovery with a residual strain of about 20.3%. The best MWNT dispersion composites (CP2000) processed at a high-shear rate yield a slightly higher residual strain of about 22.6%. However, the residual strain for the composites processed under low shear is 34.4%, indicating the deteriorated elasticity of the composites.

The mechanical properties of the neat SBBS and the composites are listed in Table 1. The mechanical properties of the composites depend greatly on the screw rotation speed during processing. The difference in these properties can be attributed to the different dispersion states of MWNTs in the SBBS matrix. A higher screw rotation speed results in better carbon nanotube dispersion in the matrix, leading to the improved physical properties.

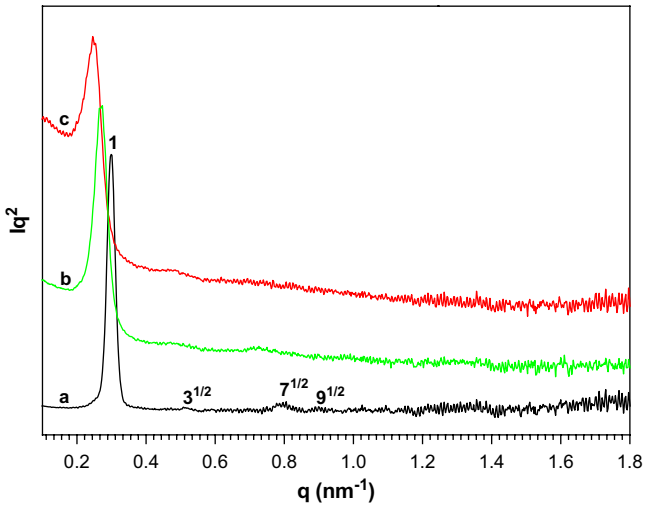

Fig. 3. Lorentz-corrected SAXS profiles of (a) neat SBBS, (b) CP1000, and (c) CP2000.

4. Summary

The effects of screw rotation speed on the dispersion of pristine MWNTs in a SBBS matrix have been investigated. The dispersion is significantly improved upon increasing the screw rotation speed. A homogenous dispersion was achieved when the screw rotation speed was 2000 rpm. Mechanical tests show that the tensile modulus, tensile strength and elasticity of the composites with fine CNT dispersion processed at a high-shear rate are much higher than those of the composites

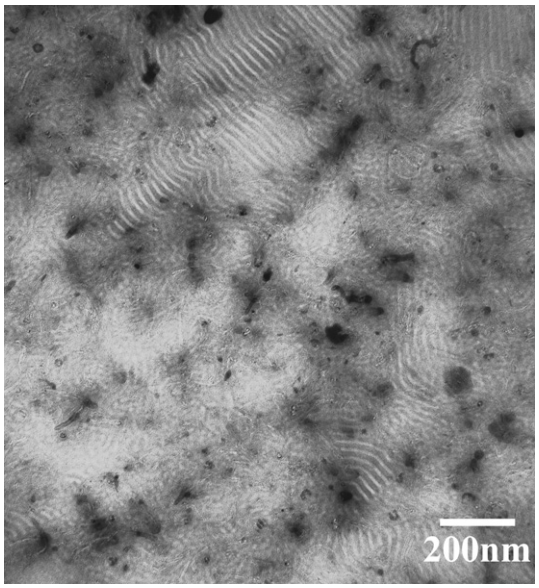

Fig. 4. TEM image of CP2000.

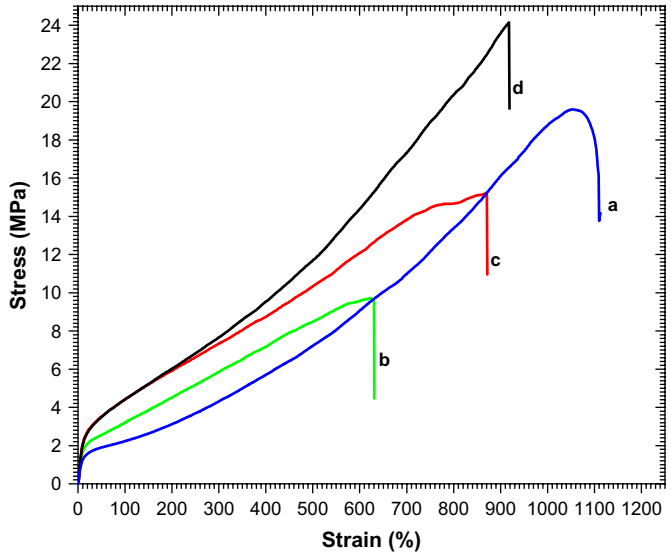

Fig. 5. Stress–strain curves of (a) neat SBBS, (b) CP300, (c) CP1000, and (d) CP2000.

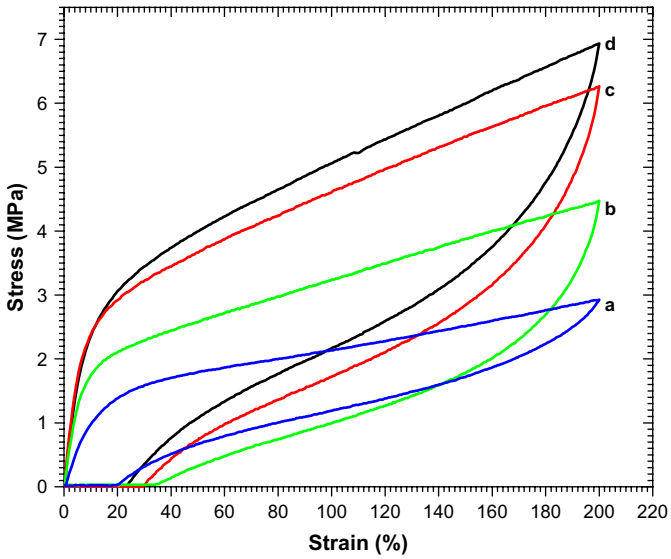

Fig. 6. Strain recovery curves of (a) neat SBBS, (b) CP300, (c) CP1000, and (d) CP2000.

Table 1
Summary of mechanical properties of neat SBBS and its nanocomposite processed at various screw shear rates containing 3 wt% unmodified multiwalled carbon nanotubes

	Modulus (MPa)	Elongation at break (%)	Strength (MPa)	Residual strain (%)
Neat SBBS	12.50	1108	19.59	20.34
CP300	14.31	628	9.45	34.41
CP1000	23.74	870	14.99	30.22
CP2000	25.31	917	24.08	22.63

processed at a low shear rate. The results indicate that high-shear processing is an effective method of improving the dispersion of unmodified CNTs in a polymer matrix. Detailed investigations on the effect of the adding MWNTs on the microphase separated structure and the strengthening mechanism are still in progress.

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