Properties of Surface-Modified Multiwalled Carbon Nanotube Filled Poly(ethylene terephthalate) Composite Films

Sang Hyun Jin,[1] Kwan Han Yoon,[1] Young-Bin Park,[2] Dae Suk Bang[1]

[1]*Department of Polymer Science and Engineering, Kumoh National Institute of Technology, 1 Yangho-dong, Gumi, Gyeongbuk 730–701, Korea*
[2]*Department of Industrial and Manufacturing Engineering, Florida Agricultural and Mechanical University - Florida State University College of Engineering, 2525 Pottsdamer Street, Tallahassee, Florida 32310–6046*

ABSTRACT: Poly(ethylene terephthalate) (PET)/multiwalled carbon nanotube (MWCNT) composites were prepared by *in situ* polymerization. To improve the dispersion of MWCNTs in the PET matrix, functionalized MWCNTs having acid groups (acid-MWCNTs) and acetic groups (acetic-MWCNTs) on their surfaces were used. The functional groups were confirmed by infrared spectrometry. Scanning electron microscopy showed that acetic-MWCNTs had a better dispersion in the PET matrix than pristine MWCNTs and acid-MWCNTs. A reaction between PET and acetic-MWCNTs was confirmed by a shift of the Raman G band to a higher frequency and an increase of the complex viscosity in the rheological properties. The composites containing functionalized MWCNTs showed a large increase in their tensile strengths and moduli. The values of the strengths and moduli of the PET/acetic-MWCNT composites were higher than those of the PET/acid-MWCNT composites. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1163–1168, 2008

Key words: mechanical properties; nanocomposites; polyesters; reinforcement; rheology

INTRODUCTION

Carbon nanotubes (CNTs) have attracted much attention worldwide because they show superior physical and electrical potentials, which allow them to be applied to hydrogen storage,[1] chemical sensors,[2,3] nanoelectronic devices,[4,5] and flat-panel field-emission displays.[6] CNTs have been also used as extremely strong nanoreinforcements for composites, which possess extraordinarily high strength with low weight and moderate electrostatic discharge properties.[7] However, the application of CNTs for composites has been largely hampered by their poor dispersion in polymer resins and weak interfacial bonding with polymer matrices.[8] To achieve optimal enhancement of the properties of CNT/polymer composites, chemical modification of the CNT surface has been used. The compatibilities of CNTs and carbon nanofibers in organic solvents, aqueous solutions, or polymeric matrices have been enhanced by covalent attachment to nylon,[9] amino-terminated polyimide,[10] aminopolymer poly(pionylethylenimine-co-ethylenimine),[11,12] tethered pyrene,[13] diamine-terminated oligomeric poly(ethylene glycol),[14] and poly (vinyl alcohol).[15] Over the past decade, the use of as-received CNTs and carbon nanofibers as reinforcement in polymer matrices (in fiber, film, or bulk form), such as polypropylene,[16,17] poly(ethylene terephthalate) (PET),[18] and epoxy,[19] has gained popularity and has led to some success in the enhancement of the mechanical properties while not adversely affecting composite processing. More recently, the influence of the functionalized CNTs on the properties of poly(methyl methacrylate),[20] epoxy,[21] polyamide 6,[22] polyimide,[10,23] and PET[24] has been studied. These results indicate that functionalization leads to good dispersion in the polymer matrix and show improved mechanical properties due to the improved interaction between the functionalized nanotubes and the polymer matrix.

In this study, PET/multiwalled carbon nanotube (MWCNT) composites were prepared by *in situ* polymerization. To improve the dispersion of MWCNTs in the PET matrix, the purification and functionalization of the MWCNTs were carried out. After the acid treatment of MWCNTs, further functionalization was performed with acetic anhydride. The reaction between PET and functionalized MWCNTs was confirmed by examination of the rheological properties, Raman spectra, and scanning electron microscopy

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(SEM). The mechanical properties, including the initial modulus and tensile strength, of the composite films were measured.

EXPERIMENTAL

Materials

The MWCNTs used in this work were manufactured by a Chemical Vapor Deposition process and were supplied from Iljin Nanotech Co. (Seoul, Korea) (purity > 97%, length = 10–50 μm, diameter = 10–20 nm). Dimethyl terephthalate and ethylene glycol (EG) were obtained from SK Chemical Co. and Dae-Jung Co., (Shiheung, Korea) respectively. The catalyst used was titanium isopropoxide.

Preparation of the functionalized MWCNTs

Pristine MWCNTs were mixed with nitric acid for 5 min and then sonicated for 1 h. The mixture was refluxed for 12 h at 110°C. MWCNTs having acid groups (acid-MWCNTs) were obtained by the washing and filtration of the mixture with distilled water. The acid-MWCNT solution was mixed again with acetic anhydride at room temperature. The mixture was reacted vigorously after 5–10 min. The unreacted acetic anhydride was removed from the reaction mixture with distilled water. The obtained solution was quenched at −84°C for 6 h and then dried in a freeze drier for 5 days. The obtained product was MWCNTs with acetic groups (acetic-MWCNTs). The reaction procedure is shown in Figure 1.

Preparation of the PET/MWCNT composites

PET/acid-MWCNT and PET/acetic-MWCNT nanocomposites were prepared by *in situ* polymerization. The acid-MWCNTs and acetic-MWCNTs prepared were first mixed with EG and then sonicated for dispersion. In a small-scale batch reactor, 100 g of dimethyl terephthalate, 65 g of EG mixture containing 1 g of MWCNTs, and catalyst were mixed. This mixture was first heated to 190°C in a silicone oil bath. This temperature was maintained for 2 h. The temperature was then increased to 210°C where it was maintained for 2 h. The reaction temperature

Figure 1 Schematic representation of the formation of acid-MWCNTs and acetic-MWCNTs.

was progressively increased to 280°C. Then, the pressure was reduced to a specified level and maintained for 0.5–1 h. The pure PET and PET/pristine MWCNT nanocomposites were also prepared by the same method for comparison. The solution viscosity values of PET and the composites ranged from 0.70 to 0.76 dL/g with the MWCNT content.

Measurements

The infrared spectra of pristine MWCNT, acid-MWCNT, and acetic-MWCNT were recorded with a Fourier transform infrared (FTIR) spectrometer (FTIR-300E, Jasco, Tokyo, Japan). The Raman spectra were obtained with a Fourier transform Raman instrument (Bruker FRA 106/S, Ettlingen, Germany). The excitation source was an argon laser with a wavelength of 1064 nm. Dynamic rheological measurements were performed with a rotational rheometer (TAARES, New Castle, DE). The measurements were carried out in an oscillatory shear mode with parallel plate geometry. Before any measurement, all samples were allowed to relax at the measuring temperature for 2 min and were then sheared at a low shear rate (0.01 s^{-1}) for 3 min under a nitrogen atmosphere. Frequency sweeps were performed from 0.1 to 100 rad/s. The morphology of the nanocomposites was examined by SEM (S-4300, Hitachi, Tokyo, Japan). The mechanical properties were measured with an Instron model 4467 universal instrument (Norwood, OH). The measurements were made at room temperature at a constant crosshead speed of 2 mm/min. Data were taken as averages of at least five measurements.

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR is a typical method for characterizing chemically modified CNTs. The FTIR spectra of pristine MWCNTs, acid-MWCNTs, and acetic-MWCNTs are shown in Figure 2 The peaks at 1721 and 1176 cm^{-1} were in correspondence to C=O, C—O stretching, respectively, which indicated the existence of carboxyl groups in the acid-MWCNTs. The same peaks in the acetic-MWCNTs were observed, which indicated the existence of carboxyl groups remaining after the reaction with acetic anhydride. The peak at 3000–2800 cm^{-1} corresponded to sp^3 C—H stretching, which indicated the existence of —CH$_3$ on the surface of the MWCNTs.

SEM morphology

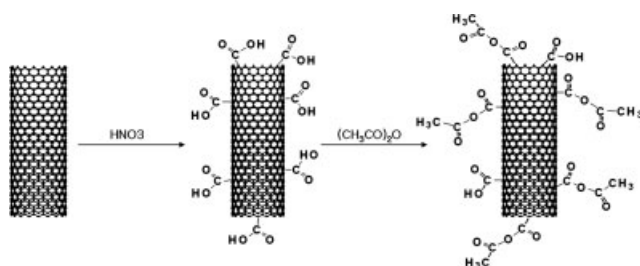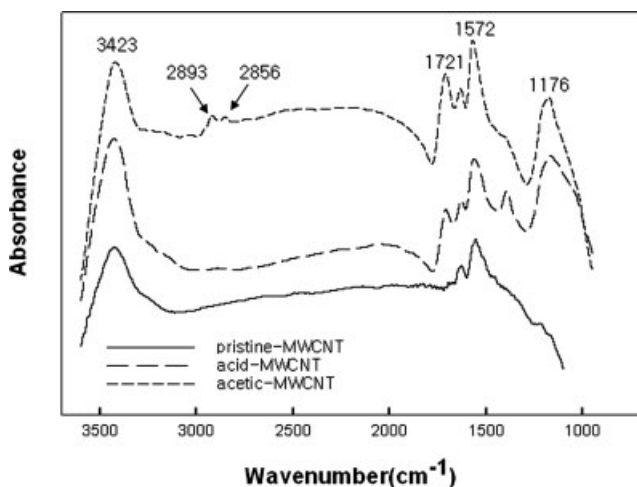Figure 3 shows the SEM images of pristine MWCNTs, acid-MWCNTs, and acetic-MWCNTs.

Figure 2 FTIR spectra of pristine MWCNTs, acid-MWCNTs, and acetic-MWCNTs.

Because of van der Waals interactions, the pristine MWCNTs were aggregated and curved. The acid-MWCNTs were cut into relatively short-length aggregates in the loser state after the treatment with nitric acid. In contrast to acid-MWCNTs, acetic-MWCNTs were aggregated, again, not as much as pristine MWCNTs after the reaction between acid-MWCNTs and acetic anhydride. The lower degree of aggregation in functionalized MWCNTs was due not only to the functional groups such as carboxyl and acetic but also their shorter lengths.

PET and PET/pristine MWCNT, PET/acid-MWCNT, and PET/acetic-MWCNT nanocomposites were prepared by *in situ* polymerization, and the solution viscosity values ranged from 0.70 to 0.76 dL/g with the MWCNT content. Figure 4 shows the SEM images of PET/pristine MWCNT, PET/acid-MWCNT, and PET/acetic-MWCNT composites; each contained 0.5 wt % of each MWCNT. In the PET/pristine MWCNT nanocomposites, the MWCNT aggregates were inhomogeneously dispersed in the PET matrix. Most MWCNTs were pulled out from the PET matrix. In contrast to pristine MWCNT, acid-MWCNT pullout was minimal. This phenomenon occurred by the increased interfacial bonding between the acid-MWCNTs and the PET matrix because of the carboxyl groups formed by acid treatment. The increased interfacial interaction was evident in PET/acetic-MWCNT nanocomposites, which resulted in the wetting of the acetic-MWCNTs into the PET matrix. We believe that the acid and acetic groups on the surface of the acid-MWCNTs and acetic-MWCNTs, respectively, may have reacted with PET during the *in situ* polymerization, which resulted in good dispersion of the acid-MWCNTs and acetic-MWCNTs.

Raman spectroscopy

Figure 5 shows the Raman spectra of PET/pristine MWCNT, PET/acid-MWCNT, and PET/acetic-MWCNT
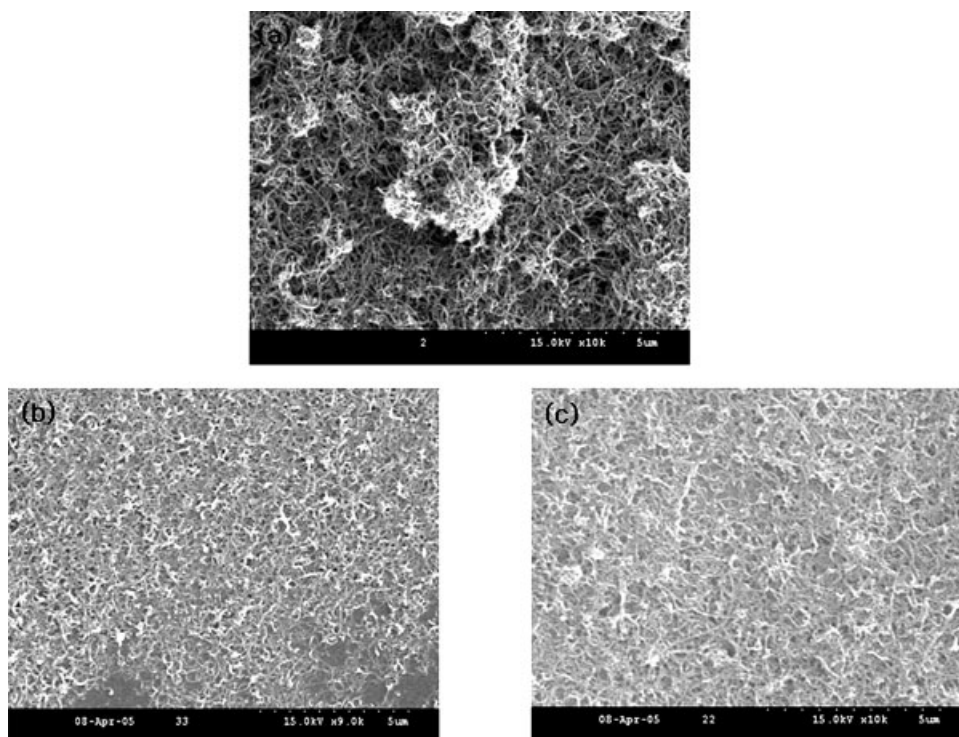

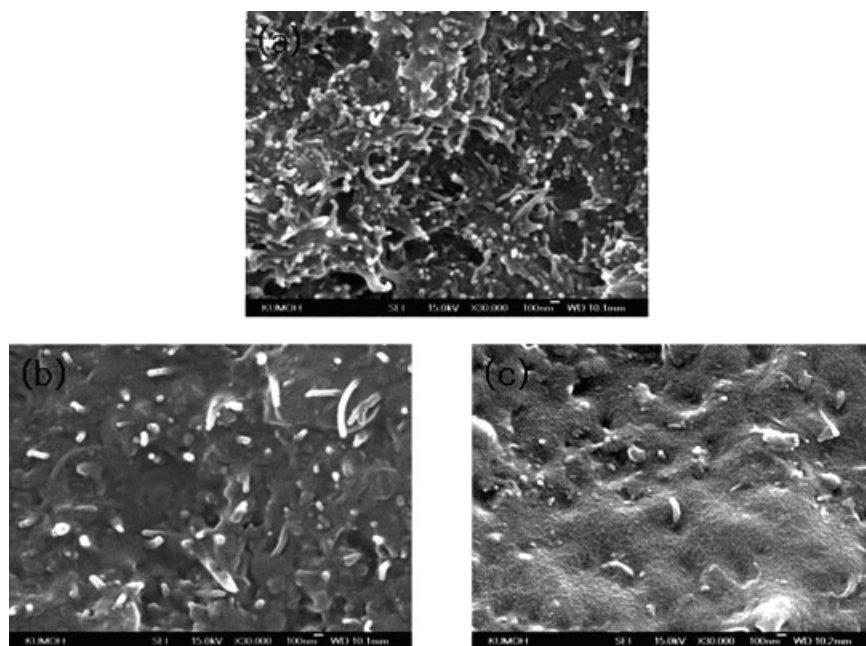**Figure 3** SEM images of (a) pristine MWCNTs, (b) acid-MWCNTs, and (c) acetic-MWCNTs.

Figure 4 SEM images of (a) PET/pristine MWCNT, (b) PET/acid-MWCNT, and (c) PET/acetic-MWCNT composites containing 0.5 wt % MWCNTs.

composites. Raman spectroscopy was used to investigate the interfacial interaction between the PET matrix and MWCNTs. The composites displayed two characteristic peaks, the first at 1286 cm^{-1} assigned the D band and derived from disordered graphite structures and the second centered at 1608 cm^{-1} assigned the G band. In contrast to the acid-MWCNT composite, the acetic-MWCNT composite showed a shifting of the G-band peak by 10 cm^{-1} to a higher frequency due to the disentanglement of acetic-MWCNTs, which resulted in the dispersion in the PET matrix as a consequence of polymer penetration into the CNT bundles during *in situ* polymerization.

Rheological properties

The frequency dependence of the shear storage modulus (G'), loss modulus (G''), and complex viscosity are shown in Figure 6 The values were measured at 265°C. It was clear that the addition of pristine MWCNT, acid-MWCNTs, and acetic-MWCNTs to PET led to an increase in the complex viscosity. However, the magnitudes of the viscosity enhancements were quite different. The PET/acetic-MWCNT nanocomposite showed the highest viscosity among all of the nanocomposites. This was due to the higher degree of agglomeration for the pristine MWCNTs and acid-MWCNTs compared to the acetic-MWCNTs. The effect of nanotubes on viscosity was most pronounced at low frequencies, and the relative effect diminished with increasing frequency

due to shear thinning. It is well known that the interconnected structures of anisometric fillers result in a plateau region in log G' versus log G'' plots at low frequencies. Only the acetic-MWCNT composites showed a plateau region, which indicated that the reaction between PET and the acetic-MWCNTs occurred more than in the other composites.

Mechanical properties

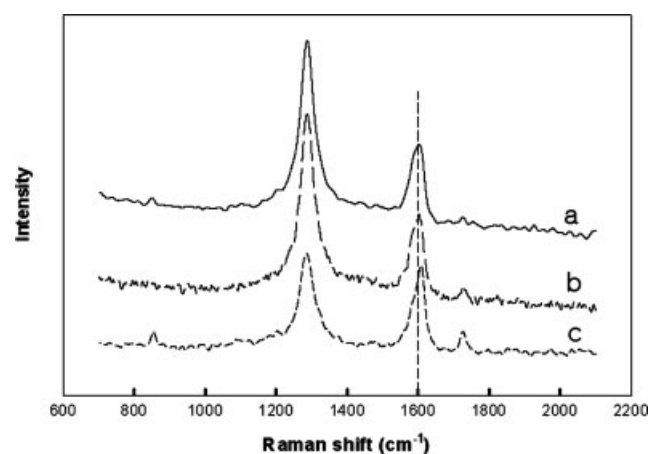Figure 7 shows the tensile strengths and moduli of PET, the PET/pristine MWCNT, PET/acid-MWCNT,

Figure 5 Raman spectra for (a) PET/pristine MWCNT, (b) PET/acid-MWCNT, and (c) PET/acetic-MWCNT composites.
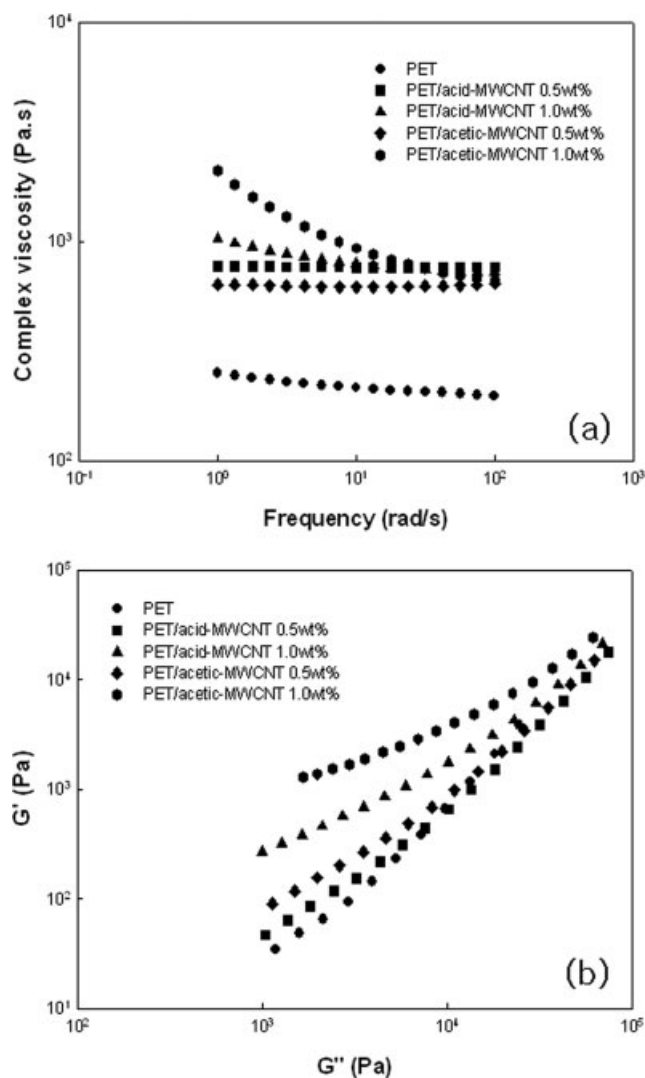
Figure 6 (a) Complex viscosities and (b) plot of log G' versus log G'' for PET and PET/pristine MWCNT, PET/acid-MWCNT, and PET/acetic-MWCNT composites with respect to frequency.

MWCNTs in the PET matrix, the purification and functionalization of the MWCNTs were carried out. After the acid treatment of MWCNTs, further functionalization was performed with acetic anhydride. We expected that carboxylic and acetic groups on the external walls and the end caps of functionalized MWCNTs participated in the reaction during polymerization, which resulted in good dispersion in the PET matrix. The increased interfacial interaction between the functionalized MWCNTs and the PET matrix were observed by SEM, Raman spectroscopy, and rheological property measurement. The increases in the complex viscosity, tensile strength, and modulus values of the PET/functionalized MWCNT composites in comparison with PET/pristine MWCNT resulted from the MWCNT–matrix reaction despite the damage and shortening of MWCNTs introduced by the acid treatment.
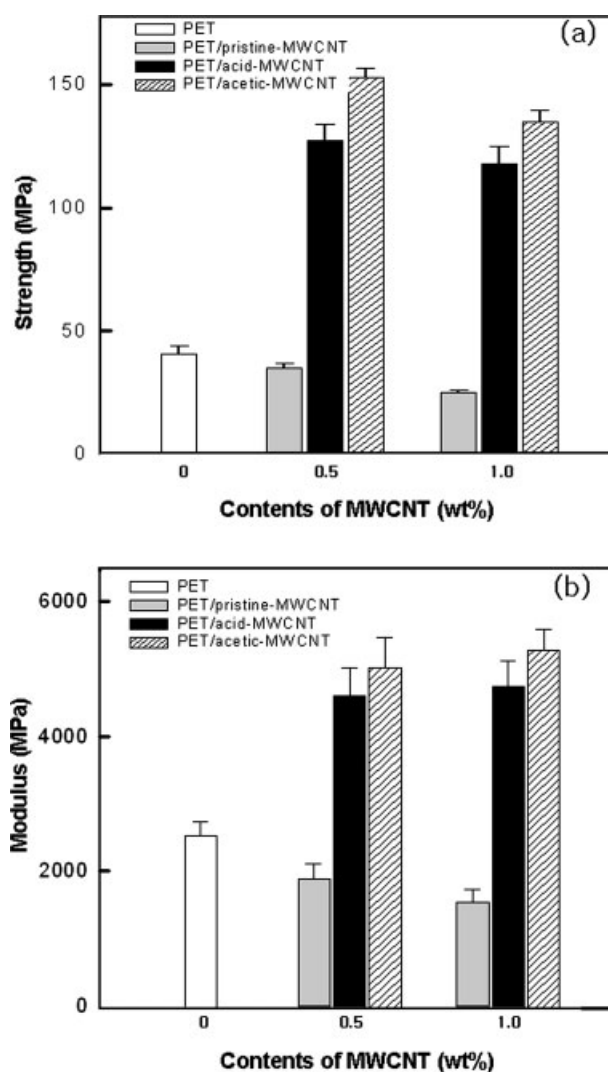
and PET/acetic-MWCNT composites. In the case of PET/pristine MWCNTs, both the tensile strength and modulus decreased with the MWCNT content. However, the composites containing functionalized MWCNTs showed significant increases in the tensile strength and modulus. The values of the strength and modulus of the PET/acetic-MWCNT composite were larger than those of the PET/acid-MWCNT composite, which was due to the better dispersion of acetic-MWCNTs due to the high reactivity between PET and the acetic-MWCNTs.

CONCLUSIONS

PET/MWCNT composites were prepared by *in situ* polymerization. To improve the dispersion of

Figure 7 (a) Strength and (b) modulus of PET, PET/pristine MWCNT, PET/acid-MWCNT, and PET/acetic-MWCNT composites with MWCNT content.

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