Surface Modification of Kevlar by Grafting Carbon Nanotubes

Wei Chen,[1] Xin-Ming Qian,[1] Xue-Qiu He,[1] Zhen-Yi Liu,[1] Ji-Ping Liu[2]

[1]State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, People's Republic of China
[2]School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, People's Republic of China

ABSTRACT: A novel and efficient method was developed for surface-modification of Kevlar fibers by multi-wall carbon nanotubes (MWCNTs). Kevlar fibers were immersed in a solution mixed with Hexamethylene diisocyanate, 1,4-diazabi-cyclo [2,2,2] octane (DABCO), and toluene to introduce pendant amine groups before the COCl-functionalized carbon nanotubes were chemically grafted onto the surface of modified fibers under ultrasonic condition. The characterization of resulting fiber involved in SEM, infrared spectroscopy, and tensile measurement. Results indicated over 20% of the fiber surface were coated by MWCNTs even after washing, which indicated a good adhesion. Furthermore, the mean value of tensile strength of Kevlar fiber was improved by 12% compared with original one. And the interlaminar shear strength (ILSS) of the fiber-reinforced bis-maleimides composite was increased by 30%. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1983–1990, 2012

Key words: fibers; nanocomposites; surfaces; mechanical properties

INTRODUCTION

Kevlar fiber is a good candidate for the reinforcement for polymer composites owing to its low density and high specific strength. However, because of high crystallinity, the surface of Kevlar fiber is chemically inert and smooth, thus its adhesion with resin matrix is poor.[1] Therefore, to use Kevlar fiber as reinforcement, surface modification is essential to enhance its reinforcing effect. In the literature, there are three approaches of surface-modification for Kevlar fiber: (a) coating with coupling agents or physical and chemical treatment to form chemical bonding with resins on the surface of the fiber[2–4]; (b) roughening the surface of the fiber to enlarge the physical interface with the resin matrix, and thus effects the mechanical anchoring[5–8]; (c) chemical activation of the fiber surface.[9–12]

However, extensive research[1,13–15] had shown that though these surface modification could to some extent increase the adhesion strength between Kevlar and a particular resin matrix, the surface and even the interior structure of Kevlar fiber would be inevitably damaged in various ways during the treatment, such as fibril splitting or breaking of macromolecular chain, leading to a decline in mechanical performance. Therefore, it is of great significance to find a way that can improve both the surface activity and mechanical properties of Kevlar fiber. O'Connor et al.[16] reported a novel method for the preparation of new, reinforced Kevlar-nanotube composites that were prepared by swelling commercially available Kevlar 129 fibers in suspensions of nanotubes in the solvent N-methylpyrrolidone (NMP). Nanotube uptake of up to 4 wt % had been observed, resulting in significant mechanical enhancement of the fibers. Moreover, a web-like deposit of nanotubes on fiber surface was also observed, which provided a possibility for the improvement of surface activity of Kevlar as the abundant polar groups in the open ends of nanotubes could help to strengthen the adhesion between fibers and resin matrix. Unfortunately, due to the weak bonding, most of these nanotubes were easily washed away in the following clean process, and only a few could remain on the fiber surface.

Herein, this article presents a novel and efficient method for surface-modification of Kevlar fibers by grafting carbon nanotubes: Kevlar fibers were immersed in a solution mixed with Hexamethylene diisocyanate, 1,4-diazabi-cyclo [2,2,2] octane (DABCO), and toluene to introduce pendant amine groups, and then the COCl- functionalized carbon nanotubes dispersed in NMP solution were chemically grafted to the surface of modified fibers under ultrasonic condition. The adhesion between fibers and nanotubes can be greatly enhanced in this way
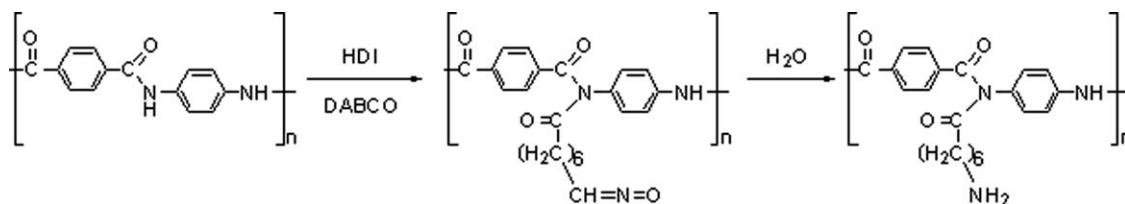
Scheme 1 Introduction of pedant amino groups to surface of Kevlar.

and the influence of COCl content of nanotubes to the grafting effect was discussed. Moreover, to investigate the mechanical properties and surface activity of the new Kevlar-MWCNTs composite materials, tensile test and single fiber pullout experiments were also carried out.

EXPERIMENTAL

Materials

Aramid 1414 (Kevlar) yarns were obtained from Yantai Spandex, China. The tensile strength of fiber is 3.4 GPa. Multi-walled carbon nanotubes (purity: 95%, length: 5–15 μm) were purchased from Shenzhen Nanotech Port, China. Hexamethylene diisocyanate (98%) and 1,4-diazabi-cyclo [2,2,2] octane (DABCO, 98%) were purchased from Sigma Chemical, USA. Bismaleimides resins were kindly provided by Beijing Institute of Fashion Technology.

Pretreatment of Kevlar fibers

Kevlar fibers were treated before proceeding different surface-modification methods. The fibers were pretreated with 1,2-dichloroethane, methanol, and distilled water for 24 h in sequence in a Soxhlet extraction apparatus, then dried it in a vacuum oven at 120°C for another 12 h.

Functionalization of MWCNTS

MWCNTs were treated in $3M$ HNO_3 at 60°C for 8 h followed by refluxing in $5M$ HCl at 120°C for 6 h.[17] The obtained MWCNTs were filtered and washed with a large amount of water, and then vacuum-dried at room temperature for overnight. The acid-treated MWCNTs were reacted with an excess $SOCl_2$ for 24 h under reflux conditions. The residual $SOCl_2$ was removed by reduced pressure distillation in conjunction with a liquid nitrogen trap to yield the acyl chloride functionalized MWCNTs (MWCNT-COCl). XPS was used to assess whether the acyl chlorination of MWCNTs had occurred as expected.

Introduction of pedant amino groups

This part of work mainly employed the approach of Chou and Penn.[18] Briefly, the Kevlar fibers, which had been washed according to the schedule described above, were immersed in a mixed solution with Hexamethylene diisocyanate and DABCO in a ratio of 100 : 1 to provide side groups. The obtained fibers were then placed in a flask which contained water and trace of DABCO to accomplish introduction of pedant amino group. After reaction, the fibers were rinsed in distilled water and then placed in a Soxhlet apparatus and extracted for 2 h with water. Finally, the fibers were placed on aluminum foil and dried at room temperature under vacuum for 24 h. The fibers obtained were expected to have pendant amine groups. The reaction was illustrated as Scheme 1.

Graft of carbon nanotubes to fiber surface

Functionalized MWCNTs were dispersed in NMP solution in a vessel by applying ultrasound using an ultrasonic generator (TCQ250). The MWCNTs concentration was set at 1mg mL^{-1} for the purpose of ensuring complete graft and standardizing experiment procedure. The fibers obtained above were then immersed into the solution and reacted for 1 h under ultrasonic condition (Scheme 2).The subsequent fibers were rinsed in distilled water and extracted with water in a Soxhlet apparatus for 2 h, and vacuum dried on aluminum foil for 24 h at room temperature. The fibers obtained were expected to have grafting MWCNTs.

Surface analysis of the fiber

The fibers were examined with a JOEL-4700 scanning electron microscope (SEM). Infrared spectroscopy (Avatar 360) was performed on the fibers after introducing pendant amino group and grafting MWCNTs, respectively. Fibers were placed over a card window and the transmission spectrum recorded with 1024 accumulations of 8-s exposures. The infrared radiation would be more highly absorbed if it passes through the center of the fibers than the edges, since there was a large path length
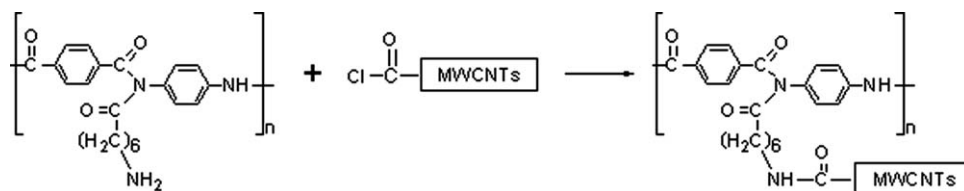
Scheme 2   Graft of carbon nanotubes to fiber surface.

within the material in the case of the former. Thus the spectra will reflect the chemistry of the surface more than the core of the fibers. A TFS-2000 ToF SIMS which had a pulse gallium ion source operated at 30 keV was used to further assess whether the amination of fiber surface had occurred as expected, the secondary ions were accelerated to 5 keV by applying a bias to the sample. To prevent the sample charging, pulsed electron flooding was used.

Preparation of the model composites

Bismaleimides resin was used to fabricate fiber composite material. Briefly, bismaleimides resin was pressed to thin circle sheets with 8-mm diameter and put inside a silicon rubber mold, which was thread by a single fiber. The obtained composite material was fixed in a mold fit for single fiber composite material and cured in vacuum drying oven by following the procedure: 115°C/25 min → 180°C/2 h → 200°C/4 h. The embedding depth could be controlled lower than 1 mm by adjusting the thickness of resin. Pullout force measurements of single fiber was made using Instron 1122 tensile tester at a cross-head speed of 2 mm min^{-1}.

Interlaminar shear strength

The interfacial adhesion between Kevlar fibers and resin was represented by interlaminar shear strength (ILSS) of a composite. The ILSS was calculated according to

$$ILSS = F/\pi DL$$

where F is the Pullout force, D is the diameter of fiber, L is embedding length.

RESULTS AND DISCUSSION

Functionalization of MWCNTS

Acyl chloride functionalization of MWCNTs was confirmed by XPS survey scan. The peaks for carbon, oxygen, and chloride are centered at around 284.30, 532.20, and 201.40 eV. After the acylation reaction with $SOCl_2$, carboxyl groups on MWCNTs surfaces were converted to acyl chloride groups. As shown in Figure 1(c), there is a noticeable presence

of Cl elements with a concentration of 3.33%. From the curve fitting of the Cl 2p peak area, the bonding energy at 201.40 and 199.80 eV, which are assigned to Cl $2p_{1/2}$ and Cl $2p_{3/2}$ respectively, indicates that the presence of Cl are in the form of C—Cl bond.

MWCNTS mass uptake against grafting time

According to O'Connor et al.,'s study,[16] soaking in NMP induces porosity in the Kevlar, allowing nanotube infiltration. Thus actually the nanotube mass uptake (expressed as nanotube mass fraction) was attributed by two parts: the internal nanotubes of the fibers and the nanotubes grafted on fiber surface. Figure 2 shows the effect of various soak time on the nanotubes mass fraction. The mass uptake was found to vary from 1.5 to 8.8 wt % and the maximum value appeared at about 70 min. Noticeably, there was little change for nanotubes mass fraction after 50 min. While the intercalation of nanotubes into the Kevlar fibers is diffusion-limited,[19] it is unlikely to reach saturation of the mass uptake just in 1 h according to a previous study.[16,20] The most reasonable explanation for this is that owing to the amido bonding interaction, most parts of the fiber surface can be coated by nanotubes in 50 min to form a web-like "barrier," which would prevent any further infiltration.

The influence of CO-Cl content on fiber modification

Considering that the CO-Cl content of MWCNTs could affect its reactivity and the grafting effect on fiber surface, several nanotube samples with various CO-Cl content were made by altering the acidizing time to investigate the influence of CO-Cl content on grafting effect. The samples with 2, 4, and 8 h HNO_3 refluxing and then thionyl chloride treatment were denoted as MWCNTs2, MWCNTs4, and MWCNTs8, respectively. And the sample treated with 4 h HNO_3 refluxing (MWCNTs0) was used as the reference substance. The CO-Cl contents were given by element analysis (Table I). From Table I, the CO-Cl content on MWCNTs increased gradually with oxidation time and a fraction of up to 4.03% was observed for MWCNTs8. It should be pointed out that over oxidation might cause MWCNTs' collapse
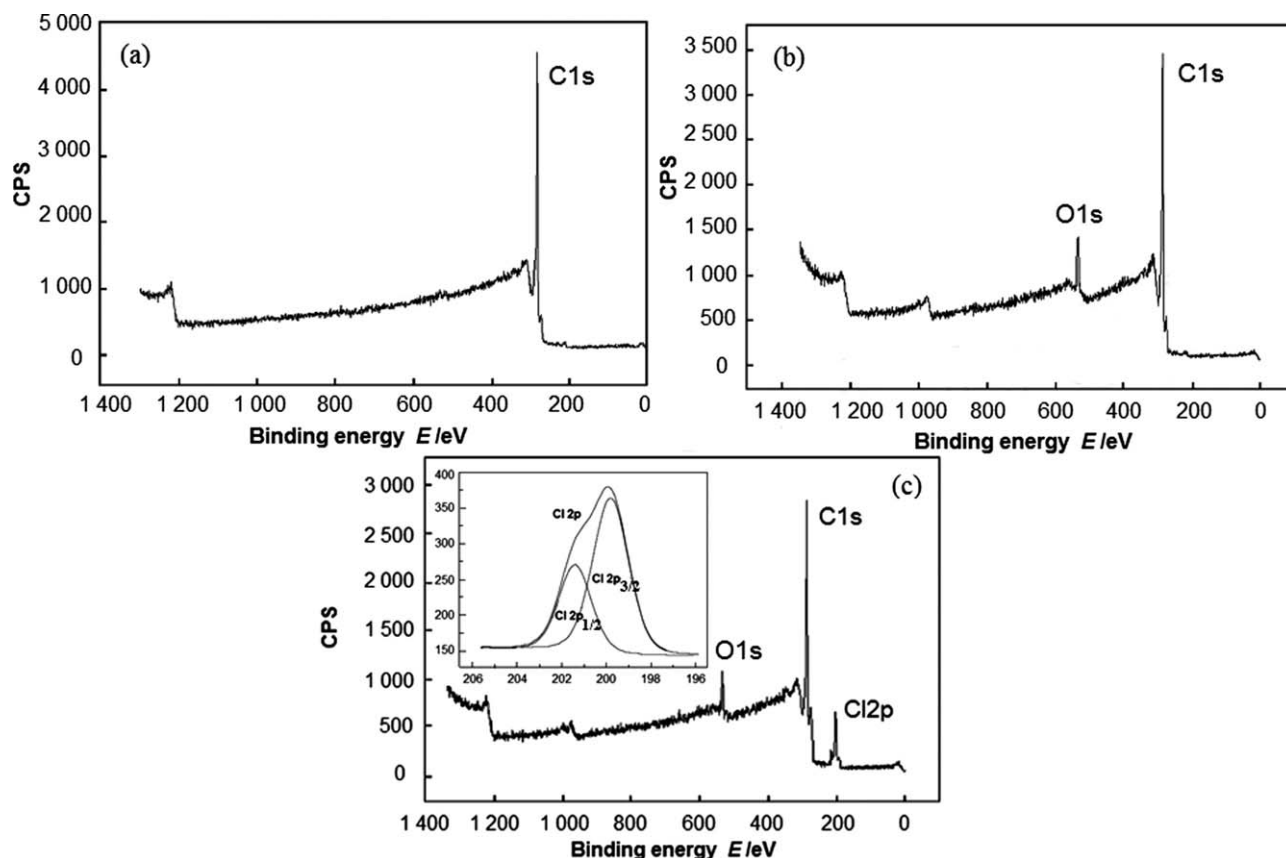
Figure 1 XPS wide scan spectra of: (a) raw MWCNTs, (b) MWCNTs after acid treatment, (c) MWCNTs after acylation reaction with SOCl$_2$.

and produce carbon species in the form of carboxylated carbonaceous fragments,[21] which will cause a significant decrease in COOH contents. Thus it is impossible to further increase the CO-Cl contents simply by prolonging the oxidation time. From the
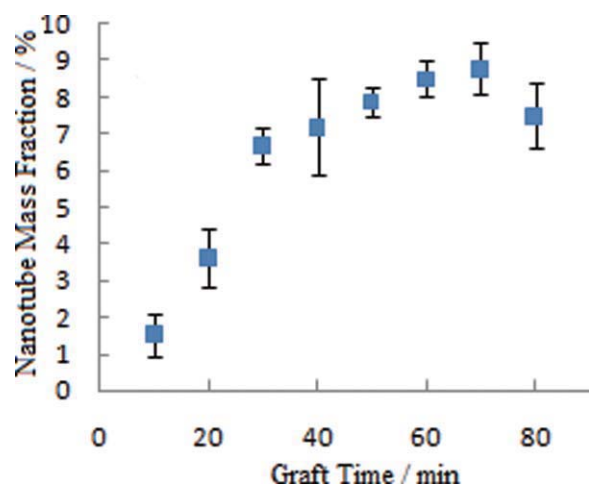
SEM photos [Fig. 3(d–g)], although the tube amount of MWCNTs4 [Fig. 3(f)] on fiber surface is indistinguishable from that of MWCNTs8 [Fig. 3(g)], it is clear that better grafting effect can be obtained with the increase of CO-Cl content on MWCNTs. And an overall impression about the MWCNTs (2.36% CO-Cl content) grafted Kevlar yarns can be obtained from Figure 4. Furthermore, Figure 5 shows the effect of various CO-Cl content of MWCNTs on the nanotube mass fraction, and the grafting time was set to 50 min. From Figure 5, surprisingly there is no apparent difference in average nanotube mass uptake despite the vast difference in grafting effect observed from SEM photos, which indicates that the increased weight is mainly attributed to the nanotubes infiltrating inside the fibers.

Figure 2 Graph of nanotube mass uptake (expressed as nanotube mass fraction) as a function of time swelling in MWCNTs suspension. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Element Analysis of MWNTs with Various CO-Cl Contents

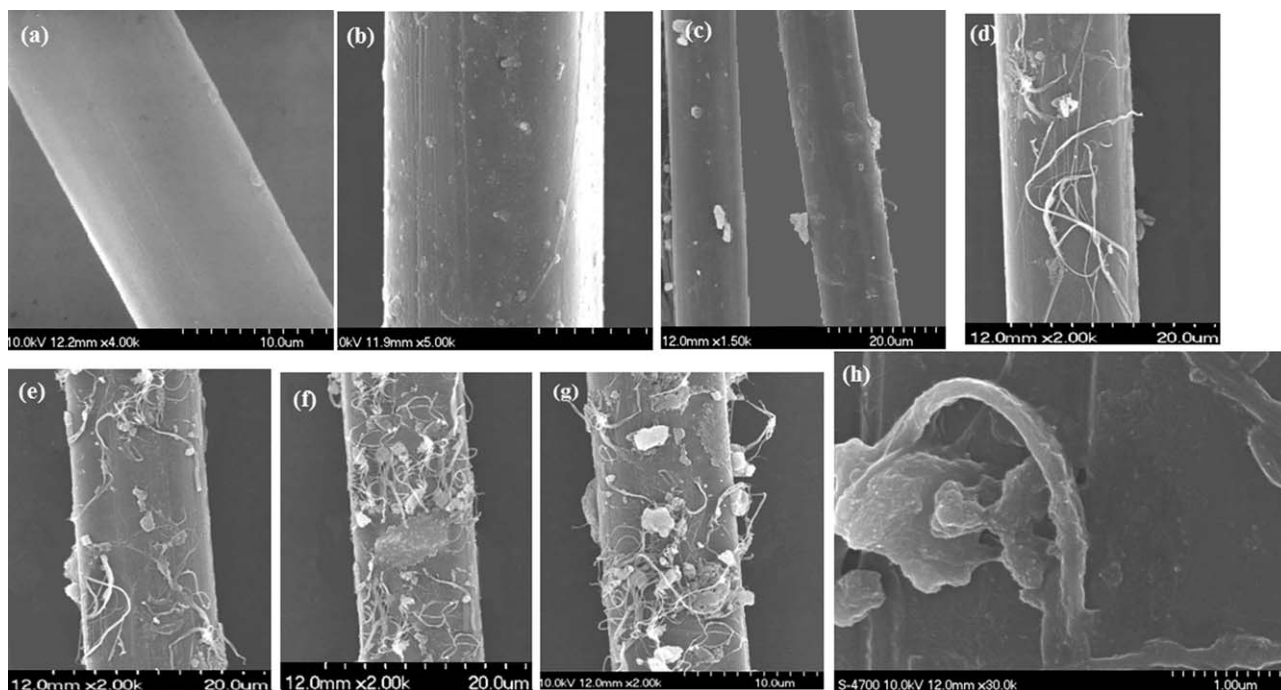| Sample	C (%)	O (%)	Cl (%)
MWNTs0	85.48	11.18	0
MWNTs2	88.46	6.35	0.91
MWNTs4	84.09	9.60	2.36
MWNTs8	81.48	10.70	4.03

Figure 3 SEM image of Kevlar fiber as-supplied (a) and after attaching amine groups to the fiber surface (b) and after treatment in 1 mg mL^{-1} MWCNTs suspension in NMP (c) and after grafting MWCNTs with 0% (d), 0.91% (e), 2.36% (f), 4.03% (g) CO-Cl content and at a magnification of 30,000 after grafting MWCNTs (h).

Mechanical performance after grafting

The yarns with various nanotube mass fractions were used for mechanical testing. Mechanical measurements were made on 10 individual fibers extracted from each of the treated yarns (five groups in all). These fibers were typically about 12 μm in diameter and were mounted in tensile tester with the aid of glue. In all cases the stress–strain curves (not shown) were linear, demonstrating brittle failure. From these stress–strain curves, we can obtain three mechanical parameters: Young's modulus, Y; tensile strength, σ_B; strain at break, ε_B; these data are shown as function of nanotube mass fraction in Figure 6(a–c). The 0 wt % curve is for untreated Kevlar fibers. For each mechanical property, both mean values, with standard deviations (closed squares), and maximum observed values (open squares) are plotted. No significant increase (significance level 0.05) in the mean values of either the Young's modulus or the strain at break is observed. In fact, hypothesis testing shows that the data set for Young's modulus and strain at break are statistically indistinguishable (significance level 0.01) for all mass fractions. However, there is a real increase in mean strength from 3.4 GPa for the Kevlar fiber to 3.82 GPa for the 7.2
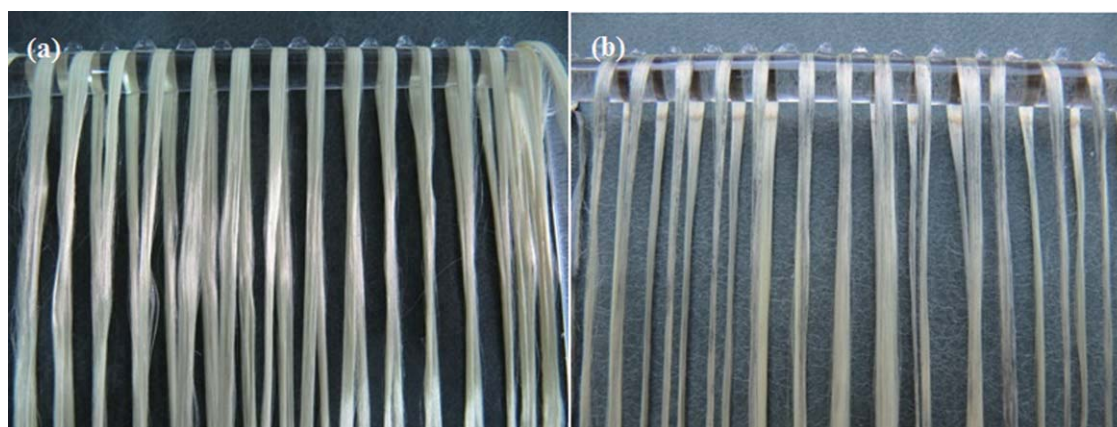

Figure 4 Photograph of Kevlar yarns as-supplied (a) and after grafting MWCNTs (2.36% CO-Cl content). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
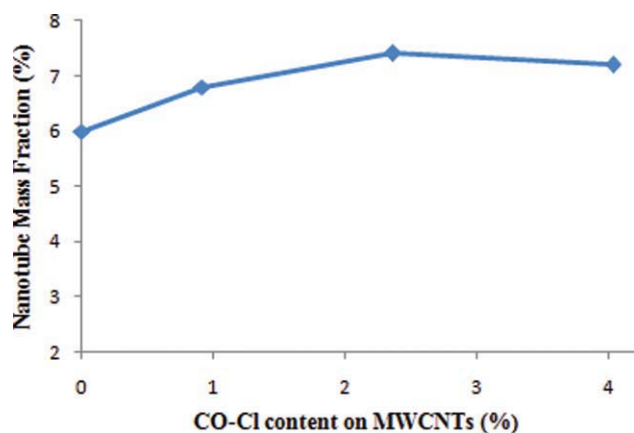
Figure 5 The effect of various CO-Cl content of MWCNTs on the nanotubes mass fraction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wt % composite fiber despite the substantial error bars. Hypothesis testing shows that for strength, both the 7.2 and 7.9 wt % data are statistically distinguishable from the pure Kevlar data (significance level 0.01). Moreover, extensive tests showed that the mean strength of fibers was decreased to 3.2 GPa after amination pretreatment, so actually the mean strength was increased by 19% for the 7.2 wt % composite fiber, and the improvement of mechanical properties should be attributed to the nanotubes infiltrating inside the fibers.[16] Furthermore, it is the maximum observed values that are of most interest as these represent the ultimate mechanical properties that are potentially achievable. The observed increases compared to the Kevlar-only fibers, were (maximum values only): strength, 3.9–4.5 GPa (7.2 wt %); Young's modulus, 76.6–84.1 GPa (7.2 wt %); strain at break, 6.6–7.1% (1.5 wt %).

Surface analysis of the fibers

ToF-Sims spectrum

Figure 7 shows positive ion SIMS spectra obtained from the fibers before [Fig. 7(a)] and after [Fig. 7(b)] the reaction to introduce amine pendant groups. A fragment with a mass of 18 amu (ND_2) was expected to be present and small pea can be observed in this position in the spectra taken after treatment [Fig. 7(b)] which is not present in the SIMS spectrum obtained before treatment [Fig. 7(a)]. Although this is also the position where water would be expected, the samples were stored for 24 h under vacuum at room temperature before analysis and so it is unlikely that there would be a significant amount of water present. Thus the analysis of the fiber surface suggests that the chemical reaction to introduce pendant amine groups was successful.

SEM analysis

Figure 3(a) is the SEM image for original Kevlar fiber, the surface of which is very smooth. Figure
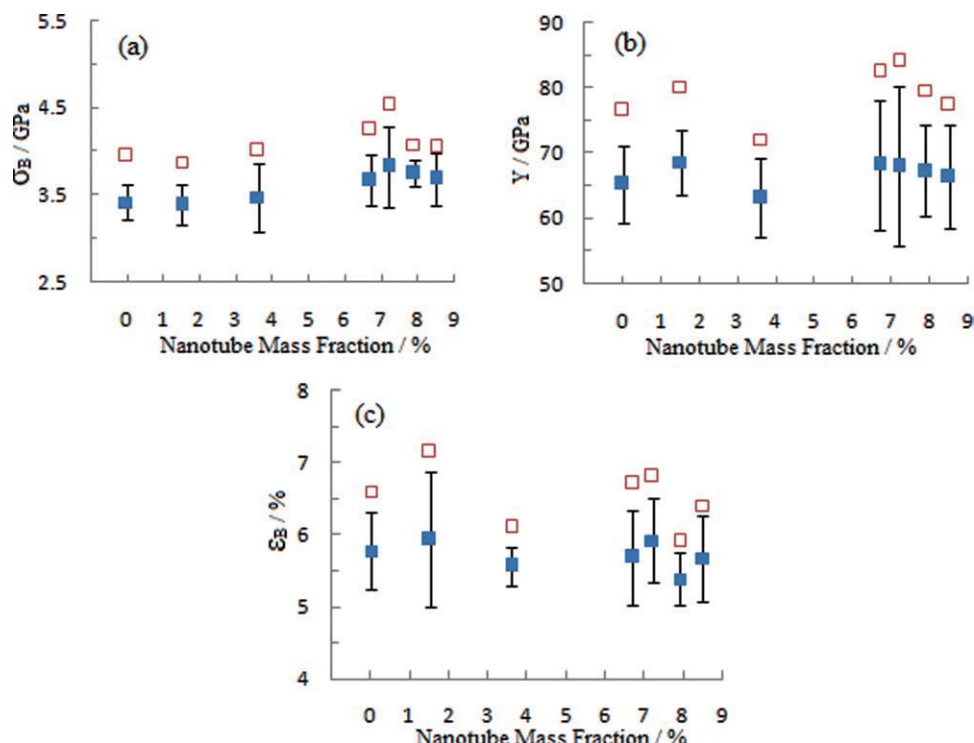

Figure 6 Strength (a), Young's modulus (b), strain at break (c) as functions of mass fraction for nanotubes in Kevlar fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
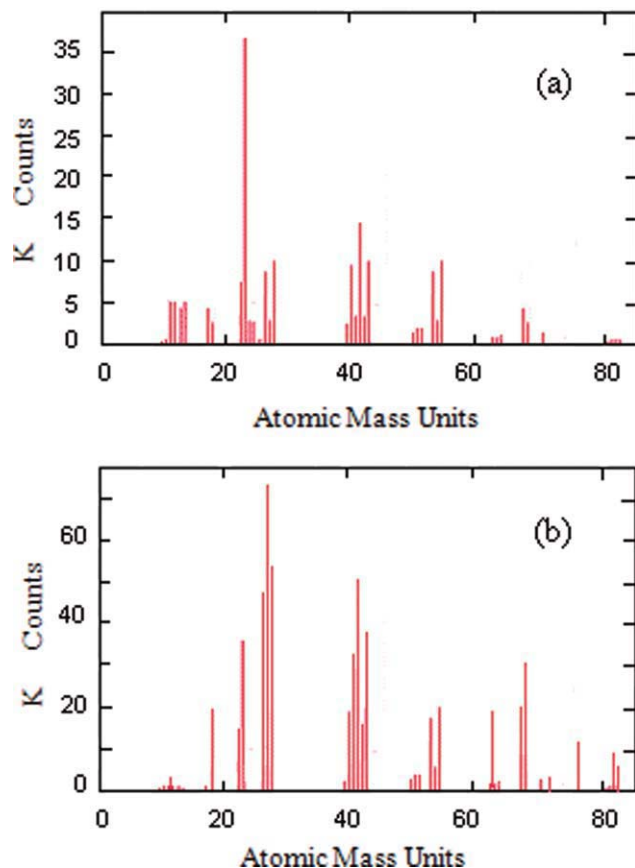
Figure 7 Positive ion ToF-SIMS spectrum from the surface of fibers following the scouring treatment (a) and the reactions to introduce pendant amine groups (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

3(b) is the SEM photo for Kevlar fiber after attaching amine groups to the surface, and the surface become a little rough. To determine the influence of amination pretreatment to grafting effect, swelling of original Kevlar fibers in nanotube suspensions without amination pretreatment [Fig. 3(c)] were also performed. From the Figure 3(c), most of carbon nanotubes were scoured away after washing because of the weak bonding with fiber, only few carbon nanotubes can remain on the fiber surface. In contrast, by grafting strategy, over 20% of the fiber surface can be coated by carbon nanotubes even after washing [Fig. 3(f,g)]. In addition, a proportion of individual carbon nanotubes can be observed which indicates a good dispersing performance in the solution. Figure 3(h) shows the MWCNTs were tightly bonded to fiber surface rather than simply deposited, which further demonstrates the efficiency of the grafting strategy used.

Infrared spectroscopy analysis

Figure 8(a) shows the infrared spectra of Kevlar fibers after scoured. Figure 8(b) shows the infrared spectra of fibers after amination pretreatment, the peak associated with primary amine in the Kevlar backbone at 3340 and 1530 cm^{-1} are of lower intensity in the treated fibers; Figure 8(c) is the infrared spectra of fibers after grafting of nanotubes. The peak around 3572 cm^{-1} is assigned to the O—H stretching vibration whereas the peak of the respective bending vibration can be found at 1430 cm^{-1}. The peak at 1730 cm^{-1} can be assigned to a C=O stretch vibration. Both the O—H and C=O groups were introduced by oxidized MWCNTs. The peak around 1768 cm^{-1} implied that the MWCNTs had been chemically bonded to the fiber surface through amido link.

Effect of grafted carbon nanotubes on ILSS

The effects of grafting MWCNTs on the interfacial adhesion between Kevlar and bismaleimides resin are illustrated in Figure 9. Figure 9(a,b) show the variation regularity for pullout force and ILSS against fiber embedding length, respectively. As amination treatment on fiber surface had been proved to be an efficient way for improvement of interfacial adhesion with resin matrix, it is unsurprising that the ILSS of fiber can be increased by 12% for 0.2-mm embedding length after introducing pedant amino groups. Specifically, the maximum ILSS for fibers with grafted MWCNTs (7.2 wt %) appears at 0.32 mm rather than 0.2 mm as expected. This might result from the fact that the MWCNTs distribution on individual fibers differ from each other. However, for the same embedding length, both pullout force and ILSS of fibers with grafted MWCNTs are higher than that of fibers with pedant amino groups, which demonstrates that the grafted MWCNTs is more efficient for improvement of interfacial adhesion than amino groups. Furthermore,
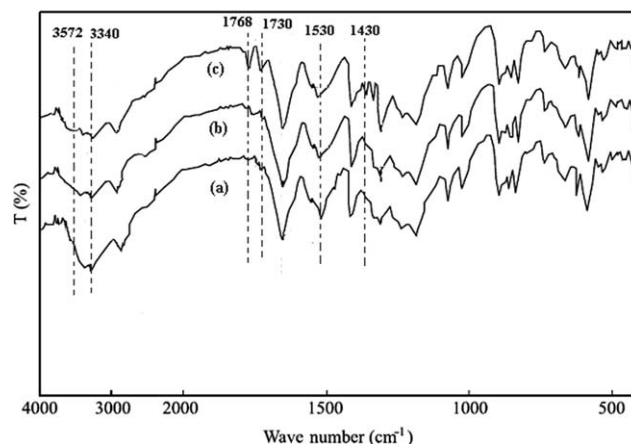

Figure 8 Infrared spectra of fibers as-supplied (a) and after the chemical modification to attach amine groups to the surface of fibers (b) and after grafting MWCNTs (c).
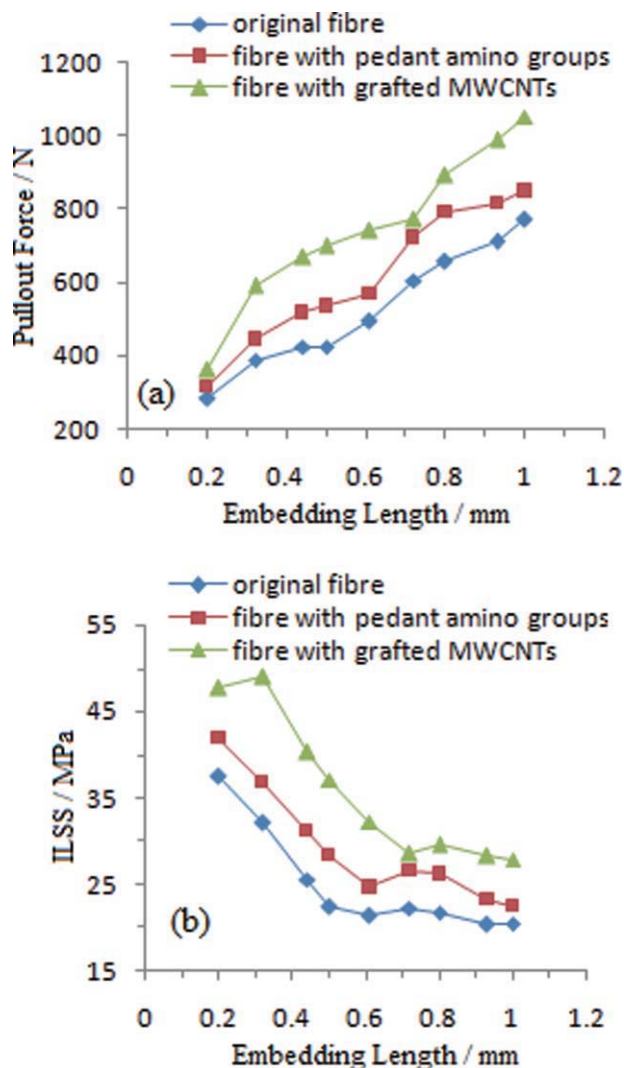
Figure 9 Pullout force (a) and ILSS (b) of the fiber composites against embedding length. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compared with original fibers, the best observed ILSS was improved from 37.5 to 49.1 MPa after grafting MWCNTs.

CONCLUSIONS

In conclusion, a new approach for surface modification of Kevlar fibers was developed using carbon nanotubes. For the fabricated Kevlar-MWCNTs composite material, mean value of tensile strength and best observed value of interlaminar shear strength were increased by 12 and 30%, respectively, compared with original fibers. Our new approach of grafting nanomaterials to surface of polymer macromaterials could be expanded and utilized for other polymer materials. We believe there will be many possible important applications for this new technique.

References

1. Lee-Sulivan, P.; Chian, K. S.; Yue, C. Y. J Mater Sci Lett 1994, 13, 305.
2. Lin, T. K.; Kuo, B. H.; Shyu, S. S. J Adhes Sci Technol 1999, 13, 545.
3. Day, R. J.; Hewson, K. D.; Lovell, P. A. Compos Sci Technol 2002, 62, 153.
4. Wu, G. M.; Hung, C. H.; You, J. H. J Polym Res 2004, 11, 31.
5. Wu, J.; Cheng, X. J Mater Sci 2005, 40, 1043.
6. Mukherjee, M.; Das, C. K.; Kharitonov, A. P. Polym Compos 2006, 27, 205.
7. Guo, F.; Zhang, Z. Z.; Liu, W. M. Tribol Int 2009, 42, 243.
8. Zhang, H. J.; Zhang, Z. Z.; Guo, F. J Appl Polym Sci 2009, 114, 3980.
9. Zhao, J. C.; Fan, G. N.; Guo, Z. A. Sci China Ser B Chem 2005, 48, 37.
10. Fan, G. N.; Zhao, J. C.; Zhang, Y. K. Polym Bull 2006, 56, 507.
11. Ai, T.; Wang, R. M.; Zhou, W. Y. Polym Compos 2007, 28, 412.
12. Li, J.; Ye, F. B. Plast Rubber Compos 2010, 39, 264.
13. Benrashid, R.; Tesoro, G. C. Text Res J 1990, 60, 334.
14. Wu, S. R.; Sheu, G. S.; Shyu, S. S. J Appl Polym Sci 1996, 62, 1347.
15. Lin, J. S. Eur Polym Mater 2002, 38, 79.
16. O'Connor, I.; Hayden, H.; Coleman, J. N. Small 2009, 5, 466.
17. Kim, H. S.; Myung, S. J Mol Cryst Liq Cryst Sci Technol 2008, 492, 385.
18. Chou, C. T.; Penn, L. S. J Adhes 1991, 36, 125.
19. Vahdat, N.; Sullivan, V. D. J Appl Polym Sci 2001, 79, 1265.
20. Fiory, A. T.; Martin, S.; Schneemeyer, L. F. Phys Rev B Condens Matter 1988, 38, 7129.
21. Yu, H.; Jin, Y. G.; Peng, F. J Phys Chem C 2008, 112, 6758.