利用界面活性劑分散奈米碳管製備超高導電率之聚亞醯胺混成薄膜

Surfactant-assisted dispersion of polyimide/multi-walled carbon nanotube nanocomposites films with ultrahigh electrical conductivity

葉珮綺 [1]、余信佩 [1]、黃奕嘉 [2]、曾怡享 [3]、蔡美慧 [1*]

Pei-Ci Ye[1]、Hsin-Pei Yu[1], Yi-Chia Huang[2], I-Hsiang Tseng[3], and Mei-Hui Tsai[1*]

[1] 國立勤益科技大學化工與材料工程系
[1] Department of Chemical and Materials Engineering,
National Chin-Yi University of Technology
E-mail*：tsaimh@ncut.edu.tw
[2] 國立交通大學材料科學與工程系
[2] Department of Materials Science and Engineering
National Chiao Tung University
[3] 逢甲大學化工系
[3] Feng Chia University
Department of Chemical Engineering
E-mail：ihtseng@fcu.edu.tw

摘要

　　一種簡單的方法來分散和穩定高負載的多壁奈米碳管(CNTs)於聚亞醯胺（PI）中。用原位聚合法合成了 PI / CNT 複合薄膜。FTIR 證明了表面活性劑並沒有妨礙聚合 PI。實驗結果表明，透過超音波震盪處理溫度為 60℃ 時，CNT 的分散效果顯著改善。因此，奈米碳管含量 40 wt.%時 PI/CNT 的導電性增加至 41.5 S/cm。

關鍵字詞：聚亞醯胺、奈米碳管、界面活性劑

Abstract

　　A facile approach to disperse and stabilize high loading of multi-walled carbon nanotubes (CNTs) in polyimide (PI) matrix is presented. PI/CNT nanocomposite films were synthesized by in situ polymerization of pyromellitic acid dianhydride (PMDA) and 4,4'-oxydianiline (ODA) in N,N'-dimethyl acetamide (DMAc) with the presence of various amounts of CNTs and the surfactant polyvinylpyrrolidone (PVP) and sodium dodecyl benzene sulfonate (SDBS). The FTIR spectroscopy proved that the surfactant did not hinder the polymerization of PI. The experimental results showed that the dispersion of CNT was significantly improved by increasing the ultrasonication temperature to 60 ^{o}C. Accordingly, the electrical conductivity of PI/CNT was increased to 41.5 S/cm for the hybrid film containing 40 wt% of CNT.

Keywords: polyimide、CNT、surfactant

1. Introduction

Polyimides (PI) are widely used in the microelectronics industry, such as flexible circuit boards, photoresist or dielectric interlayers in integrated circuits, aligning films at liquid crystal displayers [1-3].

Carbon nanotubes (CNT) have motivated many interesting fields of the research since S. Ijima initially identified the structures of CNT in 1991 [4]. CNTs have excellent mechanical [5], electrical [6], thermal properties [7], high surface area [8] and excellent chemical stability [9, 10].

Although CNT shows excellent properties but the processing of polymer/CNT nanocomposites is a crucial problem. Mnay groups have made efforts in PI/CNT nanocomposites and have reported achievements in the improvement of mechanical and electrical properties [5, 6, 11-13]. More effort is required to find methods to increase the amount of CNT with dispersed efficiently in PI/CNT nanocomposites. The well-dispersion of CNT is important for the formation of the uniform

distribution of the CNT network in the PI composites. It is a big challenge for CNT well-dispersed in polymers. Because of van der Waals forces of CNTs [14], CNTs tend to aggregate into clusters, bundles and stick together in the composites. Furthermore, poor processability, bad workability and low solubility of CNT limit applications and performances of PI/CNT nanocomposites. Compared with the chemical modification of the surface of CNT, a surfactants will not damage the inherent properties of the CNT but is likely to increase the wetting of CNT in composites Several approaches have been developed to overcome the difficulties of debunding or dispersing well in solvents with surfactants [15, 16]. Polyvinylpyrrolidone (PVP) wraps around the micelle aggregates formed by sodium dodecyl sulfonate (SDS) in water [17]. Sodium dodecyl benzene sulfonate (SDBS) and PVP interaction showed the same result in the presence of CNTs [16]. The dispersion of CNTs is also related with the type of solvent, DMAc is a good solvent for CNT dispersing. The improved dispersion of CNT in DMAc was explained by the alkyl amide group for interaction with CNTs that is why hydrophobic CNT are wetted by the organic solvent and some bundles were separated by DMAc [18].

In this paper, we used PVP and SDBS as the surfactants DMAc as solvent. Moreover, we found good dispersion of CNT with higher temperature. The surfactant-assisted in situ polymerization of PI/CNT with high CNT content is reported.

2. Experimental

2.1. Materials

The multi-walled carbon nanotubes (CNTs) with a purity of 99.5%, a diameter of 40-90 nm, a length of longer than 10 μm and an aspect ratio higher than 100 were acquired from Golden Innovation Business Co., Ltd (Taiwan). 4,4'-Oxydianiline (ODA) from Taimide Tech. Inc. (Taiwan) was used without pretreatment. Pyromellitic dianhydride (PMDA) provided by Taimide Tech. Inc. (Taiwan) was recrystallized from acetic anhydride prior to use. N,N-dimethylacetamide (DMAc) from Sigma-Aldrich was dried over night through molecular sieves. The surfactants, sodium dodecyl benzene sulphonate (SDBS, 95%, Tokyo Chemical Industry Co., Ltd) and poly-vinylpyrrolidone (PVP, Mw = 10000, Sigma-Aldrich) were used as received.

2.2 Preparation of pure PI films

A typical batch to synthesize pure PI was first to dissolve ODA (0.3829 g) in DMAc (19.2 g) in a flask. Equimolar PMDA was then added to the above solution. The polymerization reaction was kept at room temperature for 2 h to produce a poly(amic acid, PAA) solution. The resulting PAA solution was transformed into PI by step-wise thermal imidization to 300 °C.

2.3. Preparation of PI/CNT nanocomposite

The preparation procedure of PI/CNT hybrid films is shown in Fig. 1. The surfactants, SDBS and PVP with a relative weight ratio of 12:1, were mixed in the DMAc using ultrasonic treatment for 15 min.[19] Subsequently, the CNTs were dispersed in the solution containing DMAc and surfactants and treated in an ultrasonic bath at room temperature (RT) or 60 °C for 2.5 h. At the same time, ODA was added into surfactant-treated CNT solution with ultrasonic treatment keep at 60 °C and RT with stirring continued until the ODA dissolved completely in the surfactant-treated CNT solution. Equimolar amounts of PMDA were added into the flask and the mixture was stirred for a further 4 h. Then, a precursor (poly(amic acid), PAA) was prepared. A series of precursors of PAA with theoretically calculated contents of CNTs in the nanocomposites were synthesized with the same PAA solid content of 4%. The PAA/CNT dispersions were cast onto aluminum plate, which were heated on a hot at 80 °C. Subsequently, step curing (at temperatures of 80, 150, 170 and 300 °C for 1 h) was conducted to form PI/CNTs nanocomposite. The sample are encoded H-PI−X and R-PI-X, where X stands for the weight percentage of CNT in each sample, H is CNTs were dispersed in the solution containing DMAc and surfactants and treated in an ultrasonic bath at 60 °C(heat), R is room temperature (RT) dispersed it. The photos of PI/CNT composite films show in Fig. 1 H-PI-40 remains good flexibility.

2.4. Measurements

Fourier transform infrared (FTIR) spectra of pure PI, PI/CNTs nanocomposites were employed by using a Fourier transform infrared spectrophotometer (Nicolet, Protégé-460). Field emission scanning electron microscopy (FE-SEM, JEOL JSM-7401F) was acquired to observe the fractured morphology of samples. Transmission electron microscopy (TEM, Hitachi, H-7100) images were observe the morphology of samples. TEM samples were prepared by placing several

drops of pristine CNT suspension or surfactants coated CNT dispersion in DMAc on a carbon-coated copper grid and drying at room temperature. In order to determine the thermal stability of films, thermal gravimetric analysis (TGA) was performed with a thermal gravimetric analyzer (TA Instruments, Q500) under N_2 using a heating rate of 20 ℃ min^{-1} from 30 ℃ to 800 ℃ for pure PI and PI/CNT nanocomposites. The electrical conductivities of the pure PI and PI/CNT composites were measured using a four-point probe electrical measurement device (KEITHLEY, 2000).

3. Results and discussion

Fig. 2(a) shows the TEM image of pristine CNTs. The diameters of the pristine CNTs with relatively clean surface were 40-90 nm. Fig. 2(c) shows the TEM image of a typical CNTs, and it can clearly the CNTs surface coated.

The FTIR spectra of pure PI and PI/CNT hybrid films are shown in Fig. 3. All the nanocomposites are seen to show almost the same vibration bands as PI. The characteristic peaks of polyimide were observed at 1782 cm−1 (C=O asymmetric stretch), 1720 cm−1 (C=O symmetric stretch), 1373 cm−1 (C–N stretch), and 740 cm−1 (C=O bending), indicating the PI had successfully synthesized [24]. The FTIR spectra indicate that the CNTs do not hamper the formation of the PI molecular structure, even with the CNTs coated by surfactants.

Fig. 4 SEM image of the nanotube dispersion in the polyimide matrix. A representative SEM of R-PI-5 composite Fig. 4(a) shows many aggregated clusters of CNTs suggesting nonuniform dispersion of CNTs. By comparison, H-PI-5 composite show uniform dispersion of CNTs throughout the matrix, and no obvious CNTs aggregates were observed in Fig. 4(b). In fact, the observation of conductivity range of a significant degree of CNTs aggregation and dispersion in PI/CNTs composite. The aggregation of CNTs in the composite shows bigger values of conductivity error bars.

The TGA curves of PI/CNTs composites are shown in Fig. 5. The temperature at 95% weight residual was defined as the thermal decomposition temperature (Td) in this study. The Td value of H-PI-5 is 546 ℃. On the contrary, the Td value of R-PI-5 is 498 ℃. The results indicate the chain scission of the organic molecular moieties during thermal decomposition could be effectively restrained by CNT in PI with stronger interactions between surfactant and CNT.

In the majority reported methods of preparation of PI/CNT composites, CNTs are modified by acid treatment, which has been shown to reduce CNT intrinsic electrical conductivity, because of the introduced structural defects. Furthermore, decreased nanotube aspect ratio and length of acid-treated CNTs lead to a higher CNT fraction needed to form a continuous charge carrier channel in composites[25]. In our method, surfactants are adsorbed onto the CNT surface to disperse nanotube bundles into individuals without any substantial damage to the CNT length and structure. The intrinsic electrical properties and original aspect ratio of the CNTs are better preserved. Compared to other reported methods, the CNTs in our research are more easily form a conducting interconnected nanotube network in the polymer matrix.

Moreover, the absolute conductivities of our PI/CNT composites are much higher than the reported values of PI/CNT composites with the same nanotube loading. For example, for nanotube/polyimide composites with 5 wt % nanotubes, the reported conductivities are in the range of 10^{-9}—10^{-4}S cm^{-1}[26-31] which is ~ 4—9 orders of magnitude lower than our value (2.5 S cm^{-1}). Our conductivity reaches 30.3 S cm-1 at 30 wt % CNT loading and 41.5 S cm-1 at 40 wt %

CNT loading, which is ~ 17 orders of magnitude higher than that of neat PI. The electrical conductivity of our PI/CNT composites is tunable from 10-16 S cm-1 to 41.5S cm-1 by varying the nanotube content. Fig. 6 shows the conductivity of PI/CNT composites, measured at room temperature, as a function of CNT loading. The aggregation of CNTs in the composite shows bigger values of conductivity error bars.

4. Conclusion

In summary, we report the effect of 60 ^{o}C dispersion CNT shows better dispersibility and electrical conductivity of CNT than room temperature dispersion CNT. Surfactants is a highly effective dispersion of CNTs. H-PI/CNT composite films made by the conventional solution casting technique show outstanding electrical properties. The electrical conductivity of the composites reaches 41.5 S cm^{-1} at a CNT loading of 40 wt %. The excellent electrical and thermal properties, combined with the facile fabrication technique, make this H-PI/CNT composite a promising material for many potential applications, such as flexible printed circuit boards, electromagnetic interference shielding, and electrostatic dissipation.
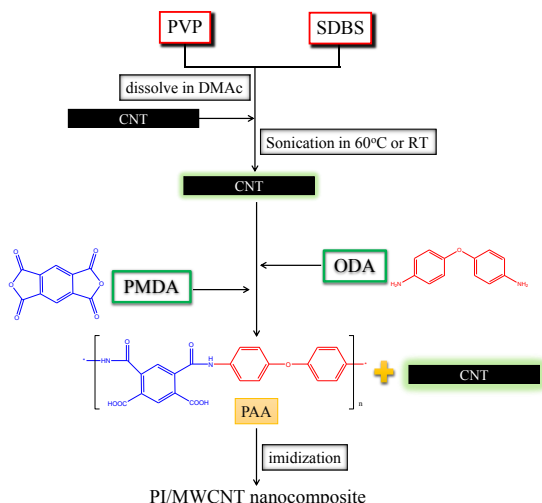

Fig.1.Reaction scheme for synthesizing polyimide/CNT hybrid films.
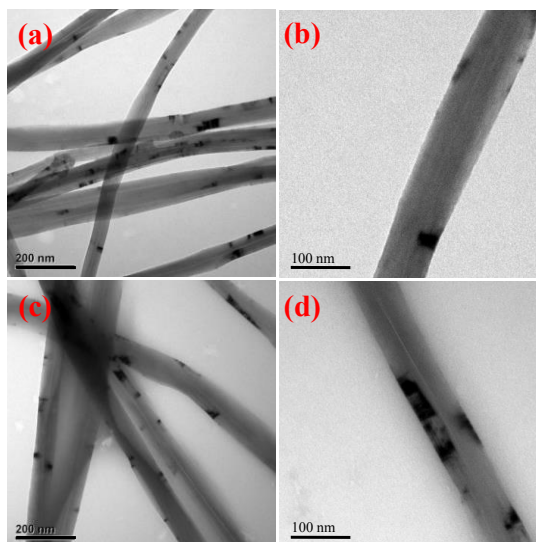

Fig. 2 TEM images of CNTs (a) with out surfactant; (b) enlarged image of a selected region in panel a; (c) with surfactant; (d) enlarged image of a selected region in panel c.
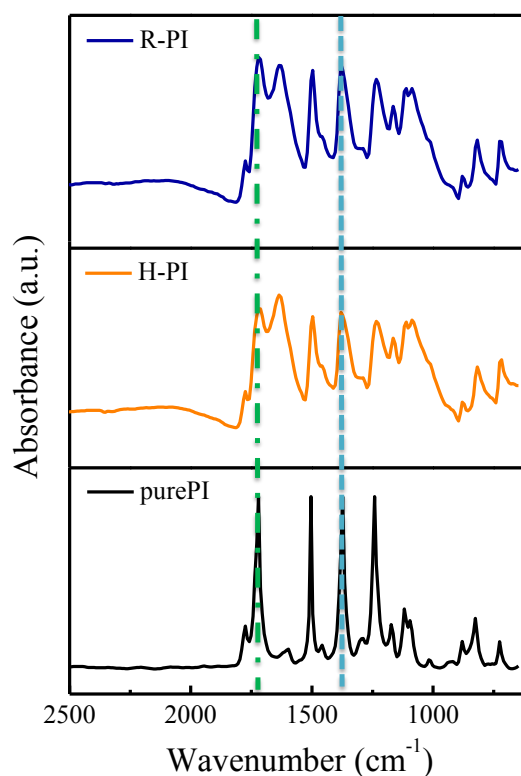

Fig. 3. FTIR spectra of pure PI and polyimide/CNT nanocomposites obtained from films.
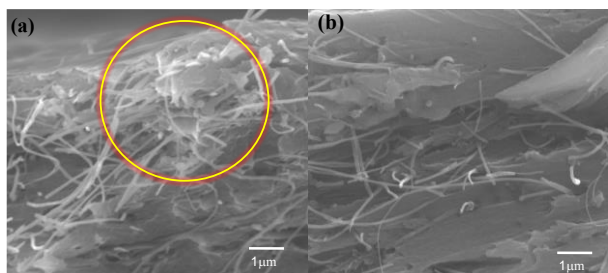
Fig. 4. SEM image of the nanotube dispersion in the polyimide matrix (a) R-PI-5; (b) H-PI-5.
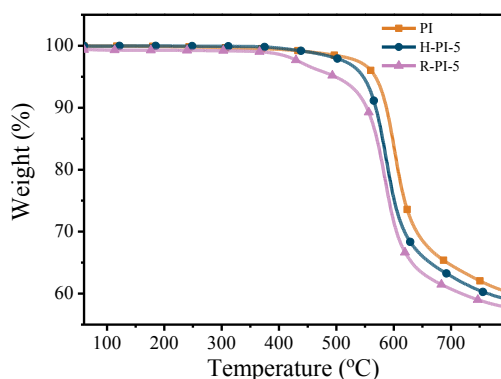

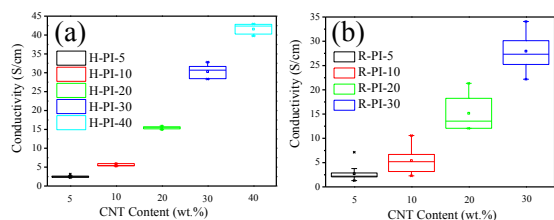Fig. 5. The TGA curves of polyimide/CNTs composites.

Fig. 6. Conductivity of polyimide/CNT hybrid films with various CNT contents, measured at room temperature.

6. 參考文獻

[1] P.C. Chiang, W.T. Whang, M.H. Tsai, S.C. Wu, Thin Solid Films 447-448 (2004) 359.

[2] C.J. Chang, M.S. Wu, P.C. Kao, Micropor. Mesopor. Mat. 111 (2008) 267.

[3] C.J. Chang, R.L. Chou, Y.C. Lin, B.J. Liang, J.J. Chen, Thin Solid Films 519 (2011) 5013.

[4] S. Iijima, Nature 354 (1991) 56.

[5] X. Jiang, Y. Bin, M. Matsuo, Polymer 46 (2005) 7418.

[6] H.H. So, J.W. Cho, N.G. Sahoo, Eur. Polym. J. 43 (2007) 3750.

[7] W.J. Chou, C.C. Wang, C.Y. Chen, Polym. Degrad. Stabil. 93 (2008) 745.

[8] A. Peigney, C. Laurent, E. Flahaut, R.R. Bacsa, A. Rousset, Carbon 39 (2001) 507.

[9] B.G. Choi, H. Park, T.J. Park, D.H. Kim, S.Y. Lee, W.H. Hong, Electrochem. Commun. 11 (2009) 672.

[10] S. Subramoney, Adv. Mater. 10 (1998) 1157.

[11] S.M. Yuen, C.C. M. Ma, Y.Y. Lin, H.-C. Kuan, Compos. Sci. Technol. 67 (2007) 2564.

[12] Q.Y. Tang, Y.C. Chan, N.B. Wong, R. Cheung, Polym. Int. 59 (2010) 1240.

[13] B.K. Zhu, S.H. Xie, Z.K. Xu, Y.Y. Xu, Compos. Sci. Technol. 66 (2006) 548.

[14] L.Y. Jiang, Y. Huang, H. Jiang, G. Ravichandran, H. Gao, K.C. Hwang, B. Liu, J. Mech. Phys. Solids 54 (2006) 2436.

[15] T. Hasan, V. Scardaci, P. Tan, A.G. Rozhin, W.I. Milne, A.C. Ferrari, J. Phys. Chem. C 111 (2007) 12594.

[16] T.J. Simmons, D. Hashim, R. Vajtai, P.M. Ajayan, J. Am. Chem. Soc. 129 (2007) 10088.

[17] K. Chari, W.C. Lenhart, J. Colloid Interf. Sci. 137 (1990) 204.

[18] B.J. Landi, H.J. Ruf, J.J. Worman, R.P. Raffaelle, J. Phys. Chem. B 108 (2004) 17089.

[19] Q.Y. Tang, Y.C. Chan, N.B. Wong, R. Cheung, Polym. Int. 59 (2010) 1240.

[20] M. Hirata, N. Kawasaki, T. Nakamura, K. Matsumoto, M. Kabayama, T. Tamura, S. Tanada, J. Colloid Interf. Sci. 254 (2002) 17.

[21] Z.L. Yang, H.Z. Chen, L. Cao, H.Y. Li, M. Wang, Mater. Sci. Eng. B-Adv. 106 (2004) 73

[22] I. Chen, H. Liu, W.A. Weimer, M.D. Halls, D.H. Waldeck, G.C. Walker, J. Am. Chem. Soc. 124 (2002) 9035.

[23] J. Chen, H. Liu, W.A. Weimer, M.D. Halls, D.H. Waldeck, G.C. Walker, J. Am. Chem. Soc. 124 (2002) 9034.

[24] M.H. Tsaia, Y.C. Huang, I.H. Tseng, H.P. Yu, Y.K. Lin, S.L. Huang, Thin Solid Films 519 (2011) 5238.

[25] W. Yuan, J. Che, M.B. Chan-Park, Chem. Mater. 23 (2011) 4149.

[26] S.M. Yuen, C.C.M. Ma, C.L. Chiang, C.C. Teng, Y.H. Yu, J. Polym. Sci. Part A: Polym. Chem. 46 (2008) 803.

[27] S.M. Yuen, C.C.M. Ma, C.L. Chiang, Y.Y. Lin, C.C. Teng, J. Polym. Sci. Part A: Polym. Chem. 45 (2007) 3349.

[28] A.I. Isayev, R. Kumar, T.M. Lewis, Polymer 50 (2009) 250.

[29] M. Lebron-Colon, M.A. Meador, J.R. Gaier, F. Sola, D.A. Scheiman, L.S. McCorkle, ACS Appl. Mater. Interfaces 2 (2010) 669.

[30] T. Ogasawara, Y. Ishida, T. Ishikawa, R.

Yokota, Composites, Part A 35 (2004) 67.

[31] B.K. Zhu, S.H. Xie, Z.K. Xu, Y.Y. Xu, Compos.

Sci. Technol. 66 (2006) 548.