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Investigation of the modification of solvent-containing two-component polyurethane coating by carbon nanotubes

Abstract

Purpose - The purpose of this paper was to investigate the effects of carbon nanotubes (CNTs) on the mechanical, thermal and colour properties of solvent-containing two-component polyurethane (PU) coating.

Design/methodology/approach - Fourier transform infrared spectroscopy and observation of dispersion stability were employed to assess the effects of acid treatment on CNTs. The CNTs and PU composite coating was synthesised by *in situ* polymerisation and blending polymerisation, and the mechanical, thermal and colour appearance properties of coating were characterised.

Findings - It was found that desirable modifications to CNTs occurred after acid treatment, thus mainly carboxylic acid groups were introduced onto the surface of CNTs. It was also found that the acid treated CNTs could improve the mechanical and thermal properties of PU coating, and the properties of composite coating were improved more successfully by *in situ* polymerisation than blending polymerisation.

Practical implications - The investigation established a method to synthesise CNTs and PU composite coating. The study developed a method to improve the mechanical and thermal properties of PU coating by the inclusion of CNTs.

Originality/value - The study established a method to synthesise CNTs and PU composite coating by *in situ* polymerisation and blending polymerisation. The study also gained understanding of the effects of CNTs on modifying mechanical, thermal and colour properties of PU coating.

Keywords Carbon nanotubes, Polyurethane, Solvent-containing, Two-component coating

Paper type Research paper

Introduction

Carbon nanotubes (CNTs) were discovered by Iijima (Iijima *et al.*, 1991). CNTs are cylinder-shaped macromolecules having a radius as small as a few nanometres, which can be grown up to 20cm in length. The walls of these tubes are made up of a hexagonal lattice of carbon atoms analogous to the atomic planes of graphite. They are capped at their ends by one half of a fullerene-like molecule (Balasubramanian *et al.*, 2005).

Carbon nanotubes have attracted increasing attention due to their unique structure, excellent electrical and thermal conductivity, together with their excellent mechanical properties (Xia *et al.*, 2006; Jung, 2006; Niu *et al.*, 2007). The unique properties of CNTs make them attractive for applications in many scientific and technological fields such as electronic structures, polymer composites, biological systems and coatings (Liu, 2005; Jiang *et al.*, 2005; Chen *et al.*, 2006; Xiong *et al.*, 2006; Yang *et al.*, 2006; Fan *et al.*, 2006; Sun *et al.*, 2006).

In order to prepare polymer/CNTs composites, chemical modification of carbon nanotubes is necessary since CNTs are insoluble in common solvents and have a weak interfacial interaction with the polymer matrix. Surface modification of CNTs has attracted significant interest recently (Baskaran *et al.*, 2005). Among various functional groups, carboxyl group is more attractive due to the possibility of further covalent and non-covalent functionalisation of CNTs (Chen *et al.*, 2007; Saito *et al.*, 2002; Liu *et al.*, 2006).

In this paper, detailed studies of CNTs and PU composite coating including the acid treatment on CNTs, and the synthesis and characterisation of composite coating to understand the effects of CNTs on the mechanical, thermal and colour properties of PU coating, are reported.

Experimental

Materials and instrument

The CNTs used were supplied by Shenzhen Nanotech Port Co. Ltd. The nanotubes had a specified diameter of 40-60 nm and a specified length of 5-15 μm, with a purity greater than 95%. The trimethylolpropane (TMP) used was supplied by Sinopharm Chemical Reagent Co. Ltd. The toluene-2,4-diisocyanate (TDI) used was supplied by Tianjin Yuanli Chemical Engineer Co. Ltd. The castor oil used was supplied by Tianjin Kermel Chemical Reagent Co. Ltd. The dibutyltin dilaurate used was supplied by Shanghai Shanpu Chemical Engineering Co. Ltd. The isobutyl acetate (standard reagent grade) used was supplied by Tianjin BASF Chemical Engineering Co. Ltd. The sulphuric acid (95-98 wt% standard reagent grade) and nitric acid (65-68 wt% standard reagent grade) used were supplied by Harbin Xintian Chemical Reagent Co. Ltd.

Fourier transform infrared spectroscopy (FT-IR) measurement of sample prepared was performed on a Magna-IR 560 E.S.P FT-IR spectrometer (supplied by Nicolet Co. Ltd). Mechanical properties of the coatings were obtained on a CMT5504 tensile testing machine (supplied by Shenzhen SANS Measurement Technology Co. Ltd) at room temperature using 110×10×1 mm^3 samples with a gauge length of 50 mm and a crosshead speed of 50 mm/min. Dynamic mechanical analysis (DMA) of sample prepared was performed on a DMS6100 DMA unit (supplied by SII Nano Technology Inc.) with an operating temperature range from 20°C to 120°C, the heating rate was set at 3°C/min, a frequency of 1 Hz was applied, and the sample size was proximately 50×10×1 mm^3. Determinations of hardness, flexibility, impact resistance were according to GB/T 1730-93, GB/T1731-93, GB/T1732-93 standards of China, respectively. The colour depth of coating was obtained using a Kangguang SC-80C spectrophotometer (supplied by Beijing Kangguang Instrument Co. Ltd).

Procedures of acid treatment of CNTs

CNTs, 1 g, were dispersed in a mixture of 50 ml HNO_3 and 150 ml H_2SO_4, and the mixture was sonicated in a water bath for 30 minutes at ambient temperature, then stirred at 60°C for 4 hours. After cooling to ambient temperature, the sample was diluted with deionised water and vacuum filtered, the solid matter collected was dispersed in deionised water and vacuum filtered for several times until no acid on the sample was detected. The final solid was dried in a vacuum oven at 80°C to a constant weight (Jiang *et al.*, 2009), the yield was 77%.

The schematic illustration of the acid treatment of CNTs is shown in Scheme 1.

(Take in Scheme 1)

Synthesis of PU coating

TMP, 5 g, was stirred and dissolved in 30 ml isobutyl acetate at 55°C, then 16 ml TDI was introduced into the solution. Then, the system was heated to 80°C and stirred for 4 hours, then the isocyanates was synthesised. The isocyanates and 30 g castor oil were diluted with isobutyl acetate, respectively. Then, the diluted isocyanates and castor oil were mixed and stirred for 10 minutes, and polymerised at ambient temperature for 2 days.

A schematic illustration of the PU coating synthesis is shown in Scheme 2.

(Take in Scheme 2)

Synthesis of CNTs and PU composite coating by *in situ* polymerisation

Acid-treated CNTs were sonicated in 10 ml isobutyl acetate in a water bath for 30 minutes at ambient temperature. TMP, 5 g, was stirred and dissolved in 20 ml isobutyl acetate at 55°C, then 16 ml TDI was introduced into the solution. After 10 minutes, the CNTs (0.05 wt% of TMP and TDI) dispersion was introduced to the system and the system was heated to 80°C and stirred for 4 hours, and then the CNTs-isocyanates composites were synthesised. The

CNTs-isocyanates composites and 30 g castor oil were diluted with isobutyl acetate, separately. Then, the diluted CNTs-isocyanates composites and castor oil were mixed and stirred for 10 minutes, and polymerised at ambient temperature for 2 days.

A schematic illustration of CNTs and PU composite coating synthesis is shown in Scheme 3.

(Take in Scheme 3)

Synthesis of composite coating by blending polymerisation

TMP, 5 g, was stirred and dissolved in 30 ml isobutyl acetate at 55°C, then 16 ml TDI was introduced into the solution and the system was heated to 80°C and stirred for 4 hours, then acid-treated CNTs (0.05 wt% of TMP and TDI) were introduced to the isocyanates and sonicated in a water bath for 30 minutes at ambient temperature. The CNTs-isocyanates and castor oil were diluted with isobutyl acetate, respectively. Then, the diluted isocyanates and castor oil were mixed and stirred for 10 minutes, and polymerised at ambient temperature for 2 days.

Results and discussion

FT-IR analysis of raw and acid-treated CNTs

The FT-IR analysis results of raw and acid-treated CNTs (for 4 hours) are shown in Figure 1.

(Take in Figure 1)

From Figures 1, it can be clearly seen that the FT-IR spectra of raw CNTs showed peaks with very low intensity at around 3446, 1711, and 1209 cm^{-1}, corresponding to OH, C=O, and C-C-O stretching present in carboxylic groups (COOH), respectively. In the case of acid-treated CNTs, these characteristic bands appeared with significantly greater intensity. This was attributed to the increased number of carboxylic acid groups that had been successfully attached to the surface of the CNTs after acid treatment in H_2SO_4/HNO_3 mixture. And the peak at 1574 cm^{-1} is attributed to the vibration of carbon skeleton (C-C stretch) of the bulk CNTs. Therefore, it was considered that carboxylic groups (-COOH) had been attached onto the surface of the CNTs by acid treatment successfully.

Observation of dispersion stability of CNTs in deionised water

Raw and acid-treated CNTs were sonicated in deionised water in a water bath for 30 minutes at ambient temperature. Photographs of such CNTs were taken a day later, which are shown in Figure 2.

(Take in Figure 2)

From Figures 2, it can be clearly seen that acid-treatment improved the dispersion stability of CNTs in deionised water, which is due to the carboxylic groups (-COOH) on the surface of the CNTs improving the polarity of the CNTs.

From the above analyses, it was clear that (1) the carboxylic groups (-COOH) were attached onto the surface of the CNTs via acid treatment; (2) such carboxylic groups could react with TDI to synthesise CNTs-PU composite coating; and (3) the acid-treated CNTs could impart excellent mechanical and thermal properties to the composite coating.

Mechanical properties of the coating

The results of the analyses of the mechanical properties of the coating obtained are shown in Table I.

(Take in Table I)

From Table I, it can be clear seen that the elastic modulus, the tensile strength, and the hardness of the coating were improved by the inclusion of the CNTs, and the flexibility and impact resistance of the coating were not compromised by the inclusion of the CNTs. It can also be seen that the mechanical properties of the composite coating were improved more successfully by *in situ* polymerisation than blending polymerisation.

The improved elastic modulus, tensile strength and hardness of the composite coating were due to the excellent mechanical properties of CNTs. The acid-treated CNTs and PU could form copolymer due to the presence of carboxylic groups on the surface of acid-treated CNTs thus imparting excellent mechanical properties of CNTs to the coating system successfully.

The improvement to composite coating by *in situ* polymerisation was significant compared to blending polymerisation. This was due to the fact that the CNTs could be utilised more efficiently and could form copolymer more easily with PU by *in situ* polymerisation compared to blending polymerisation, thus benefiting more effectively from the excellent mechanical properties of CNTs.

Also, it could be seen that the flexibility and impact resistance properties of the composite coating were not compromised by the inclusion of the CNTs.

Dynamic mechanical analyses (DMA) of coating

The results of the DMA of coating are shown in Figures 3 and 4.

(Take in Figure 3 and 4)

Compared to the PU coating, the position of the loss factor (tanδ) peak for the composite coating significantly shifted towards high temperature, indicating that the glass transition temperature (T_g) of the composite coating was greatly increased. The improvement in T_g was mainly attributed to the excellent mechanical and thermal properties of CNTs and the bonding between the CNTs and the rigid segments of PU.

From the data of the storage modulus (E') of the PU coating and that of the composite coating, it was clear that there was some difference between the storage modulus of the PU coating and that of the composite coating. Above T_g, there was no obvious difference in storage modulus, while below T_g the CNTs had a strong influence on the elastic properties of the PU coating increasing the storage modulus, which may be caused by the extremely high modulus of CNTs and their interactions with the PU coating.

And also the improvement to composite coating by *in situ* polymerisation was significant compared to blending polymerisation.

Colour strength of the coating

The L* values of the coatings are showed in Table II.

(Take in Table II)

From the L* values, it was clear that CNTs made the composite polyurethane coating darker than the PU coating, of which the extent was more significant for the *in situ* polymerisation than for the blending polymerisation. This was due to the better dispersion of CNTs in PU coating during the *in situ* polymerisation than the blending polymerisation.

Conclusion

It can be concluded that CNTs could be modified via acid (H_2SO_4:HNO_3 = 3:1 in volume) treatment at 60°C for 4 hours. Through acid treatment, carboxylic groups (-COOH) could be successfully introduced onto the surface of CNTs.

The mechanical properties of the composite coating were improved by the inclusion of CNTs in the PU coating, and the glass transition temperature and the storage modulus of the composites were increased also. The flexibility and impact resistance properties of the composite coating were not compromised by the CNTs included.

The improvement of the mechanical and thermal properties of the composite coatings as a result of the inclusion of the CNTs was more prominent when employing *in situ* polymerisation compared to blending polymerisation.

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References

Balasubramanian, K. and Burghard, M. (2005), "Chemically functionalized carbon nanotubes", *Small*, Vol. 1 No. 2, pp. 180-92.

Baskaran, D., Mays, J.W. and Bratcher, M.S. (2005), "Polymer adsorption in the grafting reactions of hydroxyl terminal polymers with multi-walled carbon nanotubes", *Polymer*, Vol. 46 No. 14, pp. 5050–7.

Chen, W., Tao, X. and Liu, Y. (2006), "Carbon nanotube-reinforced polyurethane composite fibers", *Composites Science and Technology*, Vol. 66 No. 15, pp. 3029–34.

Chen, X., Chen, X., Lin, M., Zhong, W., Chen, X. and Chen, Z. (2007), "Functionalized multi-walled carbon nanotubes prepared by in situ polycondensation of polyurethane", *Macromolecular Chemistry and Physics*, Vol. 208 No. 9, pp. 964-72.

Fan, L., Cai, Y., Shen, X., Cui, S. and Yuan, L. (2006), "Fabrication and properties of acrylate/carbon nanotube conductive coatings", *Development and Application of Materials*, Vol. 21 No. 2, pp. 5-8.

Iijima, S. (1991), "Helical microtubes of graphic carbon", *Nature*, Vol. 354 No. 6348, pp. 56-8.

Jiang, G., Wang, L., Chen, C., Dong, X., Chen, T. and Yu, H. (2005), "Study on attachment of highly branched molecules onto multiwalled carbon nanotubes", *Materials Letters*, Vol. 59 No. 16, pp. 2085–9.

Jiang. X., Gu, J., Bai. X., Lin. L. and Zhang. Y. (2009), "The influence of acid treatment on multi-walled carbon nanotubes", *Pigment and Resin Technology*, Vol. 38 No. 3, pp. 165-73.

Jung, Y.C. (2006), "Polymeric nanocomposites of polyurethane block copolymers and functionalized multi-walled carbon nanotubes as crosslinkers", *Macromolecular Rapid communications*, Vol. 27 No. 2, pp. 126-31.

Liu, P. (2005), "Modification of carbon nanotubes with polymers", *European Polymer Journal*, Vol. 41 No. 11, pp. 2693-703.

Liu, Y., Du, Z., Li, Y., Zhang, C., Li, C., Yang, X. and Li, H. (2006), "Surface covalent encapsulation of multiwalled carbon nanotubes with poly(acryloyl chloride) grafted poly(ethylene glycol)", *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 44 No. 23, pp. 6880-7.

Niu, L., Luo, Y. and Li, Z. (2007), "A highly selective chemical gas sensor based on functionalization of multi-walled carbon nanotubes with poly(ethylene glycol)", *Sensors* *and Actuators Chemical B*, Vol. B126 No. 2, pp. 361-7.

Saito, T., Matsushige, K. and Tanaka, K. (2002), "Chemical treatment and modification of multi-walled carbon nanotubes", *Physica B*, Vol. 323 Nos. 1-4, pp. 280-3.

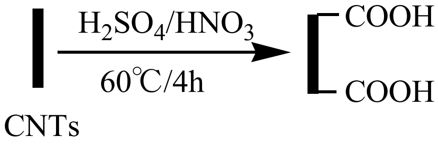
Sun, X., Yu, Y., Liu, Y. and Zhu, Z. (2006), "Nano radar absorbing materials with broad band", *Materials for Mechanical Engineering*, Vol. 30 No. 1, pp. 66-70.

Xia, H., Song, M., Jin, J. and Chen, L. (2006), "Poly(propylene glycol)-grafted multi-walled carbon nanotube polyurethane", *Macromolecular Chemistry and Physics*, Vol. 207 No. 21, pp. 1945-52.

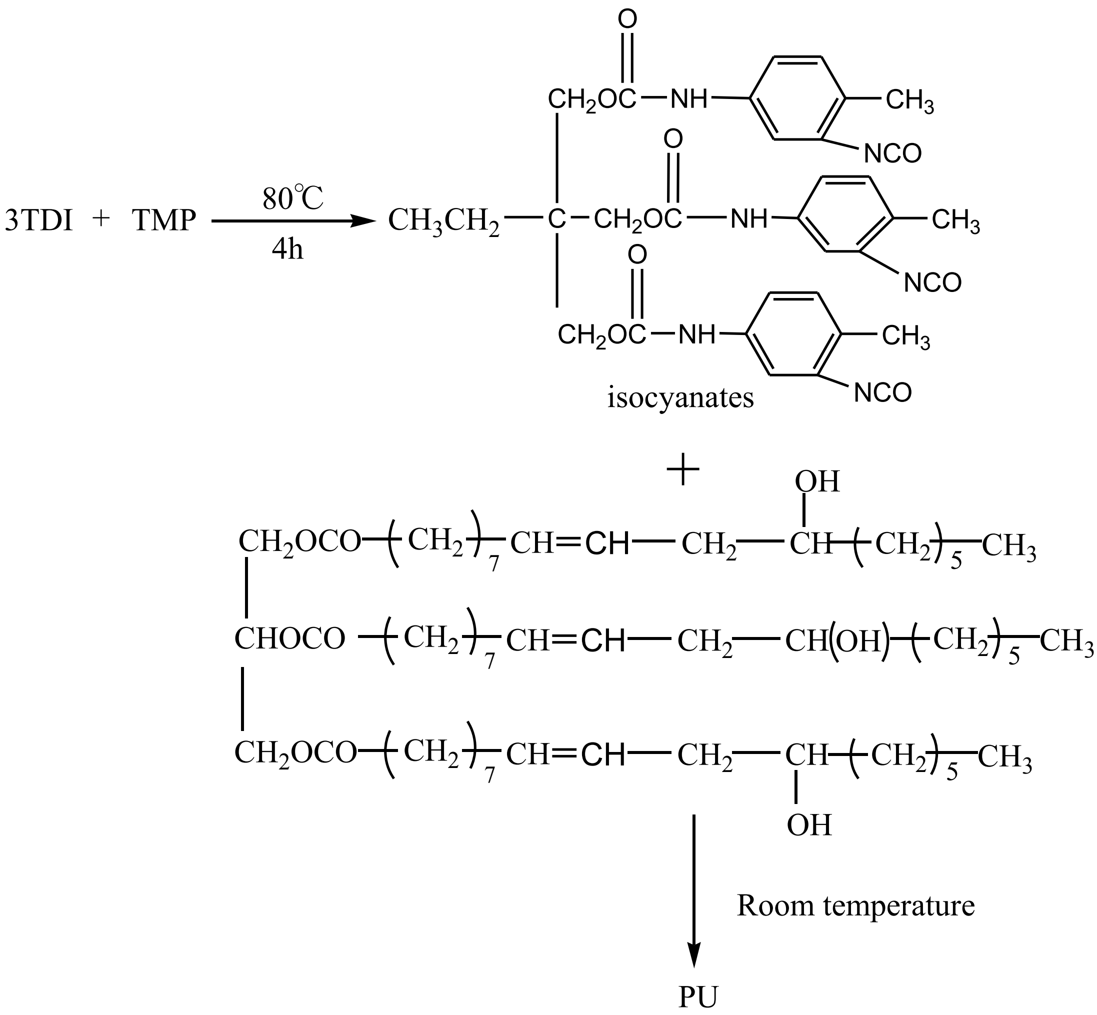
Xiong, J., Zheng, Z., Qin, X., Li, M., Li, H. and Wang, X. (2006), "The thermal and mechanical properties of a polyurethane/multi-walled carbon nanotube composite", *Carbon*, Vol. 44 No. 13, pp. 2701–7.

Yang, Y., Xie, X., Wu, J., Yang, Z., Wang, X. and Mai, Y. (2006), "Multiwalled carbon nanotubes functionalized by hyperbranched poly(urea-urethane)s by a one-pot polycondensation", *Macromolecular Rapid Communications*, Vol. 27 No. 19, pp. 1695–701.

Scheme 1 Reaction scheme of the acid treatment of CNTs



Scheme 2 Reaction scheme of the synthesis of the PU coating



Scheme 3 Reaction scheme of the synthesis of acid-treated CNTs and PU composite coating by *in situ* polymerisation

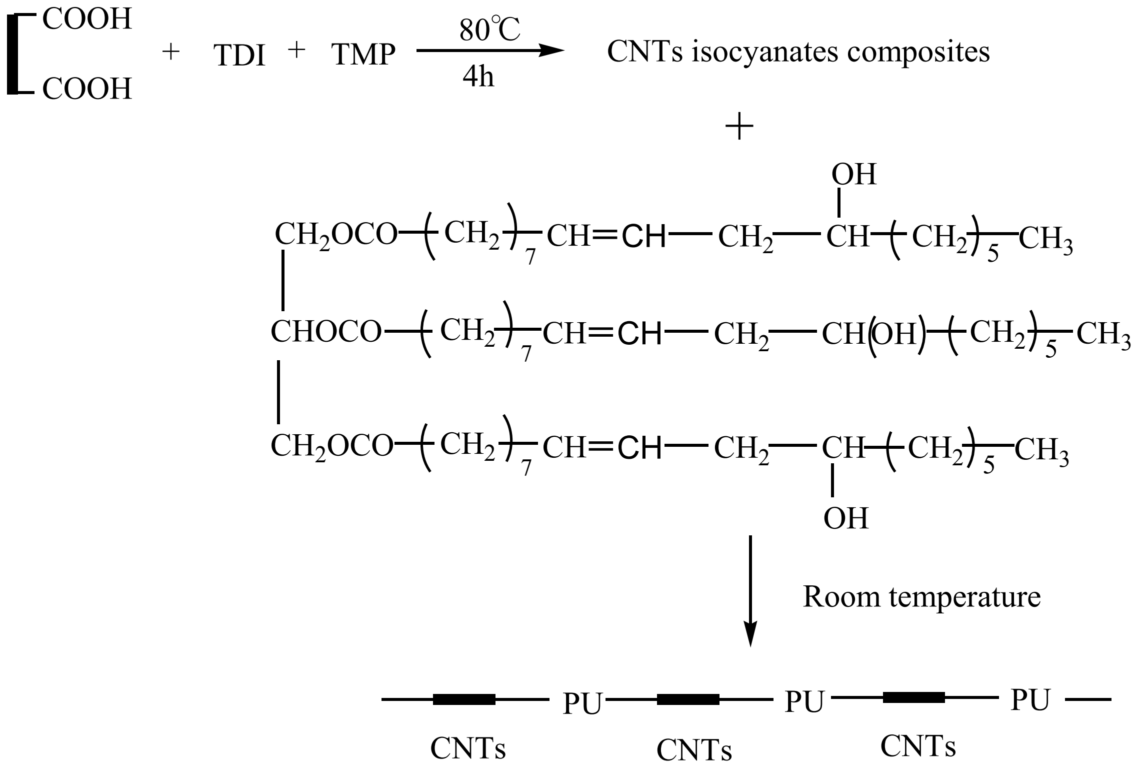
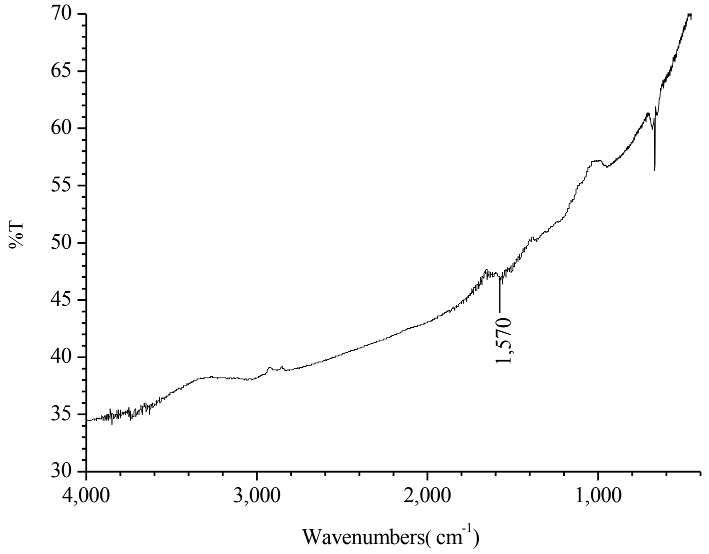
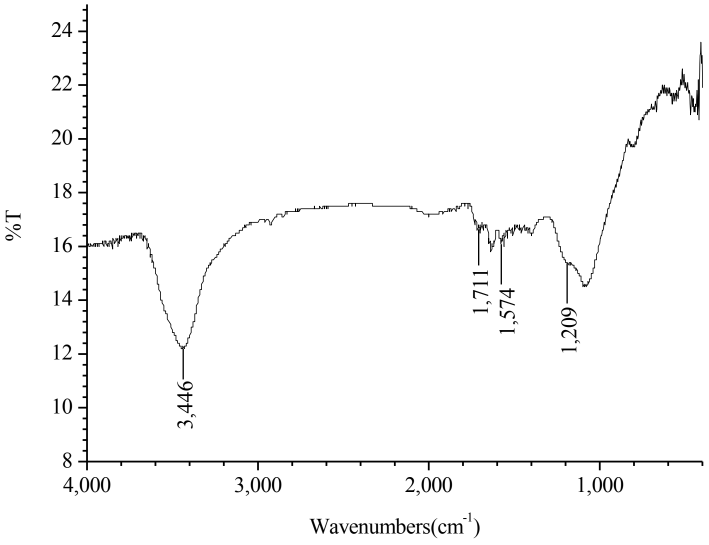


Figure 1 FT-IR spectrum of raw and acid treated CNTs



(a) Raw CNTs



(b) CNTs treated for 4 hours at 60°C by acid

Figure 2 Observation dispersion stability of raw and acid-treated CNTs in deionised water

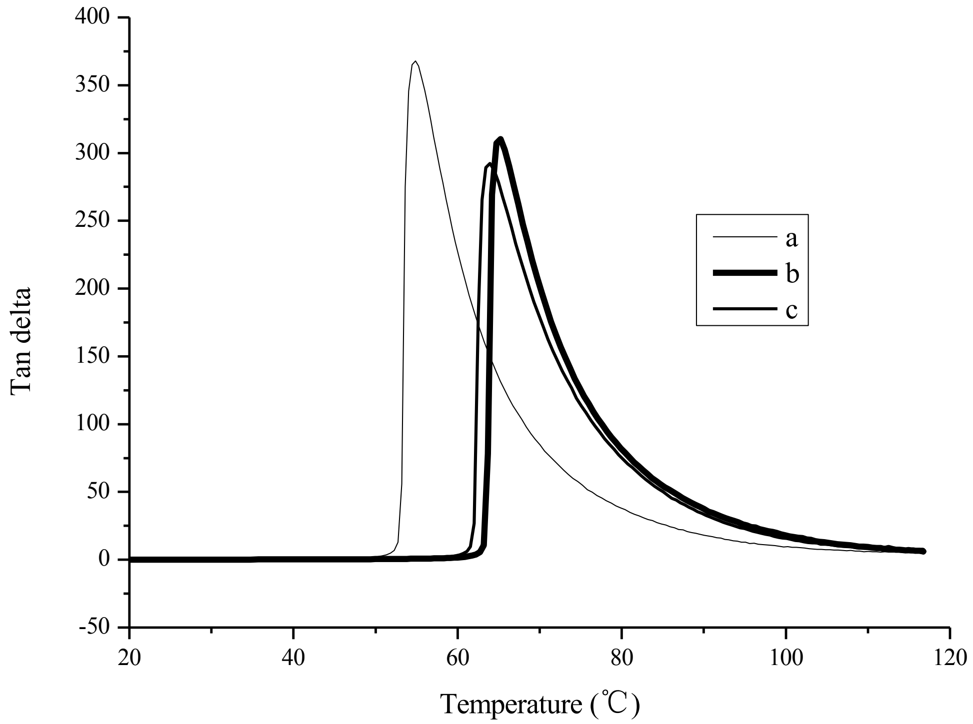
(a) Raw CNTs

(b) CNTs treated for 4 hours at 60°C by acid

Table I Mechanical properties of PU and composite coating

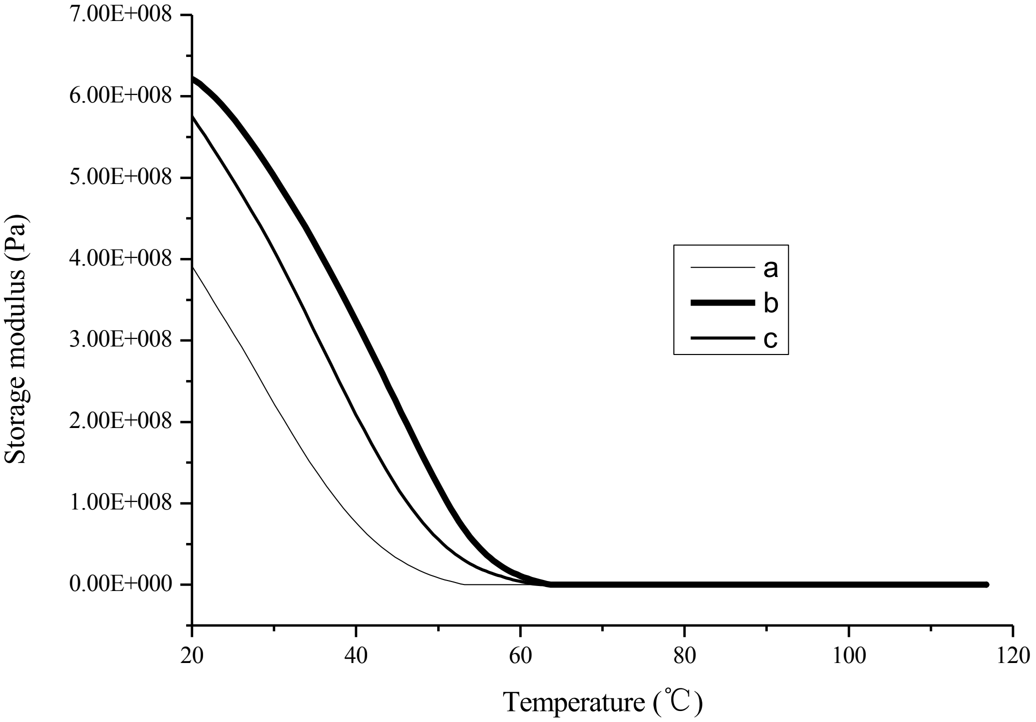
Sample	Elastic modulus (MPa)	Tensile strength (MPa)	Hardness	Impact resistance	Flexibility
Polyurethane coating	227.94	13.20	0.28	50	1
Composite coating by *in situ* polymerisation	462.56	17.29	0.40	50	1
Composite coating by blending polymerisation	356.96	15.05	0.38	50	1

Figure 3 DMA curves of PU and composite coating for loss factors



(a) PU coating; (b) composite coating by *in situ* polymerisation; (c) composite coating by blending polymerisation

Figure 4 DMA curves of PU and composite coating for storage modulus



(a) PU coating; (b) composite coating by *in situ* polymerisation; (c) composite coating by blending polymerisation

Table II Colour strength of PU and composite coatings

Sample	L*
Polyurethane coating	82.51
Composite coating by in situ polymerisation	64.64
Composite coating by blending polymerisation	70.54