

Modification Methods and Applications of CNTs/WPU Composite Material

Yunong Gao^{1,*}

¹School of Textile Science and Engineering, Xi'an Polytechnic University, Xi'an, 710000, China

Abstract. Carbon nanotubes have lots of good properties, and occupy a great position in the field of science today. However, they also have some disadvantages, such as the existence of Van der Waals forces between the nanotubes bundle, which can result the attraction between the bundles and finally will cause more serious agglomeration. So researchers make the CNTs and WPU into the composite via solution blending, melt blending and in situ polymerization, in order to give play to the excellent properties of the two materials. This paper is aimed at summarizing various modification methods of CNTs/WPU composite material in the current research status and show the effects after each modification method. Finally, it can be concluded that there were differences between composites and the results of modification methods were affected.

1 Introduction

Carbon nanotubes (CNTs) is a one-dimensional material curled up by graphite carbon atomic layer, which was found in 1991 by Japanese NEC scientists in the study C60 structure [1]. Its weight is lighter, its hexagonal structure is excellent, and its radial length can reach nanoscale, axial length can reach micron grade. There are also five-membered ring and seven-membered ring structures in the carbon nanotubes structure, which make the wall of the carbon nanotubes concave and form a curved part. In addition, Carbon atoms mainly exist as sp² hybridization and sp³ hybridization, so they have excellent mechanical, electrical and chemical properties. Its application is also extensive. For example, in the field of electronics, carbon nanotube materials can be used as batteries, precision electronic devices. In the field of adsorbent, it can be used as adsorbing pollutants in water and hydrogen storage materials. Polyurethane (PU) is mostly made by diisocyanate and oligomer alcohol via condensation polymerization, and the constitutional repeating unit is —NHCOO—. Because of its unique structure, polyurethane material has good toughness and mixed with high polymer material. Waterborne polyurethane(WPU)is a kind of material in which polyurethane particles disperse in water to form an aqueous solution. It not only has the excellent properties of polyurethane, but also has the characteristics of low toxicity, low pollution, easy modification and construction. Its due field has adhesive field, coating material field.

Although carbon nanotubes have a lot of good properties and occupy a great position in the field of

science today, they also have some disadvantages. Such as the existence of Van der Waals forces between the nanotubes bundle, which can result the attraction between the bundles, therefore, it will cause more serious agglomeration. This disadvantage will make the dispersion of carbon nanotubes in the composite material worse, the cost of preparation is increased. However, waterborne polyurethane also have the defects of poor water resistance, poor solvent resistance and poor mechanical properties. Therefore the modification to carbon nanotubes and waterborne polyurethane is needed to offset the shortcoming so that the composite can perform better and different modification methods will bring different effects to the composite.

2 Modification methods of CNTs/WPU composite

2.1. Organic alcohol-modified multi-walled carbon nanotubes

Shaohui Wang's group [7] treated MWCNTs with a mixed acid of concentrated sulfuric acid and concentrated nitric acid 3:1 to graft them into the organic segment —COOH. And then mixed and dispersed the carboxylated MWCNTs with N,N-dimethylformamide. After that, SOCl₂ was added to make the MWCNTs acyl chlorinated. Then acyl chlorinated MWCNTs were polymerized with ethylene glycol(EG), glycerol alcohol(GL) and dimethylolpropionic acid(DMPA), respectively, to form MWCNTs grafted at different organic alcohol chain segments. Finally, composite materials were synthesized

*905246707@qq.com

by solution blending with waterborne polyurethane. The results showed that the diameters of carbon nanotubes were significantly increased after esterification with polyols. MWCNTs grafted to —COOH organic chain segment began to decompose at 206°C, and the Thermo-gravimetric rate of MWCNTs grafted to —COOH at 800°C was 7.8%. The TG rate, Zeta potential and the increase in tensile stress(compared with WPU) of MWCNTs grafted to EG, GL and DMPA was showed in table 1.

Table 1. The TG rate, Zeta potential and tensile stress of 1.5% MWCNTs(compared with WPU)

	TG rates at 800°C	Zeta potential	Tensile stress of 1.5%
EG	19.8%	-38.8eV	60%
GL	38.9%	-41.5eV	67%
DMPA	39.6%	-49.7eV	72%

The higher the TG rate was, the larger the molecular weight of alcohol is, the more organic chain segments are grafted. Because the surface energy of MWCNTs was decreased by grafting hydrophilic groups, the higher the grafting rate was, the higher the absolute value of Zeta potential was. Therefore, the hydrophilicity of MWCNTs-DMPA was better than that of the other two organic alcohol segment grafted MWCNTs. The change of particle size of MWCNTs in WPU was followed by the largest size of unmodified MWCNTs, MWCNTs—COOH takes second place, and the smallest size of MWCNTs modified by organic alcohols. However, the particles size of MWCNTs modified by different organic alcohols was different from that of DMPA<GL<EG, indicating that the higher the graft rate of the organic alcohol chain segment is, the smaller the particle size of MWCNTs in WPU composite emulsion is. In the mechanical properties. The organic grafted make MWCNTs and WPU have better binding ability, and the more the amount of the hydrophilic groups grafted, the more the tensile stress increased. In the conductivity of the composites, the conductivity of composite of MWCNTs' mass fraction is 1.5% was $9.4 \times 10^{-8} \text{S/cm}$. The conductivity of the composite grafted to the organic chain segment —COOH was reduced to $1.8 \times 10^{-8} \text{S/cm}$, and that of the MWCNTs grafted to the organic alcohol group was enhanced to above $6.3 \times 10^{-5} \text{S/cm}$, improved by nearly three orders of magnitude, the higher the graft rate is, the higher the conductivity of the composite is.

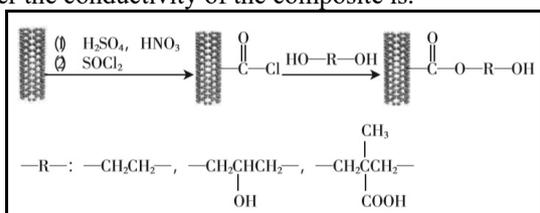


Figure 1. Synthesis route of modified MWCNTs(From Shaohui Wang [2])

2.2. Organosilicon modified multi-wall carbon nanotubes

Cui Gao's group first treated MWCNTs with mixed acid, grafted the organic chain segment —COOH, and then mixed the oxidized MWCNTs with silane polyethylenedrunk(s-PEG) to make the two esterification reaction and reach the surface of MWCNTs to graft the organosilicyl groups. Then the composite was prepared by solution blending. Results show that s-PEG covering the surface MWCNTs, wall became coarse, as the surface coverage reached 25%. When the s-PEG-MWCNTs content was 1%, the tensile strength and elongation at break of composite materials is 15.8Mpa and 585%, compared with pure WPU increased by 597% and 152%. The introduction of organic silicone group makes the dispersion properties of the composite increased greatly and interface between the MWCNTs and WPU combined with together increase. So the tensile properties increased, so as to improve the mechanical properties of the composite material. The conductivity of the composite increase with the increase of MWCNTs' content. When the amount of MWCNTs reaches 5%, the conductivity of the composite increases 9 orders of magnitude compared with the pure WPU material. The better dispersion performance of MWCNTs in WPU, the better power network structure can be formed in the composite material, thus reducing the resistivity of the composite material. However in the unmodified composites, MWCNTs were agglomerated to a certain extent in WPU, leading to the failure of forming a good electrified tunnel. Therefore, the conductivity of the modified organosilicone composite was significantly higher than that of the unmodified composite.

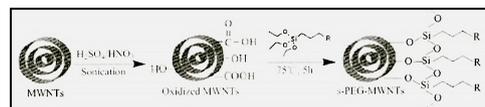


Figure 2. Synthetic procedures for s-PEG-MWCNTs(From Cui Gao [6])

2.3. Epoxy modified MWCNTs

Huafeng Duan's group treated MWCNTs with H2SO2-FeSO4, grafted hydroxyl groups and then grafted epoxy groups by coupling reaction with γ -glycidyl ether oxypropyl trimethoxysilane. Finally, the carboxylated PU material with alcohol as solvent and the modified MWCNTs were cross-linked to produce the composite material KH560-MWCNTs/WPU. The hydroxylated MWCNTs and 3-amino-propyltriethoxysilane were then reacted in the same way, and the composites E51-MWCNTs/PU were prepared by ultrasonic dispersion after they were added to epoxy resin E51. The results showed that the agglomeration of MWCNTs was significantly weakened and the tube wall was significantly thickened under scanning electron microscope. The initial thermal decomposition temperatures and the TG rates at 800°C were showed in table 2.

Table 2. Initial thermal decomposition temperatures and TG rates at 800°C

	Initial thermal decomposition T	TG rates at 800°C
KH560-MWCNTs	180°C	11.3%
E51-MWCNTs	182°C	22.5%

Table 3. Tensile strength and elongation at break of 1.5%MWCNTs content composites

1.5% MWCNTs content	Tensile strength	Elongation at break
Unmodified	17.2Mpa	517%
KH560	28.2Mpa	533%
E51	24.8Mpa	542%

Table 2 indicated that the graft rate of E51-MWCNTs was higher than that of KH560-MWCNTs. The tensile strength and elongation at break of the 1.5% unmodified MWCNTs' composites were showed in table3. It shows that the addition of epoxy groups can improve the dispersion property of MWCNTs in PU, improve the mechanical property and reduce the elongation at break. In the field of electrical properties, the resistivity of the unmodified composite material decreased with the increase of increased of the addition of MWCNTs. When the addition of MWCNTs reached 2%, the resistivity of the unmodified composite material was $2.3 \times 10^8 \Omega \cdot \text{cm}$, the resistivity of the KH560-MWCNTs decreased to $2.5 \times 10^5 \Omega \cdot \text{cm}$, and the resistivity of the E51-MWCNTs decreased to $8.6 \times 10^5 \Omega \cdot \text{cm}$. This indicates that the modified MWCNTs are more uniformly dispersed in PU, forming a conductive network. However, when the graft rate is high, the resistivity between energized tunnels will also increase due to the insulation of the grafted organic matter, so the resistivity of E51 is higher than that of KH560.

2.4. MWCNTs modified by amination

Zhenglong Yang's group first treated MWCNTs with mixed acid to graft them to the organic chain segment—COOH, and then reacted with sulfoxide chloride to acyl

Table 4. Data on mechanical properties

	SDBS-MWCNTs content/%						
	0	0.1	0.3	0.5	0.9	1.2	1.5
Tensile strength Mpa	25.3	22.9	27.7	25.6	25.7	22.1	20
Elongation at break	387%	464%	499%	477%	440%	435%	458%

The results show that with modified MWCNTs are added, composite materials tensile strength and elongation at break increased after decreased, when SDBS-MWCNTs content is 0.3%, the mechanical properties of composite materials to achieve the optimal conditions, the tensile strength and elongation at break increased by 9% and 29%, TG showed that after modification of the surface of MWCNTs alkyl chain interact with WPU soft chain segment, MWCNTs reduces the soft even the period of crystallization.

chlorination of carboxylated MWCNTs. Then they were mixed with ethylenediamine and triethylamine to make amine-modified MWCNTs, and then prepared composite materials by solution blending. The results showed that the introduction of amine groups improved the dispersion of MWCNTs in water, and the interaction ability of MWCNTs with WPU materials was also significantly improved. The particle size of the composite increases with the increase of the amount of MWCNTs and the viscosity also increases. Thermal stability properties of the composites increased, their initial thermal decomposition temperature and the temperature of the maximum thermal weightlessness rate increased with the increase of MWCNTs, 0.1% of MWCNTs composite material of two kinds of temperature than the unmodified composites of two kinds of temperature raised 20°C. The mechanical performance, itself MWCNTs and WPU composite can improve the mechanical properties of composite materials, and amino modified MWCNTs reinforcement for mechanical properties of ascension. In addition, the ultraviolet absorption capacity of the composites of such doped MWCNTs was also significantly improved, for example, the visible light transmittance of the composites of 0.1% MWCNTs reached about 80%.

2.5. SDBS modified MWCNTs

Zhiqian Xie's group mixed sodium dodecylbenzenesulfonate (SDBS) and MWCNTs were mixed ground and centrifuged to obtain SDBS modified MWCNTs. The composites were prepared by solution blending according to the amount of modified MWCNTs (0%, 0.1%, 0.3%, 0.5%, 0.9%, 1.2%, 1.5%). Date on mechanical properties was showed in table 4.

Table 5 showed that the composites' TG (when the composites mass loss reach 50%). It indicated that when the MWCNTs were added, WPU's heat stability decreased. It may be due to the good thermal conductivity of carbon nanotubes, and after being combined with polyurethane, the external heat is easily transferred through the carbon nanotubes to the polyurethane matrix, leading to the easier decomposition of polyurethane and the reduction of the decomposition temperature of composite materials.

Table 5. The TG of composites

	WPU	0.3%	0.5%	0.9%
Temperature/°C	356	351	346	348

In terms of electrical properties, when the content of modified MWCNTs was 0.9%, the conductivity of the composite increased by nearly 9 orders of magnitude.

3 Application field of carbon nanotubes/waterborne polyurethane

3.1. Application of mechanical properties

Carbon nanotubes have high mechanical strength and elasticity. They are more than 100 times stronger than steel, but have 1/6 of the density of steel. They are excellent carbon-dimensional materials, better than any fiber. The composite materials with waterborne polyurethane have most of the excellent properties of carbon nanotubes, which can be used as reinforcing materials for metal materials, giving more durability and strength to industrial products in industry. Its elasticity can also be used in the textile field, making the textile more durable, elastic and ductile

3.2. Application of electrical performance

Carbon nanotubes/waterborne polyurethane composite shell in electrical and electronic components application field is very broad, polyurethane as electrical shell material has a light texture, easy processing, the advantages of low cost, and large specific surface area of the carbon nanotubes, to a certain range of electromagnetic wave absorption characteristics, thus achieved the effect of electromagnetic shielding electromagnetic, the effect is also electrical and electronic components an integral part of preventing electromagnetic interference. In addition, it can be used as a coating material on military aircraft, so that the military aircraft achieve a "stealth" effect. The structure of carbon nanotubes also determines that the composite material has the properties of both metal and semiconductor. Therefore, the composite material can be used as a semi-conductor device, a conductor of a microcircuit, a nanoscale transistor and other microelectronic components.

3.3. Application of adsorption performance

The carbon nanotubes as a new type of adsorbent and have become one of the excellent properties of composite materials with WPU. Their adsorption of heavy metal ions, such as Pb^{2+} , Cd^{2+} , Cr^{6+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Hg^{2+} , As^{3+} and Ni^{2+} , can purify industrial wastewater and domestic water. In addition to the adsorption of metal ions, they also adsorb some organic pollutants. In addition, composite materials for hydrogen has become a kind of hydrogen storage material, and composite material of hydrogen energy is a kind of efficient, clean and pollution-free new energy source. For hydrogen storage, it is divided into two kinds of high pressures and liquefaction storage method, but these methods all have

make the risk of a hydrogen explosion, so can be used as a hydrogen storage material of carbon nanotubes/waterborne polyurethane composite materials become one of the hot composite material.

3.4. Application of biomedicine

Polyurethane materials in human body and has good blood compatibility, therefore, in the field of medicine, it is widely applied to promote bone tissue repair and production of artificial organs such as artificial heart, muscle fiber material, the current study was to improve the physiological activity of polyurethane material surface to improve its contact with the blood, but both in physical and chemical methods to make the new graft hydrophilic groups and physiological active substances, bacteria can get together ammoniac material mechanical performance is affected, while the MWCNTs can compensate for this defect, so the composite material is a kind of both can and blood compatibility and new medical material with good mechanical properties.

3.5. Energy saving materials

Carbon nanotubes in directional carbon nanotubes/waterborne polyurethane composites are vertically arranged, and there are long and narrow gaps between CNTs, The size of CNTs is exactly in line with the wavelength range of visible light. When the sunlight is incident, CNTs will constantly reflect into the film and cannot escape. Therefore, the composite material has a strong absorption and heat conduction effect on sunlight, and can be used as a kind of energy saving material for effective use of solar energy.

4 Development prospect and technical improvement of composite materials

Carbon nanotubes/waterborne polyurethane composites can greatly improve the excellent properties of carbon nanotubes and waterborne polyurethane and make the shortcomings of the two materials complement each other. The unique properties of both materials can be used better and more efficiently. In the future, the technical improvement of carbon nanotubes/waterborne polyurethane composites can be divided into the following aspects: 1)The modification method can reduce the use of and dependence of acid and other organic substances that are polluted to environment. 2)To explore the modification methods of polyurethane materials to improve the dispersibility of carbon nanotubes in them. At present, most of the research methods are modification of carbon nanotubes, while modification methods of polyurethane are rarely studied. Currently, the preparation and characterization of composites are mostly studied, but the enhancement mechanism of composites by carbon nanotubes is rarely introduced. 3)To improve the modification effect of physical methods on carbon nanotubes and to explore the modification effect of some equipment without the help of chemical reagents is also one of its research directions. Modification methods of

carbon nanotubes in composites materials will become the key to the development of composite materials in the future. The development trend of carbon nanotubes/waterborne polyurethane composite modification technology is to explore new technologies and adopt more diverse modification methods to find the optimal process to improve the composite properties.

5 Conclusion

Currently, the most commonly used modification method is to modify MWCNTs with acid. Studies have shown that, for MWCNTs grafted with —COOH, its mechanical properties, thermal stability and conductivity are not as good as those grafted with silicon group, epoxy group, amino group, and other chain segments. This paper mainly summarizes five methods of modified MWCNTs: organic alcohol modification, organosilicon modification, epoxy modification, animation modification and SDBS modification. In the field of carbon nanotubes/waterborne polyurethane composite material, there are a lot of methods. The results obtained by different modification methods are also obviously different. But in terms of simple experiment theory data, it is difficult to compare which modified method is better than other modification methods, only roughly drawing the advantages and disadvantages of each modification methods. Because when researchers prepare the composites, each method may be different due to synthetic method, experimental location, experiment condition and distribution of polyurethane soft and hard segments. Finally it caused the different between modified carbon nanotubes and differences in mechanical properties between polyurethanes. So it can be concluded that there were differences between composites and the results of modification methods are affected. In the future, the researchers will hammer at research on the modification of waterborne polyurethane and get rid of the acid dependence of the modification method.

Acknowledgement

In nearly two months, I finally finished this paper, which brought me unprecedented experience and gained a lot in the process full of struggle. With the help of my teachers and classmates, I overcame it one by one. In particular, I would like to express my strong gratitude to my thesis advisor. Without her tireless guidance and help, I could hardly finish this thesis. Finally, thanks to the monographs and academic terms quoted in this paper, it would be very difficult to complete this paper without the inspiration of these research results.

References

1. Ljima S. Helical microtubules of graphitic carbon[J]. *Nature*, 1991, 354(6348): 56-58.
2. Shaohui Wang. Chemical Functionalization of Carbon Nanotubes and the Properties of their Waterborne Polyurethane Composites[D]. Shanxi

- Taiyuan, Taiyuan University of technology, 2019. 1-38, 59-69, 75-83(In Chinese)
3. Feng Tong. Review on research progress of waterborne polyurethane[J]*Chinese Journal of Spectroscopy Laboratory*, 2000, 17(1), 56-59(In Chinese)
4. Jing Chen, Jianjun Yang, Qingyun Wu, et al. Preparation and properties of surface functionalized carbon nanotubes modified waterborne polyurethane composites[J]. *Polymer materials science and Engineering*(In Chinese)
5. Shaohui Wang, Caiying Hou, Guozhang Ma, et al. Organic alcohol modified multi-walled carbon nanotubes/waterborne polyurethane composites[J]. *Thermosetting Resin*, 2018, 33(6), 36-42.
6. Cui Gao, Xiaofei Zeng, Jianfeng Chen. Surface modification of multi-wall carbon nanotubes and its application in waterborne Polyurethane system[J]. *Chemical Reaction Engineering and Technology*, 2012, 28(3), 245-249(In Chinese)
7. Huafeng Duan, Shaohui Wang, Caiying Hou, et al. Properties of MWCNTs and their chemical crosslinked polyurethane composites modified by epoxy groups[J]. *Function materials*, 2019, 6(50), 155-159(In Chinese)
8. Zhenglong Yang, Shen Qin, Hongting Pu et al. Preparation and properties of a water-based polyurethane dispersion doped with carbon nanotubes[J]. *Function material*, 2008(06): 1030-1033. (In Chinese)
9. Caixia Zhao, Dongcheng Sun, Bin Yang et al. Preparation and application of carbon nanotubes/polyurethane functional composites[J] *CHEMICAL INDUSTRY AND ENGINEERING PROGRESS*, 2006, 25(8), 880-884
10. Zhiqian Xie, Yangyang Shi, Feilong Han et al. Preparation and characterization of waterborne polyurethane/SDBS modified multi-wall carbon nanotubes(MWCNTs) composites[J] *Water-based raw material technology*, 2017.10.23-26. 112-116.