Preparation and Characterization of Polyimide/Multiple-wall Carbon Nanotubes Composites

Fen Zhang 1, Xiaoqi Chen 1, Xiaojian Li 2, Haijun Zhou 1, Cangxu Li 2, Mengmeng Zhou 1, Lu Bai 3, Yantao Li 1,*

1 Institute of Energy Source, Hebei Academy of Science, Shijiazhuang, China
2 Hebei Huami Rubber Technology Co., Ltd, Xingtai, China
3 Hebei University of Science and Technology, Shijiazhuang, China

*Corresponding author e-mail: xiaojj@hebust.edu.cn

Abstract. The PI/MWNTs composites are prepared by using pyromelic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 4,4'-diaminodiphenyl ether (ODA) and multi-wall carbon nanotubes (MWNTs) through the ultrasonic in-situ polymerization method. The effect of MWNTs on the molecular structure, mechanical performance and chemical resistance performance are studied. The result shows that the carboxylated long MWNTs could improve the tensile performance of the composites, and the adding of MWNTs will not affect the molecular structure and the chemical resistance performance of polyimide (PI) material.

1. Introduction
Because of the special aromatic ring and heterocyclic ring structure, polyimide (PI) shows excellent mechanical, electrical, chemical and high heat performance, and has been widely used in aerospace, microelectronics, automobile and other high-tech areas.[1-3] To expand the application areas or further improve the mechanical performance of the PI resin, more and more researchers focus on the modification of PI by using functional fillers or additives. Carbon nanotubes (CNTs) are excellent reinforcing fillers in many materials for their high aspect ratio, nanosize in diameter, low density and excellent physical properties, and the combination of CNTs with high performance polymers has become one of the research focus.[4-8] Hu et al.[9] studied the effect of amino functionalized multi-wall carbon nanotubes (MWNTs) in PI resin and achieved good dispersion by using in-situ polymerization method. Adbehgah et al. [10] used MWNTs with -COOH functional groups to modify fluorinated PI, and the mechanical performance improved significantly.

In order to further improve the mechanical performance of the PI resin, four kinds of MWNTs are tried in the present study. The ultrasonic in-situ polymerization method is used to disperse MWNTs which could achieve good dispersion in PI resin. The tensile performance is studied by using the four kinds of MWNTs and by varying the loading of MWNTs, and the effect of MWNTs on the chemical resistance performance is also studied.
2. Experimental

2.1. Materials
Multi-wall carbon nanotubes (MWNTs) are supplied by Beijing Boyu High-tech New Materials Technology Company, the 4,4'-diaminodiphenyl ether (ODA) is obtained from Nantong Huishun Chemical Co., Ltd, the 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) is obtained from Shijiazhuang Haili Chemical Co. Ltd, and the pyromelic dianhydride (PMDA) is obtained from Rugao Leheng Chemical Co., Ltd. These raw materials are all dried in vacuum oven at 105 °C for 6hrs before using. N, N-dimethylacetamide (DMAC) is obtained from Tianjin Yongda Chemical Reagent Co., Ltd and used as received.

2.2. Preparation of PI powder
10wt% of ODA/DMAC solution is added to a four-neck flask equipped with mechanical stirring. Then a mixture of BPDA/PMDA with molar ratio of 2/1 is added to the flask at 20℃ under stirring. After reacting for 4 hours, a kind of viscous yellow polyamic acid solution is obtained. Then adding xylene and catalyst, the mixture is stirred uniformly and heated up for refluxing. After refluxing for 3 hours, the mixture is cooled down and filtered to get the powder. The powder is washed three times with acetone to remove the unreacted monomers, and then put into oven for thermal imidization to obtain the pure PI powder.

2.3. Synthesis of PI/MWNTs composites powder by ultrasonic in-situ polymerization
The MWNTs are added to DMAC and ultrasonic for 1h with power of 400 W, then adding ODA to the dispersion. After ODA is completely dissolved, a mixture of BPDA/PMDA with molar ratio of 2/1 is added. After reacting for 4 hours, a viscous black polyamic acid/MWNTs solution is obtained. Similar as that of the PI powder preparation, adding xylene and catalyst, the mixture is stirred uniformly and heated up for refluxing for 3 hours, then the mixture is cooled down and filtered to get the powder. The powder is washed three times with acetone to remove the unreacted monomers, and then put into oven for thermal imidization to obtain the PI/MWNTs composites powder.

2.4. Testing bar preparation
A certain amount of PI powder or PI/MWNTs composites powder is weighed and placed into a mold, and then heating up the machine to 420℃ for the testing bar preparation through hot pressing process.

2.5. Characterization
The molecular structure of PI and PI/MWNTs composites is tested by the Fourier transform infrared spectroscopy (FT-IR, Spectrum 100 infrared spectrometer). The tensile performance and Flexural performance of the PI/MWNTs composites is tested by the universal tensile testing machine according to standard GB/T 1040-92 and standard GB/T 9341-2008 respectively. Scanning Electronic Microscopy (SEM) is used to characterize the morphology of the pure PI and MWNTs filled PI material.

3. Results and discussion

3.1. FT-IR analysis of pure PI and PI/MWNTs composites
PI/MWNTs composites made with four kinds of MWNTs, long MWNTs with -COOH functional group (MWNTs\textsubscript{L-COOH}), short MWNTs with -COOH functional group (MWNTs\textsubscript{S-COOH}), long MWNTs without functional group (MWNTs\textsubscript{L}) and short MWNTs without functional group (MWNTs\textsubscript{S}) are all analyzed by the FT-IR spectrometer. And Figure 1 shows the molecular structure of pure PI and PI/MWNTs composites.
Figure 1. FTIR spectrum of pure PI and PI/MWNTs composites

Seen from Figure 1, the four PI/MWNTs composites all show similar FT-IR curves as that of the pure PI resin, and the characteristic absorption peaks of PI resin are all appeared: the peaks of the asymmetric and symmetric stretching vibration of C=O group in the imine ring at 1773 cm\(^{-1}\) and 1707 cm\(^{-1}\), the peak of the stretching vibration of C-N at 1365 cm\(^{-1}\), the peak of the bending vibration of C=O group at 729 cm\(^{-1}\), and the peak of the stretching vibration of C-O-C at 1234 cm\(^{-1}\). So the addition of MWNTs has little effect on the imidization of polyamide acid, and the PI/MWNTs composites powder are prepared successfully through the ultrasonic in-situ polymerization method.

3.2. Effect of MWNTs category on the mechanical property of PI/MWNTs composites

The effect of MWNTs category on the mechanical property of PI/MWNTs composites is studied by using four kinds of MWNTs through the ultrasonic in-situ polymerization method.

The tensile property of the four prepared PI/MWNTs composites is studied, and results are shown in Table 1. It can be seen that the sample with 0.5 wt% of MWNTs COOH-L shows the best tensile performance. The tensile strength increases to 108.9 MPa and tensile elongation increases to 4.5%, with about 26% tensile strength improvement and 23.6% tensile elongation improvement than that of the pure PI sample, while the other 3 MWNTs do not show much improvement on tensile strength performance, and also decrease the tensile elongation performance. Long MWNTs have higher contact area with PI resin, which helps to sustain much higher tension before part breaking. Furthermore, the COOH functional group on the MWNTs surface may form hydrogen bond and covalent bond with the C=O and -O- groups on the PI polymer chains, which will need more energy to break the part during the tensile test. For the MWNTs COOH-S modified PI material, the short length MWNTs will lead to more defect points for the PI resin, and thus decrease the tensile elongation performance. For the MWNTs without -COOH functional groups, because of the lack of the hydrogen bond and covalent bond between MWNTs and PI interface, the MWNTs will not have much interaction with the PI resin, and thus affect the tensile elongation performance.
Table 1. Effect of MWNTs category on the mechanical property of PI/MWNTs composites

| Sample                         | Tensile strength/MPa | Tensile elongation at break/% |
|--------------------------------|----------------------|-----------------------------|
| Pure PI                        | 86.4                 | 3.6                         |
| PI/0.5wt% MWNTs\(_{COOH-L}\)   | 108.9                | 4.5                         |
| PI/0.5wt% MWNTs\(_{COOH-S}\)   | 88.2                 | 2.6                         |
| PI/0.5wt% MWNTs\(_L\)          | 93.2                 | 3.5                         |
| PI/0.5wt% MWNTs\(_S\)          | 89.6                 | 2.8                         |

MWNTs\(_{COOH-L}\): long MWNTs with 2wt% -COOH functional group; MWNTs\(_{COOH-S}\): short MWNTs with 2wt% -COOH functional group; MWNTs\(_L\): long MWNTs without functional group; MWNTs\(_S\): short MWNTs without functional group.

3.3. Effect of MWNTs content on the mechanical property of PI/MWNTs composites

Since the tensile performance of PI/MWNTs composites can be improved by using MWNTs\(_{COOH-L}\), the loading amount of MWNTs\(_{COOH-L}\) is also studied in this part by using the ultrasonic in-situ polymerization method to prepare the composites powder. Figure 2 shows the effect of MWNTs content on the tensile performance and Figure 3 shows the SEM analysis for the morphology of the PI/MWNTs composites.

As shown in Figure 2, as the loading of MWNTs\(_{COOH-L}\) increases from 0.2wt% to 1wt%, the tensile strength performance first increases and then decreases, and tensile strength achieves to the maximum value 108.9MPa at 0.5wt% loading, while the tensile elongation performance changes from decrease to increase and then to decrease, and tensile elongation performance also reaches to the maximum value 4.5% at 0.5wt% loading. Comparing with the pure PI materials, the tensile strength and tensile elongation performance increases 26% and 23.6% respectively. Too lower loading of MWNTs\(_{COOH-L}\) cannot have the strength effect on the PI resin, while too much MWNTs\(_{COOH-L}\) is not easy to be dispersed homogeneously and might aggregate together to form the defect points, which is not good for the part mechanical performance. As shown in Figure 3, for the morphology of the cross-section of the tensile bar, PI without additives shows very smooth surface, while adding MWNTs\(_{COOH-L}\) will cause rough surface for the cross-section of the PI/MWNTs composites, and when the MWNTs\(_{COOH-L}\) loading increases to 0.8wt%, there will be MWNTs\(_{COOH-L}\) aggregation happened, which corresponds to the varying trend of the tensile performance shown in Figure 2. Therefore, the optimized PI/MWNTs composites could be achieved with 0.5wt% loading of MWNTs\(_{COOH-L}\) through the ultrasonic in-situ polymerization method.

![Figure 2. Effect of MWNTs content on the tensile performance of PI/MWNTs composites](image-url)
Figure 3. SEM analysis for the morphology of the PI/MWNTs composites

3.4. Effect of MWNTs on chemical resistance property of PI/MWNTs composites

PI resin has very good chemical resistance performance. To check the effect of MWNTs on the chemical resistance performance of PI/MWNTs composites (with 0.5wt% MWNTs loading), Flexural performance is used to do the test before and after immersing into chemicals for certain time, and deionized water, lubricating oil, kerosene and gasoline are used to do the immersion test by following the test condition shown in Table 2. After the immersion test, no erosion is found on the part surface, and Flexural test is to done to check the performance change after the immersion by following the GB/T 9341-2008 standard. Table 2 shows the Flexural testing results. It can be seen that PI/MWNTs composites could maintain very good Flexural performance after the immersion test, no obvious performance dropping is found, even after immersing in lubricating oil for 70h, Flexural performance
still could maintain about 96%. Since only 0.5wt% MWNTs exists in the composites, no significant effect is found for the Flexural performance of the PI/MWNTs composites after immersing into the selected chemicals, which also indicates that small amount of MWNTs has little effect on the chemical resistance performance of the PI/MWNTs composites.

### Table 2. Effect of MWNTs on chemical resistance property of PI/MWNTs composites

| Chemicals         | Flexural strength/MPa | Immersion test condition |
|-------------------|-----------------------|--------------------------|
| No chemical       | 109                   | 23°C                     |
| Deionized water   | 108                   | 23°C*48h                 |
| Lubricating oil   | 105                   | 23°C*70h                 |
| kerosene          | 100                   | 23°C*24h                 |
| Gasoline          | 103                   | 23°C*1h                  |

### 4. Conclusion

By using the ultrasonic in-situ polymerization method, the PI/MWNTs composites with optimized mechanical performance are prepared. The adding of MWNTs does not affect the imidization of PI resin. The tensile strength and tensile elongation performance could increase 26% and 23.6% respectively with 0.5 wt% loading of long MWNTs with -COOH function groups compared with that of pure PI material. For the prepared PI/MWNTs composites, the chemical resistance performance could be maintained in deionized water, lubricating oil, kerosene and gasoline.

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