Effect of MWCNTs’ Content on the Properties of Polyimide Composite Molding Materials

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Abstract. A series of MWCNTs/PI composite molding powders with different MWCNTs contents were prepared by ultrasonic dispersion in situ polymerization and blending method, and the samples were prepared by molding. In this experiment, 3,3’, 4,4’-biphenyltetracarboxylic dianhydride (BPDA), pyromellitic dianhydride (PMDA) and 4,4’-diaminodiphenyl ether (ODA) are taken as the main raw materials and MWCNTs as reinforcement materials. The molecular structure, thermal stability, mechanical properties, wear resistance and hardness of the composites were characterized. Results showed that mechanical properties of the composite molding materials prepared by ultrasonic dispersion in situ polymerization are better than those prepared by dry mixing method. The composite molding materials showed the best properties at the MWCNTs content of 0.5wt%. What’s more, the tensile strength and elongation at break are 108.9MPa and 4.5%, which are 26% and 23.6% higher than those of pure PI.

1. Introduction
Polyimide (PI), as a kind of high performance engineering plastics, has excellent mechanical properties, electrical properties, chemical stability, high radiation resistance and high temperature and low temperature resistance. Various application fields have placed higher demands on polyimide materials, and conventional polyimide materials have been unable to meet the demand. In order to meet higher requirements, more and more researchers focus on the performance modification of PI. Multi-walled carbon nanotubes (MWCNTs) as the tubular structure, with excellent mechanical, electrical and chemical properties and specific self-lubricating function, etc., have been developed into an ideal modified material for many materials [1-5]. In recent years, the combination of MWCNTs with high-polymers such as polytetrafluoroethylene [6], ultrahigh molecular weight polyethylene, polyurethane [7] and bismaleimide [8] has become the research focus.

Therefore, in this paper, functionalized MWCNTs was used to modify PI composite molding materials. Effects of ultrasonic in-situ polymerization method and blending method on the properties of MWCNTs/PI composite molding materials were studied, and the effects of MWCNTs’ content on the mechanical property, thermal stability, wear resistance and hardness of PI composite molding materials were discussed.
2. Experimental

2.1. Materials
Carboxylated multi-walled carbon nanotubes (MWCNTs) was supplied by Beijing Boyu High-tech New Materials Technology Company with carboxyl group content of 0.2 wt% to 1.0 wt%, the diameter of 20 nm to 30 nm, the length of 10 to 30 um, and purity of 95%. The 4, 4'-diaminodiphenyl ether (ODA) were obtained from Nantong Huishun Chemical Co., Ltd, the 3,3', 4, 4'-biphenyltetracarboxylic dianhydride (BPDA) were obtained from Shijiazhuang haili Chemical Co., Ltd and the pyromelic dianhydride (PMDA) were obtained from Rugao Leheng Chemical Co., Ltd. The raw materials were all dried in an vacuum drying oven at 105℃ for 6 h. N, N-dimethylacetamide (DMAc) were obtained from Tianjin Yongda Chemical Reagent Co., Ltd.

2.2. Preparation of PI molding materials
10 wt% ODA/DMAC solution was added to a four-neck flask equipped with mechanical stirring. Then an equimolar mixture of BTDA/PMDA (nBPDA/nPMDA=2/1) at 20℃ was added into system. 4 hours later, a kind of viscous yellow polyamic acid (PAA) solution was obtained. Then xylene and catalyst were added. The mixture was stirred uniformly and heated up. After refluxing for 3 hours, the mixture was cooled and filtered to obtain powders. The powders were washed three times with acetone, suction filtered and placed in an oven for thermal imidization to obtain a pure PI molding powder. Lastly, a certain amount of PI molding powder was weighed, put into the mold, and PI material sample was obtained by hot pressing machine.

2.3. Synthesis of MWCNTs/PI composite molding materials by ultrasonic in-situ polymerization
Firstly, the MWCNTs were added to a quantitative DMAc and ultrasonically dispersed for 1h at a power of 400 W, then ODA was added to the dispersion. After the ODA was completely dissolved, an equimolar mixture of BTDA/PMDA(nBPDA/nPMDA=2/1) at 20℃ was added into system. After reacting for 4 hours, a viscous black MWCNTs/PAA solution was obtained. Then xylene and catalyst were added, the mixture was stirred uniformly and heated up. After refluxing for 3 hours, the mixture was cooled and filtered to obtain powder. The powder was washed three times with acetone, suction filtered and placed in an oven for thermal imidization. Finally, a series of MWCNTs/PI composite molding powders with different MWCNTs content were obtained. Lastly, a certain amount of PI molding powders were weighed and placed in a mold, and samples of the MWCNTs/PI composite molding material was obtained by hot press molding machine.

2.4. Synthesis Process of Carbon MWCNTs/PI Composite Molding Materials by Blending Method
The MWCNTs and pure PI molding powders were added to a high-speed mixer in different mass ratios, and mixed at a high speed of 25000 r/min for 1 min to obtain a series of PI composite molding powders. A certain amount of powder was placed into a mold, and a sample of MWCNTs/PI composite molding material was obtained by a hot press molding machine.

2.5. Characterization
The molecular structure of PI and MWCNTs/PI composites was tested on Fourier transform infrared spectroscopy (FT IR, Spectrum 100 infrared spectrometer test). The thermal stability of composites was tested by TGA under nitrogen atmosphere with heating rate of 20℃/min and Test range of 30℃-900℃. The mechanical properties of composites were tested by universal tensile testing machine according to GB/T 1447-2005. Rockwell hardness of composite materials was tested with a plastic Rockwell hardness tester according to GB/T 3398.2-2008. And the wear resistance of composite materials are tested by the plastic sliding friction tester according to the provisions of GB/T 3960-2016.
3. Results and Discussions

3.1. FT IR analysis of PI and MWCNTs/PI composite materials
The molecular structures of PI molding powder and MWCNTs/PI composite molding powders were determined by infrared spectrometer in Figure 1.

![Figure 1. FTIR spectrum of pure PI and MWCNTs/PI composites materials.](image)

As was known in Figure 1, in infrared spectrum of pure PI, 1773 cm⁻¹ and 1707 cm⁻¹ is the asymmetric and symmetric stretching vibration peaks of C=O on the five-membered imine ring, and 1365 cm⁻¹ is the stretching vibration peaks of C-N, and 729 cm⁻¹ is the bending vibration peak of C=O, and 1234 cm⁻¹ is the stretching vibration peaks of C-O-C. Compared with Infrared spectrum of MWCNTs/PI composites materials, the characteristic absorption peak of MWCNTs/PI composite molding materials is basically the same as that of pure PI, and the addition of MWCNTs has little effect on the imination of polyamide acid.

3.2. Effects of different preparation processes on mechanical property of MWCNTs/PI composite molding materials
In this paper, ultrasonic in-situ polymerization method and blending method were used, and two different MWCNTs/PI composite molding materials were prepared separately. Effects of different MWCNTs content on their mechanical property were discussed in Table 1.

| MWCNTs content/ (wt%) | Ultrasonic in Situ Polymerization Method | Blending Method |
|------------------------|----------------------------------------|-----------------|
|                        | Tensile strength/MPa | Elongation at break % | Tensile strength/MPa | Elongation at break % |
| 0                      | 86.4                  | 3.6               | 86.4                  | 3.6               |
| 0.2                    | 91.6                  | 2.6               | 89.6                  | 1.73              |
| 0.5                    | 108.9                 | 4.5               | 92.9                  | 1.97              |
| 0.8                    | 106.6                 | 4.4               | 90.5                  | 1.69              |
| 1.0                    | 95.9                  | 3.7               | 86.9                  | 1.50              |
As shown in Table 1, the tensile strength and elongation at break of MWCNTs/PI composite molding materials prepared by ultrasonic in-situ polymerization increased first and then decreased with the increasing of MWCNTs content. The tensile strength (108.9MPa) and elongation at break (4.5%) of the composites reached the highest, which was 26% and 23.6% higher than pure PI when the content of MWCNTs is 0.5 wt%. Comparing with pure PI, the tensile strength (93MPa) of MWCNTs/PI composite molding materials prepared by blending method had a small improvement, reaching the maximum when MWCNTs content was 0.5wt%. While its elongation at break showed a decreasing trend. The above results showed that the MWCNTs can not be well dispersed into PI material simply by blending, and even became a defect in the composite molding materials. Through ultrasonic in-situ polymerization, MWCNTs can be uniformly dispersed into the molecular structure of PI, and the MWCNTs/PI composite molding materials prepared had excellent performance. Therefore, the MWCNTs/PI composite molding materials were finally prepared by ultrasonic in-situ polymerization, and the thermal stability, friction performance and hardness of the MWCNTs/PI composite molding materials were discussed.

3.3. Effects of MWCNTs content on thermal stability of MWCNTs/PI composite molding materials
The effects of different MWCNTs content on the thermal properties of MWCNTs/PI composite molding materials were shown in Figure 2. With the increasing of MWCNTs content the thermal decomposition temperature of composites increased gradually. When the amount of MWCNTs was 1wt%, the thermal decomposition temperatures of MWCNTs/PI composite molding materials on Td5 and Td10 were 580℃ and 600℃ respectively, while the thermal decomposition temperatures of pure PI on Td5 and Td10 were 574℃ and 596℃. Therefore, the addition of MWCNTs was beneficial to improve the thermal stability of MWCNTs/PI composite molding materials, but the low MWCNTs content had little effect on the thermal stability of MWCNTs/PI composite molding materials.

![Thermogravimetric curve of pure PI materials and MWCNTs/PI composite molding materials](image)

**Figure 2.** Thermogravimetric curve of pure PI materials and MWCNTs/PI composite molding materials

3.4. Effects of MWCNTs content on wear resistance of MWCNTs/PI composite molding materials
The influence of different MWCNTs content on the wear resistance of MWCNTs/PI composite molding materials was studied. As can be seen from table 2, it was beneficial to improving the wear resistance of MWCNTs/PI composite molding materials by adding MWCNTs. When the MWCNTs content was 0.5wt%, the effect was most obvious, and the friction coefficient of the composite was only 0.22. That was because MWCNTs was a tabular structure with a good load transfer capacity. During the sliding process, a transfer film can be better formed on the friction surface and the wear resistance of MWCNTs/PI composite material can be improved.
Table 2. The effect of MWCNTs content on wear resistance of composite molding materials

| Sample | MWCNTs Content/ (wt%) | Friction Coefficient |
|--------|----------------------|---------------------|
| 1      | 0                    | 0.32                |
| 2      | 0.2                  | 0.30                |
| 3      | 0.5                  | 0.24                |
| 4      | 0.8                  | 0.27                |
| 5      | 1.0                  | 0.27                |

3.5. Effects of MWCNTs Content on the hardness of MWCNTs/PI Composite Molding Materials

Table 3. The effect of MWCNTs content on the hardness of MWCNTs/PI composite molding materials

| Sample | MWCNTs Content/ (wt%) | Rockwell Hardness |
|--------|----------------------|-------------------|
| 1      | 0                    | 105.4             |
| 2      | 0.2                  | 104.5             |
| 3      | 0.5                  | 106.5             |
| 4      | 0.8                  | 107.7             |
| 5      | 1.0                  | 107.4             |

Table 3 showed the influence of different MWCNTs content on the Rockwell Hardness of MWCNTs/PI composite molding materials. The addition of MWCNTs was beneficial to increase the hardness of MWCNTs/PI composite molding materials. When the addition amount of MWCNTs was 1.0 wt%, the hardness of MWCNTs/PI composite molding materials reached 108.4, which increased slightly comparing with pure PI.

4. Conclusion

Comparing with ultrasonic in-situ polymerization and blending method, the MWCNTs/PI composite molding materials which were prepared by ultrasonic in-situ polymerization had a better mechanical property. The tensile strength and elongation at break of MWCNTs/PI composite molding materials were 108.9 MPa and 4.5% respectively when the MWCNTs content was 0.5 wt%. And comparing with pure PI materials, those were increased by 26% and 23.6% respectively. Due to the small amount of MWNTs added, the thermal stability, wear resistance and hardness of PI materials are improved, but the improvement range is small.

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