Study on Molding Process of Ether Anhydride Type Polyimide Materials

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Abstract. The main molding process of ether anhydride type polyimide materials which synthesized by the main materials of pyromellitic dianhydride (PMDA), 3,3',4,4'-tetracarboxydiphthalic dianhydride (OPDA) and Diamine diphenyl ether (ODA) was researched. The effects of molding temperature, molding time and molding pressure on the tensile properties of molded products were investigated. And the effects of dianhydride ratio on the properties and molding process of ether anhydride type polyimide materials was discussed. Results showed that samples molded by polyimide molding powder appeared the best comprehensive performance when the molar ratio of PMDA and OPDA was 2:1, with the tensile strength of 93.5 MPa, the elongation at break of 10.1%, the vitrification transition temperature of 340 ℃ and the thermal decomposition temperature of 5% was 574 ℃. And molding process is under that the molding temperature is 410 ℃, the molding pressure is 4.0Mpa and the molding time is 15min.

1. Introduction
Polyimide (PI) was a kind of special engineering plastics with high application value, which could competed with some kinds of metals. It had excellent properties such as high dielectric property, high strength and high modulus at high temperature [1-2]. It was widely used in aviation, aerospace, national defense, military and microelectronics and other high-tech fields [3-6]. Because of the rigid structure of most polyimides chains, the interaction between the chains was so strong that no melt flow or even softening occurs at the decomposition temperature, making it very difficult to form.

In this paper, main materials of pyromellitic dianhydride (PMDA), 3,3', 4,4'-tetracarboxydiphthalic ether dianhydride (OPDA) and 4, 4'-diaminodiphenyl ether(ODA) were used to synthesize ether anhydride polyimide moulding plastics successfully by introducing a certain amount of soft groups into the polyimide molecular chain. On the basis of this research, this paper focused on the study of ether anhydride type polyimide material molding process with different dianhydride ratio, and the tensile properties and thermal stability of molded products were characterized. Then the suitable molding process for ether anhydride polyimide materials were determined.
2. Experimental

2.1. Materials
The 4, 4'-diaminodiphenyl ether (ODA) were obtained from Nantong Huishun Chemical Co., Ltd. The 3,3',4,4'-tetracarboxydiphthalic ether dianhydride(OPDA) were purchased from Shanghai GuChuang New Chemical Materials Co., Ltd and the pyromelic dianhydride (PMDA) were supplied by 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 ether anhydride type polyimide molding materials
ODA was added to the DMAc for completely dissolve, and a mixture of different molar ratios (4:1, 3:1, 2:1 and 1:1) of PMDA and ODPA was put into system at 0℃, respectively. Then a series of ether anhydride type polyamic acid (PAA) solutions were obtained. Through thermal imidization at 160℃~300℃ to obtain a series of ether anhydride type polyimide molding powder containing different softening groups, named PI-1, PI-2, PI-3, PI-4. The effects of molding conditions such as molding pressure, molding temperature and molding time on the tensile properties of different ether anhydride type polyimide materials were investigated.

2.3. Characterization
The vitrification transition temperature (Tg) was measured by dynamic thermo-mechanical instrument (DMA) according to ASTM E1640-2013. The thermal stability of PI was measured by TGA. Test conditions: nitrogen atmosphere, temperature rise rate: 20℃/min, test range: 30℃-900℃. Mechanical properties was tested according to the provisions of GB/T 1040.1-2006, and B1 dumbbell test bar was tested at the speed of 2 mm/min on universal tensile testing machine.

3. Results and discussion

3.1. The vitrification transition temperature analysis
The vitrification transition temperature (Tg) of the polymer was a transition temperature from the freezing to the movement of the polymer segment, which was an important parameter for polymer processing conditions and performance. The higher the vitrification transition temperature, the higher the temperature at which the material was used, but the more difficult the processing conditions. Due to the high Tg of polyimide, the Tg of ether anhydride type polyimide materials containing different molar ratio of PMDA/OPDA was determined by dynamic thermo-mechanical instrument (DMA). Result were shown on Figure 1.

![Figure 1. DMA spectra of polyimides with different molar ratios of PMDA/OPDA](image-url)
As can be seen from figure 1, with the increasing of OPDA content in polyimide molding powder, the soft structure in the molecular structure of polyimide increased. And Tg gradually decreased from 355°C to 335°C, which improved the processing performance of PI materials.

3.2. Effect of molding process on PI performance
Taking PI-3 as an example, the effects of different molding pressures, different molding temperatures, different molding times and other factors on the tensile properties of PI materials were investigated. In the case of any two influencing factors remain unchanged, only one influencing factor was changed, a series of PI samples under different molding conditions were obtained, and the tensile properties were measured. Results are shown in Table 1.

| Samples | Elongation at break (%) | Tensile strength (MPa) |
|---------|------------------------|-----------------------|
| Molding Temperatures (°C) | | |
| 350     | 5.9                    | 55.7                  |
| 380     | 6.2                    | 67.4                  |
| 410     | 10.1                   | 93.5                  |
| 440     | 7.5                    | 88.2                  |
| 2.8     | 6.3                    | 60.2                  |
| 3.4     | 9.8                    | 88.5                  |
| Molding Pressures (MPa) | | |
| 4.0     | 10.1                   | 93.5                  |
| 4.6     | 10.0                   | 93.3                  |
| 5       | 3.9                    | 61.4                  |
| 10      | 7.3                    | 77.3                  |
| 15      | 10.1                   | 93.5                  |
| 20      | 6.1                    | 75.1                  |

It can be seen from Table 1, the PI-3 polyimide molding powder had the best mechanical properties under the condition of the molding temperature of 410°C, the molding time of 15 min, and the molding pressure of 4.0 MPa. The tensile strength and elongation at break can reach 93.5MPa and 10.1%, respectively. Therefore, the optimum molding condition was obtained from above data.

3.3. Effect of dianhydride ratio on PI molding process.
As the content of ether anhydride groups in the molecular chain increased, the Tg of the polyimide decreased, and the fluidity of the melt increased, which was advantageous for the processing of the material. After a series of experiments, the best molding process for polyimide materials with different dianhydride ratios was determined, which was shown in Table 2.

| Sample | Tensile Strength (MPa) | Elongation at Break (%) | Molding Times (min) | Molding Pressures (MPa) | Molding Temperatures (°C) |
|--------|------------------------|------------------------|--------------------|------------------------|--------------------------|
| PI-1   | 72.0                   | 4.1                    | 15                 | 4.0                    | 430                      |
| PI-2   | 73.4                   | 6.5                    | 15                 | 4.0                    | 420                      |
| PI-3   | 93.5                   | 10.1                   | 15                 | 4.0                    | 410                      |
| PI-4   | 89.5                   | 8.1                    | 15                 | 4.0                    | 400                      |

As can be seen from table 2, the PI synthesized with the molar ratio of PMDA/OPDA was 4:1, 3:1, 2:1 and 1:1 under the molding pressure of 4.0MPa, the molding time of 15 minutes accorded to best molding temperature was 430°C, 420°C, 410°C and 400°C. With the increasing content of ether anhydride groups in the molecular chain, the molding temperature gradually decreased, while the molding time and pressure were almost unchanged. High temperature helped to shorten the molding
cycle and improved the comprehensive performance of the samples. However, if the temperature was too high, the surface would become black or even decompose, which degraded the performance of the sample. On the contrary, the molding temperature was too low, the melting was not perfect and the melt fluidity was reduced, which led to the dissatisfaction of the mold filling and affected the tensile properties of the sample. Therefore, the molding temperature was one of the important factors in the molding, and the selection of a suitable molding temperature was very important for the performance of the product.

It can also be seen from Table 2 that the obtained PI-3 when molar ratio of PMDA/OPDA was 2:1, the tensile strength and elongation at break reached a maximum of 93.5 MPa and 10.1%, respectively. Therefore, the elongation at break of PI increased, as the content of ether anhydride groups in the molecular chain, and its flexibility was better.

3.4. Effect of dianhydride ratio on the thermal stability of PI
The thermal weight loss of different ether anhydride type polyimide materials was measured, and the temperature at which the weight loss ratio of the polymer was 5% and 10% was recorded. The results were summarized in Table 3.

| Sample | nPMDA:nOPDA | Td5 (%) | Td10(%) |
|--------|-------------|---------|---------|
| PI-1   | 4:1         | 583     | 597     |
| PI-2   | 3:1         | 579     | 591     |
| PI-3   | 2:1         | 574     | 586     |
| PI-4   | 1:1         | 571     | 582     |

As shown in Table 3, comparing the TGA data of different dianhydride ratio polyimide molding powder, it seemed that all four kinds of polyimide molding powder had excellent thermal stability. However, with the increase of ether anhydride groups content, the thermal stability showed a slight decline. The thermal decomposition temperature of PI-1 was the highest and the thermal stability was the best, while the thermal stability of PI-4 was the worst. With the increase of ether anhydride groups content, the content of ether bond in the main chain of polyimide molecules increased, improving the flexibility of macromolecules, so the thermal decomposition temperature gradually decreased, and the thermal stability became worse. This fully showed that ether anhydride groups was the key component to improve the fluidity of molding powder and the flexibility of products. Thus PMDA was an important monomer with high thermal stability of polyimide.

4. Conclusion
Ether anhydride polyimide molding powder with different dianhydride ratios was suitable for different molding process. Polyimide molding powder PI-3(nPMDA/nOPDA = 2:1) had the best comprehensive performance. The suitable molding process was under the molding temperature of 410℃, the molding pressure of 4.0 MPa, and the molding time of 15 min. And the tensile strength of the sample was 93.5Mpa, the elongation at break was up to 10.1%, the vitrification transition temperature was 340℃, and the thermal decomposition temperature of 5% was 574℃, which had good processing performance, resulting in the preparation of mold parts with more complicated structures.

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