Preparation and Characterization of Polyimide/TiO\textsubscript{2} Nano-composites for Non-lethal Weapon

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Abstract: A series of Polyimide/ TiO\textsubscript{2} (PI/TiO\textsubscript{2}) nano-composites were successfully prepared by incorporating different nano-sized TiO\textsubscript{2} contents into PI which derived from pyromellitic dianhydride (PMDA) and a flexible diamine 4,4-bis(3-aminophenoxy)biphenyl (4,3-BAPOBP) via in-situ polymerization and a thermal imidization method. The micromorphology, chemical structure of samples were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR). The SEM results show that when the content of nano-TiO\textsubscript{2} is lower, the nano-TiO\textsubscript{2} can be distributed uniformly in the matrix by the method of this experiment scheme, and signs of agglomeration have begun to appear when the TiO\textsubscript{2} content is 12 wt.%. XRD patterns reveal the crystal structure of TiO\textsubscript{2} remains unchanged and stable after being doped into PI matrix, and the TiO\textsubscript{2} nano-particles have good compatibility with PI matrix.

1. Introduction

For the Armed Police Force, with the continuous expansion of functional tasks, higher requirements are put forward for the performance of equipment. In the diversified tasks of the armed police forces, non-lethal weapons have played an irreplaceable role. In order to improve the performance of related equipment, the use of high-performance materials is an effective way.

PI is a polymer material that owns excellent mechanical properties, dielectric properties, corrosion resistance, especially high temperature resistance. It has shown good development potential in aerospace and other demanding harsh environments. However, there is still a certain gap between the performance of pure polyimide and the actual demand. Many research groups had devoted oneself to developing PI/inorganic hybrids by embedding inorganic particles [1-5].

Among the inorganic nano-ceramic materials, nano-TiO\textsubscript{2} is non-toxic and low-cost, it has good semiconductor properties, excellent transparent properties, high surface activity, and good dispersibility in the matrix as an additive. It is a raw material with a considerable market, which has been promoted in the coatings, electronics, chemical fiber, cosmetics and medicine et al fields. In recent years, nano-TiO\textsubscript{2} has shown especially good application prospects in improving the mechanical properties of the matrix and which has also been proved by a number of studies in academia.

However, according to the research and analysis on the preparation of PI/TiO\textsubscript{2} composite materials, it has been found that there are some difficult problems during the preparation of such nano-composite materials. Such as, the inherent catalysis of TiO\textsubscript{2} causes thermal stability and other performance reduction of the composite materials; as well as TiO\textsubscript{2} nano-particles often form accumulation before they can be uniformly dispersed in the matrix. The common solution is to add a chelating agent into the TiO\textsubscript{2}
precursor to reduce the hydrolysis process. However, it is not easy to remove the excessive chelating agent from the system, which will affect the final performance of the composite material. [6-9]

In this experiment, nano-TiO$_2$ is directly used as an additive, and a variety of physical methods are used to maximize the dispersion of TiO$_2$ in the matrix. With the aid of ultrasound, strong stirring, and pre-dispersion, PI/TiO$_2$ nano-composites film was successfully prepared by strictly controlling the experimental operating process conditions, and the microstructure of the prepared samples was characterized by physical and chemical instruments; at the same time, electronic universal material testing machine was used to test the mechanical properties of the prepared samples, and the effect of the different TiO$_2$ content on the samples’ properties was systematically studied.

2. Experimental

2.1. Main raw materials and instruments
Pyromellitic dianhydride (PMDA, 98.5%) was obtained from Sinopharm Chemical Reagent Co., Ltd, China and dried at 130$^\circ$C for 3 h before use; 4,4-Bis(3-aminophenoxy)biphenyl (4,3-BAPOBP, 98%) was supplied by Heowns Biochemical Technology Co., Ltd, China and used as received; TiO$_2$ with a mean particle size of 100 nm was obtained from Guangzhou GBS High-tech & Industry Co. Ltd, China and was dried for 24 h at 100$^\circ$C; N,N-dimethylacetamide (DMAc, 99.5%) was purchased from Shanghai SSS Reagent Co., Ltd, China, purified by distillation under reduced pressure and stored over 4 Å molecular sieves prior to use.

Electronic balance, JM-B2003, Cixi Red Diamond Weighing Apparatus Co., Ltd.; Scanning Electron Microscope (SEM), Evo-50, produced by Carl Zeiss, Germany; X-ray diffraction (XRD), AXS D8, produced by Bruker, Germany; Fourier transform infrared (FTIR), FTIR-650, produced by Tianjin Gangdong Sci. & Tech. Co., Ltd, China.

2.2. Preparation of PI/TiO$_2$ Nano-composites
Before the experiment, the amount of nano-TiO$_2$ needed was calculated, then weighed and spread in a glass dish, and it was dried in a blasted high temperature box with 130$^\circ$C for 5h, then cooled to room temperature, and was encapsulated.

In this experiment, dry and clean utensils were connected and set up at room temperature according to the experimental process and requirements, and the each part was kept sealed; the N$_2$ tank valve was opened before feeding, and the pre-calculated nano-TiO$_2$ and 4,3-BAPOBP were added after 10min, with stir vigorously until it is completely dissolved; then the weighed PMDA was added into the reaction flask with continuous stirring by 6 times. After 6h, PAA/TiO$_2$ solution with a certain viscosity was obtained by continuing stirring and reacting.

Firstly, spread the prepared PAA/TiO$_2$ solution evenly on the pre-cleaned glass plate by spin coating, in order to avoid the formation of bubbles and defects in the film due to the rapid volatilization of a large amount solvent during the imidization process. Nextly, the film coated the glass plate will be kept at about 70$^\circ$C for 1 h to remove the part solvent. Then, it is placed in a program-controlled oven for thermal imidization; the programmed gradient temperature was 120, 180, 240, and 300$^\circ$C each for 1 h, and the sample was cooled to room temperature, and finally PI/TiO$_2$ composite films were obtained. The thickness of the prepared sample is approximately 25 μm. The experimental process was shown in Fig. 1.
2.3. Characterization

Scanning electron microscopy (SEM): The samples were cut to rectangular specimen (5mm×5mm), whose surfaces were sputter coated with gold and then observed with by Carl Zeiss Evo-50 Scanning Electron Microscopy.

X-Ray Diffraction (XRD): XRD studies were performed on a Rigaku D/Max 2550 instrument with CuKα radiation at 30 kV and 20 mA. The experiments were performed in the range of 2θ=10-80° with a step of 0.02°.

Fourier Transform Infrared (FTIR): FTIR spectra were recorded using a Nicolet MAGNA-IR 650 spectrometer with a KBr disk or thin film at wavelengths between 400 and 4000 cm⁻¹ at room temperature.

3. Results and discussion

3.1. SEM analysis of Nano-composites

Fig.2 (a~d) are the SEM images of the distribution of different content of TiO₂ in the PI matrix. In this group pictures, the dark color is the matrix, and the obvious white small particles are nano-TiO₂. It is not difficult to see that TiO₂ has good compatibility with the matrix, and has very good dispersibility in the matrix; in addition, with the increase of TiO₂ content, the density of TiO₂ in the matrix increases successively, and there is no obvious larger agglomerated particles; however, with closer inspection, you will notice that when the TiO₂ content is 12 wt.% signs of agglomeration have begun to appear⁶.

Fig.3 (a) and (b) are the distribution of 5,000 times (a) and 20,000 times (b) when the content of TiO₂ in the PI matrix is 15 wt.%, respectively. It can be seen from this group of pictures, the distribution has changed significantly, and the agglomeration between TiO₂ nanoparticles is prominent, which will not be conducive to the improvement of matrix performance.⁷
3.2. XRD analysis of Nano-composites

In order to further investigate the morphology of TiO$_2$ in the matrix, XRD tests were performed on the PI matrix and PI/TiO$_2$ nano-composite film samples. Fig.4 shows the XRD spectrum of pure PI. Fig.5 shows the XRD spectra of the PI/TiO$_2$ nano-composites when the TiO$_2$ content is 6, 9, and 12 wt.%, respectively. It can be seen from Fig.4 and Fig.5 that PI has a typical amorphous structure, and there is an obvious convex diffraction peak near 20=18°, which is the characteristic peak of PI[8-9]. At the same time, in the curves of Fig.5 (a~c), in addition to the characteristic diffraction peaks inherent in PI, there are obvious sharp peaks at 27°, 36°, 41°, 54.5°, 57°, and 69°, these diffraction peaks are the characteristic diffraction peaks of the TiO$_2$ crystal plane. Their appearance indicates that TiO$_2$ has been successfully composited with the PI matrix; and the diffraction peaks of TiO$_2$ gradually increase with
the increasing of its content, which indicates the crystal particles are larger when TiO₂ content is higher in the matrix; at the same time, comparing Fig.4 to Fig.5, it is found that in the XRD spectrum of PI/TiO₂ nano-composites, the 2θ position of the PI diffraction peak did not move significantly, which indicating that the microscopic morphology of the PI matrix did not change significantly after adding a small amount of TiO₂.

![XRD patterns of PI/TiO₂ hybrid films with different TiO₂ content:](image)

**Figure.5** XRD patterns of PI/TiO₂ hybrid films with different TiO₂ content: (a) 6 wt.%, (b) 9 wt.% and (c) 12 wt.%

### 3.3. FTIR analysis of Nano-composites

The FTIR spectra of PI/TiO₂ nano-composites with 3, 6, 9 and 12 wt.% TiO₂ are shown in Fig.6(a~d).

![FTIR patterns of PI/TiO₂ hybrid films with different TiO₂ content:](image)

**Figure.6** FTIR patterns of PI/TiO₂ hybrid films with different TiO₂ content: (a) 3 wt.%, (b) 6 wt.%, (c) 9 wt.%, (d) 12 wt.%

By analyzing the spectra of the samples, it is found that the most important and basic functional groups of PI are C=O and C-N-C. The symmetric and asymmetric vibration characteristic absorption peaks of C=O group are near 1728 and 1776 cm⁻¹, respectively, and the characteristic absorption peaks due to flexural vibration are near 725 and 3487 cm⁻¹. The absorption peak caused by the stretching vibration of C-N-C in the imide bond is near 1380 cm⁻¹. At the same time, characteristic absorption peak of PAA was not observed near 1678 cm⁻¹ in this diagram. These results show that the imidization process is complete [5-6].

In addition to, based on the PI characteristic peaks' spectra, we can also see that there is a continuous vibration absorption peak in the region of about 400–850 cm⁻¹, this is due to introduce the Ti-O-Ti bond by the addition of TiO₂, which forms a network structure in the system; and the presence of distinct peaks in the adjacent 1010-1240cm⁻¹ region is due to the Ti-O-C bond formed when hydroxyl of TiO₂ surface polymerizes with the macromolecular branched chain; and at the far left of the spectrum, the obvious absorption peak is about 3647cm⁻¹, which is the hydroxyl' contribution of TiO₂ surface[7-9].
The intensity of these absorption peaks caused by TiO$_2$ is closely related to the content of TiO$_2$. When the content of TiO$_2$ is larger, the vibration amplitude of the peaks is larger; when the content of TiO$_2$ is larger, the vibration amplitude of the peaks is smaller, and the vibration amplitude of the peaks is smaller.

All the above results show that the PI/TiO$_2$ nano-composites can be successfully prepared by this method.

4. Conclusion

(1) A series of PI/TiO$_2$ nano-composites can been successfully prepared via in-situ polymerization and a thermal imidization method.

(2) The SEM results show that when the content of nano-TiO$_2$ is lower, the nano-TiO$_2$ can be distributed uniformly in the matrix by the method of this experiment scheme, and signs of agglomeration have begun to appear when the TiO$_2$ content is 12 wt.%.

(3) The XRD patterns show that the morphology of TiO$_2$ doped in PI matrix does not change and the TiO$_2$ nano-particles have good compatibility with PI matrix.

(4) The FTIR spectra analyses show that the intensity of the characteristic absorption peak of TiO$_2$ increases with the increasing of TiO$_2$ content.

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