Preparation and characterization of copolyester-TiO₂ nanocomposites ultra-thin films

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Abstract. A series of ultra-thin films were prepared by dip-coating method, with the copolyester-TiO₂ nanocomposites as solute and chloroform-trifluoroacetic acid as solvent. The thickness, surface morphologies and thermal properties of the films were studied. The results indicated that the thickness of the ultra-thin films was improved with the increase of the concentration of solution. The glass transition temperature declined from 64.2 °C to 51.2 °C with the decrease of film thickness from 3.275 μm to 22 nm.

1. Introduction
In the polymer-inorganic nanocomposites, controlling the inorganic nanofiller as the form of the dispersed phase is the core technology for realizing the nano-effect of the inorganic filler and improving the material properties [1]. It is of great significance in both theoretical research and practical application. The polymer solution is a homogeneous structure system in which a polymer is dispersed together in a molecular state and a solvent. It is a subject that people often deal with in life practice and scientific research. The dissolution of a polymer in a solvent generally involves two processes: swelling and dissolution. The solvent molecules first penetrate into the polymer molecular chain by diffusion, so that the volume of the polymer material expands, thereby weakening the interaction force between the molecular chains [2]. When the molecular chain is gradually stretched and dispersed, the movement tends to be free, and a completely dissolved solution system is formed.

In the solution state, the movement of the polymer molecular chain tends to be free, and the molecular self-organization process is remarkable. When the solvent of the polymer solution is volatilized to form a film, various structures can be formed depending on the operating conditions [3]. The method of film formation of a polymer solution mainly includes solution casting method [4], spin-coating method [5], dip coating method [6], and so on. The solution casting method refers that a polymer solution is injected into a certain shape mold, and the film is obtained with the same shape after evaporation of the solvent [7], but the disadvantage is that the thickness of the film is thick. The spin coating method is applied by using a spin coating instrument. There are many limitations, but it has high advantages in terms of the flatness and precise thickness control of thin films [8]. The dip coating method is more commonly used because of its simple operation. Besides, it has high production efficiency and is easy to realize mechanization of coating process [9].

In this paper, the copolyester-TiO₂ nanocomposites [10] were dissolved in a mixed solvent of chloroform-trifluoroacetic acid, and the ultra-thin films with different thicknesses loaded on the glass
sheets were prepared by dip coating method. The effects of the concentration of polymers solution on the thickness, surface morphology and the glass transition temperature of the ultra-thin films were investigated.

2. Materials and methods

2.1. Materials
Chloroform and acetone were purchased from Tianjing Guangfu Fine Chemical Research Institute, China. Trifluoroacetic acid and ethyl alcohol were obtained from China National Pharmaceutical Group Corporation. The reagents mentioned above were of analytical grade and used without further purification. The copolyester-TiO₂ nanocomposites were synthesized according to our previously established literature [10]. In this experiment, polyethylene terephthalate copolyester combined 0.4 wt% TiO₂ (CPT-0.4) was used as the experimental sample.

2.2. Preparation of ultra-thin films
Solvent was prepared with chloroform: trifluoroacetic acid volume ratio of 6:1 and stored in reserve. CPT-0.4 samples were washed with acetone, dried in vacuum at 130 °C and crushed, then passed through a 200-mesh standard sieve. Samples of sieved powder were weighed to prepare the solution with mass concentration of 0.1%, 0.2%, 0.4%, 0.6% and 1.0%. Ultra-thin films were prepared by immersing the glass sheets in above solution at 45° for 3 s, taking them out and standing them for 3 s, then repeating them three times. Finally, the resulting ultra-thin films were naturally dried for 30 min and then vacuum dried at 25 °C for 12 h.

2.3. Characterization of ultra-thin films
The glass sheets loaded with different concentrations of ultra-thin films were frozen in liquid nitrogen for 5 min and then broken with tweezers. The cross-sections and surface were respectively coated with a thin layer of gold. The thickness and surface morphology of ultra-thin films were observed under scanning electron microscope (SEM, FEI Quanta 200F). Glass transition temperature of these ultra-thin films was determined using differential scanning calorimeter (DSC, NETZSCH 204 F1 Phoenix, Germany). The ultra-thin films were heated from 0 °C to 90 °C at a heating rate of 10 °C/min in N₂ atmosphere.

3. Results and Discussion

3.1. Analysis of ultra-thin film thickness
Cross-sectional SEM images of CPT-0.4 nanocomposites ultra-thin films prepared by dip-coating method in organic solvent are shown in Figure 2. It is clearly seen that the film thickness is only 22.64 nm (Fig. 2a) when the concentration is 0.1 wt%. As the concentration of the solution increases, the thickness of the film rapidly increases to 280 nm (Fig. 2d) when the concentration is 0.6 wt%. The thickness reached 3275 nm (Fig. 2e) when the concentration reached 1.0 wt%.
Figure 2. Cross-sectional SEM images of CPT-0.4 composite thin films prepared by dip-coating method in organic solvent (a: 0.1 wt%, b: 0.2 wt%, c: 0.4 wt%, d: 0.6 wt%, e: 1.0 wt%).

Furthermore, the effect of different CPT-0.4 contents loaded in organic solvent on the ultra-thin films thickness is shown in Figure 3. It is obvious that the thickness-concentration relationship is basically linear when the solution concentration is low (<0.6 wt%). When the concentration is high (>0.6 wt%), the thickness increases rapidly with the increase of concentration. This curve can be used as a reference for preparing ultra-thin films with certain thickness.

Figure 3. The effect of different CPT-0.4 contents loaded in organic solvent on the thickness of the ultra-thin films.
3.2. SEM surface morphology analysis

Figure 4(a)–(e) show SEM surface morphologies of the ultra-thin films with organic solvent concentration loading from 0.1 to 1.0 wt%. At the concentration of 0.1 wt%, the surface (Fig. 4a) is more difficult to form a continuous film structure, and there are a large number of voids and discontinuities, which may be due to the fact that the solvent itself is extremely volatile. The ultra-thin film can form continuous structure starting from the concentration of 0.2 wt%. At the same time, an ‘island’ phenomenon occurs on the surface of the ultra-thin film. This is due to the interaction of TiO₂ with the matrix, and TiO₂ is coated in the polyester matrix. Meanwhile, some TiO₂ is agglomerated due to the dissolution-volatilization of the sample. As the concentration increases to 0.6%, the ‘islands’ also gradually increase and connect into pieces. When the concentration is as high as 1.0 wt%, the thickness reaches the micron level, the surface tends to be flat, and the microscopic nanostructure is not obvious. Yangchuan Ke et al. [11] found that the effect of the inorganic filler on the matrix was significantly enhanced when the thickness of the film was at the nanometer level, resulting in the formation of ring-shaped or band-like ordered structure on the surface of the film. Therefore, this indicates that the smaller the thickness of the film, the stronger the interaction between inorganic filler and matrix, also the more obvious the nano-effect. When the film thickness reaches the micron level, this effect is inhibited because the nanoparticles are completely embedded in the matrix.

![Figure 4](image)

**Figure 4.** The surface morphologies of the ultra-thin films (a: 0.1 wt%, b: 0.2 wt%, c: 0.4 wt%, d: 0.6 wt%, e: 1.0 wt%).

3.3. Analysis of glass transition temperature of the ultra-thin films

Figure 5 shows the heating curves of CPT-0.4 ultra-thin films with different thicknesses. The data obtained are summarized in Table 1. The glass transition temperature (T_g) is the basic property of polymer materials. Glass transition of amorphous materials is a molecular relaxation phenomenon, which is the transition state of polymer from glass state to high elastic state. The molecular chain movement ability is stronger when the glass transition temperature is low. It can be seen from Figure 5 that the T_g of films formed in different concentration solutions is quite different. Table 1 shows that when the film thickness is low, the T_g is small. The 22 nm thick film has the T_g of only 51.2 °C. As
the thickness of the film increases, the $T_g$ also gradually increases [12]. When the film thickness is increased to 3275 nm, the glass transition temperature reaches to 64.2 °C. The results indicate that the molecular chains have strong activity at lower temperatures. That is, it can accept less energy to overcome the energy barrier and reduce the activation energy of molecular chain motion. This reduction in activation energy provides the basis for further crystallization rearrangement of molecular chains.

![Figure 5. The DSC curves of the ultra-thin films.](image)

### Table 1. The data of thermal properties of the ultra-thin films.

| Solution concentration (wt%) | Thickness (nm) | Glass transition temperature (°C) |
|-----------------------------|---------------|----------------------------------|
| 0.1                         | 22            | 51.2                             |
| 0.2                         | 42            | 53.8                             |
| 0.4                         | 86            | 56.7                             |
| 0.6                         | 280           | 60.5                             |
| 1.0                         | 3275          | 64.2                             |

### 4. Conclusion

In this work, the copolyester-TiO$_2$ nanocomposite was dissolved in the organic solvent prepared from chloroform-trifluoroacetic acid, the ultra-thin films were successfully formed on the glass substrate by dip coating organic solvent method. The effects of different concentrations of polymer solution on film thickness, surface morphology and glass transition temperature were investigated. The thickness of the prepared nanocomposite ultra-thin films were 22 nm, 42 nm, 86 nm, 280 nm, and 3275 nm when the concentration of the organic solvent were 0.1 wt%, 0.2 wt%, 0.4 wt%, 0.6 wt%, 1.0 wt%, respectively. SEM displayed surface morphologies of films with different thicknesses. This indicated that the TiO$_2$ nanoparticles were embedded in the copolymer matrix when the film thickness was thick (3275 nm). As the film thickness decreased to 280 nm, the embedded TiO$_2$ particles formed the heterogeneous ‘island’ structure with the matrix macromolecule. The thickness of the film reached the nanometer scale, the interaction between the TiO$_2$ particles and the matrix was enhanced, and the ‘island’ phenomenon was more obvious. In addition, the film thickness had a large influence on the glass transition temperature. The glass transition temperature decreased as the thickness of the film decreased, and the molecular chain's mobility was enhanced, which was favorable for the polymer crystallization.
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