Abstract

In this paper, the influence of nano-graphite and nano-TiO$_2$ with the content of 0.5wt.% to 2wt.% on the thermal properties of polymerized cyclic butylene terephthalate (pCBT) resin was investigated by Differential scanning calorimetry (DSC) and Thermo gravimetric analysis (TGA), respectively. The experiment results show that the degree of crystallinity of the material decreases with the increasing of nano-particles content. Furthermore, it is found that two melting peaks appearing during the second heating in DSC curves. Meanwhile, with the increasing of nano-TiO$_2$ content, the decomposition rate of the resin decreases slightly in TGA curves.

Keywords: Thermal performance; nano-fillers; pCBT resin; DSC; TGA

1. Introduction

Composites materials are being more frequently used in a wide range and variety of structures, such as automotive and aerospace components. Generally, in these applications, composite materials often demand a unique combination of properties such as high thermal and oxidative stability, toughness, solvent resistance and low dielectric constant [1]. Thermoplastic composites and thermosetting composites are the two main composite materials that used in the real engineering areas. However, these two types of composites usually differ in polymer structure and result in different properties and processing techniques. It should mentioned that thermoplastic composites are an interesting material class since they combine good mechanical properties with a low density, and this further results in a series of excellent specific properties. Thermoplastic composites are generally manufactured...
first polymerized and then processed in their molten state, and then lead to the final product. In terms of thermosetting polymers, it was believed that they are polymerized during the production. Thus, the shape and properties of thermosetting composites cannot be altered anymore once the polymerization occurred [2]. However, the disadvantage of thermoplastic resin is their temperature-sensitive properties. Hence, it is essential to investigate the thermal history of thermoplastic resin and find out an effective approach by which the thermal properties can be enhanced.

Recently, with the increasing application of composite materials in marine engineering, requirements on the thermal performance of polymers become more stringent, and the temperature at which the composites are produced and the effect of various additives (such as flame retardants) on the decomposition process become more important [3]. Polymer nano-composites are considered to offer significant advantages over the conventional materials such as the outstanding flame retardancy. Actually, it is known that nanoparticles can enhance the thermal degradation of polymer composites and further enhance the overall mechanical performance in high temperature environment [4].

Cyclic butylene terephthalate (CBT) oligomers have stimulated a great interest because of their water-like viscosity and the ability to be readily polymerized to form the engineering thermoplastic poly(butylene terephthalate) (pCBT). Commonly, PBT resin is obtained through industrial processes based on the polycondensation of dimethylterephthalate and 1, 4 butanediol. However, it needs two stages under controlled temperature and pressure to get high molecular weights of PBT. As comparison, entropically-driven ring-opening polymerization of CBT into linear high molecular weight PBT can be obtained in a shorter time scale under isothermal conditions [5-6]. Therefore, CBT oligomers represent the best alternative to polymerize PBT under milder conditions, and their ultra-low viscosity makes them well suited for numerous processes, such as composite processing [7].

The aim of the present paper is to study the thermal performance of pCBT resin with different nano-fillers. Meanwhile, the effect of nano-particle content on the thermal stability of pCBT nano-composites is investigated with the emphasis on finding out an effective way by which the thermal stability of pCBT polymers can be enhanced.

2. Experiment

2.1. Materials

CBT resin (CBT 100) is bought from Cyclics Corporation together with 0.6wt.% Tin-based catalyst (PC-4101). The nano-TiO₂ and nano-graphite particles, with an average diameter D of 50nm and 100nm respectively, are provided by Degussa AG. All materials are dried at 100°C in the vacuum drying oven for 10h to remove the residual moisture, which could interfere with the polymerization reaction of CBT oligomer. Samples with 0.5wt.% and 1wt.% nano-graphite and 1wt.% and 2wt.% nano-TiO₂ are prepared.

2.2. Test method

The crystallization and melting behavior of pCBT are examined with differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). The mass of samples is cut from bulk sample in the range of 7-15mg. Nitrogen is used as the purge gas in the hot stage during all measurements and thermal treatments. Each sample is heated to 260°C at a rate of 20°C/min, cooled to 20°C, and reheated to 260°C at the same rate in DSC test, while the temperature ranges from room temperature to 550°C is adopted in TGA test.

The degree of crystallinity is defined as follow,

\[ \chi_c = \frac{\Delta H_m}{\Delta H_f} \]  

(1)

where \( \Delta H_m \) is the melting enthalpy of the polymer. \( \Delta H_f \) is the melting enthalpy of the fully perfect crystal of pCBT, which is found in literature to be 142 J/g.
3. Results and discussion

3.1. DSC test

Fig.1 shows the curves obtained in DSC tests for pCBT resin with 0.5wt.% and 1wt.% nano-graphite and 1wt.% and 2wt.% nano-TiO2, respectively. The curves are achieved for the first time during heating and cooling process.

![DSC test curves](image)

From Fig.1, there are no obvious differences of the tendency both in the heating and cooling are observed. Even though the filler categories as well as their contents are not the same, it seems that all the graphs have same tendency in DSC test. However, the crystallinity calculated form Fig.1 by Eq.1 shows some difference. It should be mentioned that when pCBT resin with same nano-filler, the crystallinity decreases with the increasing mass content of the nano-filler. In terms of pCBT with nano-graphite, its crystallinity decreases from 34.9% to 30.7% when the nano content increases from 0.5wt.% to 1wt.%. Similarly, the crystallinity of pCBT with nano-TiO2 decreases from 31.56% to 29.5%. On the other hand, crystallization point of the polymer with different nano-filler in it decreases approximately 5°C as listed in Table 1. While the melting point of all the samples are nearly the same. By comparison, it can be concluded that the diameter and mass content of nano-filler in the polymer are the two main factors that can influence the thermal behavior of the material. High content of nano-filler in the polymer could interfere the course of crystallization due to the fact that molecular chains have to promote the fillers and then finish their crystallization. Moreover, since there are more kinetic energy is needed to push the fillers that with larger diameter, crystallization of pCBT with nano-graphite shows a fast decline.

### Table 1 Thermal parameters of the samples obtained in DSC tests.

| Condition          | First heating |           |          | Second heating |           |
|--------------------|---------------|-----------|----------|----------------|-----------|
|                    | Melting peak  | Crystallization peak | Crystallinity | First peak | Second peak |
| 0.5wt% graphite    | 225.15        | 185.21    | 34.9     | 215.94        | 225.02    |
| 1wt% graphite      | 226.53        | 185.15    | 30.7     | 216.42        | 224.86    |
| 1wt% nano-TiO2     | 226.35        | 180.29    | 31.5     | 214.63        | 224.34    |
| 2wt% nano-TiO2     | 225.63        | 180.2     | 29.5     | 214.05        | 224.08    |

During the second heating process of the samples in DSC test, tendencies appear an obvious difference. It can be clearly observed the double peaks in Fig.2. The peak shape of the sample with same filler is very similar, while it is very different when the filler is different. Moreover, melting point of all the samples obtained in the second heating is around 224°C, hence it seems that the content of nano-fillers has no influence on the melting point. The authors
believe that the appearance of the two peaks in the second heating is the result of the agglomeration of nano-fillers occurred in the first heating process. As the viscosity of the resin is small in high temperature, the fillers in the resin are adsorptive each other during the first heating. As a result, the polymer chain near the nano-cluster in the sample is first melt and followed by the melting process of the chains far from the fillers. As a result, the curves turn out to be double peaks in the second heating as shown in Fig.2.

![Fig.2 DSC tests for pCBT with various content of (a) nano-graphite and (b) nano-TiO2 during the second heating.]

3.2. TGA test

TGA tests allow us to investigate the thermal decomposition of the material. The results are given in Fig.3 and Fig.4. In Fig.3, no obvious difference can be found in the curves of samples with nano-graphite. Both the two curves reclosed each other with increasing of heating temperature. Also, the same tendency is found in the curves of mass decomposition. Thus, it can be concluded that for sample with 0.5wt.% and 1wt.% nano-graphite, the thermal decomposition behavior is the same. However, some differences can be found in the figure when pCBT resin with nano-TiO2 in Fig.4. Firstly, even though the tendency of the weight lost curve is the same, but the left mass is different when the heating temperature is 500°C. The sample with high content of fillers in it left more residue in the figure, this is because that 2wt.% nano-TiO2 cannot melting during the heating and were left as residue. On the other hand, it is clearly that the maximum decomposition rate of the sample with 2wt.% nano-TiO2 is small than that of 1wt.% sample. This means that the addition of nano-TiO2 can enhance the usage temperature of the material. Table 2 lists the calculate results that obtained in TGA curves, we can find that with the increasing of the nona-fillers, the decomposition temperature decrease. Moreover, sample with TiO2 has a lower decomposition temperature than graphite, which is 420.5°C and 418.3°C, respectively. On the other hand, the 5% mass lost temperature is nearly the same for all the four samples. The maximum decomposition rate of the sample with TiO2 is a little higher than that of graphite, which is about 2.5% and 2.35%, respectively.
Table 2. Thermal parameters of the samples obtained in TGA tests.

| Sample           | Decomposition temperature (°C) | 5% mass lost temperature (°C) | Max decomposition rate (°/°C) |
|------------------|---------------------------------|-------------------------------|-----------------------------|
| 0.5wt% graphite  | 420.52                          | 378.07                        | 2.35%                       |
| 1wt% graphite    | 418.36                          | 379.73                        | 2.36%                       |
| 1wt% nano-TiO₂   | 416.20                          | 378.90                        | 2.53%                       |
| 2wt% nano-TiO₂   | 415.49                          | 377.30                        | 2.44%                       |
4. Conclusion

The influence of different types of nano-fillers with different content on the thermal properties of (pCBT) resin is investigated by DSC and TGA, respectively. From the experiment results, it can be concluded that the melting point of pCBT resin are enhanced by the nano-fillers. Nanoparticle category and its content are the two key factors that cause the difference in the thermal performance of pCBT resin.

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