Glass transition of PCBM, P3HT and their blends in quenched state

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Abstract
In this work the thermal behavior with the glass transition of phenyl-C_{61}-butyric acid methyl ester (PCBM), poly(3-hexylthiophene) (P3HT) and their blends was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Both TGA and DSC measurements show that PCBM contains around 1% residual solvent in the crystalline structure. The glass transition of PCBM, P3HT and their blends was determined by quenching techniques. The quenched state of the materials has a strong effect on the glass transition of the materials, especially in the case of PCBM. In all blend compositions only one glass transition temperature was found. These results indicate that PCBM and P3HT are thermodynamically miscible in all blend compositions.

Keywords: PCBM, P3HT, glass transition, quenched state

Classification numbers: 2.03, 5.10

1. Introduction

The worldwide demand for energy has grown enormously over recent years. Because of the limited supply of fossil energy sources such as crude oil and coals, as well as concern about global warming and climate change, the development of renewable energy sources such as solar cells has a great priority [1, 2].

Organic solar cells are a promising alternative to silicon solar cells because they are inexpensive, flexible and large areas of solar cells can be made with organic solar cells. However, the energy conversion efficiency of organic solar cells is still too low compared to that of conventional silicon solar cells [3, 4]. The energy conversion efficiency of solar cells based on the bulk heterojunction concept is only about 5% [4, 5]. The main reasons for low energy conversion efficiency by bulk heterojunction solar cells are the short exciton diffusion length (around 10–20 nm) and low mobility of charge carriers [6–9]. One of the approaches to improve the energy conversion efficiency by bulk heterojunction solar cells is to control the morphology formation of the donor materials such as (2-methoxy-5-(3,7-dimethyloctyloxy)poly-1,4-phenylenevinylene) (MDMO-PPV), poly(3-hexylthiophene) P3HT and acceptor materials such as PCBM. The desire is to form a co-continuous phase morphology at the nanoscale [10–12]. This means that the miscibility of the components will play a very important role for the phase morphology formation of blends.

In this work the thermal behavior and the glass transition of PCBM, P3HT and their blends in quenched state was investigated. The glass transition behavior of the blend could give important information about the thermodynamical miscibility of the blends.

2. Experimental

2.1. Materials and chemicals
PCBM, purity >99%, was purchased from Solenne company and P3HT (molecular weight $M_w = 65.5\, \text{kg mol}^{-1}$ and $M_w/M_n = 2.04$) was from Merck company. The chemicals are analytical grade and were used as received.

2.2. Blend preparation and characterization methods
The blends were prepared by solution method. A mixture of PCBM and P3HT in different weight portions was dissolved in chlorobenzene (CB) to make a solution of 2%. The blend solution was then coated on glass substrate, dried at room temperature for several hours and finally collected.
In order to prepare the quenched morphology of polymers, the polymer was placed in DSC cells closed by a cover. The sample was thermally treated at different temperatures using a heat plate for 3 min. The coolant was prepared by mixing of liquid nitrogen with methanol to reach the temperature of −50 °C. After heating, the polymer sample was placed in a ceramic cup and then the ceramic cup was rapidly immersed into the coolant for 90 s. A rapid cooling process was introduced in the polymers, resulting in their quenched morphology.

The TGA measurements were carried out on the TGA instrument with the heating rate of 10 K min$^{-1}$, in N$_2$ atmosphere. The Fourier transform infrared (FTIR) spectra were recorded on a Bruker instrument at room temperature.

The DSC measurements were performed on the DSC Q1000 instrument using modulated temperature mode (MTDSC). The heating and cooling rate was 5 K min$^{-1}$ and N$_2$ gas was used as media.

3. Results and discussions

3.1. Thermal behavior of PCBM and P3HT

Figure 1 shows the TGA diagrams of PCBM and P3HT. P3HT begins thermally to degrade clearly at 420 °C. In contrast, two weight loss steps are observed by PCBM. The first step is about 244 °C with the weight loss of about 1% and the second weight loss step is about 398 °C.

For an explanation for the PCBM thermal gravimetric behavior, its structure was investigated. FTIR spectra of PCBM before and after annealing at 280 °C for 5 min were recorded. This annealing temperature of 280 °C was chosen on purpose. It is higher than the temperature at the first weight loss step but lower than the temperature at the second weight loss step in order to study the structure of PCBM after the first weight loss step. Figure 2 shows the FTIR spectra of PCBM before and after this thermal treatment.

The FTIR spectra of PCBM before and after thermal treatment are basically identical. For PCBM the characteristic peaks of butyric acid methyl ester are shown for the carbonyl group (C=O) at 1740 cm$^{-1}$ and the ether group (C–O–C) at 1144 cm$^{-1}$. It is clear to see that these peaks also appeared with the thermally treated PCBM. It implies that the chemical structure of butyric acid methyl ester was unchanged by the thermal treatment. It also indicates that the first weight loss step does not result from the thermal decomposing of PCBM. It is believed that this weight loss is from the residual solvent contained in the crystalline structure of PCBM. This kind of residual solvent in the crystalline structure has been reported by Tung et al [13] for polyaniline (PANi) crystallite. The presence of residual solvent in the crystalline structure of PCBM can be seen again by DSC measurements as discussed below. It is concluded that the chemical structure of phenyl-butyric acid methyl ester in PCBM was thermally decomposed at 398 °C.

To characterize the melting behavior of PCBM and P3HT, figure 3 shows the MTDSC thermograms of PCBM and P3HT.
The melting temperature of P3HT crystallite is 233.7 °C. For PCBM, several peaks are observed. It is interesting to note that the endothermic peak at 241.4 °C disappeared by the second heating cycle. This temperature is nearly the same temperature for the first weight loss step of PCBM discovered by TGA measurements as mentioned above. It reconfirms the evaporation of residual solvent in the PCBM crystalline structure. The melting temperature of PCBM crystallite is about 279.5 °C.

3.2. Glass transition of PCBM, P3HT and their blends

It is well known that the glass transition temperatures of P3HT and PCBM are hard to determine using DSC measurement. Zhao et al [14] reported that the glass transition temperatures of P3HT, PCBM and their blends could be determined by quenching technique. In this work, the effect of quenched state on the glass transition of PCBM and P3HT was systematically investigated. Figures 4 and 5 show the effect of quenching temperature on the glass transition of P3HT and PCBM.

The effect of the quenching temperature on the glass transition of P3HT and PCBM is significant, especially in the case of PCBM. With a quenching temperature of 200 °C, the glass transition of PCBM cannot be determined. With a quenching temperature of 280 °C the glass transition of PCBM is visible and can be determined to be 118.3 °C. At this temperature the crystallite of PCBM melts and thus a high amorphous state of the polymer is obtained after the quenching process. The glass transition of P3HT is also more visible at higher quenching temperature (280 °C) and the glass transition temperature being determined at 9.3 °C. The glass transition temperatures of PCBM and P3HT determined in this study are close to those of the same polymers reported by Zhao et al [14].

The glass transition of the polymers, especially PCBM, depends strongly on the quenched state of the polymers. Figure 6 shows the first and second heating cycle of P3HT.

It is seen that the second heating curve of P3HT is basically the same as the first heating curve. That implies that morphology of P3HT in the second heating cycle is almost
In all PCBM/P3HT blends, only one glass transition temperature is observed for all compositions. It implies that P3HT and PCBM are miscible in all compositions. The dependence on PCBM content of glass transition temperature of PCBM/P3HT blends is shown in figure 9.

With increasing PCBM content, the glass transition temperature of the blend increases. This trend of $T_g$ depending on PCBM content is in agreement with the result reported by Zhao et al [14].

4. Conclusion

The PCBM contains around 1% solvent in the crystalline structure as seen by both TGA and DSC measurements. The glass transition of P3HT and PCBM in normal state is undetectable in MTDSC measurements. However, it could be seen for their quenched state. In all PCBM/P3HT blends, one glass transition temperature was observed. This implies that P3HT and PCBM could be miscible in all compositions.

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