



Preparation and characterization of in situ grafted/crosslinked polyethylene glycol/polyvinyl alcohol composite thermal regulating fiber

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ABSTRACT

In this study, an in situ grafting/crosslinking method was employed to prepare form stable thermal regulating fibers (TRFs). The fibers were made from polyvinyl alcohol (PVA, as fiber polymer), polyethylene glycol (PEG, as phase change material) and butane tetracarboxylic acid (BTCA, as crosslinking agent) and spun by dry spinning. The addition amount of BTCA and thermal treatment temperature for preparation were optimized by studying the reaction kinetics of PVA/BTCA and PEG/BTCA composite systems. The structures and properties of PEG/PVA/BTCA composite fibers were characterized by differential scanning calorimeter (DSC), two-dimensional wide angle X-ray diffraction (WAXD) and scanning electron microscope (SEM). Results show that small amounts of BTCA can form adequate chemical bonds to fix PEG in the PEG/PVA/BTCA composite at proper temperatures in the thermal treatment. In composite fibers, the crystallization of PVA promotes the phase separation between PVA and PEG, and the crosslinkages confine the crystallization of PEG. In the as-spun fiber, the crystallization of PEG occurred along the normal direction of the fiber axis. During the stretching, the original orientation of PEG crystals in fibers was destroyed and then new crystalline orientation formed along the fiber axis. The cross-sections of the composite fibers are almost round; after being extracted, the fibers crosslinked by BTCA are denser and have fewer defects than un-crosslinked PEG/PVA fiber, which demonstrated that the PEG can be fixed steadily in PVA fiber matrix by the in situ grafting/crosslinking method.

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1. Introduction

The shortage of energy will be more serious in the future than at any time in the past [1]. In order to utilize the energy more effectively, phase change materials (PCMs) have played an increasingly important role because of their energy storage and conservation [2,3]. PCMs absorb and release the energy over a defined temperature range. They can solve the contradictions between the energy supply and the demands in time and space. These materials, due to their unique thermal control and energy conservation properties, can be widely applied in various thermal energy storage (TES) applications [4–6]. Thermal regulating fiber (TRF) [7,8] is one of the applications of PCMs, it was conceived by the National Aeronautic and Space Administration (NASA) in the 1980s and first applied in space suits to maintain an equilibrium temperature for astronauts in the ferocity environment of outer space [9]. TRFs are usually prepared by

combining PCMs with fiber polymers, and the PCMs endow the fibers with the functions of energy storage and thermal regulation. Nowadays, the TRF is regarded as a promising material for preparing intelligent textiles which can improve our living environment and save energy.

As most of PCMs are not form-stable materials, it is hard to composite PCMs with fiber polymers and prepare fibers with stable properties [2,10,11]. Researchers have developed many methods to prepare TRFs. These methods can be mainly divided into physical composite methods and chemical composite methods. Physical composite methods include composite spinning [12,13], hollow fiber filling [14], fabric coating [15] and microcapsule composite spinning [16]. TRFs prepared by physical methods normally have high thermal regulating properties but are not stable, because there are no chemical bonds between PCMs and polymers, and PCMs tend to be lost during long term use of these fibers. Chemical composite methods are virtually based on polyethylene glycol (PEG) which is a kind of PCM with high latent heat and low thermal hysteresis. Moreover, the active hydroxyl terminated structure makes PEG easy to be grafted with some fiber polymers, and the chemical bonds provide PEG grafted TRFs with more durable and stable thermal properties.

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There are two typical ways to prepare PEG grafted TRFs [17–20]. One is to synthesize PEG grafted polymers first, and then to spin these functional polymers into TRFs. Even though this approach seems very feasible, the contradictories between the spinnability and the grafting ratio restrict its application. The other is to graft PEG with formed fibers. Generally, the grafting ratio of TRFs prepared by this way is very low because of the inefficiency of the heterogeneous reaction. Considering the factors above, a new approach should aim at elevating the grafting ratio of PEG without deteriorating the spinnability of fiber polymers.

In this study, an in situ grafting/crosslinking method was developed to prepare TRFs with high and stable performance. Polyvinyl alcohol (PVA) was chosen as fiber polymer and PEG as PCM to prepare PEG/PVA TRF by dry spinning. During preparation, a small amount of butane tetracarboxylic acid (BTCA) was added into the PEG/PVA composite fiber as an in situ grafting/crosslinking agent. In the spinning solution, PVA was just mixed with PEG and BTCA, and was not grafted before spinning, so the spinnability of PVA did not change much. After spinning, the composite as-spun fiber was subjected to a thermal treatment at an appropriate temperature, and BTCA would react in situ with the hydroxyl groups of PEG and PVA, which leads to the grafting or crosslinking between PEG and PVA. This method has the advantage of both the physical and the chemical composite methods, simplifies the preparation process of TRF and makes it possible to prepare TRF with high and permanent thermal storage performance.

2. Experiment

2.1. Materials

PVA (DP = 1700 ± 50, alcoholysis degree > 99%), industry degree, was provided by Sinopec Sichuan Vinyon Works. PEG (Mr 2000 and 200), reagent grade, was purchased from Kelong Chengdu Inc. BTCA, reagent grade, was purchased from Aladdin Shanghai Inc. All the chemicals (except PEG200) were applied without further purification. Deionized water was used in all preparations.

2.2. Preparation of samples for grafting/crosslinking reaction kinetics study

2.2.1. Preparation of PEG/BTCA sample

PEG200 was dried in vacuum freeze dryer for 24 h. PEG and BTCA (the mole ratio between hydroxyl in PEG and carboxyl in BTCA is 2:1) were mixed at 50 °C for 4 h in nitrogen atmosphere. The mixture was then vacuum dried at 50 °C for 4 h. The sample was sealed and kept in the dryer before testing. PEG200 is intended to substitute PEG2000 in kinetics study experiment. The concentration of hydroxy groups in PEG2000 is too low for kinetic study, so PEG200 which has higher hydroxyl content is used to observe the reaction heat between it and BTCA.

2.2.2. Preparation of PVA/BTCA sample

PVA was dissolved in water with a concentration of 12 wt% at 98 °C for about 4 h, BTCA was then added into PVA solution (the mole ratio between hydroxyl in PVA and carboxyl in BTCA is 2:1) and mixed to form a homogeneous solution. The resultant solution was then made into a film by a casting method. The film was then vacuum dried at 50 °C for 4 h. The sample was sealed and kept in the dryer before testing.

2.2.3. Preparation of PEG/PVA/BTCA sample

PVA was dissolved in water with a concentration of 12 wt% at 98 °C for about 4 h. Certain amount of PEG and BTCA were then added into PVA solution and mixed to form a homogeneous solution.

(The mass ratio among PEG/PVA/BTCA is 3:10:0.5). The obtained solution was manufactured into films by the casting method. The films were vacuum dried at 50 °C for 4 h. Then, the films were heat treated in different temperatures (140, 160, 180, 200, 220, and 240 °C) for 10 min to accomplish the grafting/crosslinking reaction. The films were weighed respectively after that.

The treated films were extracted with Soxhlet extractor for 24 h to remove the non-grafted/crosslinked PEG, and ethyl alcohol was used as an extractant. After extracting, the resultant films were vacuum dried at 50 °C for 4 h and then were weighed.

Weighing method was used to calculate the grafting ratio of PEG according to the following equation:

$$G = 1 - \frac{M_1 - M_2}{KM_1} \quad (1)$$

where G is the grafting ratio of PEG;

M_1 is the weight of PEG/PVA/BTCA samples after thermal treatment;

M_2 is the weight of PEG/PVA/BTCA samples after extraction;

$K = 3/13$ (the mass ratio of PEG and PVA is 3:10);

KM_1 means the initial content of PEG in the films;

$M_1 - M_2$ means the weight loss of PEG.

2.3. Preparation of TRFs

PVA was dissolved in water with a concentration of 30 wt% at 98 °C for 4 h. PEG and BTCA (30 wt%, 5 wt% to the weight of PVA respectively) were then added into the solution and mixed together. The obtained spinning dope was extruded from the spinneret into dry heated air to form the PEG/PVA/BTCA as-spun composite fiber. Then, the as-spun fiber was stretched with different drawing ratio and thermal treated at 200 °C for 10 min to complete the in situ grafting/crosslinking reaction. The PVA/PEG composite fibers for comparison were prepared as above, without adding BTCA. The flow chart of the preparation process of TRFs is shown in Scheme 1

2.4. Testing and characterization

2.4.1. The chemical structures of PEG/PVA/BTCA composite samples

The in situ Fourier transform infrared spectrometer (in situ FTIR) (Nicolet Is10 spectrometer, Thermo Fisher Scientific, USA) was used to observe chemical structure changes of the composite sample during thermal treatment. The test was conducted in transmission mode with a resolution of -2 cm^{-1} . The KBr disk technique was used in the samples preparation. The temperature was increased at the rate of 5 °C/min from 100 °C to 240 °C by a miniature controller. Spectra were recorded every 30 s.

2.4.2. Non-isothermal reaction kinetics

Differential scanning calorimeter (DSC) (DSC204F1, Netzsch, Germany) analysis was carried out to study the non-isothermal kinetics of esterification reactions between BTCA and PVA or PEG. The samples were sealed in crucibles for about 8 mg each and tested by DSC at different heating rates (6, 8, 10, 12, 14, and 16 °C/min) in nitrogen atmosphere. The peaks of reactions were recorded and analyzed for reaction kinetics study.

2.4.3. Thermal properties of composite fibers

Thermal properties of the composite fibers were further studied by DSC. The tests were performed in nitrogen atmosphere with a heating rate of 10 °C/min from 0 °C to 300 °C. The phase change latent heat of PEG and the melting enthalpies of PVA were obtained by integrating the peaks in DSC curves.

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