

Solvent Vapor Annealing Induced Polymorphic Transformation of Polybutene-1^{*}

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Abstract Solvent annealing is a facile method for changing the aggregated microstructure and physical properties of polymer materials. In this paper, we addressed the effects of solvent vapor annealing, including chloroform and water vapor, on the polymorphic transformation in both hot-pressed film and electrospun nonwoven of isotactic polybutene-1 (PB-1) by means of *in situ* Fourier transform infrared spectroscopy (FTIR). The pretty rapid transition rate caused by the increased motion of molecular chains under chloroform vapor is associated with a lowest crystallinity. Also, a decreased crystallinity with the crystal transition occurred in electrospun nonwovens resulting from the relaxation of the stretched molecular chains into amorphous state rather than realignment into crystal form I predominating the crystal transition process.

Keywords: Polybutene-1; Crystal transformation; Solvent vapor annealing.

INTRODUCTION

Isotactic polybutene-1 (PB-1), a semi-crystalline polymer well known for its superior creep resistance, toughness, tear strength, flexibility, and high temperature resistance attracts great industrial attention in pressurized tanks, tubes, and hot water pipes, *etc*^[1]. Primarily, another attracting characterization of PB-1 is the typical polymorphic behavior, in particular, the pronounced crystal-crystal transition^[2, 3]. Depending on the solidification conditions, four crystal modifications characterized as different chain conformations and packing modes: the twined hexagonal form I, untwined hexagonal form I', tetragonal form II, and orthorhombic form III have been identified in PB-1 materials^[4]. Among them, form I and form II are the most attractive modifications for application due to metastable form II, a kinetically favored form generally occurred with melt crystallization and spontaneously transforming into the ultimately stable form I as samples aging in air^[5]. Such phase transformation may take days to several weeks to complete under atmosphere pressure. Since each microstructure imparting different densifications and mechanical properties^[6], undesirable effect, such as shrinkage of the molded objects may be accompanied with the crystal phase transition from form II to form I^[7].

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Accordingly, an advanced strategy to manipulate and accelerate the crystal-crystal transition accounts for the improved performance, and in turn the improved applications of PB-1 in some aspects.

The crystal transition process has not been understood very well yet nevertheless the addition of specific additives^[8, 9], copolymerizing with other monomers^[10, 11], blending with other polymers^[12, 13] widely used for the acceleration of crystal transition. Certainly, it is believed that the crystal transition from form II to form I is the result of conformational changes of PB-1 molecular chains^[14]. Any route for promoting the mobility of molecular chains is beneficial to the increase in crystal transformation rate, such as the employment of external stress^[15] and thermal^[16]. It is well-known that a large extent stretching accelerates the polymorphic transformation^[17], and even an inverse I to II phase transition may be observed during a stress-induced melting-recrystallization process^[18, 19]. A maximum transition rate was found around the edge of those large spherulites while crystallization of PB-1 occurred at high temperatures and soon quenched to low temperatures for further crystallization^[20]. As known, solvent annealing also has a profound effect on the movement of molecular chains, and developed to be a main and efficient approach for tailoring the microstructure of block copolymers by self-assembling molecular chains. It is, however, unfortunate that only a few works have dealt with the investigations involving the effects of solvent vapor on the crystal transition in PB-1 materials.

Fundamentally, a solute polymer chain expands in a good solvent, and collapses in a poor solvent. As reported that the transformation rate was increased slightly in the presence of water and ethanol, but significantly in the presence of liquids that are solvents of PB-1 at elevated temperatures or by temperature cycling^[21]. It is speculated that absorbed gas molecule may increase the free volume fraction of the polymer and then promote the motion of the polymer chain in the amorphous region, which may in turn induce the tensile stress on the molecular chains in the crystalline lattice^[22]. The yielded stress in the crystalline would cause the elongation of the chain helix and subsequently increase the phase transition rate. Thereof, an alternative to establish solvent atmosphere, in which mobility of the PB-1 molecular chains may be increased at some degree and then self-orienting of molecular chains to form aligned micro-domain is enhanced, deserves a detailed study to achieve not only a rapid process of crystal transition but also a detailed understanding of some scientific interest.

In this paper, we focused on the evolution of crystal transition in hot-pressed film and electrospun nonwoven of PB-1 upon chloroform or water vapor annealing. The crystal transitions of PB-1 hot-pressed film and electrospun nonwoven that aging in air were also recorded by *in situ* FTIR as controls. This is the first experimental observation of the crystal transition of PB-1 induced by solvent vapor atmosphere at room temperature. The crystal transition rate and the plateau value of crystal form I in PB-1 nonwoven were analyzed to evaluate the effects of solvent and framework of PB-1 materials.

EXPERIMENTAL

Materials

Isotactic polybutene-1 (PB-1) was supplied by Shandong Dongfang Hongye Chemical Co., Ltd., China. The melt flow rate (MFR) of PB-1 is 4.32 g/10min (190 °C, 2.16 kg) and the isotacticity is 97.7 wt%. All other chemical agents were used as received.

Sample Preparation

Hot-pressed film: PB-1 was firstly heated to 150 °C for 5 min to erase the heat history, and then compress-molded at 5 MPa to yield a film of 110 μm in thickness followed by quenching to 25 °C at 5 MPa for 10 min. The as-obtained quadrate trimmed samples with dimensions of 10 mm × 10 mm were used immediately for the following investigation on crystal transition under different solvent vapor.

Electrospun nonwoven: PB-1 was dissolved in a mixture solvent containing cyclohexane and *N,N*-dimethylacetamide (DMAc) with volume ratio of 90/10 at 70 °C to get a 0.04 g/mL of solution concentration. The dope was subsequently electrospun at 20 kV of electric voltage, 15 cm of collecting distance and 60 μL/min of feeding rate. The collected electrospun nonwovens with a thickness of 80 μm were vacuum dried at room temperature for 14 h to remove the remained solvent and then were cut into a 10 mm × 10 mm dimension before the investigation of crystal transition under different solvent vapor.

Solvent Vapor Annealing

5 mL of chloroform or water was previously put into a sealed chamber with cover to assure the chamber filled with solvent vapor, respectively (Figs. 1a and 1b). Then, both PB-1 hot-pressed films and electrospun nonwovens were laid aside in the spare space of the chamber to ensure that the samples were immersed in solvent vapor (Fig. 1c). Finally samples were taken out from the chamber to characterize the crystal phase at the given interval (Fig. 1d).

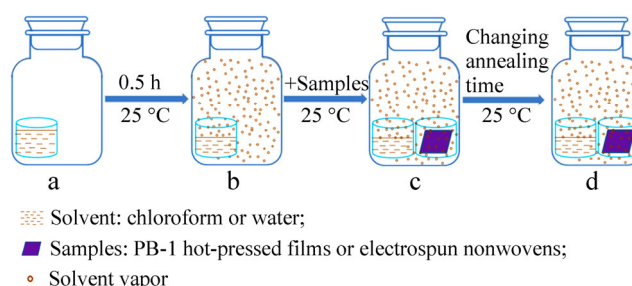


Fig. 1 Schematic diagram of the solvent vapor annealing

Characterization

Morphology of electrospun fibers was observed using a scanning electron microscope (SEM, JSM-7500F) after platinum sputter coated. FTIR spectra were recorded on a Bruker VERTEX 70 FTIR spectrometer from 400 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans.

RESULTS AND DISCUSSION

In situ Observation of Crystal Transformation in PB-1 Hot-pressed Film

Crystal transformation of metastable phase II of PB-1 is frequently associated with the conformational variations. FTIR coupling with the vibrational modes has prevailed for analyzing the changes in microstructure along with the crystal transformation. Basically, the band at 905 cm^{-1} is assigned to the vibration of crystal form II. The band at 923 cm^{-1} is characteristic of the vibration of crystal form I or I'^[23]. In this experiment, the band at 923 cm^{-1} can be attributed to form I combining the DSC and XRD analyses (data not shown here). Therefore, the change on the intensity of the peak at 905 cm^{-1} and 923 cm^{-1} can be used to monitor the transformation between crystal form II to form I of PB-1.

Figure 2 shows the FTIR spectra of PB-1 hot-pressed film as a function of annealing time under different vapor including chloroform, water and air. As expected, form I, the thermodynamically stable modification is seldom predominated by directly crystallizing from PB-1 melt without any preconditions or additives. Both peaks with comparable intensity at 905 cm^{-1} and 923 cm^{-1} are present before annealing (0 h of samples), indicating the coexistence of crystal form II, and form I which transformed from form II during the handing process. The band at 905 cm^{-1} gradually diminishes till they totally disappear, meanwhile the peak at 923 cm^{-1} becomes strong as annealing process proceeded. These results suggest that the occurrence of crystal transformation from crystal form II to crystal form I was a spontaneous process regardless of the environment conditions. Interestingly, the crystal transformation rate from form II to form I was dependent on the solvent atmosphere, and can be accelerated by solvent vapor annealing. Evidently, the disappearance of peak at 905 cm^{-1} was observed after 0.5 h of chloroform vapor annealing in comparison to more than 48 h of water vapor annealing or 96 h of aging in air.

Notably, the band at 1152 cm^{-1} represents the bending vibrations of backbone CH_2 and has no obvious change with the occurrence of crystal transformation. Consequently, the peak height ratios of H_{905}/H_{1152} and H_{923}/H_{1152} denoted as the $H_{\text{II}}/H_{\text{C}}$ and $H_{\text{I}}/H_{\text{C}}$ can be marked to quantitatively evaluate the relative content of crystals form I and form II. By calculating, the origin values of $H_{\text{I}}/H_{\text{C}}$ and $H_{\text{II}}/H_{\text{C}}$ in PB-1 hot-pressed film are around 0.7 and 1.15, respectively. A sharp decrease of the value of H_{905}/H_{1152} instantaneously associated with a

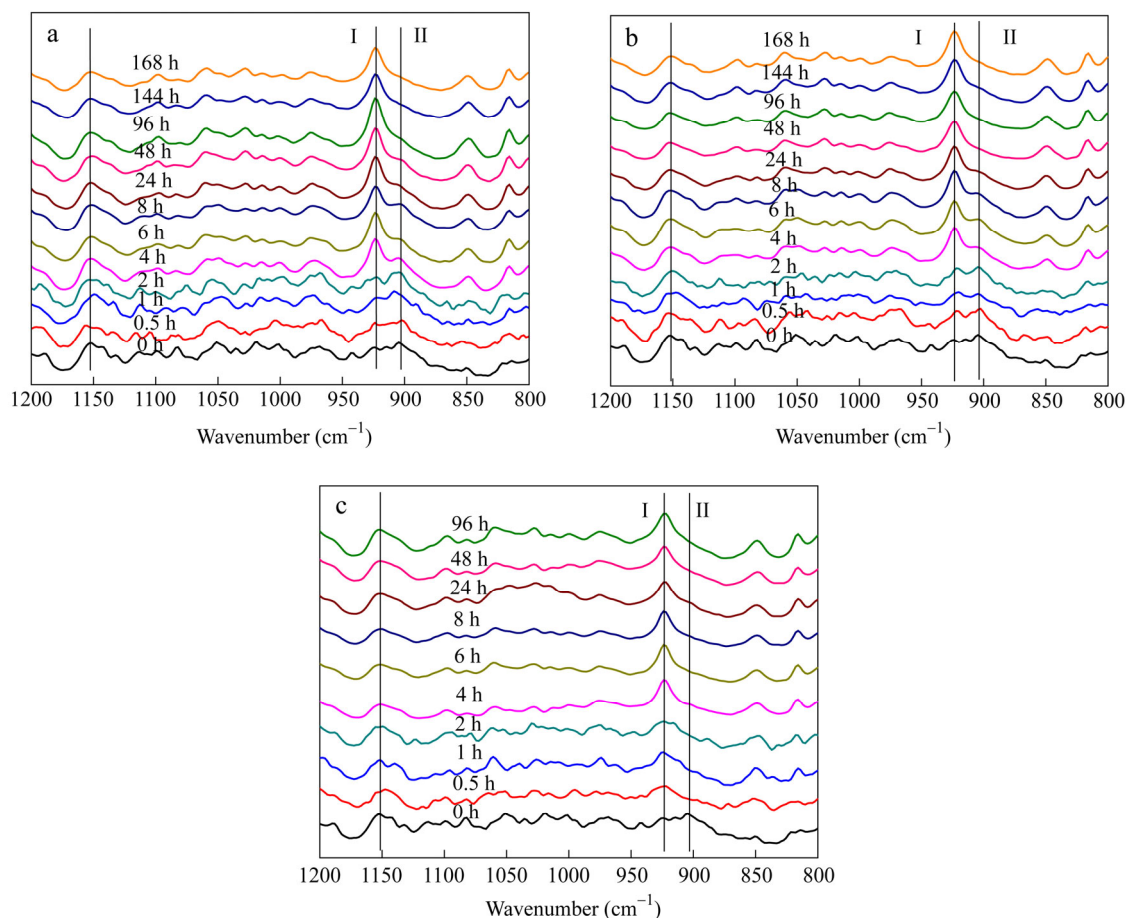


Fig. 2 FTIR spectra of PB-1 hot-pressed films annealed at room temperature in (a) air atmosphere (control), (b) water vapor and (c) chloroform vapor as a function of time

steep increase of H_{923}/H_{1152} is observed within the first 12 h (Figs. 3a and 3b). Basically, the crystal transformation involves the disappearance of crystal form II and the deferred growing of crystal form I, and both of them are proceeding simultaneously. Thereof, the diminishing rate of crystal form II can be indicative of the crystal transition rate. Figure 3(a) shows that H_{II}/H_C in PB-1 hot-pressed film downgrades to zero after less than 1 h of chloroform vapor annealing. However, the value of H_{905}/H_{1152} did not reach zero until the samples of PB-1 were annealed more than 50 h in water vapor or more than 100 h in air. This further demonstrates that the slow crystal transformation rate of PB-1 in air was accelerated by solvent vapor annealing, in particular organic solvent vapor annealing. Interestingly, the values of H_I/H_C upon the H_{II}/H_C downgrading to near zero are different for the same sample but annealed in chloroform vapor, water vapor and air, respectively. A lowest value of H_I/H_C appeared in sample that annealed in chloroform vapor, but a highest value observed in sample that aging in air. Clearly, the order of H_I/H_C from high to low was contrary to the diminishing rate of crystal form II with different solvent vapor annealing.

It is commonly believed that the phase transition between crystals form II and form I is a solid-solid phase transition that occurs in the crystalline region, but the motion of chains and diffusion of chain segments in the amorphous region play an important role in conformational transition and dynamical conformational disorder^[23]. Although both chloroform and water are poor solvents for PB-1, chloroform, a weak polar organic solvent showing more phiphilicity to PB-1 than water, induces a more rapid molecular motion of amorphous chains than water. Also, the diffusion and sorption of small molecules may cause the uniaxial compression, which in turns may result in some tensile deformation of the amorphous regions in the lateral direction^[21]. Nevertheless, water,

a strong polar solvent has a weakened interaction with PB-1 molecular chains, but it may still penetrate into the PB-1 hot-pressed film, and expand the amorphous regions, thus creating a tensile stress on the taut tie molecules^[24].

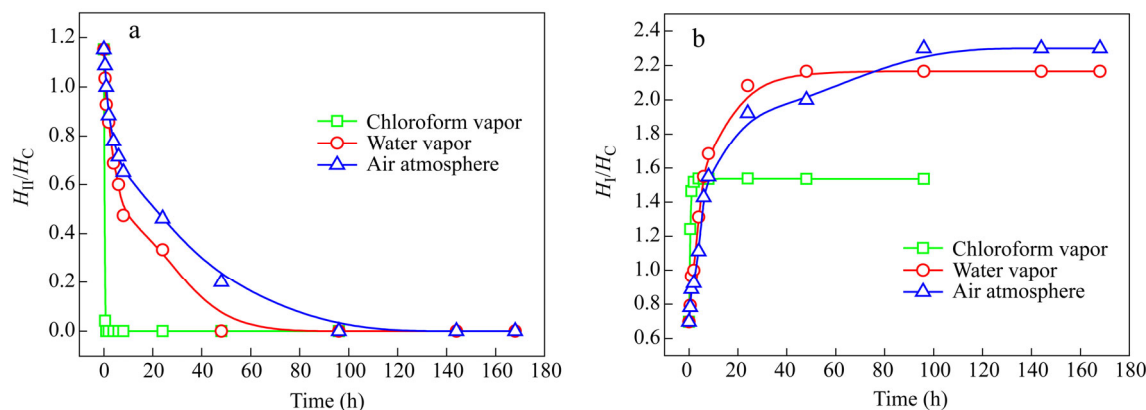


Fig. 3 Variation of crystal form content in hot-pressed film of PB-1 as a function of annealing time under different solvent vapor: (a) form II and (b) form I

In situ Observation of Crystal Transformation in PB-1 Electrospun Nonwoven

Electrospinning is a simple and feasible technique to fabricate nanostructured polymer materials^[25, 26]. It has been reported that bringing materials into nano-scale facilitates not only the improved material properties^[27], but also the occurrence of new advanced characteristics that is not observed in bulk materials^[28]. Herein, the morphology of the electrospun nonwovens of PB-1 is shown in Fig. 4. Due to the low conductivity of PB-1 electrospinning solution, irregular fibers with spindle structure were collected^[29]. Additionally, the demixing and different evaporation rates between the two kinds of solvents of electrospun solution may result in the collapsed and complicated fiber morphology. Meanwhile, both chloroform and water are poor solvents for PB-1, and there is no distinct variation in morphology before and after annealing process.

Considering the stretched polymer chains by electric field, the reported alignment of polymer chains along the axis of nanofibers may result in the totally different crystal behavior comparing to the bulk materials^[30]. It has been found that electrospun nonwovens have different crystal modifications with PB-1 casting films even though they come from the same solutions^[31]. The crystals in electrospun nonwoven are crystal form II and form I rather than form III and I' that always occurred in casting films of PB-1 (Fig. 5). The stretching of molecular chain under the electric field contributes to the compact orientation of molecular chain, and thereby the predominant of crystal form I. The final disappearance of the peak at 905 cm^{-1} for PB-1 electrospun nonwovens was 1/6 h of chloroform vapor annealing, 1 h of water vapor annealing and 4 h of aging in air. The much larger surface area of electrospun nonwoven may result in the increased contact area between solvent vapor and materials, thereby the increased crystal transition rate during solvent vapor annealing.

The origin values of H_I/H_C and H_{II}/H_C in PB-1 electrospun nonwovens are around 2.64 and 0.82, respectively, further suggesting that the kinetically predominant crystal in electrospun nonwovens is form I (Fig. 6). As shown in Fig. 6(a), a relatively flat curve of H_{II}/H_C in the first hour represents a slow transition rate when electrospun nonwovens aging in air. In contrast, an enhanced crystal transition in PB-1 electrospun nonwovens is also observed as samples annealed in solvent vapor, especially in chloroform vapor. A lowest value of H_I/H_C occurred in samples that annealed in chloroform vapor. The recorded value of H_I/H_C in PB-1 nonwovens is 2.9 closing to the origin value of H_I/H_C (2.64) after 168 h or chloroform vapor annealing. The slight increase of H_I/H_C was also observed in PB-1 electrospun nonwoven while aging in air or annealing in water vapor. It is noted that the polymorphic transformation accompanied by the vacuum process of electrospun nonwovens is inevitable.

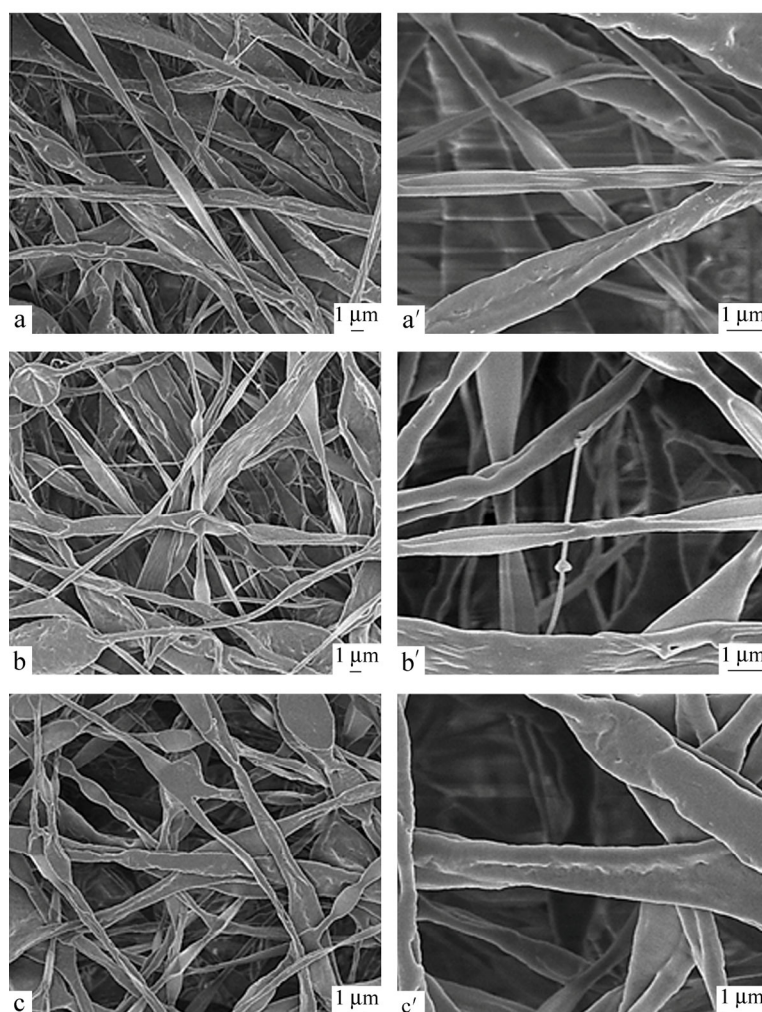


Fig. 4 SEM images of PB-1 electrospun nonwoven after 168 h of solvent vapor annealing: (a, a') air atmosphere as a control, (b, b') water vapor and (c, c') chloroform vapor (a–c: low magnification; a'–c': high magnification)

As shown in Fig. 7, for electrospun nonwoven, the final value of H_I/H_C with 168 h of chloroform vapor annealing was 2.9, and 3 or 3.25 of water vapor annealing or aging in air. The final value of H_I/H_C is 1.54, 2.17 and 2.3, respectively for the hot-pressed film after 168 h of chloroform vapor annealing, water vapor annealing, or aging in air. Evidently, a rapid crystal transition with chloroform vapor annealing is accompanied with a low content of final crystal form I. The change value of H_I/H_C denoted as the content of crystal form I may come from not only the contributions of the realignment of molecular chains to crystal form II, but also the participation of amorphous aggregated molecular chains into ordered alignment. The rapid disappearance of crystal form II just means the fast relaxation of molecular chains in crystal form II. However, the realignment of molecular chains both from the crystal form II and amorphous aggregation into crystal form I may involve the new nucleation and crystal growth^[32]. Since the rapid diminishing of samples annealing in chloroform vapor illustrates an enhanced motion of molecular chains in chloroform environment, the low value of H_I/H_C can be reasonably attributed to the rapid motion of molecular chain in a short time under solvent vapor for the hot-pressed film, and the electrospun nonwoven as well.

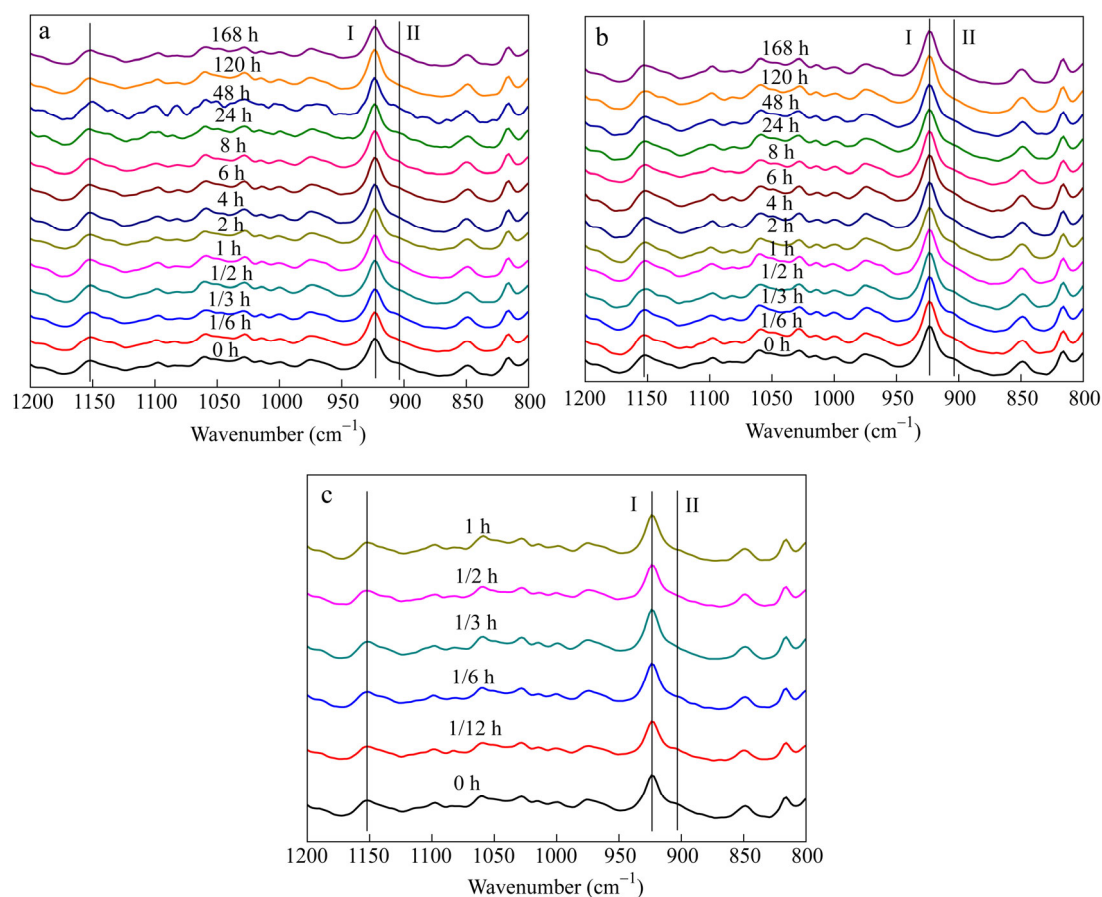


Fig. 5 FTIR spectra of PB-1 electrospun nonwoven annealed at room temperature in (a) air atmosphere (control), (b) water vapor and (c) chloroform vapor as a function of time

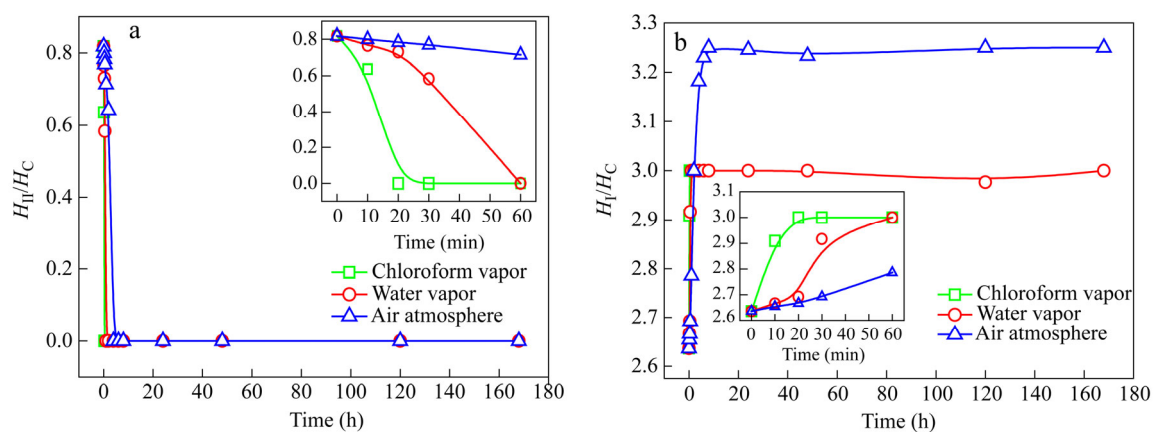


Fig. 6 Variation of crystal form content in electrospun nonwoven of PB-1 as a function of annealing time under different solvent vapor: (a) form II and (b) form I

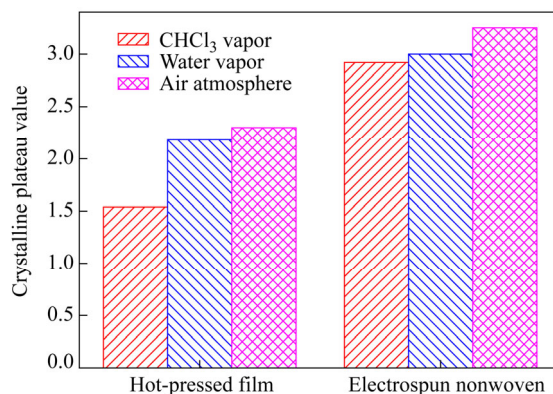


Fig. 7 The recorded values of H_I/H_C in hot-pressed film and electrospun nonwoven after 168 h of solvent vapor annealing

Another highlighted difference between hot-pressed film and electrospun nonwoven is shown in Figs. 8(a) and 8(b), and it depicts the variation tendency of H_{I+II} which can be a rough quantitative description of crystallinity during crystal transformation. For hot-pressed film (Fig. 8a), an increased value of H_{I+II} is observed while a decreased H_{I+II} presents in electrospun nonwoven (Fig. 8b) as solvent vapor annealing proceeding. This indicates that molecular chains of amorphous domain in hot-pressed film of PB-1 participate in the ordered realignment with the transformation of crystal form II into form I. However, a reverse process was pronounced in electrospun nonwoven with the relaxation of highly ordered molecular chains in crystalline region into disordered amorphous aggregation during solvent vapor annealing. Additionally, a lowest H_{I+II} presented with chloroform vapor annealing while a highest H_{I+II} appeared as aging in air for both hot-pressed film and electrospun nonwoven. As known that the value of H_{I+II} is relevant with not only the fast disappearance of crystal form II but also the reforming of crystal form I during the crystal transformation. Although a slow crystal transition rate of samples aging in air was observed as a slow disappearance of crystal form II, a relatively rapid reforming of crystal form I is induced by the slow motion of molecular chains.

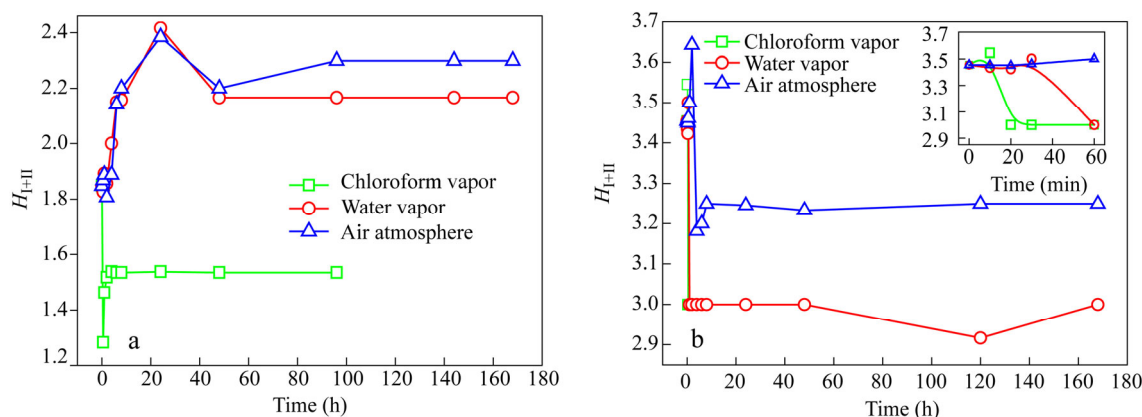


Fig. 8 Variation of total crystal as a function of annealing time under different solvent vapor: (a) in PB-1 hot-pressed film and (b) in PB-1 electrospun nonwoven

CONCLUSIONS

The influence of solvent vapor annealing on the crystal transformation from form II to form I of PB-1 hot-pressed film and electrospun nonwoven was investigated. The results showed that solvent vapor annealing increased polymorphic transformation rate of PB-1 from form II to form I. Although chloroform annealing promoted a pretty fast crystal transition rate, the lowest crystallinity is observed due to the rapid motion of

molecular chains in PB-1 samples. The stretched molecular chains in electrospun nonwovens relaxed into amorphous rather than alignment into a more compact crystal form I also resulted in a decreased crystallinity during the crystal transition process.

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