Effects of Stress Level and Temperature on the Time Dependent Morphological and Physical Properties of PVA Fibers

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Abstract: The effects of the stress level and heat treatment temperature on the morphological and physical properties of poly(vinyl alcohol) (PVA) fibers were investigated with regard to treatment time. The PVA fibers were heat treated at three different temperatures (210, 220, and 230°C) and stress levels (0.05, 0.15, and 0.25 g/d). Increase in shrinkage was observed with an increase in the heat treatment time when treated at 220 and 230°C beyond 15 min, while a little extension was observed at 210°C. The shrinkage in the PVA fibers heat treated at 230°C increased with a decrease in stress levels, exhibiting a different dependence of the shrinkage on the heat treatment time. The WAXS patterns of the PVA fibers heat treated at 230°C at 0.15 g/d showed that the crystalline peaks became sharp with time up to 15 min beyond which they became dull. The degree of crystallinity, determined from the density measurement, was maximum when heat treated for 5 min regardless of the temperature and the stress level. However, the degree of crystallinity when further treated at 220 and 230°C decreased, while that showed little change when treated at 210°C. In addition, the variation of the degree of crystallinity with heat treatment time was in good agreement with that of the degree of amorphous orientation. In the DSC thermograms, a greater dependence of the melting temperature and the heat of fusion on the heat treatment time was observed at higher heat treatment temperatures and lower stress levels.

Keywords: PVA fibers, heat treatment, shrinkage, crystalline structure, orientation

1. Introduction

Among various high performance fibers, PVA fibers attract great attention in the industrial areas because of its superior properties such as high thermal stability, excellent creep characteristics and tensile properties, weatherability, chemical resistance, and adhesion to matrices [1–4]. In addition, PVA fibers have very economical and ecological advantages compared with other high performance fibers. However, some drawbacks of PVA fibers including poor mechanical properties at high temperature and in hot water limit their applications even though they have lots of desirable properties. Thus, PVA fibers has mostly been applied in the industrial fields where high strength is not critical factor such as building materials instead of asbestos, coating materials, reinforced rubber, medical substitute, adhesives, and other composites [4–7]. Therefore, efforts to complement the demerits of PVA fibers are needed to make them widely applicable in various areas.

PVA which has hydroxyl groups as pendant groups can
take a planar zigzag conformation resulting in the second highest theoretical crystal modulus next to polyethylene. The reported tensile properties, however, fall much shorter of theoretically predicted values although various efforts have been made including ultrahigh drawing of gel-spun fiber [8], zone drawing [9,10], multi-step drawing [11], hot drawing [12,13], and cross linking spinning method [14]. Aside from those techniques associated with fiber spinning process, the heat treatment at an appropriate condition is another essential process to maximize the mechanical properties of fibers by reducing or eliminating residual stresses, strains and defects. In the case of semicrystalline polymers, the heat treatment gives rise to the change of microstructure of fibers resulting in different physical properties [15–21]. Thus, it is important to understand the variation of physical properties of PVA fibers with heat treat conditions for the actual applications. However, there are few reports on the combined effects of various heat treatment conditions on the physical properties of high strength PVA fibers, associating them with changes in their microstructure. In this work, PVA fibers prepared by dry-jet wet spinning and subsequent drawing process were heat treated varying stress level and temperature. The influence of the heat treatment conditions on morphological and physical properties of PVA fibers was investigated with regard to treatment time.

2. Experimental

2.1. Sample Preparation

PVA resin (number average degree of polymerization=1735, degree of saponification=99.5 mol%) for the fiber spinning was prepared by bulk polymerization of vinyl acetate at 60 °C using azobisisobutylonitrile (AIBN) as an initiator. The gel-like spinning dope was prepared by dissolving the PVA in 80/20 (by wt%) DMSO/water mixture at 120 °C under nitrogen atmosphere. Dry-jet wet spinning (nozzle diameter=0.1 mm) at an air gap of 5 mm at 75 °C and subsequent drawing process at 210 °C were performed to obtain high performance PVA fibers [22]. The coagulation was performed at -20 °C in the bath draft of 2.0 using 80/20 (by wt%) methyl alcohol (MeOH)/DMSO mixture. The heat treatment was performed on the 120 filaments at one time using the tailor-made apparatus equipped with measuring devices of the tension and length change of fiber specimen and a heating tube as shown in Scheme 1. One end of the fiber specimen was fixed by jog and a constant stress was imposed on the other end. Both ends of the heat treatment tube were insulated with Teflon. The heat treatment was carried out at three different temperatures (210, 220, and 230 °C) and stress levels (0.05, 0.15, and 0.25 g/d) for 60 min.

2.2. Measurement of Physical Properties

The change in fiber length ($L_c$) with time during heat treatment was calculated by equation (1):

$$L_c = L/L_o$$

(1)

where $L$ is the fiber length at time $t$ and $L_o$ is the initial fiber length.

The crystallization and orientation behavior of fibers were examined by wide angle X-ray scattering (WAXS) diffractometer (MX18, MAC Science Co.). The diffraction pattern was obtained at a scanning rate of 1 °/min at 45 kV and 250 mA. The test specimen was prepared in a thickness of 0.5 mm and a width of 5 mm.

The density of PVA fibers was measured at 23 °C with a density gradient column constructed with benzene and carbon tetrachloride. The degree of crystallinity of PVA fiber ($X_c$) was determined by equation (2):

$$1 - \frac{\rho}{\rho_c} = (1-X_c) \frac{\rho_a}{\rho_c}$$

(2)

where $\rho$ is the sample density, and $\rho_c$ and $\rho_a$ are the density of crystalline (1.345 g/cm$^3$) and amorphous (1.269 g/cm$^3$) parts of PVA, respectively.

The degree of crystal orientation was obtained from (100) and (020) planes by azimuthal scanning of WAXS. The degree of amorphous orientation was then evaluated by combining X-ray results, the degree of crystallinity obtained from density, and optical birefringence data measured by a Zeiss polarizing microscope. Amorphous orientation factors were calculated by equation (3):

$$\Delta n = x_c \Delta n f_c + (1-x_c) \Delta n f_a$$

(3)

where $\Delta n$ is the measured birefringence, $\Delta n_c$, and $\Delta n_a$ the intrinsic birefringence of the crystalline (51.8×10$^{-5}$) and amorphous (43.8×10$^{-5}$), respectively, $x_c$ the degree of crystallinity of the fibers, and $f_c$ and $f_a$ the crystalline and amorphous orientation factors, respectively. The birefringence of form ($\Delta n_f$) is neglected [11].

Thermal properties of PVA fibers were measured by differential scanning calorimeter (Perkin Elmer DSC 7) at a scanning rate of 10 °C/min under N$_2$ atmosphere. Indium was used for the calibration.

3. Results and Discussion

Figure 1 shows the variation of shrinkage of PVA fibers with heat treatment time at three different temperatures of
210, 220, and 230 °C at a stress level of 0.15 g/d. Little change in shrinkage is observed in the beginning of heat treatment up to about 15 min at all temperatures. However, further heat treatment at 220 and 230 °C increases the shrinkage with time, while a little extension is observed at 210 °C. Overall shrinkage is associated with the disorientation in the amorphous regions by chain folding [23,24]. At relatively low temperature where there is low molecular mobility chain extension in the amorphous region might favorably happen under some tension after a given time rather than chain folding. Occurrence of only a small shrinkage even at 230 °C near melting temperature (234 °C) suggests that amorphous regions are highly oriented representing high thermal stability of the fiber. However, heat treatment at 230 °C for more than a critical time causes noticeable dependence of shrinkage on time. Long heat treatment at elevated temperature promotes the chain folding due to high mobility of polymer chain resulting in a large amount of shrinkage.

The effects of stress level applied during heat treatment at 230 °C on the shrinkage with regard to time are shown in Figure 2. The shrinkage increases with decreasing the stress level showing different dependence of shrinkage on heat treatment time. At the lowest stress level of 0.05 g/d, the shrinkage increases significantly with heat treatment time even from the beginning while shrinkage occurs slightly at 0.15 g/d after a given time and a little extension occurs at the highest level of 0.25 g/d rather than shrinkage. Under relatively low tension applied during heat treatment there is more chance for the molecules to be folded and disoriented, resulting in high shrinkage. A great dependence of the shrinkage of PVA fibers on stress levels might be attributed to the alteration of orientation behavior during heat treatment and some of crystalline structure.

In Figure 3 the WAXS patterns of PVA fibers heat treated at 230 °C under 0.15 g/d represent the variation of crystalline structure and orientation behaviors with time. The diffraction patterns of 5 to 45 ° and 65 to 85 ° are obtained by equatorial and meridian scanning, respectively. PVA fibers present the characteristic peaks at 2θ values of 11.1, 16.0, 19.6, 22.4, and 74.8 ° corresponding to (100), (001), (101), (200), and (020) planes, respectively. The crystalline peaks become sharp with heat treatment time up to 15 min, indicating that the heat treatment increases perfectness of the crystal structure. For
heat treatment beyond 15 min, however, the crystalline peaks become dull, resulting from rerandomness of oriented chains in the amorphous regions and partial thermal degradation which are more noticeable at longer heat treatment time. As shown in Figure 1, the shrinkage of the fiber heat treated at 230 °C does not occur up to 15 min, a little shrinkage occurs up to 30 min, and its notable dependence on time is then observed by further treatment. There is a good agreement between the shrinkage data and WAXS results. The intensity of crystal planes (100), (001), (101), and (200) increases slightly with heat treatment time up to 15 min while that of the crystal plane (020) increases notably. This indicates that heat treatment under tension has a more significant influence on the short crystal lattice (020) in the direction parallel to the fiber axis than crystal lattices (100), (001), (101), and (200) in the direction perpendicular to the fiber axis. Generally, heat treatment in a free state increases the dimensions of crystallites, especially in the direction perpendicular to the fiber axis. On the contrary heat treatment under tension affects a parallel and perpendicular crystallite dimensions in a different manner. The parallel dimension increases considerably while the perpendicular dimension increases slightly or decreases [25].

Figure 4 shows the variation of the degree of crystallinity of PVA fibers heat treated at three different temperatures at 0.15 g/d with time. The degree of crystallinity of untreated PVA fiber is increased from 67% to 78% by heat treatment at 220 and 230 °C for 5 min. However, further heat treatment at the temperatures decreases the degree of crystallinity with increasing treatment time. In particular, heat treatment at 220 and 230 °C beyond 30 min gives even lower degree of crystallinity than untreated fibers, while little change is shown at 210 °C over the heat treatment time. This suggests that the heat treatment at the elevated temperatures more than a critical time gives rise to a partial degradation, that is, demolition of crystal structure, which is accelerated with increasing heat treatment time and temperature.

Figure 5 shows time dependent degree of crystallinity of the PVA fibers varying stress level applied during heat treatment at 230 °C. The degree of crystallinity increases up to 78% over all stress levels by heat treatment for 5 min beyond which it decreases with increasing heat treatment time. Little dependence of the degree of crystallinity on the stress level is observed up to 15 min but a greater decrease in the degree of crystallinity is caused at 0.05 g/d by further heat treatment than at 0.15 and 0.25 g/d. It is worth noting that variation of the degree of crystallinity obtained from density measurement discords with that of the X-ray patterns. The intensity of crystalline peaks decreases more than 15 min in the X-ray pattern, while the degree of crystallinity calculated from density decreases more than 5 min. The discrepancy in the critical time might be caused by the methodological difference between wide angle X-ray diffractometer and density gradient column. X-ray diffraction patterns are mostly affected by crystalline region, while the density is sensitively affected by both amorphous and crystalline regions. Therefore, it implies that the time difference is associated with the disorientation in the amorphous region. The amorphous regions are rapidly crystallized in the beginning of heat treatment up to 5 min, which is followed by the disorientation of the unstable crystalline structure formed in the amorphous regions during further heat treatment.

Figures 6(a) and (b) show the variation of the degrees of crystal and amorphous orientation with heat treatment time, respectively, for (100) and (020) crystal planes of PVA fibers heat treated at 230 °C at 0.15 g/d. The degree of crystal orientation increases with heat treatment time up to 15 min and then levels off by further heat treatment. The degree of crystal orientation of untreated fiber is 92% and 95 for (100) and (020) plane, respectively and the heat treatment for a
proper time increases it as high as 96 and 98%. It is noteworthy to mention that the degree of crystal orientation is unusually high in comparison with most of fibers made of flexible polymers representing the high performance of PVA fibers. On the contrary, the degree of amorphous orientation increases more than the degree of crystal orientation giving maximum value at 5 min and then decreases with further heat treatment. The variation of the degree of amorphous orientation with heat treatment time agrees well with that of the degree of crystallinity. This indicates that heat treatment of PVA fibers at elevated temperature under tension affects preferably the amorphous regions. In other words, variation in degree of crystallinity by heat treatment is mostly associated with alteration of the amorphous region rather than that of the crystalline region.

The DSC thermogram of PVA fibers heat treated at the
stress level of 0.15 g/d at 230 °C is given in Figure 7. The
endothermic peak becomes sharp with increasing time up to
15 min giving little changed melting temperature ($T_m$) at
c.a.234 °C. However, further heat treatment increases the $T_m$
with broadened $T_m$ peak. Similar results are also obtained at
the stress levels of 0.05 and 0.25 g/d. This coincides with the
WAXS patterns where the crystalline peak becomes broad
from 15 min heat treatment.

Figure 8 presents the effects of temperature and stress level
on $T_m$ and heat of fusion ($\Delta H$) of PVA fiber with regard to
heat treatment time. For the heat treatment at 210 °C, little
change in $T_m$ and $\Delta H$ is observed with time as shown in
Figure 8(a). For the heat treatment at 220 and 230 °C,
however, the $T_m$ increases and the $\Delta H$ decreases. In particular,
at 230 °C, the greatest dependence of $T_m$ and $\Delta H$ on heat
treatment time is observed, giving 7 °C higher $T_m$ and 27% reduced $\Delta H$ at 60 min heat treatment than those of untreated
fiber. This suggest that large crystallite is obtained and the
number of crystallites is reduced at an elevated temperature
of 230 °C which is favorable condition for the growth of
crystallite and unfavorable condition for nucleation. As
shown in Figure 8(b) $T_m$ increases notably more than 15 min
heat treatment over three different stress levels but $\Delta H$
decreases. Particular at the lowest stress level of 0.05 g/d
much greater change is observed than at the other stress
levels. The low stress level produces the large crystallite by
improving the molecular mobility. In addition, imperfect
crystal structures in the amorphous regions favorably formed
under low tension appear to be destroyed when the fiber is
heat treated more than 15 min leading to a decrease in $\Delta H$.

4. Conclusion

PVA fibers were heat treated varying temperature and
stress level and resulting changes in morphological and
physical properties were examined with regard to heat
treatment time. Shrinkage was more notably observed at
higher temperature at lower stress level after the heat
treatment of a critical time. This is associated with promoted
chain folding due to high mobility of polymer chain at the
conditions. Heat treatment under stress had more noticeable
influence in the direction parallel to the fiber axis than in
the direction perpendicular to the fiber axis exhibiting more
increased intensity of crystal plane (020) with heat treatment
time. In the WAXS pattern the intensity of crystalline peaks
decreased by the heat treatment beyond 15 min while the
degree of crystallinity calculated from density of the fiber
decomposed by that beyond 5 min. This time difference was
attributed to the disorientation in the amorphous region
mostly contributing to the density change rather than WAXS
pattern. The degree of amorphous orientation increased
more than the degree of crystal orientation exhibiting
maximum value at 5 min and then decreased with further
heat treatment time, which agreed well with the changes in
degree of crystallinity. The temperature and stress level applied
during heat treatment had a more significant effect on the
melting temperature and heat of fusion at higher temperature
and lower stress level. When the heat treatment at elevated
temperature at proper level of tension is done for a critical
time the performance of PVA fibers might be maximized
resulting from enhanced crystallinity and orientation.

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응력수준과 온도가 PVA 섬유의 시간 의존적인 형태학적 및 물리적 특성에 미치는 영향

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