THERMAL EFFECT ON THE UNIAXIAL TENSILE PROPERTIES AND STRUCTURE OF POLY (VINYL ALCOHOL) FILMS

Baki Aksakal, Önder Yargi

Yildiz Technical University, Department of Physics, Davutpasa Campus, Esenler 34210, Istanbul, Turkey

Abstract

Influence of heating or annealing at different temperatures from 25 to 140 ℃ on the uniaxial tensile properties of polyvinyl alcohol (PVA) thin films was investigated by using tensile testing method. It was observed that especially the shape of initial part (up to 10% strain) of the stress-strain curve changed significantly which indicates the formation of a transition point at a low strain value of around 1-2% strain with increasing anneal temperature. Besides, initial or Young's modulus increased from 0.26 GPa to around 1 GPa as the temperature increased from 25 ℃ to around 100 ℃ and then it decreased slightly down to around 0.7 GPa. Ultimate tensile stress increased significantly from around 16 to 39 MPa. Moreover, toughness of the PVA films were improved from around $144*10^4$ to $3942*10^4$ J/m^3 for the anneal temperatures from 80 to 130 ℃. By using the FT-IR/ATR spectral results, the increase in tensile strength and toughness is assumed to be due to increase in the degree of crystallization and absorbance ratio of hydrogen bonded OH groups, that is, the increase in the more ordered structural units and reformation and/or breakage of intra- and inter-molecular hydrogen bonds during heating process.

Key words: *poly (vinyl alcohol), tensile properties, thermal effect, Young's modulus, hydrogen bond*

1. INTRODUCTION

Poly vinyl alcohol (PVA) being a water soluble biodegradable synthetic polymer the structure of which has a formula of $[CH_2CH(OH)]_n$ is commonly used in the food industries as a binding, coating agents, and food packaging (Baker et al. 2012), the textile industries as a sizing and finishing agent (DeMerlis et al. 2003), for paper products manufacturing (DeMerlis et al. 2003), and in the production of polarizer films. Besides, in medical devices, due to its biocompatible, noncarcinogenic, nontoxic, swelling properties, and bioadhesive characteristics, PVA is used as a biomaterial (Hassan et al. 2000). PVA has been also used to treat vascular embolisms (Covey et al. 2005; Tadavarthy et al. 1975) and as tissue adhesion barriers (Weis et al. 2004; Hiraizumi et al. 1995; Lang et al. 2007). It is well known that PVA is widely used to produce nanocomposites with different chemical structures such as graphene oxides, carbon nano tubes, titanium dioxide in order to improve not only optical and electrical properties but also mechanical properties. Although mechanical properties of PVA films having different concentration and composition of different materials such as carbon nanotubes were investigated (Paiva et al. 2004; Xu et al. 2009; Zhan et al, 2014; Ni et al. 2006; Chen et al. 2005; Bahrami et al. 2005), the influence of heating on the uniaxial tensile properties and corresponding changes in the structure of PVA films have not been investigated much. Moreover, the relationship between the changes in the structure and tensile properties of PVA films due to heating was not examined which could be quite important to understand the reasons leading the changes on the stress-strain behaviors and mechanical characteristics of PVA films.

In this study, the influence of heating at different temperatures on the uniaxial tensile properties and stress-strain behaviors of PVA films was investigated by using Tensile testing method. The changes in the structure and absorbance values of infrared bands of annealed PVA films were examined by FT-IR/ATR spectroscopy. The relationships between structural changes and mechanical changes in PVA films were tried to set.

2. MATERIALS AND METHODS

2.1 Preparation of PVA Films

Commercially available Polyvinyl alcohol (PVA) was purchased from Boysan Co., Turkey, which includes Acetic acid ethenyl ester, polymer with ethanol, 92-100 % and has powder form, white color, and is water soluble with melting point about 220-240 $^{\circ}$C and PH at around 4.5-6.5. It was used as supplied in white powder form. A solution of PVA was prepared as follows: PVA was dispersed in deionized water in the proportions of 0.01 gr PVA with 1 ml water by bath sonication for 3h. Then, by dropping the same amount of PVA on the rectangular PP films with the size of 0.5x4cm^2, the PVA films were prepared and then the films were kept at room conditions for one day for allowing the water to evaporate.

2.2. Tensile Testing Method

Uniaxial tensile tests of PVA films having a gauge length of 20 mm were made on a Lloyd tensile testing machine LF Plus (AMETEK Lloyd Inst., UK) with a crosshead speed of 20 mm/min at room conditions (T=25 °C; RH=60%). The tested PVA films had the same width of 5 mm and the thicknesses of 165±5μm. In order to see the influence of heating, the films were heated at the temperatures from 80 to 140 °C for 15 min.

2.3. FT-IR/ATR Spectroscopic Measurements

The Fourier transform infrared / attenuated total reflectance (FT-IR/ATR) experiments were carried out on a Perkin–Elmer Fourier transform spectrometer "Spectrum One" (Perkin Elmer, Inc. USA) by using the ATR cell. The FT-IR/ATR spectra of the PVA film samples were recorded in the 650–4000 cm^{-1} range at a resolution of 4 cm^{-1} with 4 scans for each measurement. In order to examine the effect of heating on the spectra of the samples, the spectra of the PVA film samples were recorded after the samples were separately heated at different temperatures from 80 to 140 °C.

3. RESULTS AND DISCUSSION

The influence of heating on the shape of stress-strain curve of PVA films is shown in Figure 1 and the changes in the tensile properties of these annealed PVA films are tabulated in Table 1. Considering the changes on the stress-strain curves, it is clear that the prominent changes are seen in the initial part (up to around 10% strain) of the stress-strain curves. As seen in Table 1 and in Figure 2, the Young's modulus of the PVA films showed a great increase from around 0.3 GPa up to around 1 GPa for the temperatures from 25 to 80-100 °C. Then it decreased to around 0.6 GPa with increasing anneal temperature higher than 100 °C.

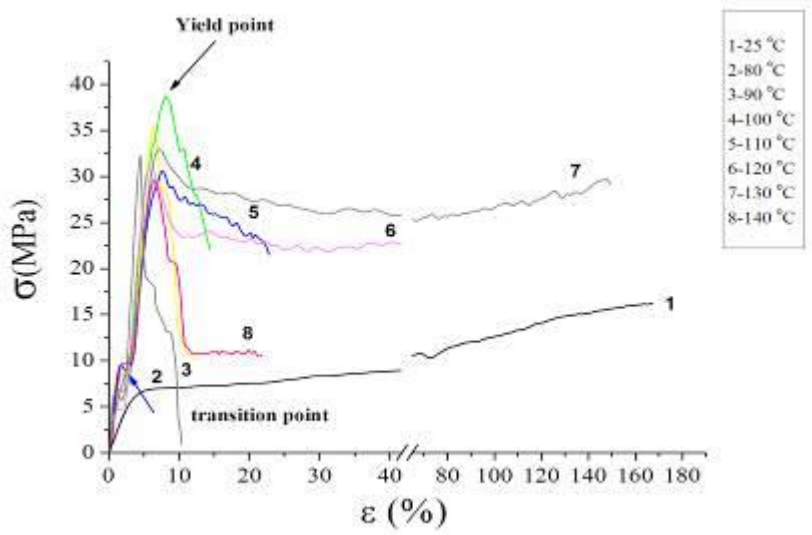


Figure 1. Stress-strain curves of PVA heated at different temperatures.

The increase in the Young's modulus can be due to that the structure passes from the amorphous structures (as for the case of T=25° C) to more ordered structure which increases the intra- and intermolecular interactions between polymer chains.

Table 1. Tensile properties of PVA films heated at different Temperatures.

T (°C)	E_y (GPa)	ε_t (%)	σ_t (MPa)	ε_y (%)	σ_y(MPa)	ε_r (%)	σ_T (MPa)
25	0.26	-	-	6.35	6.93	167.44	16.23
80	1.16	0.74	6.22	4.48	32.17	10.35	32.17
90	1.00	1.32	8.64	6.45	35.53	12.31	35.53
100	1.09	1.12	6.98	8.08	38.65	14.42	38.65
110	0.73	1.7	9.52	7.6	30.65	22.8	30.65
120	0.60	1.22	4.6	6.02	31.13	61.64	31.13
130	0.46	2.51	9.45	7.16	32.93	149.36	32.93
140	0.72	2.05	9.67	6.37	29.67	21.8	29.67

As seen in Figure 1 and Table 1, although it was not observed in the stress-strain curve of unheated PVA films, a kind of transition point was observed at strain values of about 0.8 which shifted to higher strain values up to around 2% which has the corresponding stress values changing from around 6 to 10 MPa with increasing anneal temperature. Besides, it was observed that the yield stress which also determines the ultimate tensile strength of the annealed PVA films increased from around 7 MPa to ~39 MPa for the temperatures increasing from 25 to 100 °C. After that, it showed a slight decrease down to ~30 MPa. It is clear that after such yield stress and yield strain values, the irreversible structural processes, that is, plastic deformations are seen in the structure.

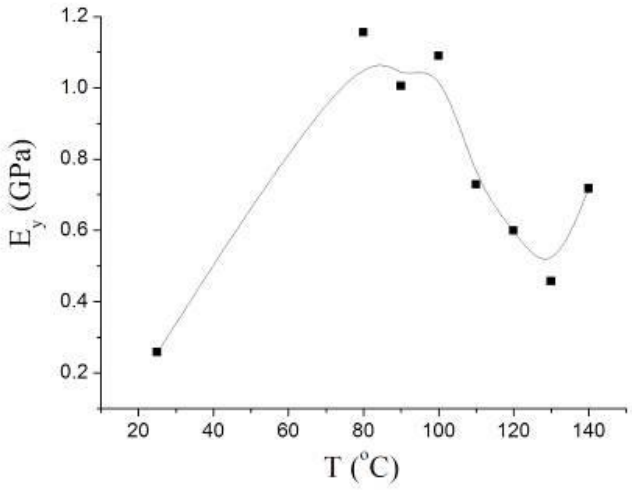


Figure 2. The change of Young's modulus of PVA films with increasing anneal temperature.

Apparently seen in Figure 3, with increasing anneal temperature, ultimate tensile strength showed an increasing tendency up to around 39 MPa and then a slight decrease. This indicates that heating enhanced the mechanical strength of PVA films greatly when compared with the case of unheated PVA films and it was also seen that further heating at temperatures higher than 100 °C did not change much the ultimate tensile strength of the PVA films. Moreover, if the breaking extension is compared for the samples heated at temperatures from 80 C to 130 °C, it is seen that the breaking extension also increased.

Furthermore, as tabulated in Table 2 and illustrated in Figure 4, toughness values of PVA films increased greatly with increasing anneal temperature up to around 130 °C. That is, heating process increased apparently the rigidity and the toughness of PVA films which is a measure of the absorbed energy per volume taken by the sample up to rupture.

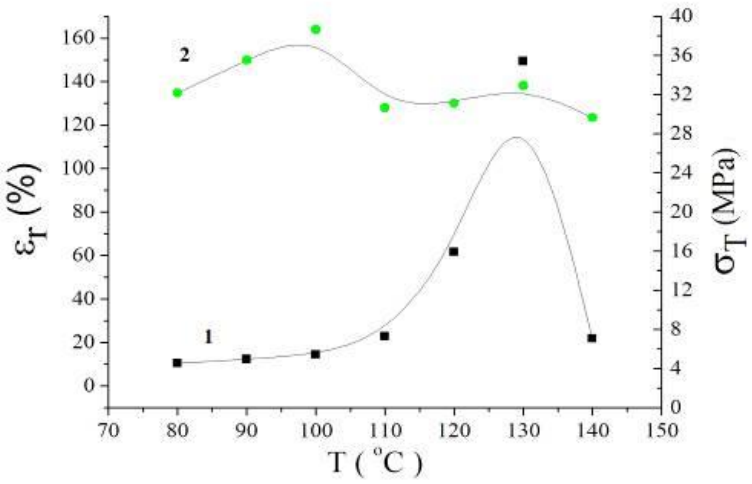


Figure 3. (1) The change of breaking extension (ε_r) and (2) ultimate tensile strength of PVA films with increasing anneal temperature.

Table 2. The change of toughness (U_T) of PVA films heated at different Temperatures

T (°C)	**U_T (Jm^{-3})*10^4**
80	143.66
90	219.67
100	355
110	514.71
120	1379.42
130	3942.04
140	305.4

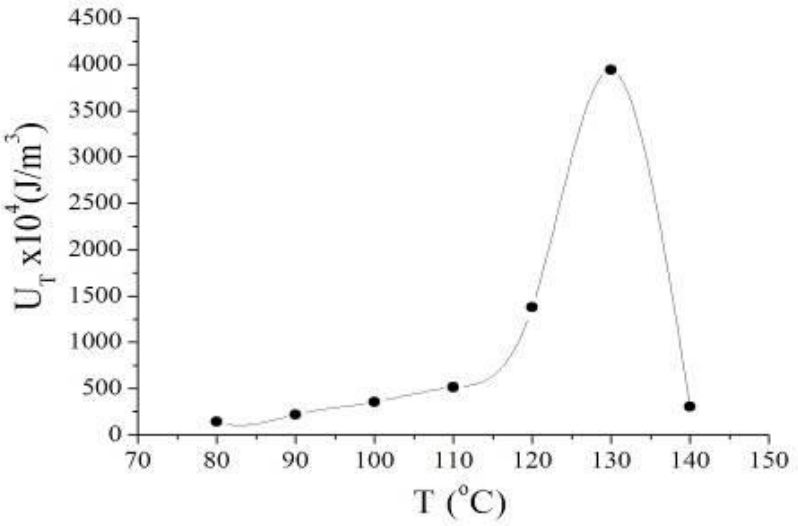


Figure 4. The change of toughness of PVA films with increasing anneal temperature.

On the other hand, in order to see how the crystalline and amorphous regions as well as intra and inter molecular interactions change with heating, the absorbance values of the related bands in different wave number ranges of 850 to 1170 cm^{-1} and of 2800-3700 cm^{-1} were analyzed.

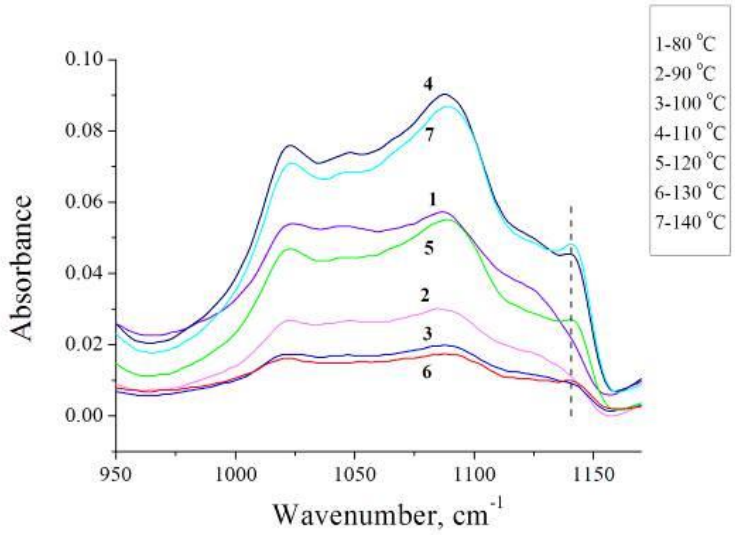


Figure 5. FT-IR /ATR spectra of PVA films in the range of 850-1170 cm^{-1} after being annealed at different temperatures.

Figure 5 shows the FT-IR/ATR spectra of PVA films annealed at different temperatures in the wavenumber range of 950 to 1150 cm^{-1}. The band at around 1142 cm^{-1} is known to be crystallization sensitive band (Kenny et al. 1966) and also crystallinity band (Tretinnikov et al. 2012). This band was also assigned to ν(C–O) stretching vibrations in C–OH groups of the crystalline polymer phase and to ν(C–C) stretching vibrations of the carbon framework of the polymer chain in the crystalline phase (Tretinnikov et al. 2012; Ahmad et al. 2013; Kumar et al. 2014). In the spectra, another broad band at 1094 cm^{-1} is assigned to ν(C–O) stretching vibration (Tretinnikov et al. 2012; Ahmad et al. 2013, Tsukada et al. 1994; El-Hefian et al. 2010; Shehap 2008; Jabbar et al. 2010; Raju et al. 2007) which was taken as a reference band for the calculation of crystallinity ratio (Tretinnikov et al. 2012). Table 3 shows the change in the ratio of the absorbance intensity of the band at 1144 to that at 1094 with increasing anneal temperature.

Table 3. Absorbance intensity ratio (A_{1144}/A_{1094}) values for the PVA films heated at different temperatures.

Anneal Temperature, °C	**A_{1144}/A_{1094}**
80	0.312
90	0.360
100	0.449
110	0.461
120	0.477
130	0.524
140	0.517

It is clearly seen in Table 3 the absorbance ratio (A_{1144}/A_{1094}) which is related with the crystalline parts or degree of crystallization of the PVA film structure increased significantly from around 0.31 to 0.52 with increasing temperature of annealing. This also indicates that the PVA films still have a great amount of amorphous phase in the structure after annealed at temperatures of 80-140 °C. It is also

revealed that due to increasing ratio (A_{1144}/A_{1094}) the film structure can be assumed to obtain more ordered, rigid, and crystallized structural units which significantly contribute to the mechanical strength of the PVA films as it is seen in Table 1.

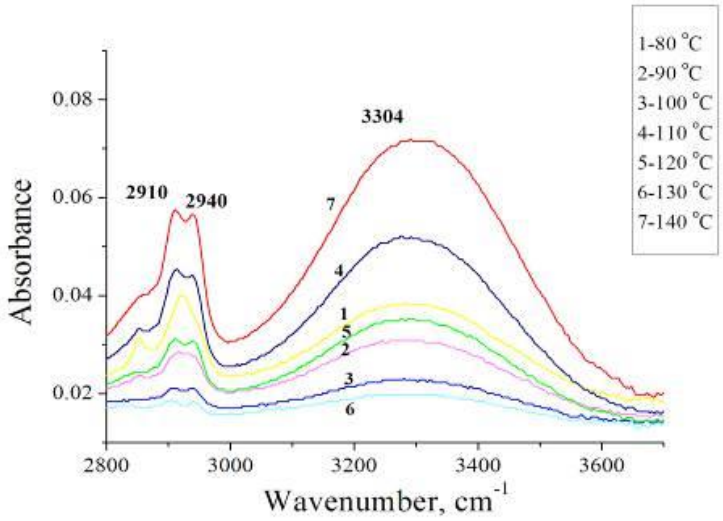


Figure 6. FT-IR /ATR spectra of PVA films after being annealed at different temperatures in the wavenumber range of 2800-3700 cm^{-1}.

On the other hand, figure 6 shows the FT-IR/ATR spectra of PVA films in the wavenumber range of 2800-3700 cm^{-1}. The absorption bands at around 2940 and 2910 cm^{-1} correspond to anti-symmetric and symmetric stretching bands of CH_2 groups respectively (Ahmad et al. 2013; Shehap 2008; Attia et al. 2013; Chan et al. 2009). It was stated that a broad band observed between (3220-3600) cm^{-1} is due to OH stretching vibration of the hydroxyl groups being either non-bonded or hydrogen bonded (Ahmad et al. 2013; ; Kumar et al. 2014; Tsukada et al. 1994; El-Hefian et al. 2010, Jabbar et al. 2010; Sakellariou et al. 1993; Korbag et al. 2016; Chen et al. 2010) and similarly, it was also stated that the band at around 3293 cm^{-1} is the stretching vibration of hydroxyl group with strong hydrogen bonding of pure PVA films (Korbag et al. 2016; Chen et al. 2010).

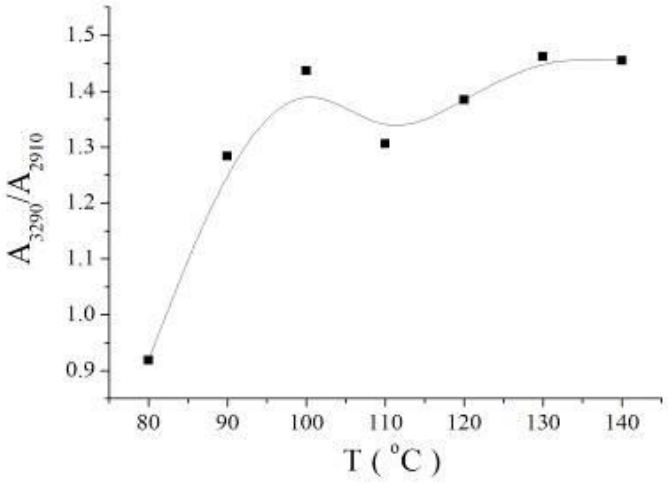


Figure 7. The change in the ratio of the absorbance of the band at 3290 cm^{-1} to that of the band at 2910 cm^{-1} of PVA film with increasing anneal temperature.

Figure 7 shows the absorbance ratio of the band at around 3290 cm^{-1} corresponding to OH stretching of hydroxyl groups with strong hydrogen bonding to the band at around 2910 cm^{-1} which was chosen as an internal standard band to eliminate the any thickness effect on the absorbance values. It is clearly seen that the ratio increased greatly first for the temperature up to 100 °C and then it seems to have an almost constant value or to vary slightly for the temperatures higher than 100 °C. The increase in the intra- and inter-molecular hydrogen bonding interactions may indicate that annealing increased the crystallization process which changes the form of the film structure from about glassy and amorphous state to a more ordered structure. Thus, the film obtained a more ordered structure and crystallites due to new formation and reorganization of structural units thanks to mainly increase in the number of inter- and intra- molecular hydrogen bonding due to OH groups of hydroxyl groups of adjacent chains or of the intra chain in both crystalline and amorphous phases. These more ordered and stronger structural units contribute to increase in the tensile strength of the PVA films heated at temperatures from 80 to around 100 °C and then it seems that increased number of hydrogen bonding did not have a great effect on the tensile stress. Besides, it can be assumed that reorganization that is, reformation and/or breakage of intra- and inter-molecular hydrogen bonds especially between amorphous chains in amorphous parts which constitute a great amount (more than about 50%) of PVA film structure contribute to the extensibility of PVA films which is also reflected on the increase in the breaking extension as seen in figure 3. Therefore, the increase in extensibility together with the increase in tensile stress enhances the toughness of PVA films as shown in figure 4.

4. CONCLUSIONS

Considering the results of tensile testing measurements, it is seen that especially the shape of initial part of the stress-strain curve of PVA films heated at different temperatures from 25 to 140 °C changed, that is, a kind of transition point at around 1-2% strain with increasing anneal temperature was observed. Besides, heating at temperatures from 25 °C up to around 100 °C increased Young's modulus from 0.26 GPa to around 1 GPa significantly and then it decreased Young's modulus slightly down to around 0.7 GPa. It was also observed that breaking extension decreased when compared with that of unheated PVA films, but it showed an increasing tendency with increasing anneal temperature. It was thought that this increase in the breaking extension may be due to reformation and/or breakage of intra- and inter-molecular hydrogen bonds of hydroxyl groups especially between amorphous chains in amorphous parts which were shown by the FT-IR/ATR spectral results. Moreover, ultimate tensile stress increased significantly from around 16 to 39 MPa for the anneal temperatures increasing from 25 to 100 °C, after which it showed a slight decrease down to 30 MPa. The increase in the tensile strength is assumed to be strongly related with the increase in the number of more ordered structure and rigid structural units such as crystallites which were obtained with increasing degree of crystallization shown by FT-IR/ATR results (Table 3) and with intra- and inter-molecular hydrogen bonding interactions during heating process. Furthermore, the increase in the tensile stress and breaking extension values together contributed and increased the toughness of the annealed PVA films from around $144*10^4$ to $3942*10^4$ J/m^3 for the anneal temperatures from 80 to 130 °C.

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