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Uniaxial tensile and structural properties of poly(vinyl alcohol) films. The influence of heating and film thickness

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ABSTRACT: Poly(vinyl alcohol) as pure or composite materials is widely used in the food and textile industries, andbiomedical applications due to some important properties such as uniaxial tensile, biocompatibility, and noncarcinogenicity. Investigation of the influence of the film thickness and heating on the uniaxial tensile, spectroscopic, and surface properties of PVA films investigated in this study is quite important for improving the properties of such materials and their applicability in different conditions. In this study, with the influence of heating, a necking behavior was observed at around 2% for thin films and 4–9% strain for thicker PVA films for which a kind of transition point at around 1–2% strain was observed. The mechanical strength of PVA films, strain at break, and Young's modulus were enhanced greatly as the temperature increased from 80 to around 110°C, and then most of them decreased. The degree of crystallinity increased linearly with the heat temperature from around 36–40%. Although PVA thin films obtained a very smooth surface structure after being heated at 80°C, with increasing heat temperature, the surface roughness of both thin and thick PVA films increased and the PVA thin films obtained more degraded film surface. © 2017 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2017**, *133*, 44915.

KEYWORDS: FT-IR/ATR spectroscopy; mechanical properties; poly(vinyl alcohol) films; structure-property relationship; thermal effect

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INTRODUCTION

Poly(vinyl alcohol) (PVA), which is a water soluble biodegradable synthetic polymer with the structure having the formula of $[CH_2CH(OH)]_n$, is mostly used in the food industries,[1] as well as the textile industries,[2] paper products manufacturing,[2] and in the production of polarizer films due to significant uniaxial tensile and surface characteristics. Moreover, due to some important properties such as biocompatibility, noncarcinogenicity, nontoxicity, swelling properties, and bioadhesive characteristics, PVA is used as a biomaterial in medical devices.[3] PVA has also some other important applications to treat vascular emboli sms[4,5] and as tissue adhesion barriers.[6–8] On the basis of PVA, it is clear that various nanocomposite films with the use of different chemical structures such as carbon nanotubes, graphene oxides, and titanium dioxide are produced in order to obtain improved properties such as uniaxial tensile, optical, and electrical properties. Thus, it is clear that depending on the proportion of additives, crystallinity, molecular weight, and thickness of the PVA based composite films, the film formation and their properties can change. It is known that the mechanical properties of PVA films with different concentration and the composition of different materials such as carbon nanotubes and graphene oxide were investigated.[9–14] However, both the thickness and thermal effect on the uniaxial tensile as well as morphological and spectroscopic properties of pure PVA films have not been investigated in detail. In a study,[15] it is reported that with increasing thickness of the PVA films with different molecular weights, both the elastic modulus and tensile strength decreased. It is important to examine how the tensile properties such as tensile strength and extensibility, spectroscopic, morphological properties of pure PVA thin films will change with increasing thickness of PVA films exposed to heating at different temperatures to produce composite films with better characteristics and to modify them for better applicability in different conditions such as at high temperatures. In addition, the variation of such properties after heating or annealing process is quite important to obtain a relationship between mechanical and structural properties of PVA films. Due to these reasons, to produce composite films based on PVA with better characteristics and also to modify them for better applicability in different conditions, in this study, it was mainly aimed to investigate the effects of film thickness and heating on the uniaxial tensile,

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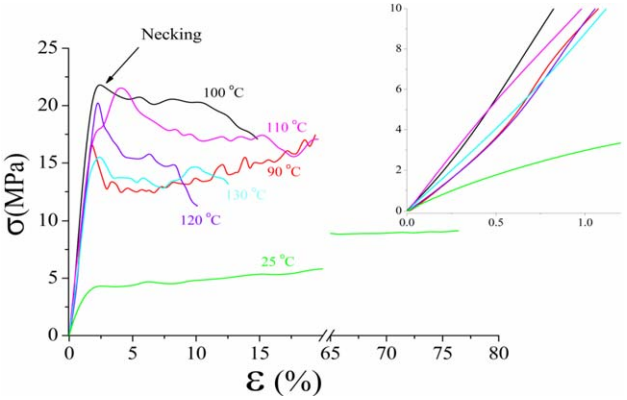


Figure 1. Stress-strain curves of PVA films having the thickness of 50 μm after thermal process at different temperatures. [Color figure can be viewed at wileyonlinelibrary.com]

spectroscopic, and morphological properties of pure PVA films in detail by using tensile testing, Fourier transform infrared (FT-IR)/attenuated total reflectance (ATR) spectroscopy, and Scanning Electron Microscope (SEM) methods. Moreover, because the structure-property relationship will be important for not only pure PVA films but also producing composite films based on PVA with better properties, the correlation between changes in the uniaxial tensile properties and structural changes such as changes in intramolecular and intermolecular interactions especially hydrogen bonding, which will be obtained in the spectroscopic as well as the film surface property measurements of heated PVA films having different thickness was tried to be determined. It was observed that although the shape of the stress-strain curves of unheated PVA films with different thickness did not change and indicated a kind of rubber like behavior, with increasing heat temperature, a necking behavior was observed on the stress-strain curves. In addition, a kind of transition point at low strain values was observed for thicker PVA films than 50 μm. In general, as the heat temperatures increased from 80°C up to around 110°C, the tensile strength, Young's modulus, and strain at break values of PVA films with varying thickness increased significantly, and beyond this temperature, most of them decreased. The role of the intermolecular interactions especially hydrogen bonding in the structure and of the degree of crystallinity and film surface structure in the change of the uniaxial tensile properties were discussed in detail.

EXPERIMENTAL

Materials

Preparation of PVA Films. Commercially available PVA was obtained from Boysan Co., Turkey. It has powder form and white color and is water soluble with melting point at about 220–240°C and has PH value at around 4.5–6.5 and includes acetic acid ethenyl ester, polymer with ethanol, 92–100%. The PVA was used as supplied in white powder form. An aqueous polymer solution of PVA was prepared as follows: first, PVA was dispersed in deionized water in the proportions of 0.01 g PVA/1 mL water by using bath sonication for 3 h. Then, to produce PVA films with different thickness from around 50 ± 5 to 170 ± 5 μm, different amounts of the PVA solution was dropped on to the PP films cut in a rectangular shape with the size of 0.5×4 cm^2. All the films were kept at ambient temperature in the laboratory for one day.

Methods

Tensile Testing Method. Uniaxial tensile tests of PVA films were carried out on a Lloyd tensile testing machine LF Plus (AMETEK Lloyd, UK) with a crosshead speed of 20 mm min^{-1} at room conditions ($T = 25$°C; RH = 60%). The test specimens had the same gauge length of 20 mm, width of 5 mm, and varying film thicknesses from 50 ± 5 to 170 ± 5 μm measured by using a digital micrometer (Mitutoyo, No 293–821-30, Japan). To investigate the influence of heating or annealing on the stress-strain behavior of the PVA films, the PVA films of different thickness were heated in an incubator (Binder, 115 lt, Germany) at the temperatures from 80 to 130°C for 15 min. The PVA films were not kept under stress in the heating process. They were heated freely after placed on a glass plate. The heated PVA films were tested at the same experimental conditions, that is, at 25°C and 60% RH. For each heat treatment, 7–8 PVA film samples having the same film thickness were tested by using the tensile tester and then the mean and standard deviation values of tensile properties of PVA films were determined.

FT-IR/ATR Spectroscopic Measurements. The FT-IR/ATR experiments were carried out on a Thermo Scientific Nicolet iS5 FT-IR Spectrometer equipped with a iD7 ATR sampling accessory. The FT-IR/ATR spectra of the PVA film samples were recorded in the 500–4000 cm^{-1} range at a resolution of 4 cm^{-1} with 32 scans for each measurement. To examine the effect of heating and film thickness on the spectra of the samples, first, the PVA film samples with different thickness were separately heated at different temperatures from 80 to 130°C for 15 min. Then, the spectra of the specimens were recorded at room conditions.

SEM Measurements. SEM analysis of the PVA films with different thickness exposed to heating at different temperatures from 80 to 130°C was done to determine the changes on the morphology and microstructure of PVA films. Before the SEM measurements of PVA film samples, these nonconductive specimens were mounted on aluminium stubs using carbon tape and gold coated with a Polaron SC7610 sputter in a vacuum. The surface morphology of the PVA films was examined by a Philips

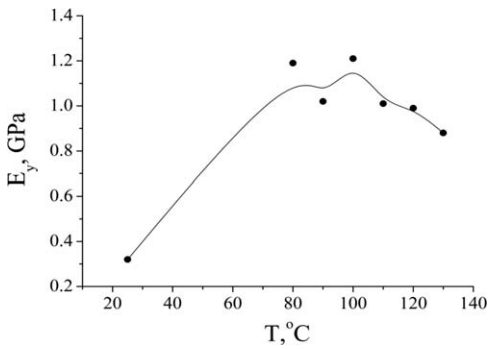


Figure 2. The change of Young's modulus of PVA films having the thickness of 50 μm with increasing anneal temperature.

Table I. The Mean and Standard Deviation Values of Tensile Properties of PVA Films Having the Thickness of 50 μm after Being Heated at Different Temperatures (T)

T (°C)	E_y (GPa)	ϵ_y (%)	σ_y (MPa)	ϵ_r (%)	σ_T (MPa)
25	0.32 ± 0.05	2.2 ± 0.44	4.3 ± 0.47	76.4 ± 15.69	9.1 ± 1.33
80	1.19 ± 0.15	2.1 ± 0.14	19.8 ± 1.60	13.5 ± 0.93	20.3 ± 1.19
90	1.02 ± 0.12	1.7 ± 0.27	17.0 ± 1.87	19.4 ± 5.15	17.0 ± 1.87
100	1.21 ± 0.12	2.3 ± 0.17	21.8 ± 0.50	14.8 ± 0.52	21.8 ± 0.50
110	1.01 ± 0.16	2.2 ± 0.21	17.7 ± 0.75	20.1 ± 1.92	21.6 ± 0.96
120	0.99 ± 0.15	2.2 ± 0.15	20.2 ± 1.35	10.1 ± 0.40	20.2 ± 1.35
130	0.88 ± 0.08	2.3 ± 0.44	15.6 ± 1.48	12.5 ± 0.35	15.6 ± 1.48

E_y: Young's modulus; ϵ_y: yield strain; σ_y: yield stress; ϵ_r: strain at break; σ_T: tensile strength.

XL30 SFEG SEM at 5 kV. They were observed using secondary electron detector under different magnifications up to 5000×.

RESULTS AND DISCUSSION

The Results of Uniaxial Tensile Tests of PVA Films

Figure 1 shows how the shape of the stress-strain curve of PVA film having the thickness of 50 μm changes with increasing heat temperature.

Here, the heat temperature was chosen from around 80°C being very close to glass transition temperature of PVA to 130°C beyond which PVA begins to be destroyed at around 150°C.

Considering Figure 1, as seen on the first curve at 25°C, it can be stated that PVA became ductile and its stress-strain curve can be divided into two parts, that is, a linear region up to around 1–2% strain, which can correspond to elastic reversible deformations of bond angles and lengths in both crystalline and amorphous regions, and another region, which can be pronounced as yield or plastic deformation region following a yield point at strain of 2.2% and at a stress of 4.31 MPa where irreversible structural processes such as alignment of crystallites and amorphous chains and their stretching take place.

After the PVA films were heated at different temperatures, in general, the stress-strain curves of the PVA films showed necking behavior on the stress-strain curves of the specimen for almost every elevated temperature which is similar to the observation of necking behavior of PVA films when the relative humidity was 20%.[16] It was also assumed that this necking formation could be associated with the rearrangements of PVA polymer chains in the crystalline region to parallel with the tensile direction.

From Figure 2 and Table I, it is seen that Young's modulus shows an increasing tendency for the anneal temperature from 25 up to around 100°C and beyond this temperature it decreased significantly.

As seen in Figure 3, as the anneal temperature increased, while strain at break values decreased greatly from around 80–10%, tensile strength was enhanced from around 9–22 MPa and then it slightly decreased. Here, the mechanical behavior changed from like a kind of ductile to more brittle with increasing heat temperature.

When the film thickness was increased from 50 to 125 μm, as seen in Figure 4, in addition to the necking formation, different from the case of PVA films with thickness of 50 μm, a kind of transition point at around 2% strain on the stress-strain curves was observed. This transition point may be considered to form as a result of weakening of intermolecular interactions.

As the temperature increased from 80 to around 100°C, the PVA films extended significantly more than the PVA films with 50 μm in thickness. It was assumed that this can be associated

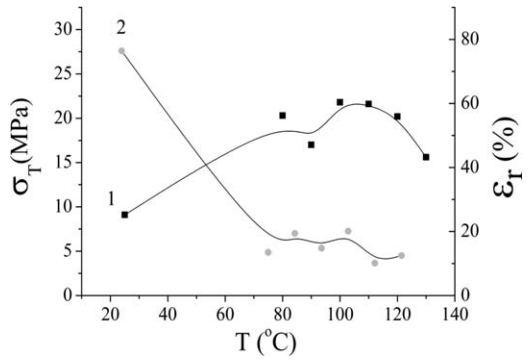


Figure 3. The change of tensile strength (1) and strain at break (2) of PVA films having the thickness of 50 μm with increasing anneal temperature.

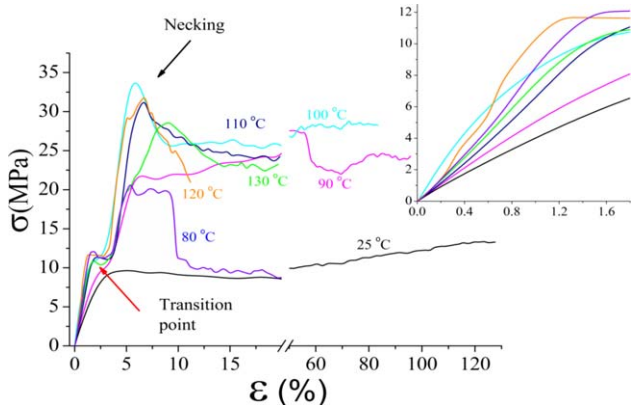


Figure 4. Stress-strain curves of PVA films having the thickness of 125 μm at different temperatures. [Color figure can be viewed at wileyonlinelibrary.com]

Table II. The Mean and Standard Deviation Values of Tensile Properties of PVA Films Having the Thickness of 125 μm at Different Heat Temperatures (T)

T (°C)	E_y (GPa)	ϵ_t (%)	σ_t (MPa)	ϵ_y (%)	σ_y (MPa)	ϵ_r (%)	σ_T (MPa)
25	0.47 ± 0.04	-	-	3.9 ± 0.55	9.6 ± 0.60	127.6 ± 19.32	13.3 ± 1.88
80	0.79 ± 0.14	1.8 ± 0.12	12.1 ± 1.30	5.4 ± 0.36	20.5 ± 0.44	21.8 ± 2.67	20.5 ± 0.44
90	0.5 ± 0.08	2.5 ± 0.42	9.5 ± 0.80	6.6 ± 0.55	21.7 ± 1.90	95.7 ± 2.66	27.5 ± 2.41
100	0.76 ± 0.13	2.0 ± 0.11	10.9 ± 0.22	6.0 ± 0.35	33.6 ± 0.72	83.4 ± 6.87	33.6 ± 0.72
110	0.70 ± 0.07	2.2 ± 0.10	11.4 ± 0.18	6.7 ± 0.49	31.1 ± 1.00	38.2 ± 5.45	38.2 ± 1.26
120	1.03 ± 0.16	1.3 ± 0.039	11.6 ± 0.58	5.1 ± 0.50	29.1 ± 1.74	11.2 ± 1.12	31.7 ± 1.90
130	0.72 ± 0.05	1.8 ± 0.17	10.8 ± 0.14	9.0 ± 0.93	28.5 ± 1.78	34.3 ± 1.72	28.5 ± 1.78

with the changes of the intermolecular interactions such as hydrogen bonding between polymer chains themselves and/or between polymer chains and water molecules, which can be present in the amorphous regions found in the volume of the PVA films and evaporate upon heating. Similarly, tensile strength also increased greatly. These changes imply that thicker PVA films became stronger and can extend more. For the temperatures higher than 100–110°C, although the strain at break decreased greatly as seen in Table II, tensile strength of the PVA films decreased slightly as shown in Figure 5(b).

As the temperature increased up to 120°C, although Young's modulus has an increasing tendency up to around 1 GPa, as also seen in Figure 5(a), it decreased slightly for the higher temperatures.

However, Table III shows the uniaxial tensile characteristics of PVA films having the thickness of 170 μm at different anneal temperatures. It is seen that Young's modulus of unheated PVA films decreased considerably with increasing film thickness when compared with that of unheated PVA films with thickness of 50 μm at 25°C. This decreasing tendency in Young's modulus at 25°C from around 0.32 GPa to around 0.17 GPa is compatible with the decreasing tendency while the thickness of the PVA films increased as given in the study.[15] However, the Young's modulus of PVA films with thickness of 170 μm also showed an increasing tendency for heating temperature up to 100°C as seen also in Figure 6(a). After heating at higher temperatures than 100°C, Young's modulus decreased greatly.

With increasing anneal temperature; strain at break values increased greatly which resulted in an increase in tensile strength significantly except for a slight decrease, that is, 7–8 MPa for higher temperatures than around 100°C. It is seen that in general, heating at elevated temperatures improved the strength and extensibility of the PVA films, as the film thickness increased. That is, the PVA films can withstand higher stress and strain values due to obtaining more ordered structural units, for example, crystallites, as a result of crystallization process and extensible amorphous chains.

FT-IR/ATR and SEM Analysis of PVA Films

To see the changes in spectroscopic properties used to determine structural changes, the FT-IR/ATR spectra of the films shown in Figures 7 and 8 were recorded in the wavenumber range of 500–4000 cm^{-1}, each of which was vertically translated for better illustration in the Figures, after the PVA films having different thickness were heated at some elevated temperatures.

In these spectra, the bands at around 920 and 840 cm^{-1} correspond to ν_r (CH_2) rocking vibration and ν (C—C) stretching vibration.[17] Other two bands at about 1328 and 1244 cm^{-1} correspond to wagging vibration of CH_2 and CH, respectively.[17] Symmetric bending mode ν_δ (CH_2) is observed at around 1423 cm^{-1}.[17,18] The bands at 1715 and 1574 cm^{-1} are assigned to C═O stretching vibration of carbonyl group, which are due to absorption of the residual acetate groups due to the manufacture of PVA from hydrolysis of polyvinyl acetate.[19,20] Moreover, other two absorption bands occurring at around 2937 and 2917 cm^{-1} correspond to anti-symmetric and symmetric stretching bands of CH_2 groups, respectively.[17,21–23] In some works,[21,24–28] a broad band observed between (3200–3600) cm^{-1} was assigned to O—H stretching vibration of hydroxyl

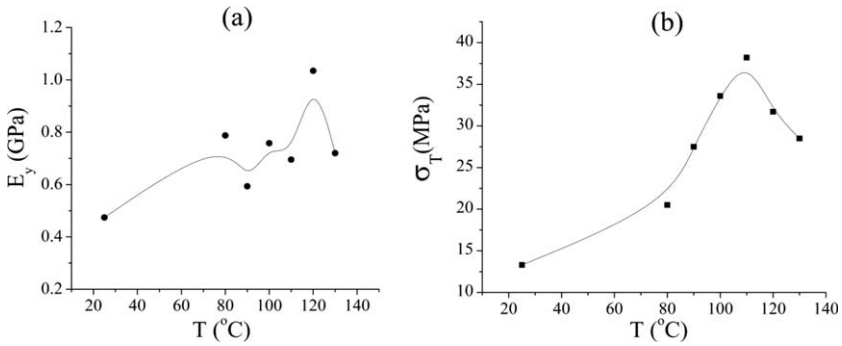


Figure 5. The change of (a) Young's modulus and tensile strength (b) of PVA films having the thickness of 125 μm with increasing anneal temperature.

Table III. The Mean and Standard Deviation Values of Tensile Properties of PVA Films Having the Thickness of 170 μm at Different Heat Temperatures (T)

T (°C)	E_y (GPa)	ϵ_t (%)	σ_t (MPa)	ϵ_y (%)	σ_y (MPa)	ϵ_r (%)	σ_T (MPa)
25	0.17 ± 0.02	-	-	5.1 ± 0.42	6.7 ± 0.11	167.4 ± 16.39	16.2 ± 2.23
80	1.17 ± 0.26	0.7 ± 0.16	6.2 ± 0.78	4.5 ± 0.51	33.0 ± 2.79	10.4 ± 1.83	32.9 ± 2.78
90	1.00 ± 0.11	1.3 ± 0.02	8.6 ± 0.60	6.6 ± 0.44	35.8 ± 3.14	12.3 ± 2.54	35.8 ± 3.14
100	1.09 ± 0.28	1.1 ± 0.06	7.0 ± 0.17	8.1 ± 0.37	38.7 ± 0.82	14.4 ± 1.86	38.7 ± 0.82
110	0.78 ± 0.04	1.7 ± 0.12	9.5 ± 0.12	7.5 ± 0.36	30.8 ± 0.70	22.8 ± 4.43	30.8 ± 0.70
120	0.79 ± 0.12	1.2 ± 0.04	4.6 ± 0.22	6.1 ± 0.79	31.8 ± 1.60	61.6 ± 9.89	31.8 ± 1.60
130	0.46 ± 0.03	2.5 ± 0.23	9.5 ± 0.13	6.8 ± 0.17	34.7 ± 1.05	149.4 ± 11.84	34.7 ± 1.05

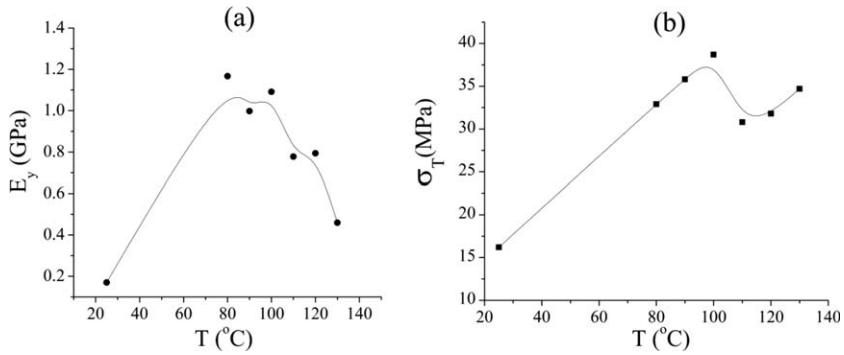


Figure 6. The change of (a) Young's modulus and tensile strength (b) of PVA films having the thickness of 170 μm with increasing anneal temperature.

group being either nonbonded or hydrogen bonded. It was also stated[22,23,25] that the band at around 3290 cm^{-1} is the stretching vibration of hydroxyl group with strong hydrogen bonding of pure PVA films. To understand how the structural changes occur depending on both heat temperature and film thickness, the degree of crystallinity and changes in the hydrogen bonding interactions in the structure were determined by analyzing the spectra in the range of 950–1200 cm^{-1} and 2400–3800 cm^{-1} carefully. In Figure 9, the band at around 1141 cm^{-1} is known to be crystallization sensitive band[17,29] and crystallinity band,[30] which was considered to calculate the degree of crystallinity.[29,30] 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 by different researchers.[17,21,26,30] In the spectra, another broad band at 1088 cm^{-1} is assigned to ν(C—O) stretching vibration,[17,18,21,24,27,28,30] which was taken as a reference band for the calculation of the degree of crystallinity.[30] Here, the degree of crystallinity was calculated by using the following equation obtained by Tretinnikov and Zagorskaya[30]

$$\alpha(\%) = -13.1 + 89.5\left(A_{1141}/A_{1088}\right) \quad (1)$$

where α denotes the degree of crystallinity and A_{1141} and A_{1088} are the absorbance intensity of the crystallinity band and the reference band, respectively. The intensity values of these peaks

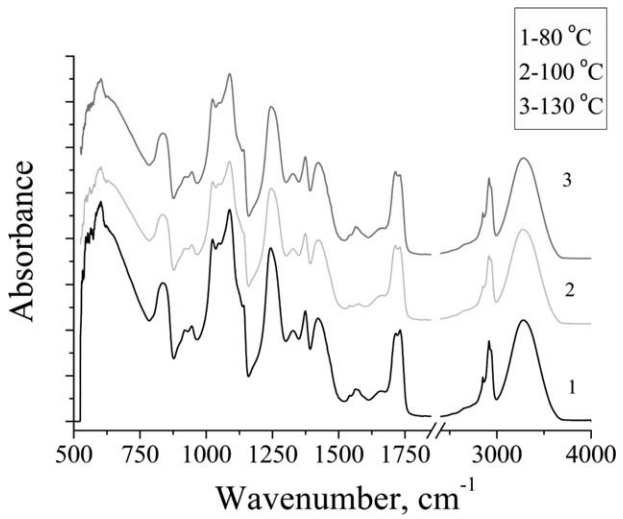


Figure 7. Changes in the FT-IR/ATR spectrum of PVA films having the thickness of 50 μm with respect to heat temperature.

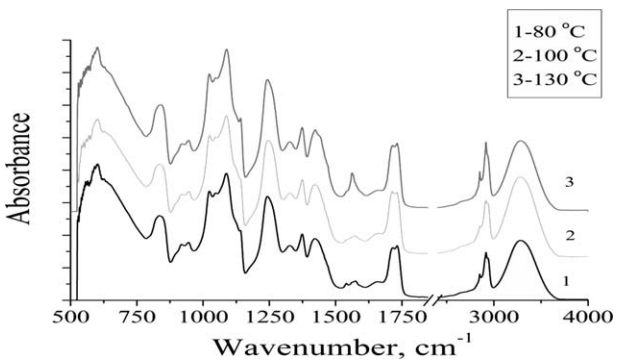


Figure 8. Change of FT-IR/ATR spectrum of PVA films having the thickness of 170 μm with respect to heat temperature.

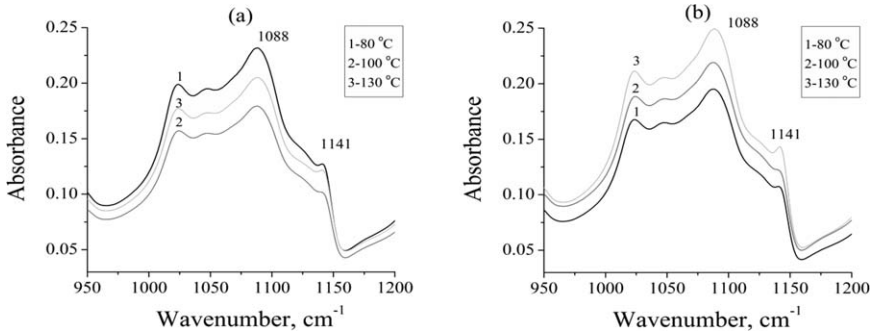


Figure 9. Changes in the FT-IR/ATR spectrum of PVA films having the thickness of (a) 50 and (b) 170 μm with respect to heat temperature.

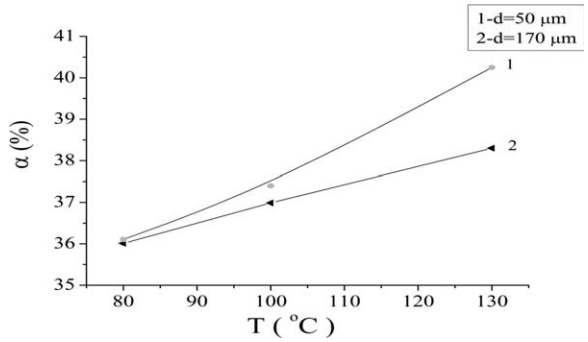


Figure 10. The change of degree of crystallinity of PVA films having different thickness with respect to heat temperature.

are originally recorded intensity values, which were not calculated by using any baseline method in this region.

Figure 10 shows the change in the degree of crystallinity of PVA films with increasing heating temperature for the PVA films having different film thickness. It is seen that for both thickness, with increasing temperature, the degree of crystallinity increases, which indicates a linear relationship between the degree of crystallinity and temperature, the linear equation of which can be written with different slope. Since the PVA films were kept at elevated temperatures for only 15 min, the heated samples did not crystallize much and had a great amount of amorphous chains, which can contribute to extensibility of PVA films. Because with increasing temperature, the degree of crystallinity had lower values while the film thickness increased, the thicker PVA films obtained more amorphous chains. This can be a reason why the PVA films having thickness of 170 μm had higher strain at break values which indicates higher extensibility property of PVA films than that of the PVA films having lower thickness such as 50 μm. It was also deduced that an increase in the degree of crystallinity implies more rigid and stronger crystalline structural units, which had a significant contribution to the increase in the Young's modulus of the PVA films. In addition to the changes in the degree of crystallinity, the changes in the absorbance of the OH stretching mode which will lead to estimate the changes in the intermolecular and intramolecular hydrogen bond interactions due to hydroxyl groups in the structure of PVA film.

Figure 11 shows the changes in the FT-IR/ATR spectra of PVA films with different thickness in the wavenumber range of 2400–3800 cm^{-1} as heating temperature increases. By using the absorbance values of the band at around 3290 cm^{-1} corresponding to stretching of hydrogen bonded OH groups and the band at around 2917 cm^{-1}, which was chosen as an internal standard band,[30] the change in the absorbance ratio, A_{3290}/A_{2917} with respect to heating temperature for the PVA films with different thickness was displayed in Figure 12.

It is clearly seen that the ratio increased greatly first for the temperature up to 100°C and then it decreased for both film thickness. This may indicate that annealing increased the crystallization process, which strengthened the structural units by means of changing the distributions of the intramolecular and/or intermolecular interactions, that is, hydrogen bonding due to OH groups of adjacent chains or intra chain in both crystalline and amorphous phases.

Due to existing water molecules in the volume of PVA films, changes in the hydrogen bonding between water molecules and PVA polymer chains in amorphous regions should be also considered. It should be noticed that the increasing tendency of the

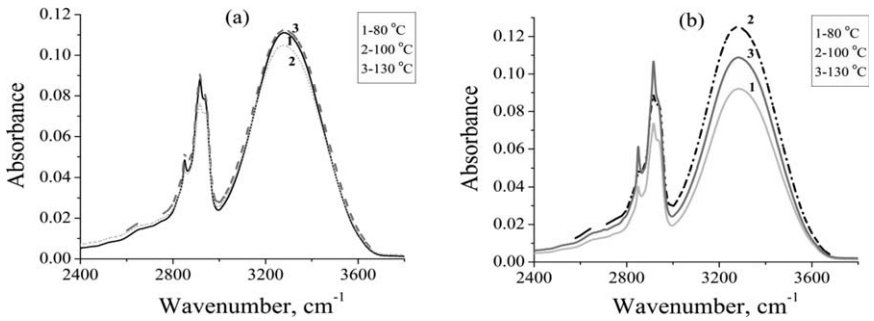


Figure 11. Change in the FT-IR/ATR spectrum of PVA films with the thickness of (a) 50 and (b) 170 μm with respect to heat temperature in the wavenumber range of 2400–3800 cm^{-1}.

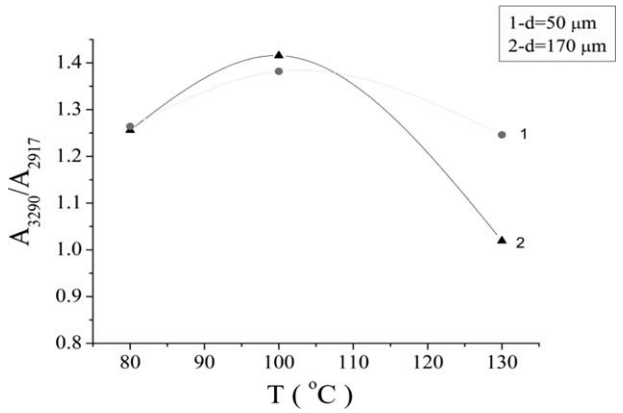


Figure 12. The change in the ratio of the absorbance of the band at 3290 cm^{-1} to that of the band at 2917 cm^{-1} of the PVA film with different film thickness (d) with respect to increasing heat temperature.

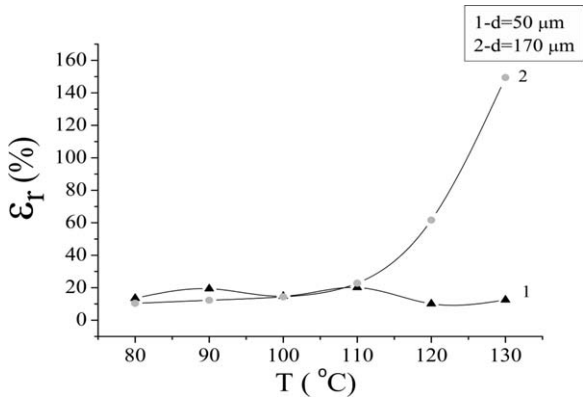


Figure 13. The change in strain at break (ϵ_r) of PVA films having different film thickness (d) with respect to increasing anneal temperature.

absorbance of OH stretching groups is in a good agreement with the increasing tendency in the degree of crystallinity as seen in Figure 10 and proves the important role of intramolecular and intermolecular hydrogen bonding interactions during the formation of crystallites in crystallization process. It can be said that the structure of PVA film changed from about a glassy or amorphous state to a more ordered structure. During crystallization process, due to new formation and reorganization of structural units, at higher temperatures, it is seen that the number of hydrogen bonded OH groups decreased more for the thicker PVA films than thinner films, which indicated the presence of polymer chains with more amount of free OH groups due to breakage of intramolecular or/and intermolecular hydrogen bonds especially in amorphous chains.

Especially for such thicker PVA films, due to weakening of intramolecular and intermolecular hydrogen bond interactions in especially amorphous chains, the amorphous chains easily slip on each other upon stretching, hence they contributed greatly to the strain at break or extensibility of PVA films, as it is seen in Figure 13, which compares the strain at break values for PVA films with thickness of 50 and 170 μm. As seen in Figure 13, while the strain at break values for the PVA films with the thickness of 50 μm did not change much for temperatures

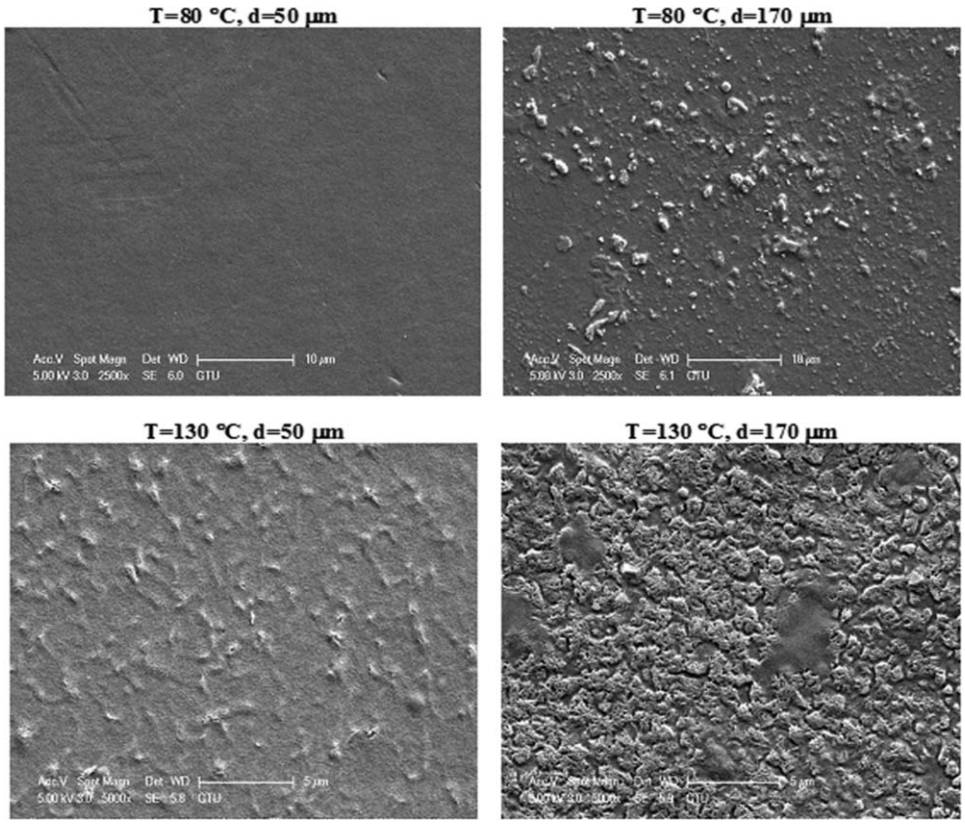


Figure 14. SEM images of PVA films with different thickness (d) exposed to heat treatment at different temperature (T).

greater than 110°C, strain at break values increased significantly for the PVA films having the thickness of 170 μm, which has a good agreement with the decrease in the absorbance ratio of OH stretching of the hydrogen bonded OH groups as shown in Figure 12.

However, Figure 14 illustrates how the surface structure of PVA films with different thickness changed with increasing heating temperature.

It is seen that while the film surface of The PVA film with $d = 50$ μm heated at $T = 80$°C became quite smooth, which could indicate the better film formation and more homogenous surface structure, for thicker PVA films, that is, $d = 170$ μm, the surface roughness increased significantly, which could lead to worse film formation and to hinder the formations of more ordered structural units. Due to the formations of rougher surface structure for thicker PVA film, it was needed to apply higher tensile stress values to cause a necking formation and to break the film sample as shown with the comparison of the tensile characteristics of PVA films having the thickness of 50 and 170 μm in Tables I and III. For the case of heating temperature, $T = 130$°C, it is seen that the film surface of both PVA films were affected significantly by heating. It was noticed that as the film thickness increased, the surface roughness increased greatly. It can be assumed that such greater amount of rougher formations on the film surface can have a significant contribution to increase the tensile strength of both necking formations and rupture of the film sample and to decrease the Young's modulus. These changes are apparently seen from the comparison of tensile characteristics for the PVA films with the thickness of 50 and 170 μm in Tables I and III.

CONCLUSIONS

The results of the uniaxial tensile tests of the PVA films revealed that after the influence of heating PVA films of varying thickness from 50 to 170 μm at different temperatures, the shape of stress-strain curves changed significantly; that is, a necking formation was observed at around 2% for thin films and 4–5% strain for thicker PVA films, which shifted to higher strain values as the heat temperature increased. Moreover, for the thicker PVA films, also a kind of transition point at around 1–2% strain was observed. In general, the strength and the strain at break values of the PVA films with different thickness were enhanced greatly as well as a slight increase in Young's modulus, as the temperature increased from around 80°C close to glass transition temperature to around 110°C, and beyond this temperature, most of them decreased. The results of the FT-IR/ATR spectra showed that the degree of crystallinity increased linearly with the heat temperature from around 36–40% with a slow rate. However, higher the film thickness, lower the degree of crystallinity was. Thicker PVA films obtained more amorphous PVA chains, which had more free OH groups and contributed to the extensibility of thicker PVA films greatly. Thus, it was emphasized that the intermolecular and intramolecular interactions, especially hydrogen bonding interactions have an important role in the change of tensile properties of heated PVA thin films of different thickness. As consequences of SEM analysis, as the heat temperature increased, the surface roughness of both thin and thick PVA films increased apparently and the PVA films obtained more degraded film surface. It was noticed that higher the film thickness, the bigger the size of such formations on the surface was.

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