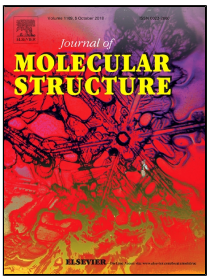
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Altan Bozdoğan, Baki Aksakal, Utkan Şahintürk, Önder Yargı

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Influence of Heating on spectroscopic, mechanical, and thermal properties of reduced graphene oxide-poly(vinyl alcohol) composite films

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ABSTRACT

The spectroscopic, uniaxial tensile, and thermal properties of reduced graphene oxide (rGO)-poly(vinyl) alcohol (PVA) composite films produced by using rGO synthesized using modified Hummer's method with varying weight ratio of rGO up to 10% were investigated by using an uniaxial tensile tester, Fourier Transform Infrared (Ft-IR)/Attenuated Total Reflectance (ATR) spectroscopy, and Differential Scanning Calorimeter (DSC) methods after heating process at different temperatures from room temperature to 200 ^{o}C. For unheated composite films, with increasing rGO weight ratio up to 10%, the Young's modulus of rGO-PVA films increased by approximately 2-3 times, conversely the strain at break values decreased greatly by about 40-50%. The heating process led to the significant improvement in the tensile strength and the Young's modulus, and great decrease in extensibility with respect to the unheated samples, e.g., the tensile strength and Young's modulus increased by 3-4 times and 8-10 times, respectively, for the heating temperatures up to 150 °C. With increasing heating temperature, the stress-strain curve of rGO-PVA composite films turned from that of ductile and amorphous polymer to that of more brittle and rigid polymers. With increasing rGO content, the glass transition, the crystallization, and the melting temperatures increased and heating process generally shifted these temperatures to higher values. The great contribution of rGO content and the heating to the improvement of especially mechanical properties of rGO-PVA composite films thanks to the strong intermolecular interactions of rGO nanosheets with the PVA matrix molecules through hydrogen bonding and to the changes in the crystallinity ratio of PVA was shown in detail in the analysis of the spectral results. The relationship between the changes in the mechanical, structural, and thermal properties of the studied composite films was determined by using tensile testing, Ft-IR/ATR, and DSC methods.

Keywords: Mechanical properties, Young's modulus, reduced graphene oxide, poly(vinyl) alcohol, hydrogen bonding, crystallinity.

1.Introduction

Graphene being a two dimensional monolayer of sp2-bonded carbon atoms has not only conductive properties due to high electrical conductivity, but also extremely high mechanical, electronic and thermal properties [1-4]. Because graphene does not exist naturally, it can be produced inlarge quantities by the chemical reduction of graphene oxide (GO), by using graphite as a raw material [5]. It is known that GO is the intermediate formed during graphite chemical processing consists of oxygen-containing functional groups, hydroxyls, carboxyls, carbonyls, and epoxides [5,6]. Reduced graphene oxide (rGO) is synthesized by using modified Hummers method [7-9]. Due to quite high values of Young's modulus(~1000 GPa), elastic modulus (0.25 TPa) [10], thermal conductivity(~5000Wm^{-1} K^{-1}) [11], charge carrier mobility (~2630 m^2 g^{-1}) [12], low density and high aspect ratio, graphene have many applications like in solar cells, sensors, super capacitors etc. Graphene and graphene oxide are used in the production of nanocomposites in order to improve the mechanical, thermal, dielectric, and water vapor barrier properties by using different polymers such as poly vinyl alcohol (PVA) [13-19]. Poly(vinyl alcohol) (PVA) being a water soluble biodegradable synthetic polymer is used in many different fields from the food industries [20] and the textile industries [21] to the production of polarizer films due to significant uniaxial tensile and surface characteristics. In addition, because of biocompatibility, non-carcinogenicity, nontoxicity, swelling properties, and bioadhesive characteristics, PVA is also used as a biomaterial in medical devices [22]. Although there are some studies to improve the thermal, mechanical and other properties such as dielectric properties of PVA/GO or composites [13-19], within our knowledge there are a few studies investigating thermal, mechanical and protective properties of rGO-PVA and graphene-PVA composite films [7,23-26]. In the study [24] the effect of graphene loading ranging from 0 to 3vol% on the mechanical and structural properties were investigated and it was reported that tensile strength increased from around 15 MPa to 45 MPa, and strain at break decreased from around 200% to 75-80 % strain, with increasing graphene content. However, within our knowledge content of graphene or graphene oxide loading remained at low amount and the effect of heating on the mechanical, thermal, and spectroscopic properties of rGO-PVA composite with changing rGO content up to very high loading were not investigated. However, the heating effect is quite important to produce rGO-PVA composite films with enhanced mechanical, thermal, and optical

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properties and to modify these properties for the application of these composites in various fields. Thus, this study is aimed to investigate the influence of heating at different temperatures on the spectroscopic, mechanical, and thermal properties of rGO-PVA composite films with varying weight ratio from 0 to 10% by using mainly tensile testing, Ft-IR/ATR spectroscopy, and differential scanning calorimeter (DSC) methods. The role of rGO loading and heating on the intermolecular interactions between graphene nanosheets and PVA matrix molecules which lead to changes on the spectroscopic, mechanical, and thermal properties of rGO-PVA composite films were examined in detail.

2. Materials and methods

2.1 Materials

2.1.1.Preparation of reduced Graphene Oxide (rGO)

rGO material was prepared with microwave assisted reduction of GO to rGO. Firstly, graphene oxide was prepared from the graphite powder (Alfa Aesar Graphite flake, natural, -325 mesh, 99.8 % metal basis) with the method on the basis of modified Hummer's method [8,9]. Then, a stock of GO suspension of 20 mg/mL was prepared by bath ultrasonication in distilled water for 2 h. The pH value of the pure GO solution was measured as 2.60 with pH meter (Thermo Fisher Scientific, Orion Star A211). A specific amount of Hydrazine monohydrate (Sigma Aldrich, N_2H_4, 64-65 %, reagent grade, 98%) were added to GO solution for adjusting at pH value of 10.00. The ratio of N_2H_4/GO is equal to (135µl/400 mg). Afterwards, the suspension was ultrasonicated for 5 min followed by microwave-assisted reduction. The reduced graphene oxide material was prepared by reducing graphene oxide during the microwave-assisted synthesis reactions carried out in a microwave accelerated reaction system (CEM, Mars 5). The Microwave irradiation was applied in a microwave oven with 1600W power at % 50 yield, 2450 MHz) for duration time is 5 min.

2.1.2. Preparation of rGO-PVA films

The PVA which was used in the production of rGO-PVA composite films was obtained from Boysan Co., Turkey. It has powder form and white color and is water soluble and has PH value at around 4.5–6.5 and includes acetic acid ethenyl ester, polymer with ethanol, 92–100%. Then, the sufficient amount of rGO-PVA film solution with different ratios were prepared by adjusting the weight amount of rGO with respect to that of PVA from 1Wt% up to 10Wt% to produce rGO-PVA composite films. After the preparation of mixture solutions

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following some sonication and stirring procedures, the rGO-PVA mixture solution of different weight ratios was poured into rectangular plastic thin boxes, each of which has the dimension of 2.5cmx6cm. Later, the samples were left to dry completely at room conditions for 3 days.

2.2. Methods

2.2.1. Tensile testing method

Uniaxial tensile tests of untreated and heated rGO-PVA films with varying percent weight ratio (rGO/PVA) from 1% up to 10% were carried out on a Lloyd tensile testing machine LF Plus(AMETEK Lloyd, UK) with a crosshead speed of 20 mm/min at room conditions (T=25°C; RH=60%). The test samples had the same gauge length of 20 mm, width of 3 mm measured by using a digital micrometer (Mitutoyo, No 293–821-30,Japan). Tensile tests of 6-8 samples from each kind of rGO-PVA films were done and average values of tensile characteristics were determined.

2.2.2. Heating method

Prior the tensile, FT-IR/ATR spectral, and DSC tests of heated rGO-PVA films, all the films having different weight ratios from 1% to 10% were placed and heated in an incubator (Binder, 115 lt, Germany) at each desired temperature from 50 to 200 °C for 30 min, after each rectangular sample was cut into smaller ones with the size of 3 mm x 60 mm and stuck on thin glasses from the ends in order to hinder bending or deformation of samples during heating process. After heating, the samples were left to be cooled down at room conditions.

2.2.3. Thermal Analysis

Thermal analysis of untreated and heated rGO-PVA film samples were carried out in a Differential Scanning Calorimeter (DSC) instrument (Perkin-Elmer Pyris-1 DSC 6) under a nitrogen flow at a rate of 20 mL/min. The rGO-PVA sample of ~7-8 mg was put in an aluminum pan of 50 µl and tested in the instrument following 3 cycles in order to determine thermal behavior such as melting and crystallization. For the first cycle, the sample was heated from initial temperature, 30 °C up to 250 °C at a heating rate of 10 °C/min, in the

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second cycle the heated sample was cooled down to initial temperature, 30 °C at a rate of 10 °C/min. In the third cycle, the same sample again was heated up to 250 °C with the same heating rate. The curves from second and third cycles were used to determine thermal behavior and characteristics of the samples.

2.2.4. FT-IR/ATR spectroscopic method

The FT-IR/ATR experiments were carried out on a Thermo Scientific Nicoleti S5 FT-IR Spectrometer equipped with a iD7 ATR sampling accessory. The FT-IR/ATR spectra of the rGO-PVA film samples with different rGO ratios were recorded in the 600–4000 cm^{-1} range at a resolution of 4 cm^{-1} with 32 scans for each measurement. In order to investigate the influence of heating on the spectra of the samples, the rGO-PVA samples after being heated at each different temperature from 50 to 200 °C were tested at the same experimental conditions.

3. Results and discussion

3.1. Effect of heating on the thermal properties of rGO-PVA composite films

Fig. 1 presents the DSC curves of 1Wt% rGO-PVA composite films and the effect of heating process at high temperature, 200 °C on DSC curves. These curves show the thermal behavior of the samples during cooling down from 250 to 30 °C following first heating cycle and last heating step following cooling. It is seen that the glass transition temperature (T_g), the melting peak (T_m), and crystallization temperature (T_c) determined by using exothermic peak were shifted from 69.96 to 70.53 °C, 114.33 to 120.24 °C, and 161.02 to 164.81 °C after the sample was heated at 200 °C.

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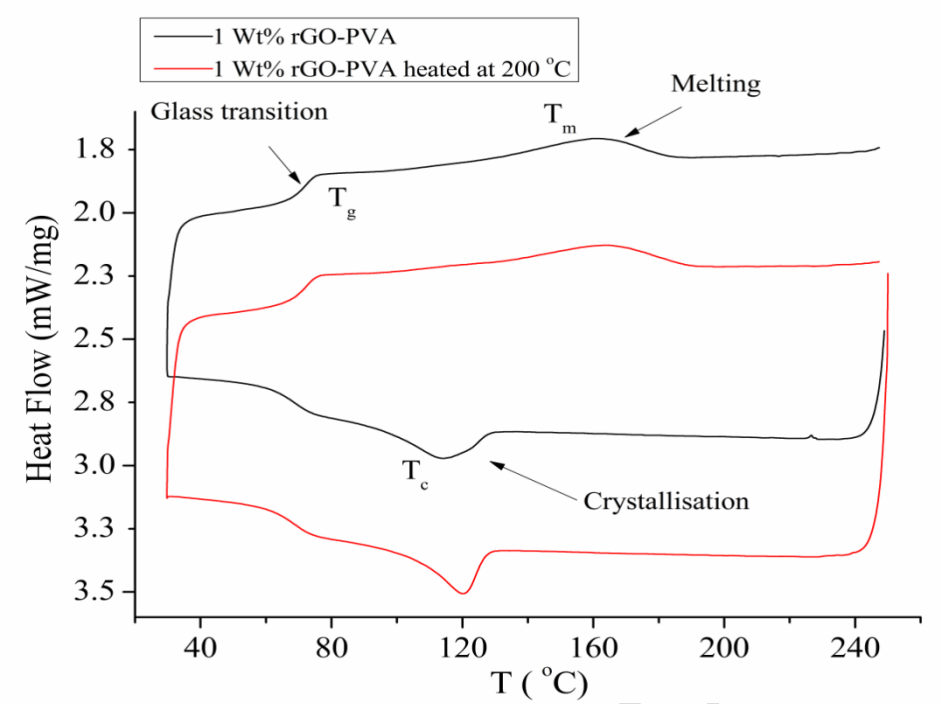


Fig.1. DSC curves of untreated and heated 1 Wt% rGO-PVA films.

Similarly, when the content of rGO increases to 2.5% in rGO-PVA composite films, similar DSC curves are observed as shown in Fig. 2. A similar shifting effect on the characteristic temperatures was observed after the sample was heated at 200 °C. The T_g, T_c, and T_m values are tabulated in Table 1.

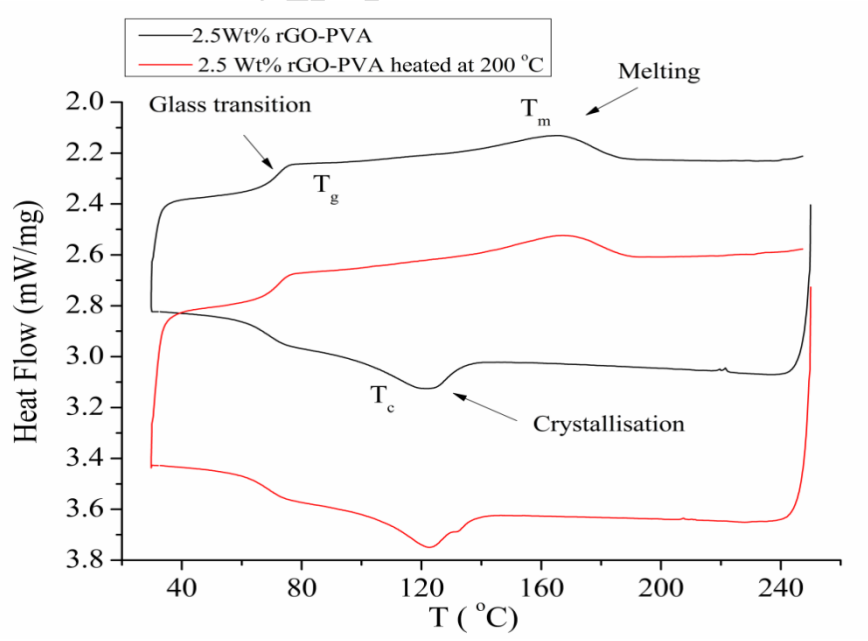


Fig. 2. DSC curves of untreated and heated 2.5 Wt% rGO-PVA films.

Table 1. Thermal characteristics of rGO-PVA composite films and the influence of heating at a high temperature (200 °C) on these values

Sample	T_g(ºC)	T_c(ºC)	T_m(ºC)
1Wt% rGO-PVA	69.96	114.33	161.02
1Wt% rGO-PVA heated at 200 ºC	70.53	120.24	164.81
2.5Wt% rGO-PVA	71.18	122.08	166.58
2.5Wt% rGO-PVA heated at 200 ºC	72.05	123.03	168.83
10Wt% rGO-PVA	76.17	129.12	162.73
10Wt% rGO-PVA heated at 200 ºC	78.24	116.75	152.56

The shifts to higher temperatures of these characteristics values, with increasing rGO content is also compatible with previous studies [7,26]. Moreover, if the rGO content becomes 10 wt%, similar thermal behaviors of the composite films were observed as presented in Fig. 3 and Table 1. However, although the T_g value is shifted to higher value, T_m and T_c values are shifted to lower values for the 10 wt% rGO-PVA films heated at 200 °C. In general with increasing rGO content, shifts toward higher temperatures of the T_g, T_m, and T_c, indicated the degree of polymer crystallization of the rGO–PVA composites becomes better. These results show that with increasing amount of graphene, the intermolecular interactions between polymer matrix and graphene oxide increases greatly which result in the stronger structure. Here, it is thought that segmental dynamics of polymer chains, especially PVA chains is strongly influenced by intermolecular interaction with embedded rGO particles. Thus, this emphasizes that as the amount of rGO increases, especially hydrogen bonding interactions between PVA polymer chains and rGO molecules increase significantly which will greatly improve the mechanical properties of rGO-PVA composites. On the other hand, because the heating the samples at 200 °C leads generally higher T_g, T_m, and T_c values for the samples, it can be thought that heating also improved the intermolecular interactions between polymer matrix, that is PVA structure and graphene sheets which will affect the mechanical characteristics of the rGO-PVA composite films after heating process. Here, it is thought that heating process enhanced the formations of more ordered structures and crystallization process by increasing segmental motions and mobility of PVA polymer molecules and intermolecular interactions between PVA and rGO molecules especially via hydrogen bonding.

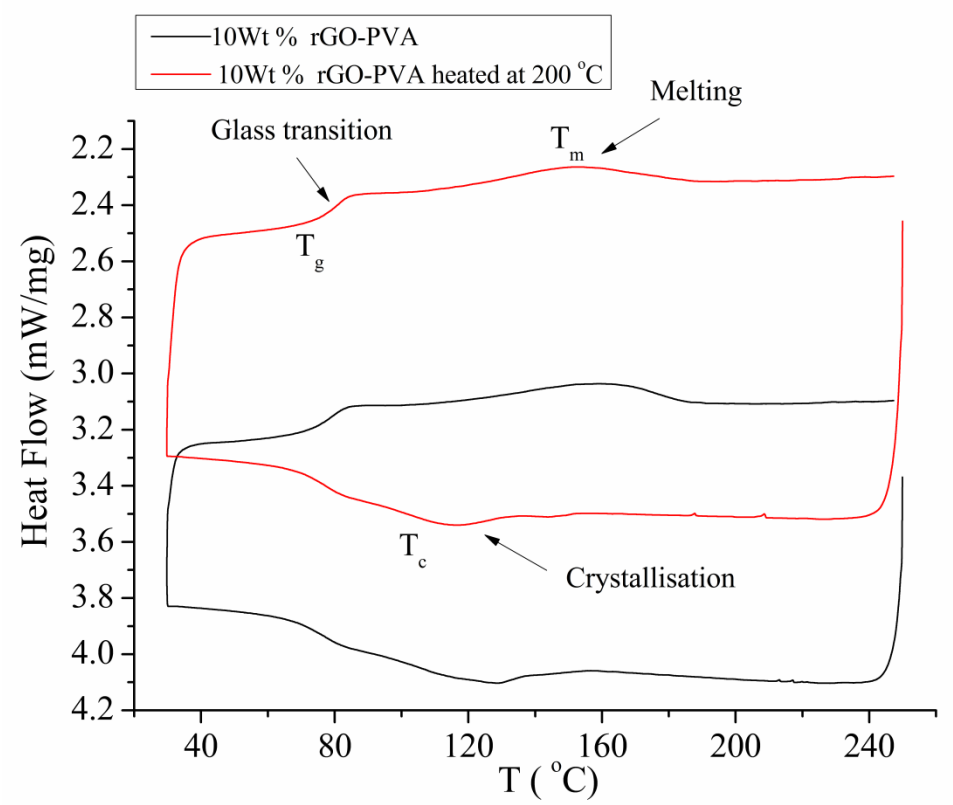


Fig. 3. DSC curves of untreated and heated 10 Wt% rGO-PVA films.

3.2. Influence of Heating on the Mechanical Properties of rGO-PVA composite films

Fig.4 shows the optical images of the samples of rGO-PVA composite films used in the uniaxial tensile tests. It is obviously seen that with increasing rGO content, following incorporation of rGO, the color of the composite films changed from white and transparent for pure PVA films to brown color for low rGO content (1Wt%) and then darker color for higher rGO weight ratios. Therefore, optical transparency of the nanocomposites decreased with increasing rGO content.



Fig. 4. The optical images of the untreated rGO-PVA composite films having different rGO content: a-pure PVA; b-1 wt% rGO-PVA; c-5 wt% rGO-PVA; d-10 wt% rGO-PVA.

Fig.5 presents the stress-strain curves of rGO-PVA composite films at ambient temperature and corresponding uniaxial tensile properties are tabulated in Table 2. In general, the shape of the stress-strain curve of pure PVA did not change much with increasing rGO content, but tensile characteristics changed greatly. That is, Young's modulus (E_y) increased from around 207 MPa to 437 MPa and tensile strength (σ_T) enhanced slightly.

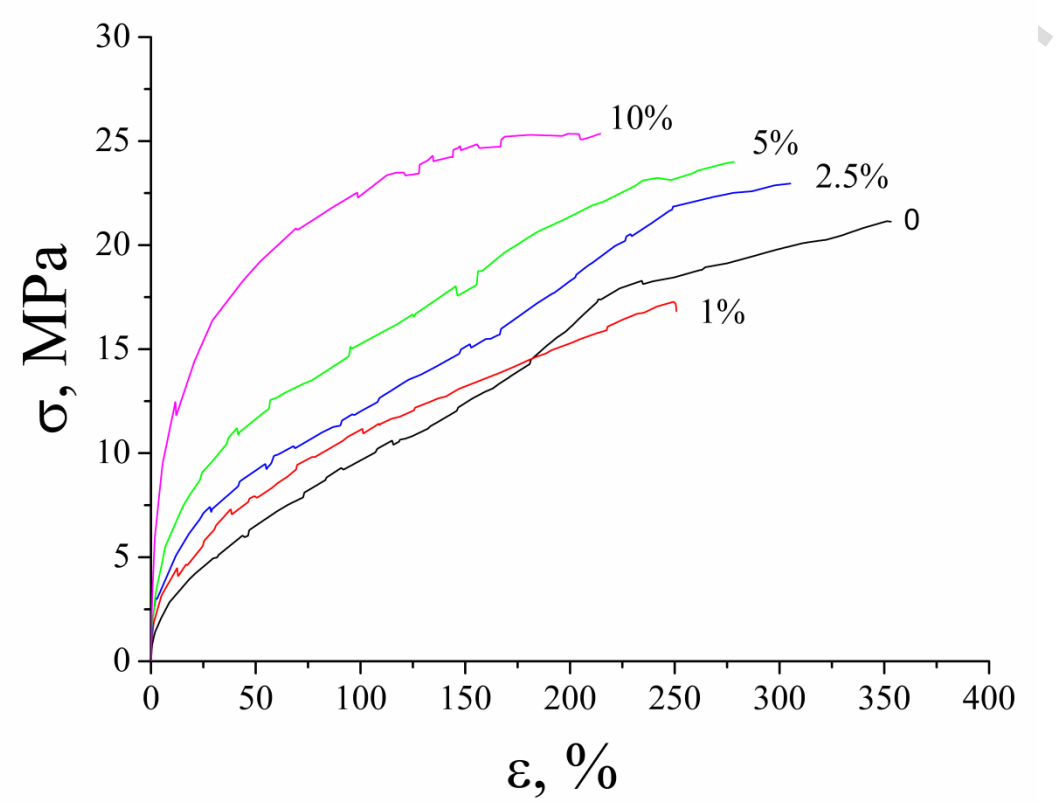


Fig.5.representative stress-strain curves of rGO-PVA composite films with different wt% rGO content.

Table 2. Tensile properties of rGo/PVA composite films with respect to wt% rGO content.

Wt%rGO	**E_Y (MPa)**	**σ_T (MPa)**	**ε_b (%)**	**U_T, 10^4 (J/m^3)**
0	206.90	21.13	353.12	4242.34
1	226.10	17.03	250.76	2898.73
2.5	241.60	22.96	305.105	3987.96
5	369.13	24.00	278.29	4937.07
10	436.54	25.356	214.43	4447.67

Due to increasing stiffness and rigidity, the extensibility of the sample, that is, the strain at break value (ε_b) reduced from around 353 to 214%. Although the toughness (U_T) being the required energy per volume to break the sample shows a decrease for the low rGO content, it

shows an increasing tendency for the higher content values. It is known that PVA is a semi crystalline polymer which contains more ordered crystalline units and more flexible amorphous chains. At room temperature lower than the glass transition temperature, the PVA has more amorphous domains than ordered units. Thus, the stress-strain curve of pure PVA is regarded as after the initial elastic region at small strain values of about 1-2%, the extension of the flexible amorphous chains and alignment of crystalline units along stretching direction which is considered as plastic deformation of the structure. High extensibility observed on the stress-strain curve of PVA is due to mostly the influence of amorphous chains. In case of addition of graphene to the PVA film structure, graphene nano sheets increase the intermolecular interactions, especially hydrogen bonding between OH groups of PVA chains and C=O groups of graphene sheets leading to increase in stronger and more rigid film structure and enhance the mechanical properties. Therefore, the stress-strain curve of rGO-PVA composite films shows the higher stress levels at a constant strain value. With increasing rGO content, strain at break is decreased because more rigid structure and more compact network not only result in less chain mobility and decreased free volume but also enhancing the rigidity of the molecular chains.

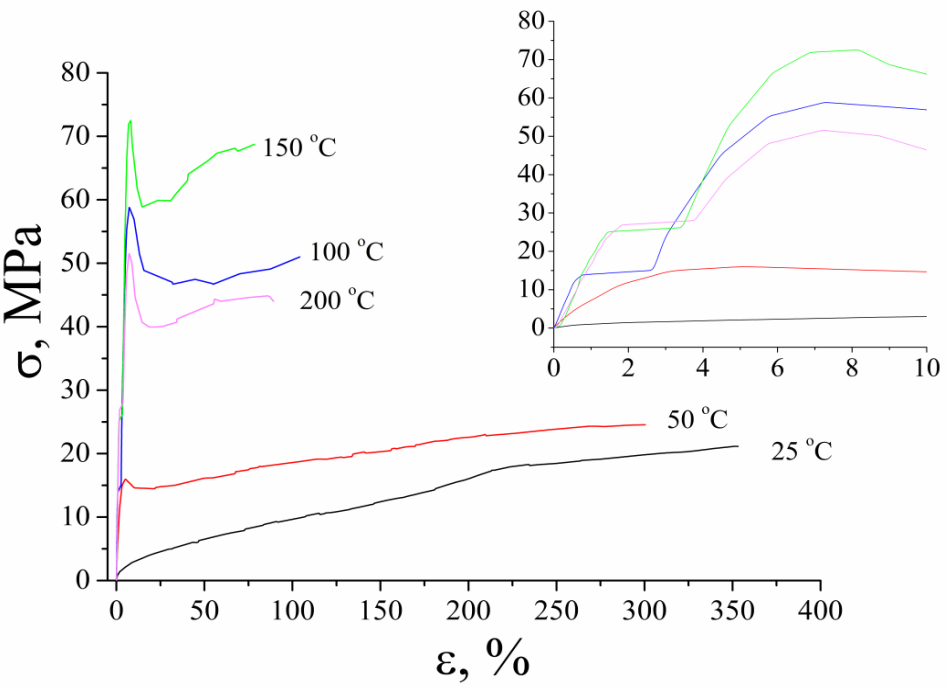


Fig.6. The effect of heating on the stress-strain curves of pure PVA films.

In order to examine the effect of heating on the uniaxial tensile characteristics of rGO-PVA composite films and to see whether or not there will be some correlations between changes in the uniaxial tensile properties and increasing rGO content, the pure PVA and rGO-PVA composite films with varying rGO content in the wide range from 1 to high content 10 wt% were tested after they were heated at different temperatures from 25 to 200 °C for 30 min.

Firstly, in case of pure PVA films heated at different temperatures, the observed changes on the stress-strain curves and in the tensile characteristics as are given in Fig.6 and Table 3, respectively.

Table 3. Tensile properties of pure PVA films heated at different temperatures.

T (°C)	E_Y (MPa)	σ_T (MPa)	ε_b (%)	U_T, 10^4 (J/m^3)
25	206.90	21.13	353.12	4242.34
50	518.41	23.17	300.44	5946.93
100	2267.15	58.821	104.14	6414.45
150	2398.66	70.74	78.42	6106.51
200	1727.06	51.45	85.89	4116.76

As seen in Fig.6, the shape of the stress-strain curve changed much especially for the films heated at temperatures higher than 50 °C which resulted in a kind of transition point at very low strain values around 2% and a necking behavior at around 6-8% strain value and a very high tensile stress having a good agreement with our previous work [27]. It was clearly observed that heating enhanced greatly Young's modulus and the tensile strength, that is almost 10 times and 3 times, respectively. It is thought that heating enhances the mobility of the polymer chains and lead to changes in the intra- and intermolecular interactions such as hydrogen bonding. Due to the reformation of hydrogen bonds and the formation of more ordered structural units, the degree of crystallization increases. This leads to stronger film structure and improved mechanical properties. Due to increasing rigidity and stronger structural interactions, the strain at break values decreased with increasing temperature. It should be noted that because the PVA structure starts thermal degradation at higher temperatures than around 150 °C [28], the weakening of intermolecular interactions and the structure leads to decrease in the mechanical characteristics as seen for the samples heated at 200 °C.

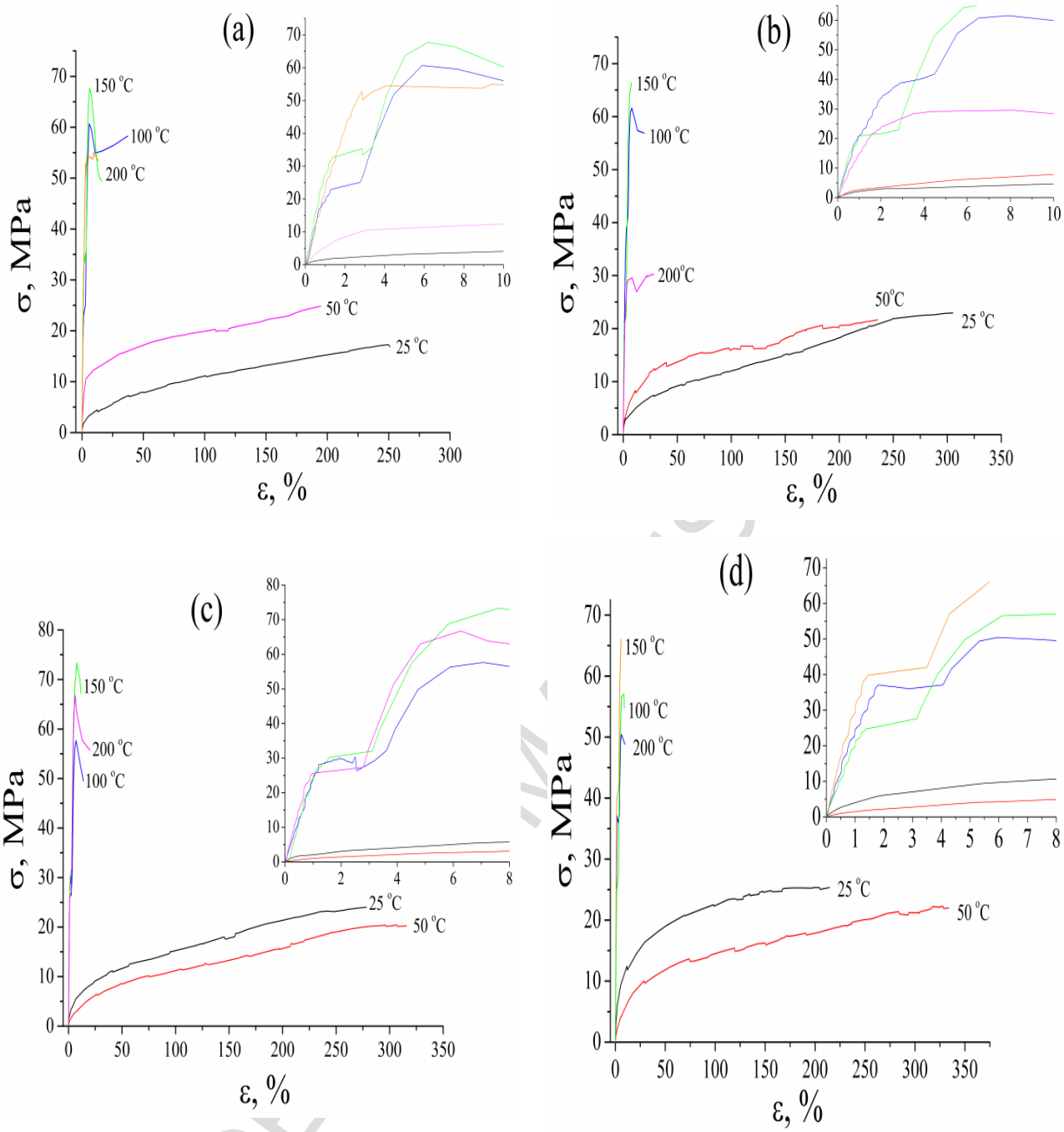


Fig. 7. The effect of heating on the stress-strain curves of rGO-PVA composite films: (a) 1 Wt% rGO-PVA, (b) 2.5 Wt% rGO-PVA, (c) 5 Wt% rGO-PVA, (d) 10 Wt% rGO-PVA

On the other hand, the influence of heating on the stress-strain curves of rGO-PVA composite films with varying rGO ratio from 1 wt% to 10 wt% and corresponding changes in the uniaxial tensile properties are given in Fig.7 and Table 4.

Table 4. Tensile properties of rGO-PVA films heated at different temperatures.

	T(°C)	E_Y (MPa)	σ_T (MPa)	ε_b (%)	U_T, 10^4 (J/m^3)
1Wt% rGO-PVA	**25**	226.10	17.03	250.76	2898.73
	50	543.82	24.838	194.52	3405.05
	100	2360.62	60.66	37.278	891.68
	150	2628.76	64.32	16.20	541.20
	200	2328.37	54.49	13.33	462.41
2.5Wt% rGO-PVA	**25**	241.60	22.96	305.105	3987.96
	50	256.68	21.645	235.16	3031.78
	100	2492.14	61.62	19.32	658.95
	150	2741.93	66.36	7.74	325.24
	200	1454.13	30.22	28.24	747.57
5Wt% rGO-PVA	**25**	369.13	24.00	278.29	4937.07
	50	98.01	20.25	315.95	4588.535
	100	2235.75	57.65	13.96	543.26
	150	2904.47	73.32	11.67	746.07
	200	2759.05	66.72	20.01	1291.93
10Wt% rGO-PVA	**25**	436.54	25.356	214.43	4447.67
	50	121.23	22.011	333.68	4956.02
	100	2502.38	50.44	9.65	325.25
	150	3253.775	66.03	5.66	263.18
	200	2128.14	57.13	8.89	354.54

As a general characteristic for the rGO-PVA composite films with different rGO content from 1W% to 10W%, it should be noticed that heating at higher temperatures than 50 °C led to a stronger and more rigid structure and to the changes of the stress-strain curve from more amorphous and glassy state to a more rigid and brittle state. As well as a necking at around 5-6% strain, a kind of transition point was observed at around 1-2% strain on the stress-strain curves. It was observed that with increasing heating temperatures up to around 150 °C, the tensile strength was improved significantly but the toughness was decreased greatly. That is, the Young's modulus increased by about 10 times and more, and the tensile strength increased by around 3-4 times for each kind of the composite samples. These improvements in the tensile strength and the Young's modulus may be due to that heating led to significant increase in the crystallinity and to the formation of more ordered structures in the rGO-PVA composite films. However, unlike the increase in the tensile strength, the strain at break value indicating the extensibility of the rGO-PVA composite film decreased almost 15 times for low rGO content (1Wt%) and decreased more like 35-40 times with increasing rGO weight ratio

when compared with that of corresponding unheated sample. Beyond heating temperature higher than around 150 °C, a softening and weakening behaviors on the stress-strain curve and in the tensile characteristics were observed. This may be due to the starting of melting and thermal degradation of the rGO-PVA composite films as shown in the previous section. These processes enhanced the chain movement and mobility and the weakening of the intermolecular interactions such as hydrogen bonding between PVA polymer chains and graphene nano-sheets. Considering the comparison of the changes in the tensile properties of the studied rGO-PVA composite films exposed to heating process at different temperatures, it can be concluded that although the tensile strength and Young's modulus have similar changing tendency for each rGO doping ratio for the range from 1% to 10% which led to the improved mechanical characteristics due to heating process, the most rigid and least extensible rGO-PVA composite films were obtained for the rGO ratio equal to 10Wt% and the heating temperature beyond 100 °C.

3.3. FT-IR/ATR spectral results

In order to analyze the structural changes due to the addition of rGO content in the rGO-PVA composite films, the Ft-IR/ATR spectra of the samples were recorded. Fig. 8 displays the Ft-IR/ATR spectra of the samples, each of which was vertically translated for a better illustration and the fundamental peaks which were analyzed in 600-3600 cm^{-1} range. Moreover, in Fig. 9, the effect of heating on the Ft-IR/ATR spectra of the rGO-PVA composite films with different doping ratio is seen.

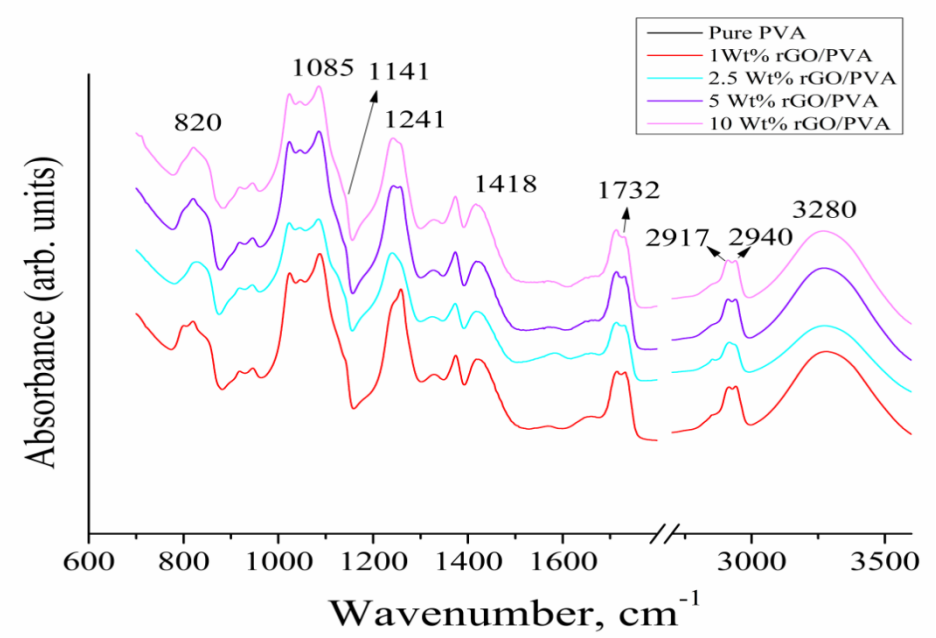


Fig. 8. Ft-IR/ATR spectra of rGO-PVA composites at 25 ºC

In these spectra shown in Fig.8, the band at around 836 cm^{-1} corresponds to ν(C-C) stretching vibration [29] and it was shifted toward 820 cm^{-1} with increasing rGO content. Another band at 1244 cm^{-1} corresponding to the wagging vibration of CH [7,27,29] was shifted to lower values of 2-3 cm^{-1}. A small shift was seen toward 1418 cm^{-1} on the band position of symmetric bending mode $\nu_{\delta}(CH_2)$ [29,30] observed at around 1423 cm^{-1} for pure PVA film. The band at 1732 cm^{-1} is assigned to C=O stretching vibration of carbonyl group, which is due to the absorption of the residual acetate groups during the manufacture of PVA from hydrolysis of polyvinyl acetate [31,32]. This band was also attributed to C=O stretching in the Ft-IR spectrum of GO [5]. 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 in pure PVA [29,33-35].

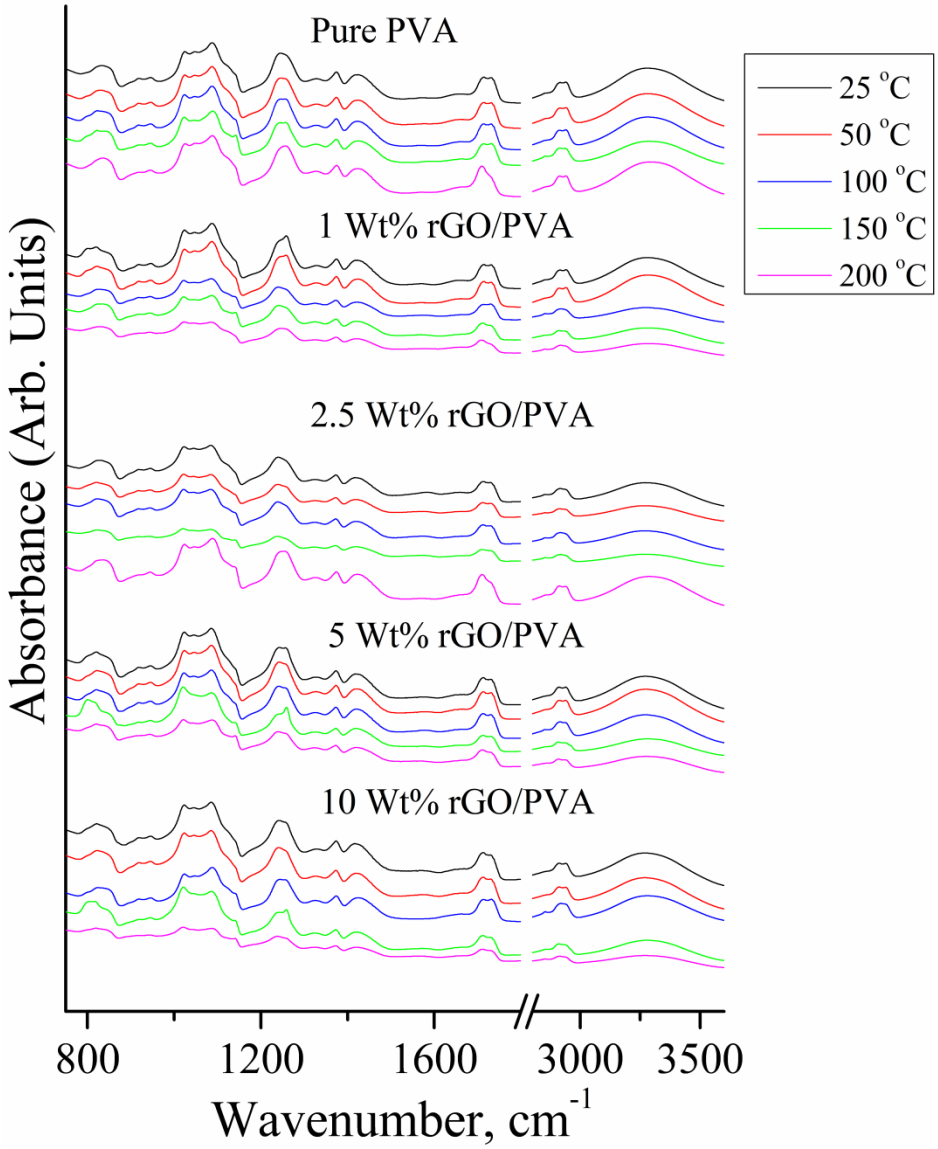


Fig. 9. Ft-IR/ATR Spectra of rGO-PVA composites heated at different temperatures.

Here, the band at around 2917 cm^{-1} attributed to aliphatic C–H stretching was also seen in GO [5]. In addition, a broad band observed between (3200–3600) cm^{-1} was assigned to O-H stretching vibration of hydroxyl group being either non-bonded or hydrogen bonded [5,33,36-40]. In the spectrum of graphene oxide, it was stated that OH stretching of hydroxyl groups was observed at around 3404 cm^{-1} [5]. It was also stated [34,35,37] that in this spectral region the band at around 3290 cm^{-1} is the stretching vibration of hydroxyl group with strong hydrogen bonding of pure PVA films. In order to comprehend how the structural changes occur depending on both rGO weight ratio and heat temperature, the degree of crystallinity based on the PVA content and the changes in the hydrogen bonding interactions in the structure were determined by analyzing the spectra in the range of 900–1200 cm^{-1} and 3000–3600 cm^{-1} carefully as well as the changes in the absorbance of C=O stretching group observed at 1732 cm^{-1}. In Fig. 8 and 9, the band at around 1141 cm^{-1} is known to be crystallization sensitive band [29,41] and crystallinity band [28], which was considered to calculate the degree of crystallinity [28,41]. Here, by different researchers [27,28,29,33,38] 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.

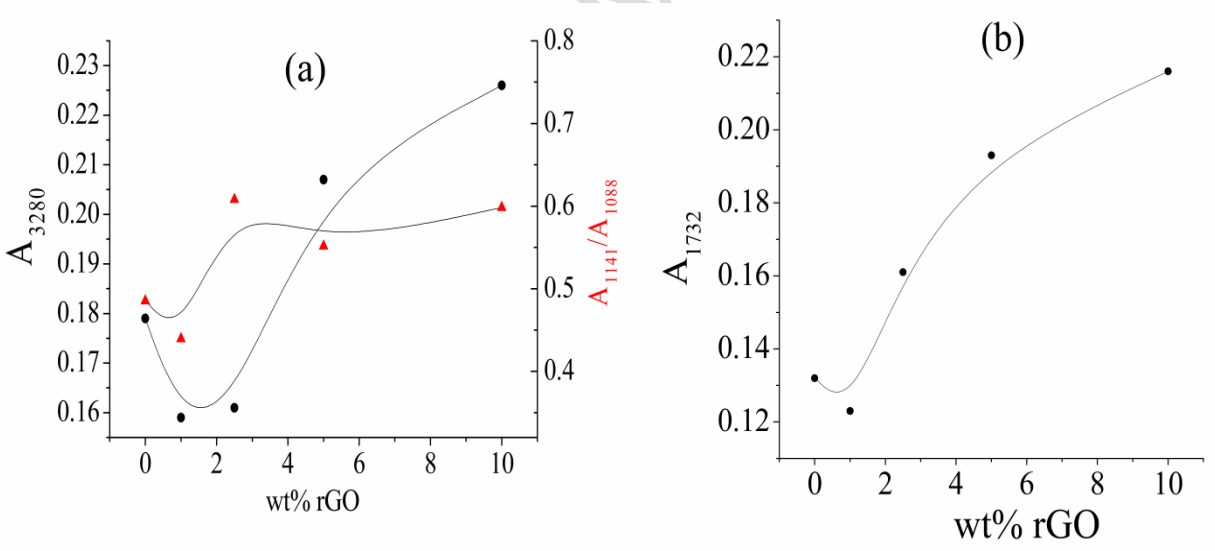


Fig.10. The changes in the absorbance of (a) OH stretching of H bonded OH groups and crystallinity ratio (A_{1141}/A_{1088}) and (b) C=O stretching of rGO-PVA composite films with increasing Wt% rGO content.

In these spectra, another broad band at 1088 cm^{-1} shifted towards to 1085 cm^{-1} with increasing rGO content as seen in Fig. 10 is assigned to ν(C-O) stretching vibration [27,28-

30,33,36,39,40] which was taken as a reference band for the calculation of the degree of crystallinity [28]. Here, the crystallinity ratio was calculated by using the absorbance ratio of A_{1141}/A_{1088} where A_{1141} and A_{1088} are the absorbance intensity of crystallinity and reference bands respectively.

Fig. 10a shows the changes in the intermolecular interactions via hydrogen bonding and crystallinity ratio of rGO-PVA composite films at 25 °C with increasing rGO content. It is clear that the increasing tendency of the absorbance of hydrogen bonded OH groups is due to the significant contribution of rGO content. Although it was mentioned that rGO nano-sheets has a "hydrogen bond barrier" effect by cutting off the present hydrogen bonds between PVA polymer chains[7], the remaining carboxylic groups present in reduced graphene oxide intensively form hydrogen bonds between the PVA molecules in PVA matrix and rGO nano-sheets. Thus, the number of hydrogen bonds increase with increasing rGO content. Besides, As seen in Fig. 10b, because the added rGO have many remaining carboxyl groups and they contribute to the absorbance of present C=O groups in PVA structure, that is, the number of C=O groups, the absorbance of stretching of C=O groups increased significantly. Because GO was considered to act as the crystallization nucleus of the PVA matrix [5] and increased the intermolecular interactions via especially hydrogen bonds, the crystallinity ratio increased for the rGO weight ratio up to around 2-3% and then it remained almost constant. It can be thought that due to improvement in the intermolecular interactions and leading to the formation of more ordered structural units with increasing rGO content at 25 °C, the uniaxial tensile properties of rGO-PVA composite films were enhanced significantly.

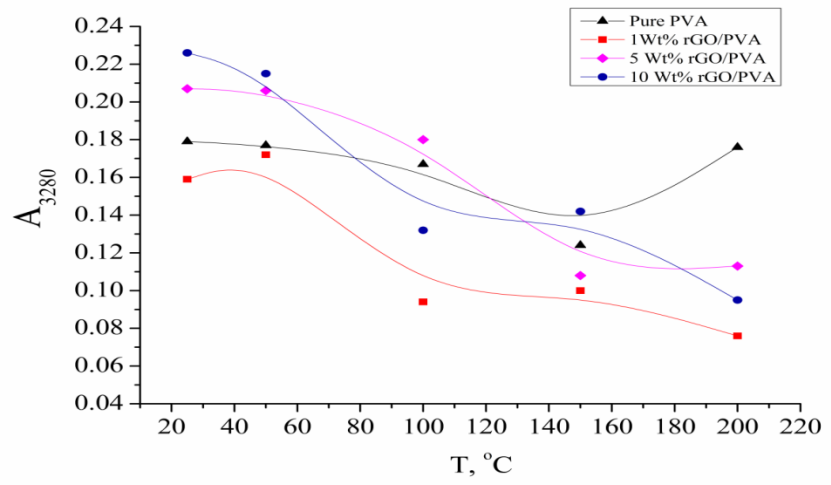


Fig. 11. The effect of heating on the changes in the absorbance of OH stretching of H bonded OH groups of rGO/PVA composite films.

Fig. 11 shows how the absorbance of H bonded OH groups changes after the rGO-PVA composite films with different rGO weight ratio were heated at different temperatures. It is clear that with increasing rGO content, starting point of the each curve, that is the beginning level of A_{3280} generally increased. This observation is understandable because as rGO content increases in PVA matrix, the OH groups present in rGO nano-sheets contribute to the number of OH groups found in PVA matrix. It is common that general changing tendency of each curve representing the behavior of each rGO-PVA composite films with increasing temperature is almost the same. That is, almost each curve has a decreasing tendency. It is known that there are oxygen-containing moieties, such as carbonyl, hydroxyl, carboxyl, ether and epoxy groups, on the surface of GO [5]. These groups can form hydrogen bonds with PVA molecules and lead to changes in the number of hydrogen bonds. However, when the nano-rGO sheets were dispersed in the PVA matrix and incorporate with PVA molecules, they cut off the present hydrogen bonds between C=O and OH groups of PVA molecules. With the addition of enhanced chain mobility of PVA and rGO molecules due to increasing heating temperature, the number of hydrogen bonds can decrease more. That is, heating can also strongly affect the formation of hydrogen bonds in the structure.

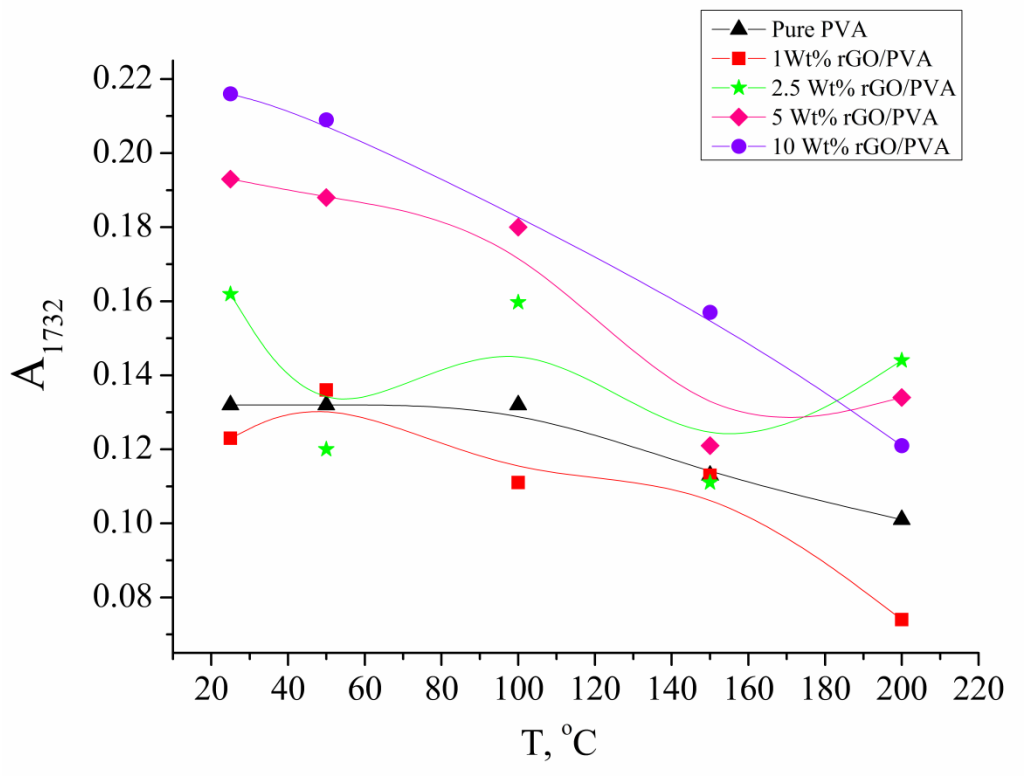


Fig. 12. The influence of heating on the changes in the absorbance of C=O stretching vibration of rGO/PVA composite films.

The effect of heating and breakage and/or reformation of hydrogen bonds in the structure also affected the absorbance of C=O groups as seen in Fig. 12. It is obvious that due to increasing rGO content which can contribute to the number of C=O groups, the beginning level of each curve became higher than one another. However, generally each curve has a decreasing tendency with increasing heating temperature. Because during the deformation and the reformation of hydrogen bonds between PVA molecules and rGO nano-sheets, some non-bonded C=O groups due to rGO nano-sheet can form new hydrogen bonds with OH groups of PVA molecules which make the structure and interactions stronger, the absorbance of C=O groups was reduced. Also, it was seen that this process was enhanced with the increasing heating which enhances the reorganization of structural units and crystallization process.

It is clear that crystallization process is very sensitive to the thermal treatment and additives. Due to the dispersion of rGO nano-sheets and strong interactions at the interface between rGO and PVA matrix, crystallization nucleus of the PVA matrix was affected by rGO content. It is seen in Fig. 13 that as the rGO weight ratio increased, generally crystallinity ratio of PVA increased.

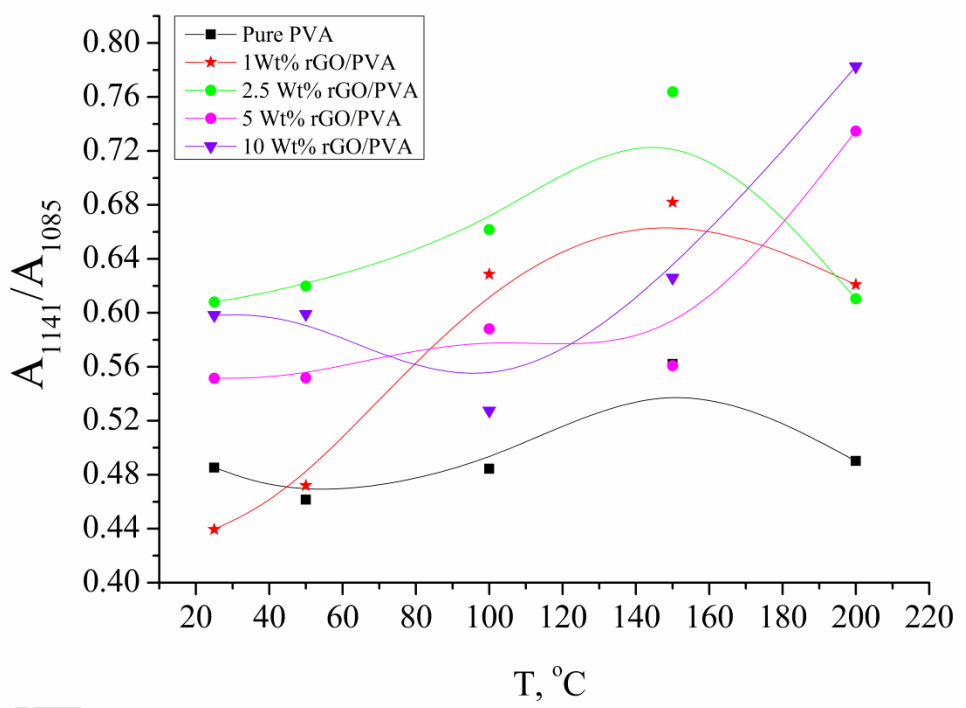


Fig. 13. The changes in the crystallinity ratio (A_{1141}/A_{1085}) of rGO/PVA composite films with increasing heating temperature.

In Fig. 13, it is observed that for the low content of rGO up to around 2.5-3%, with increasing heating temperature up to 150 ºC, the crystallinity ratio increased and then it decreased for

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higher temperatures such as 200 ºC. However, the crystallinity ratio for the rGO content higher than 2.5-3 wt% increased slightly for the temperature up to 150 ºC and it increased sharply for higher temperatures than 150 ºC. Here, it is obvious that the amount of rGO affects significantly the crystallization process. Except for some low rGO content, when extra rGO was added into the PVA matrix, the interaction between the GO sheets, mainly by van der Waals force, will help the sheets to be stacked together and form large GO agglomerates which may lead to increase in the crystallinity ratio at also high temperatures such as 200 ºC. Therefore, this excessive GO loading leads to brittle failure in the nano composites and rapid decrease in the strain at break value. It is known from the thermal characterization results, the crystallization temperature and the melting temperatures of rGO-PVA composite films became around 120 ºC and 160 ºC, respectively. Such a decrease in the crystallinity ratio at higher temperatures than 150 ºC was caused by the melting and thermal degradation process for the low rGO contents. Because graphene is considered to be one of the strongest materials with high thermal stability [7], higher content of graphene which improves the thermal properties of the polymer matrix may be considered to affect positively the formation of ordered structural units, hence the crystallinity ratio at even high temperatures.

4. Conclusion

Thermal analysis showed that with increasing rGO content, the glass transition, the crystallization, and the melting temperatures of rGO-PVA composites increased from around 70 to 76 °C, 114 to 129 °C, and from 161 to around 169 °C, respectively which indicated rGO improves the thermal stability of PVA. It was also observed that heating process shifted these values generally to some higher values. The results of the uniaxial tensile properties revealed that because the rGO nano-sheets are rigid and strong structures, the incorporation of rGO nano-sheets in PVA matrix increased the intermolecular interactions such as hydrogen bonds, thus, they improved the mechanical properties of nanocomposite films such as Young's modulus and rigidity. Conversely, the elongation at break of nanocomposites decreased with increasing rGO content. The rGOnano-sheets are considered as reinforcing materials in these nanocomposites. Moreover, heating the rGO-PVA composite samples at different temperatures increased greatly the Young's modulus by around 8-10 times and improved the tensile strength by around 3-4 times, however, a brittle fracture and rapid decrease in the elongation at break was seen after the heating temperature higher than 100-150 °C. Therefore, the typical stress-strain curve of PVA films changed from the shape of glassy and amorphous

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polymers to that of brittle polymers with increasing heating temperatures. Strong interactions of rGO nano-sheets via hydrogen bonding between C=O or OH and opposite OH and C=O sites of PVA molecules and the significant effect of heating on the absorbance of related bands and the crystallinity ratio of PVA were shown in the spectral analysis. These spectral observations correlated the responsible structural changes with the changes in the tensile properties of rGO-PVA composite films having different rGO content due to heating process.

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HIGHLIGHTS

- shifts toward higher temperatures of the T_g, T_m, and T_c due to heating rGO-PVA films up to 200 °C.
- a necking at 5-6% and a transition point at 1-2% strain on the stress-strain curves of rGO-PVA films.
- E_y and σ_T increased by about 10 times and 3-4 times for heating up to 150 °C.
- Strong interactions of rGO nano-sheets via H bonding with the PVA molecules.
- Increasing crystallinity ratio for 5-10Wt% rGO-PVA films exposed to heating process.

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Reduced Graphene Oxide- Poly(vinyl) alcohol Composite Films



10Wt% rGO-PVA
5Wt% rGO-PVA
2.5Wt% rGO-PVA
Pure PVA
1Wt% rGO-PVA

σ, MPa

ε, %

0 5 10 15 20 25 30

0 50 100 150 200 250 300 350 400