Non-Isothermal Degradation Kinetics of High Energy Protons Irradiated Polyvinyl Butyral

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This research is aimed to undertake a comparative study on stability and thermal degradation kinetics of un-irradiated and high energy protons irradiated polyvinyl butyral (PVB) based on weight loss analysis and non-isothermal approaches. The weight loss by the un-irradiated PVB upon heating was found to be in two stages but due to high energy protons accelerated exposure following by chemical etching, this weight loss transition proceeds in a major one stage with increases in the highest rate of weight loss temperature. In addition, the samples were analyzed using the FT-IR spectroscopy technique to illustrate the stability of irradiated-chemical etched PVB, and also elucidate the mechanism of degradation. The effect of irradiation on the surface of PVB films was investigated by scanning electron microscope (SEM) after and before irradiation. The kinetic triplet and other related thermal kinetic parameters of un-irradiated and irradiated-chemical etched PVB films are presented and compared together. The results showed that due to high energy protons irradiation exposure following by chemical etching, the thermal stability of the PVB film is significantly increased.

INTRODUCTION

The polymers, nowadays, have achieved interest of scientists in numerous fields of science and technology. The motivation that, not only having tremendous characteristics, but also their inherent properties can be altered to suit specific requirements by physical and chemical properties, *e.g.* heat treatment, chemical doping, and ion implantation [1,2]. In one of the modification methods of polymers, like upgrading, stabilization and changing the properties of polymers are based on the irradiation with high energy accelerated radiation (gamma rays, X-rays, and accelerated ion beams). Irradiation of polymers with high energy radiations leads to the formation of very reactive intermediates in the forms of excited states, such as ions and free radicals. These intermediate forms are almost instantaneously used up in several reaction pathways which

result in the arrangement or formation of new bond structures. The ultimate effects of these reactions are the formation of oxidized products, grafts, cross-linking and scissoring of main or side chains. The amounts or dominances of these changes depend on the type of the polymers and their conditions before, during and after irradiation treatment processing [3-6]. The ion track technology created by swift heavy ions which may be sufficiently-contiguous for chemical etching is used for the industrial production of filters, heat exchangers, printed circuit boards and anti-fraud coding. Nanochannels made-up in ion-tracked polymer membranes have a wide range of applications in sensing biomolecules, biotechnology and act as Coulter counter microchannels, molecular filters and stimuli-responsive devices of high selectivity. Solid-state nanochannels were also successfully fabricated in ion tracked polymer membranes *via* chemical etching. In this method, polymer foils were first irradiated with heavy ions. By a suitable wet chemical etching, the damaged material

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along the track can be removed faster than that from the bulk material, thus developing the ion tracks into nanochannels [3-6]. Recently, extensive studies have been undertaken for the preparation of ion-track membranes of some polymers such as polyethylene-terephthalate (PET), polycarbonate (PC), cellulose nitrate, and allyl diglycol carbonate (CR-39) as well as subsequent chemical etching with suitable enchants [7-9]. Polyvinyl butyral (PVB) has very good structural properties to be used in ion-track membranes because of its strong binding, toughness, flexibility, high mechanical strength at a low thickness, narrow pore size distribution and low content of extractable [10-12].

Polymer degradation is a complicated process and is contingent on a combination of factors like irradiance, distribution of irradiation, ambient temperature, and dose-response characteristics of the polymer. Thermal analysis methods are very important technics which help the study of the influence of the polymer morphology on the thermal stability of polymers with monitoring of the optimum temperature of the process and the other kinetic parameters associated with the degradation reactions such as activation energy, frequency factor, reaction order, *etc.* Thermogravimetry analysis (TGA) has been proved to be practically a rapid and accurate method for determination of kinetic parameters related to the thermal degradation processes [13,14]. Experimentally, solid-state reaction kinetics has been studied either isothermally or non-isothermally. Various mathematical approaches have been developed to describe the data obtained by both methods. The calculation methods are commonly classified into two categories: model-based and model-free. Historically, the former methods have been widely used because of their ability to determine the kinetic triplet, frequency factor, activation energy and degradation model, directly. It should be noted that, there are various model-based approaches for analyzing non-isothermal experimental data to get these three kinetic parameters. Mentioning that, these procedures have been used widely in solid-state reaction kinetic analysis [15,16].

Excellent investigations on the thermal characterization and thermal decomposition behavior of polyvinyl butyral have been performed. It is stated that the stability and solidity of PVB are reduced by acid materials or other substances that are easily oxidized into acids with the ring attack on 1,3-dioxane which result in the ring opening. However, it is demonstrated that PVB could be stabilized by adding various bases [17]. According to the previous works, in the thermal degradation of PVB, the reaction is initiated from the acetate group [18,19]. Study of the reaction pathways and kinetic analysis of polymers, from an engineering standpoint, is useful in gaining chemical kinetic data, maintaining outstanding end-product properties, and ensuring proper management of thermal degradation processes. Ion track technology uses to a great extent the irradiation of polymer membranes with high energy ions which are usually sufficiently contiguous for chemical etching, leading to the formation of damaged zones known as latent tracks. Thus, under these conditions it is necessary to check the stability and solidity of the polymer membranes [20,21].

In our earlier works, the physic-chemical properties of ion track-etched polyvinyl butyral (PVB) membrane have been studied based on irradiation with high energy protons [12]. In present work, a detailed study of thermal properties and its behavior such as its stability, weight loss, activation energy, frequency factor, order of degradation reaction and some thermodynamic parameters such as entropy, free energy of activation and rate constant of the PVB films are presented and compared with irradiated and chemical etched irradiated samples using a thermogravimetric analysis. As well as in accordance with the quantitative and qualitative analysis by TGA/DTG and FT-IR carried out in the present study and on the basis of the previous works [19,22-24] the possible mechanism for the thermal degradation of PVB films has been proposed.

MATERIALS AND METHODS

Materials

The polyvinyl butyral (PVB) films with a thickness of 20 μm made by Risø Co., Denmark, were used in this work. The KOH with a purity of 99% provided by Merk Company, Germany, was used as the etching reagent.

Sample Preparation & Irradiation

The PVB films were cut into small pieces and placed in Aluminum frame film holder in the proton beam tube with

the internal and external diameters of 45 mm and 75 mm, respectively, and a thickness of 27 mm. The film holder could be located in the radiation field in a manner that the film plane is perpendicular to the proton beam direction. The films were irradiated about 5 s with accelerated protons (energy of 30 MeV) on the Cyclon-30 cyclotron made by IBA Company (see Fig. 1), Belgium, in Agricultural, Medical and Industrial Research School (AMIRS). The schematic of sample preparation and irradiation processes are shown in Fig. 2.

Etching Procedure

The irradiated films were cut into a smaller size and a solution of KOH (7 normal) is used for etching at 70 °C for 15 min. Distilled water in an ultrasonic system (Fritsch Laborette 17 model) is used to clean the alkaline sediment on the films surface during the etching procedure and finally dried in the oven for 10 min (see Fig. 2).

Microscopic Technique

A scanning electron microscope (SEM) XL-30 series, made by Phillips Company, Holland, was used to study the morphology of the polymer surface in a comparative view point. By using the LaB6 filament, the magnification from 25x to 400000x is obtained. The surfaces of the samples were covered with a thin gold film prior to the SEM

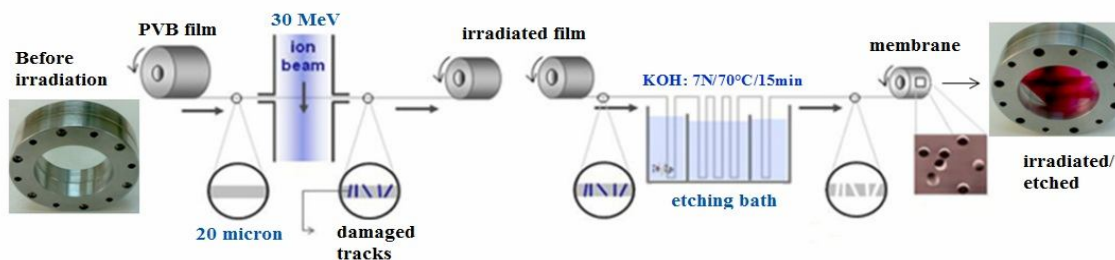**Fig. 1.** Device for proton irradiation of PVB films.

Fig. 2. The schematic of sample preparation and irradiation processes.

TGA Analyses

The thermograms of un-irradiated and irradiated/etched PVB samples were recorded in a nitrogen atmosphere (40 ml min^{-1}) at a heating rate of 10 K min^{-1} from 30-700 °C by using a thermal analyzer (Netzsch-Geratebau GmbH STA 409 PC). The effects of irradiation and chemical etching on the thermal properties and kinetic parameters of PVB films were investigated and discussed.

Fourier Transform Infrared (FT-IR) Analyses

A Fourier transmission infrared spectroscopy (FT-IR) system was used to illustrate the stability of irradiated/etched PVB, and to elucidate the mechanism of degradation, in the wave range of 400-4000 cm^{-1} using a Shimadzu 8300 apparatus.

RESULTS AND DISCUSSION

Exposure to High Energy Protons Irradiation

The physical appearance of the PVB films before and after exposure on proton beams are shown in Figs. 3a and b, respectively. Figure 4 shows, using the SEM apparatus, the porosity images on the surface of PVB film created by high-energy proton irradiation. It is very clear that the unexposed and the exposed samples are different and show changes in color and numerous defects across the polymer surface.

The FT-IR spectra of un-irradiated and irradiated/etched PVB films are presented in Figs. 5a and b, also the characteristics of FT-IR spectra are given in Table 1. In FT-IR spectrum of un-irradiated sample, the functional group analysis shows the presence of a broad band for polyvinyl alcohol (PVA) group at 3460 cm^{-1} corresponding to -OH group together with the C-H stretching band at 2950 cm^{-1}.
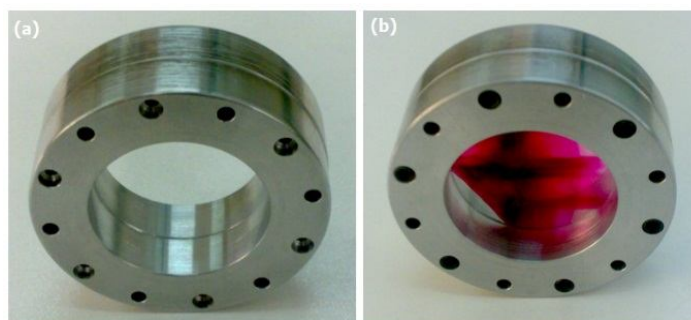

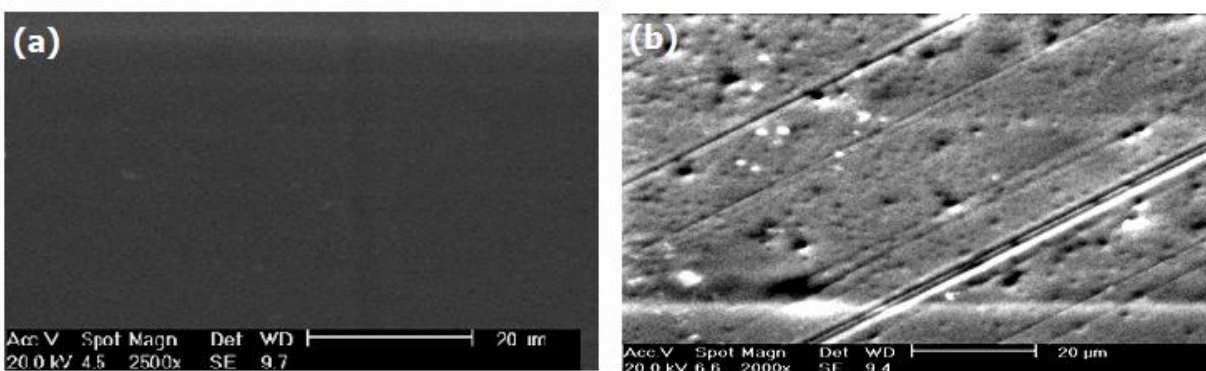**Fig. 3.** The physical appearance of the PVB films: (a) Un-irradiated and (b) irradiated.

Fig. 4. SEM micrograph of PVB films: (a) Un-irradiated and (b) irradiated.
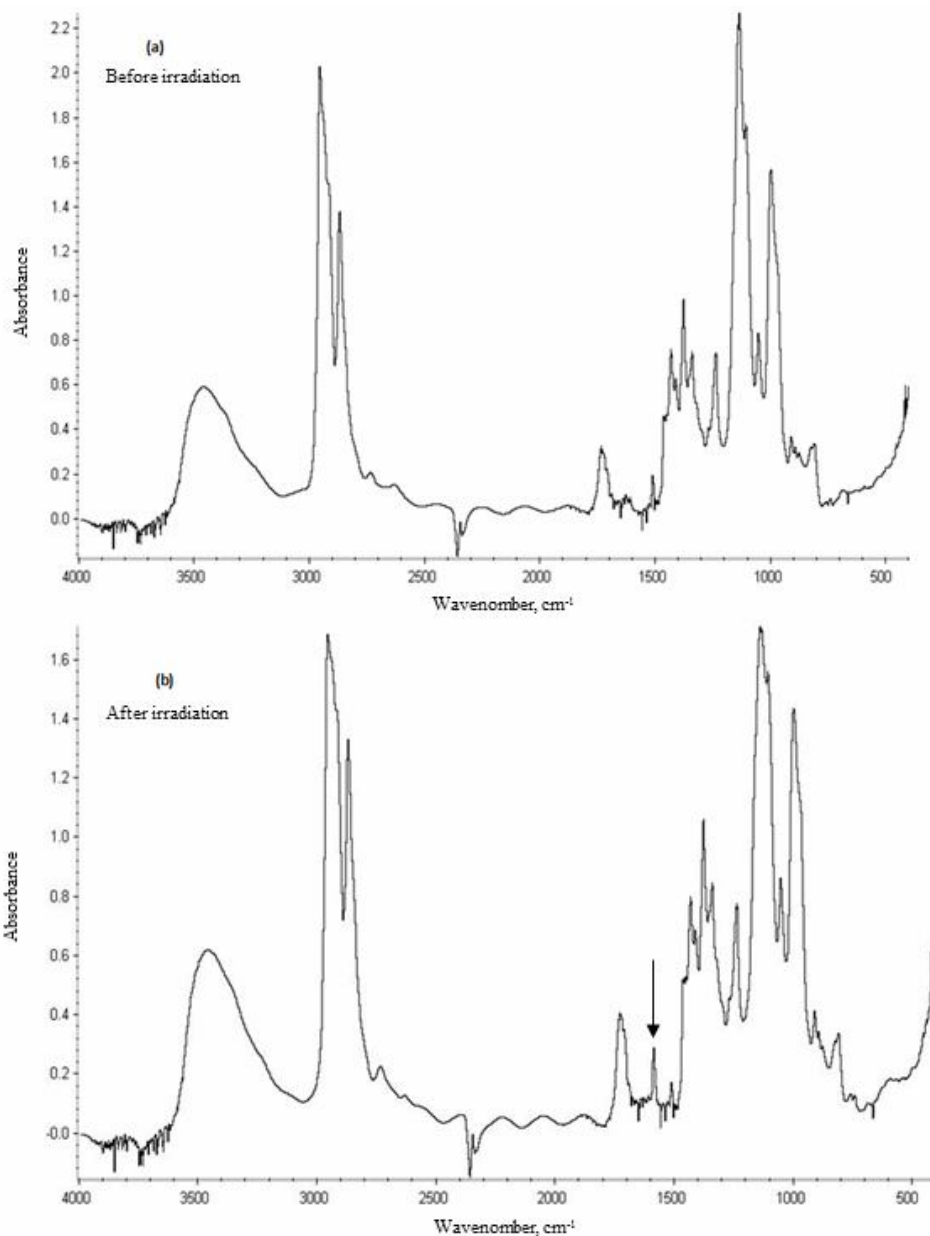
Fig. 5. FT-IR spectra of un-irradiated and irradiated/etched PVB films: (a) Un-irradiated and (b) irradiated.

Table 1. FT-IR Characteristics of Functional Groups of Un-irradiated and Irradiated/Etched PVB

Samples	-OH		C-H		C=O		C=C		C-O-C		C-O	
	cm^{-1}	p-h	cm^{-1}	p-h	cm^{-1}	p-h	cm^{-1}	p-h	cm^{-1}	p-h	cm^{-1}	p-h
Un-irradiation	3460	0.58	2950	2.02	1740	0.32	Not recognized		1140	2.26	1000	1.56
Irradiated/Etched	3460	0.62	2950	1.68	1710	0.41	1580	0.28	1140	1.70	1000	1.44

Peak-height: p-h

The band at 1740 cm^{-1} is due to the C=O stretching of acetate group. In addition, the C-O-C stretching band at 1140 cm^{-1} corresponding to acetal ring of butyral group and 1000 cm^{-1} band related to C-O stretching for acetate group are recognizable. On the other hand, thorough the existed FT-IR spectrum of irradiated etched sample one can identify a new significant band at 1580 cm^{-1} which can be assigned to the C=C stretching absorption band. Furthermore, the FT-IR spectra of irradiated sample shows that the band corresponding to acetal ring (1140 cm^{-1}) decreases in intensity (from peak-height 2.26 to 1.70), but the intensity of C=O band increases (from peak-height 0.32 to 0.41). There is a clear shift in the absorption band to lower wavelength from 1740 cm^{-1} to 1710 cm^{-1}. From the above observation, it can be concluded that, as a consequence of the irradiation of the PVB film, the acetal ring is opened and a conjugate system including a C=C band and a new C=O band is formed which changes the color of irradiated PVB film to dark pink (see Fig. 1). Also, the intensity of C-H, C-O and C-O-C stretching bands are reduced in the infrared spectra of irradiated sample (Table 1). So, it can be concluded that, during irradiation of the PVB film, some bonds of PVB chain are broken (C-H, C-O and C-O-C) and generate free radicals leading to the formation of new bonds (C=C and C=O) different from the polymeric common bonds (Fig. 6).

From these results and the basis of the previous works [11,18], the formation of stabilized PVB by high energy protons irradiation exposure following by chemical etching, is described in Fig. 6. As shown in this figure, under proton beam exposure, B1 and B2 bonds are ruptured in order to the acetal ring opening. It goes further by etching to produce butanal and the new structure of polymer chain is formed which approve the FT-IR spectrum given in Fig. 5b.

Thermal Degradation

The thermal degradation of un-irradiated and irradiated etched PVB films has been carried out using the dynamic weight loss data from the TGA in the N2 atmosphere (40 ml min^{-1}) using sample weights of 2-5 mg over a temperature range of 30-700 °C at a scan rate of 10 °C min^{-1}. The weight loss obtained by TGA apparatus and the derivative of the weight loss data of un-irradiated and irradiated etched PVB

films are shown in Fig. 7. As shown in Fig. 7 and the data presented in Table 2, the degradation of un-irradiated PVB displays a well-separated two-stage weight loss, one at temperature ranges 190-330 °C and the other between 330-550 °C, which the weight losses are about 44% and 53%, respectively. However, the degradation of irradiated etched PVB film proceeds in a major one-stage process at wich the threshold temperature, T$_{threshold}$, and the peak temperature, T$_{max}$, for the main weight loss are 301 °C and 391 °C, respectively. In present study, in accordance with the quantitative analysis obtained by TGA/DTG, and the basis of the previous works [19,23,25], the possible mechanism for the thermal degradation of PVB before and after irradiation are shown in Figs. 8a and b, respectively. As shown in Fig. 8a, the first stage degradation of un-irradiated PVB films, involves breaking of the side group C-O bonds denoted by B1, B3 and B4. These bond ruptures at the location of side-groups go to produce acetic acid and butanal confirming the weight loss of nearly 45% in TGA analysis. The rupture of C-O bonds goes further at location on the main chain of PVB polymer, denoted by B2 and B5, to produce butenal and butanol. As shown in Fig. 8b, the thermal degradation of irradiated PVB takes place in one major step by the rupture of the B1, B2 and B3 bonds giving rise to acetic acid, butenal and butanol. Many researchers [11,19,23,25] identified that the PVB degradation takes place by side-group elimination and main chain scission which produces acetic acid, butanal, butenal, butanol and C4 hydrocarbon compounds. Our present study in accordance with the quantitative analysis by TGA/DTG and FT-IR spectrum confirm them.

Determination of Kinetic Triplet

The employed kinetic analysis is based on the weight loss of PVB samples measured on a dynamic basis with the use of a thermogravimetric analyzer. The PVB degradation conversion is defined as,

$$\alpha = \frac{m_{PVB}^0 - m_{PVB}(T)}{m_{PVB}^0 - m_{PVB}^\infty}$$

(1)

where m_{PVB}^0 is the initial PVB mass, m_{PVB}^∞ is its final mass and $m_{PVB}(T)$ is the PVB mass at temperature T. To derive
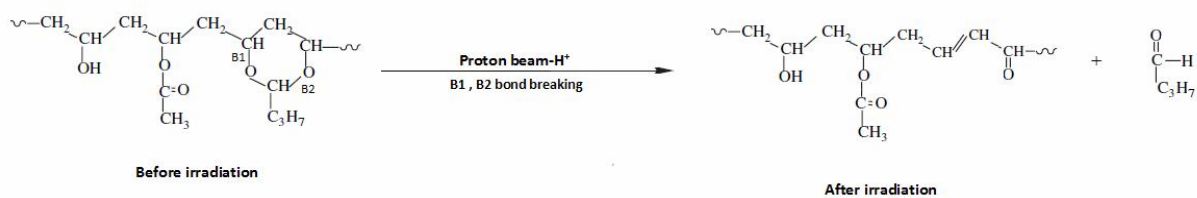
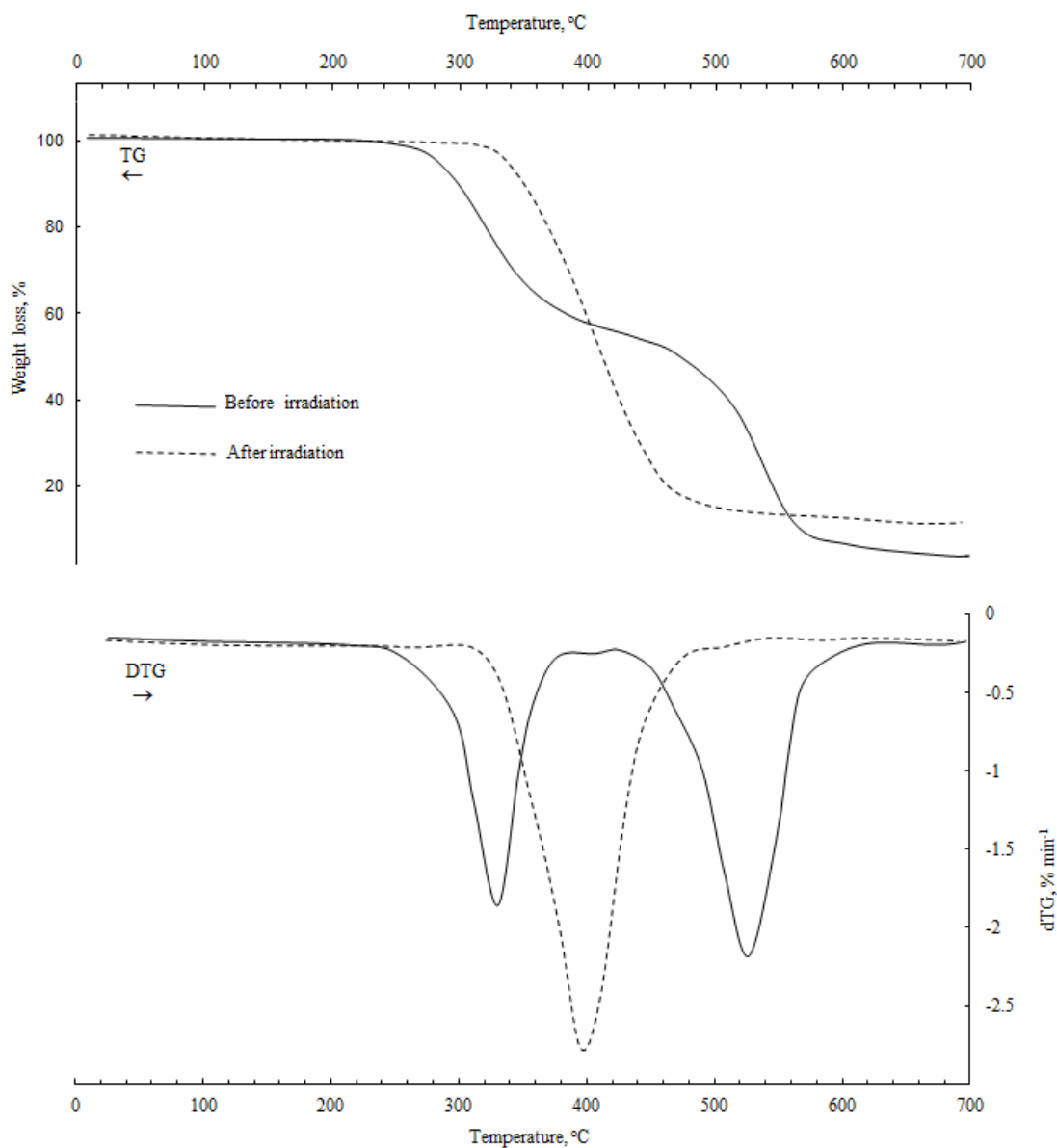**Fig. 6.** The effects of high energy protons exposure on PVB film and the formation of a new stabilized chain.

Fig. 7. TGA/DTG curves of un-irradiated and etched irradiated PVB in N_2 atmosphere at heating rate 10 K min^{-1}.

Table 2. Results of Thermal Degradation Parameters for Un-irradiated and Irradiated/
Etched PVB Films

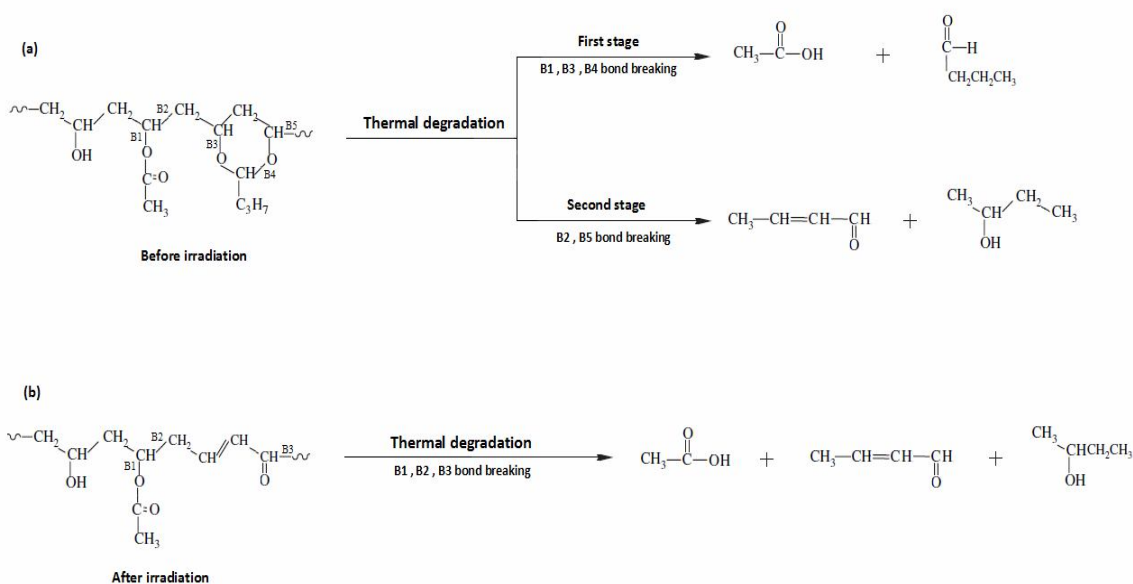| Samples		$T_{threshold}$ (°C)	T_{max} (°C)	Weight loss (%)
Un-irradiated	(1th)	239.81	324.81	44.26
	(2th)	450.08	525.01	53.52
Irradiated/etched		301.62	391.47	91.40

Fig. 8. The possible reaction pathways for the thermal degradation of PVB: (a) Un-irradiated and (b) irradiated.

the rate equation for this non-homogeneous degradation reaction, we begin with the decomposition rate of a specimen which can be presented using the rate expression as follows [24]:

$$\frac{d\alpha}{dt} = k f(\alpha) \tag{2}$$

where α α is the fraction of solid decomposed at time t, $f(\alpha)$ is a function of α which depends on the reaction mechanism and k is the rate constant given by the Arrhenius equation. If Eq. (2) is combined with the Arrhenius equation and also with the heating rate expression $\beta = dT/dt$ (K min^{-1}), which should be taken as a constant, the decomposition rate equation can be written in the differential form as presented in Eq. (3),

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{3}$$

where A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature of reaction. One can obtain the integrating of Eq. (3) as follows [26]:

$$F(\alpha) = \int_{\alpha=0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T(0)}^{T(\alpha)} \exp(-\frac{E_a}{RT}) dT \tag{4}$$

224

Where $F(\alpha)$ is defined as the integral form of the empirical function $f(\alpha)$, and by defining $z = -E_a/RT$, its differential can be written as:

$$dT = (\frac{RT^2}{E_a})dz \qquad (5)$$

by combining Eqs. (4) and (5) one can obtain Eq. (6):

$$F(\alpha) = \frac{A}{\beta} \int_{-\infty}^{z} \frac{RT^2}{E_a} \exp(z)\,dz \qquad (6)$$

Solving the integral of Eq. (6) by part, with the conditions: $\exp(z)dz = dv$, $RT^2/E_a = U$ and $dU = 2RT/E_a dt$, Eq. (7) is reached,

$$\frac{A}{\beta} \int_{T(0)}^{T(\alpha)} \exp\left(\frac{-E_a}{RT}\right) dT = \frac{A}{\beta} \frac{RT^2}{E_a} \exp(z) - \frac{A}{\beta} \int_{T(0)}^{T(\alpha)} \frac{2RT}{E_a} \exp(z) dT, \qquad (7)$$

then rearranging Eq. (7) and substituting $_{-E_a/RT}$ for z, following equation is obtained:

$$\frac{A}{\beta} \int_{T(0)}^{T(\alpha)} (1 + \frac{2RT}{E_a}) \exp\left(\frac{-E_a}{RT}\right) dT = \frac{A}{\beta} \frac{RT^2}{E_a} \exp\left(\frac{-E_a}{RT}\right). \qquad (8)$$

Since $E_a \gg 2RT$, the value of $(1 + 2RT/E_a)$ is almost unity and $(1 + 2RT/E_a)$ is assumed a constant and therefore can be transferred to the right sides of Eq. (8) as follows:

$$\frac{A}{\beta} \int_{T(0)}^{T(\alpha)} \exp\left(\frac{-E_a}{RT}\right) dT = \frac{A}{\beta} \left(\frac{RT^2}{E_a}\right) \left(\frac{1}{1 + \frac{2RT}{E_a}}\right) \exp\left(\frac{-E_a}{RT}\right). \qquad (9)$$

Finally, comparing Eqs. (9) and (4) results in the integral form of the function $f(\alpha)$ as:

$$\int_{\alpha=0}^{\alpha} \frac{d\alpha}{f(\alpha)} = F(\alpha) = \left(\frac{RT^2}{E_a}\right) \left(\frac{A}{\beta\left(1 + \frac{2RT}{E_a}\right)}\right) \exp\left(\frac{-E_a}{RT}\right). \qquad (10)$$

Rearranging Eq. (10) and taking the natural log of its

both sides lead to the rate equation degradation reaction of PVB in non-isothermal conditions as follows:

$$\ln\left[\frac{F(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta(E_a + 2RT)}\right] - \frac{E_a}{RT} \qquad (11)$$

where $(E_a + 2RT)$ is assumed to be a constant due to the extremely high value of Ea ($\sim 10^6$ j mol^{-1}) at moderate temperature. Here, we adopted the DTG results of the PVB degradation into the Eq. (11). In this data analysis, for un-irradiated and irradiated/etched PVB films an order-based model, $(F(\alpha))$, [27,28] with $F(\alpha) = (1 - \alpha)^n$ were found to yield the best fit for the data at the range of major weight loss region. The reaction order, n, are found to be 1.277 and 1.393 for un-irradiated and irradiated/etched PVB films, respectively. As shown in Fig. 9, the plot of $\ln[F(\alpha)/T^2]$ vs. $1/T$ demonstrates a straight line with the slope of $-E_a/R$, which gives the activation energy (E_a). The frequency factor (A) can be calculated from the interception on the y axis. Calculated values of the reaction order, activation energy and frequency factor for un-irradiated and etched PVB films are summarized in Table 3. The results show that the activation energy and frequency factor of PVB after irradiation following by chemical etching, are greater than that of its values before irradiation. This implies that the irradiation by high energy proton causes the higher stability for PVB.

Determination of Entropy of Activation

The difference between the entropy of the transition state and the sum of the reactant entropies is termed the entropy of activation ($\Delta S^{\ddagger}$) and calculated as follows [29,30]:

$$\Delta S^{\ddagger} = 2.303R \log\left(\frac{Ah}{kT_S}\right) \qquad (12)$$

where R is universal gas constant, h is Planck's constant, k is the Boltzmann constant and T_s is the reference temperature corresponding to $W/W_0 = 1/e$, where W_0 is the initial weight and W is the remaining weight at temperature T. The threshold temperature, $T_{threshold}$, (similar to the
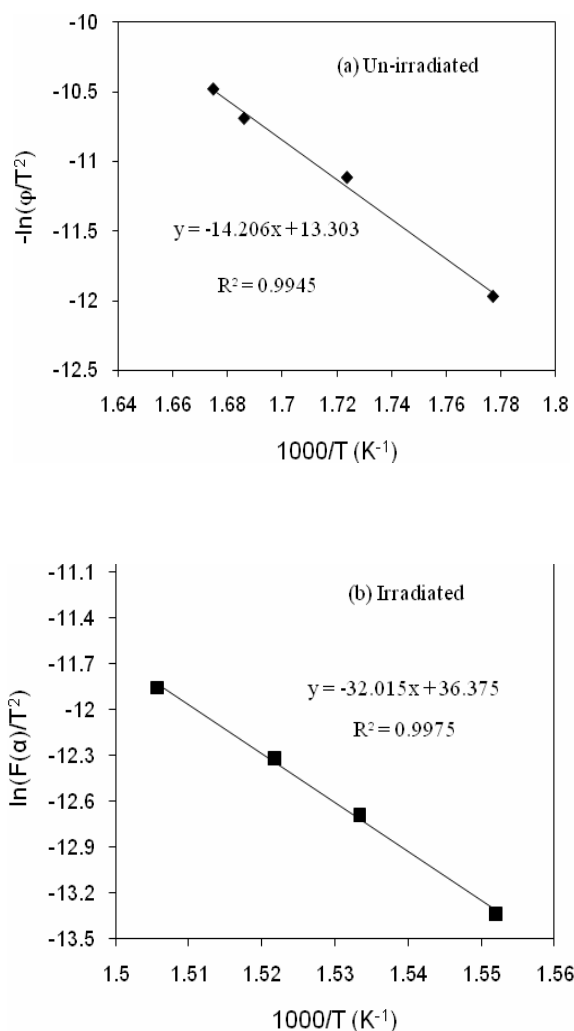
Fig. 9. Plot of $\ln[F(\alpha)/T^2]$ *vs.* 1000/T for determination of the activation energy and the frequency factor: (a) Un-irradiated and (b) irradiated.

ignition temperature in DTA/DSC anlaysis in the solid state kinetics) depends on the heating rate (β), but threshold temperature at $\beta = 0$ namely, T_s is independent of β which means the degradation temperature is β independent [31]. The calculated values of entropy of activation ($\Delta S^{\ddagger}$) and the obtained T_s are listed in Table 3. The results indicate that the entropy value of the activation PVB after irradiation is greater than the corresponding value before irradiation. The increase in the values of activation entropy for irradiated/etched PVB supports the relative stability of the PVB film using irradiation and the chemical etching process.

Determination of Free Energy Change of Activation

Free energy of activation, $\Delta G^{\ddagger}$, is given by considering the difference between the enthalpy of the transition state and the sum of the enthalpies of the reactants in the ground state, E_a, and the entropy of activation (see Eq. (13)). It may be considered as the driving force of a chemical reaction. $\Delta G^{\ddagger}$ Determines the spontaneity of the reaction. The values of $\Delta G^{\ddagger}$ are calculated using the following expression, [32,33]

$$\Delta G^{\ddagger} = E_a - T_s \Delta S^{\ddagger} \qquad (13)$$

Values obtained in this research are listed in Table 3. The positive values of $\Delta G^{\ddagger}$ signify the non-spontaneity of the degradation reaction. As can be seen, the values of $\Delta G^{\ddagger}$ for un-irradiated PVB are greater than the values of $\Delta G^{\ddagger}$ for irradiated/etched sample. This demonstrates that the

Table 3. Kinetic Analysis of Thermal Degradation for Un-irradiated and Irradiated/Etched PVB Films

Kinetic parameters	E_a (kJ mol^{-1})	log$A$ (1/s)	n	T_S (K)	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})	k (s^{-1})	R^2
Un-irradiation	118.52	8.831	1.277	592.13	116.01	49.82	0.023	0.9945
Irradiated/Etched	215.40	17.28	1.393	658.75	276.91	32.99	1.587	0.975

irradiation following by chemical etching affects the spontaneity of the degradation reaction. It may be also thought that the chemical etching process increases the values of $\Delta G^{\ddagger}$ of degradation reaction.

Determination of Rate Constant

The rate constant, *k,* can be calculated using the Arrhenius equation as in Eq. (14), [32,33]

$$k = A\exp(-\frac{E_a}{RT_s}) \tag{14}$$

The calculated values of the rate constants are listed in Table 3. The increasing trend in these values show the fast nature of the reaction with irradiation and etching process of the PVB film.

CONCLUSIONS

The thermal stability and kinetic parameters of un-irradiated and irradiated-etched PVB films have been evaluated using TGA/DTG analysis. The weight loss by the un-irradiated PVB upon heating was found to be in two stages and so that the highest rate of weight losses occurred at 324 ℃ and 525 ℃. However, due to high energy protons accelerated exposure following by chemical etching, this weight loss transition proceeded in a major one stage, so that the highest rate of weight loss took place at 378 ℃. From the obtained results, it can be concluded that the thermal stability of PVB increases with proton irradiation following by chemical etching. The possible reaction mechanism of thermal degradation of un-irradiated and irradiated-etched PVB films was discussed on the basis of the knowledge of the literature remarks and the results of this work through infra-red spectra and quantitative thermal analysis by TGA/DTG. Non-isothermal thermogravimetry was used to obtain the kinetics of thermal degradation. The increases in activation energies for thermal degradation and other related kinetic parameters like the frequency factor, order of reaction, entropy of activation and rate constant, clearly indicate the enhancement in thermal stability of PVB as an effect of high energy proton irradiation. The increases in thermal stability may be correlated with the

morphological changes induced in the PVB sample as a consequence of high energy proton irradiation which was confirmed using the FT-IR spectra. This leads to the formation of very reactive intermediates in the forms of excited states such as ions and free radicals. These intermediates are instantaneously used in several reaction pathways, resulting in the arrangement and formation of new strong bonds and stable structure of PVB. Also, the change trend of obtained kinetic parameters shows an excellent consistency with each other.

ACKNOWLEDGMENTS

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