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INFRARED STUDY OF THE THERMAL BEHAVIOR OF γ-IRRADIATED POLY-(VINYL ALCOHOL)

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Abstract

Infrared spectroscopy was applied for the investigation of the combined effects of γ -irradiation and heat on polyvinyl alcohol (PVA). The samples were exposed in an atmosphere of air at room temperature to doses ranging form 0.5 to 15 M rads. The obtained results revealed that exposure to γ-irradiation produces no considerable changes in the IR spectra of PVA apart from very slight changes in the intensities of the absorption bands. The crystallinity of the irradiated samples was determined by following the induced changes in the absorbances of the crystalline bands.

The IR spectra of PVA samples heated at 180°C exhibited two absorption bands at 1580 and 1710 cm^{-1} due to carbonyl groups. Alken double bonds and possibly also carboxyl groups.

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IR spectroscopy was also used for the examination of the effect of time of heating in air or in vacuum and also the effect of quenching of the degree of crystallinity of γ-irradiated PVA. Careful examination of the IR spectra led to the conclusion that the temperature induced changes depend on time of heating, rate of cooling and γ-dosage used. The highest crystallinity was obtained by heating in vacuum at 140°C and quenching at -40°C.

Introduction

The effect of ionizing radiation on the physical, chemical and morphological structures of PVA has been the subject of interest for several investigators[1,2] in recent years. Indeed gamma-irradiation of polymer has become one of the most common processes in graft copolymerization as a means of mixing compounds.

The study of heat effects on polymers has both fundamental and applied interest. Practically the processing and use of polymers sometimes involve rather high temperatures. Detailed knowledge of the thermal behaviour of the polymers can help to obtain improved heat resistance or at least certain harmful conditions can be avoided. Several authors[2-4] have studied the rather specific changes produced when PVA is subjected to heat. It has been accepted that one of the principal effects of heat treatment on PVA at moderate temperatures (below 160°C) is an increase in the crystalline fraction of the polymer[5]. Extensive heat treatment at higher temperatures induces chemical changes such as unsaturation, chain scission and cross-linking. The aim of the present study is to investigate the combined effects of γ-radiation and heat on PVA by using IR absorption spectroscopy.

Experimental

The polymer used in the present study is commercial polyvinyl alcohol of molecular weight 22,000 g/mol obtained from Merk LTD. The samples were ground and the powder was then sieved to a particle size of diameter ranging from 0.75 to 0.63 mm.

The samples were irradiated by ^{60}Co source. Noratom control A.S. gamma 3500 unit at a dose rate of 23 rad/s. The IR spectra were recorded on the PYE UNICAm full automatic double beam spectrophotometer model Sp 3300. The spectra of the powder were obtained by using the KBr disc technique and the UV spectra were recorded on Beckman spectrophotometer UV 5260. The obtained absorbances of the IR absorption bands are the averages of four replicate runs. The accuracy of the measured values was found to be 3%.

Results and Discussion

Fig. (1) represents example of the infrared spectra of samples of PVA before and after exposure to γ-irradiation. All spectra exhibit the characteristic absorption bands of PVA in addition to the C=O band of residual acetate groups at 1710 cm^{-1} as reported in the literature [5-7]. Careful examination of the spectra of the samples showed that there are no differences between the IR spectra of the irradiated and unirradiated samples apart from slight changes in the intensities of the absorption bands.

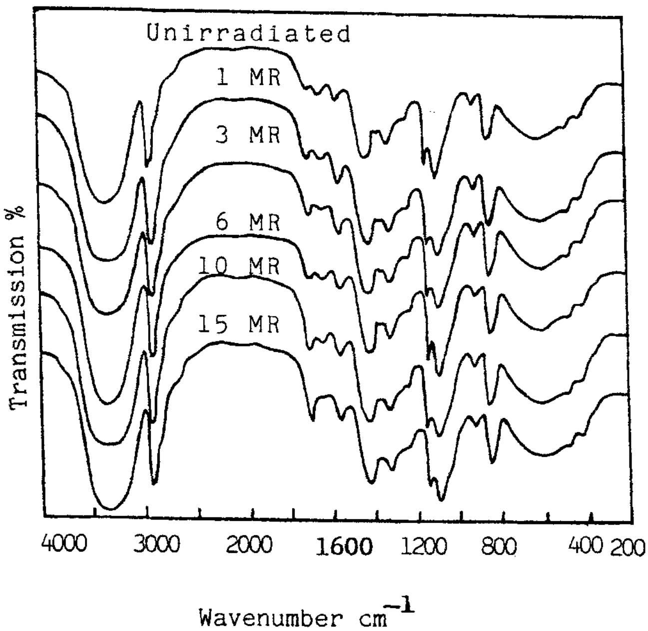

Fig.(1) IR Spectra of γ-irradiated PVA

The UV spectra of the samples under investigation were recorded Fig. (2). Analysis of the recorded spectra revealed that the spectrum of the unexposed PVA film exhibits a weak absorption band at 280 nm, this band was assigned to the carbonyl groups associated with ethylene unsaturation of the type -CO $(C=O)^{(8)}{}_2$. The exposure of PVA to different doses of gamma radiation up to 15 M rad resulted in no significant changes in the intensities of this band. Rao and Murthy[9] proposed the existence of carbonyl free radicals probably with aldehyde functional groups in γ-irradiated PVA. Bravar et al[8] mentioned out that even prolonged exposure of PVA to UV irradiation

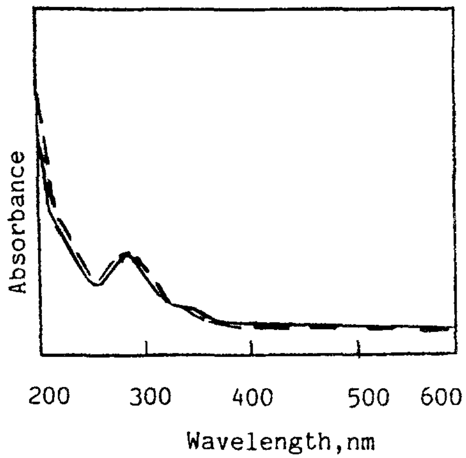

Fig.(2) UV spectra of PVA before(----)
and after(———) irradiation.

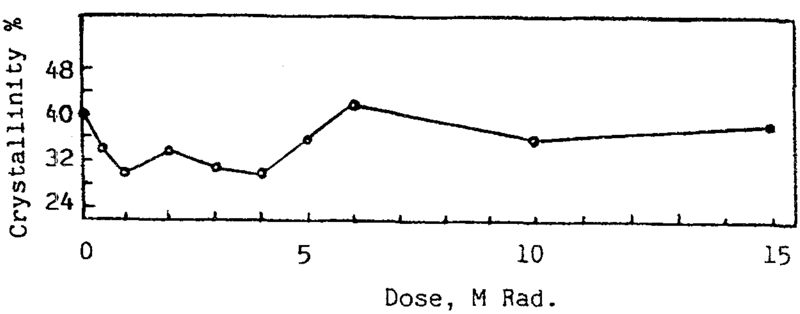

Fig.(3) Variation of crystallinity of PVA with
γ - dose.

did not provoke an increase of the existing bands nor the appearance of a new band. This means, practically that under mild conditions of irradiation the oxidation of PVA is not possible. Rabie et al[2] stated that exposure of PVA to 12 or 28 M rads produces no changes in its IR and UV spectral features.

The results of the present study confirme the statement that γ-irradiation of PVA with doses up to 15 M rads results in no observable changes in its spectral features.

The percent crystallinity of the samples was determined by using the relation[10] percent crystallinity = 92(d/c)-18 were d is the absorbance of the 1141 cm^{-1} peak and c is absorbance of the 1425 cm^{-1} peak.

The relationship between the percent crystallinity and gamma doses is shown in Fig. (3). It was found that the maximum value of crystallinity 42% is obtained by irradiation with 6 M rad, while the minimum value 29.5% is obtained by irradiation with 4 M rad. From the above mentioned data it was concluded that gamma-irradiation produces considerable changes in the crystallinity and this changes depend on the dosage used.

Samples under investigation were then heated at various temperature ranging from 25°C to 180°C in atmosphere of air for 3 hrs. Figs (4&5). Analysis of the spectra revealed that heating PVA either before or after irradiation over the range 25-120°C causes no observable changes in its spectral features while heating at 140°C causes marked increase in the intensity of the crystalline band at 1141 cm^{-1} on the other hand elevating the temperature to 160°C and 180°C causes a significant decrease in the intensity of this

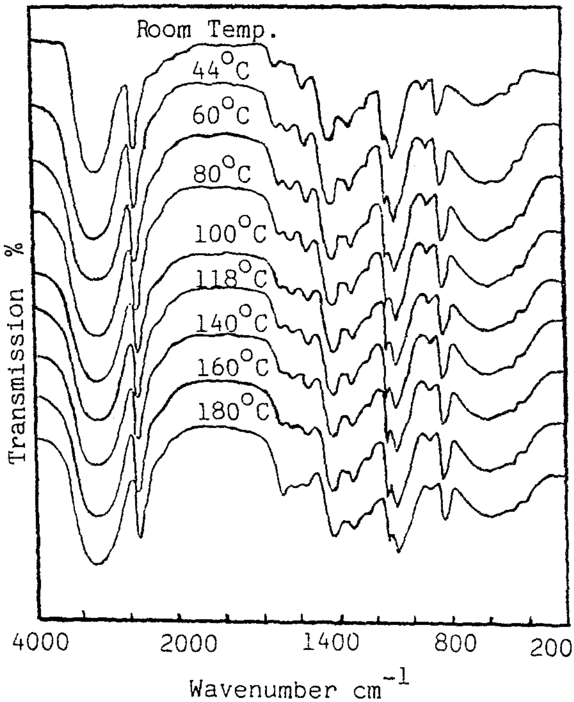

Fig.(4) IR spectra of thermally treated PVA.

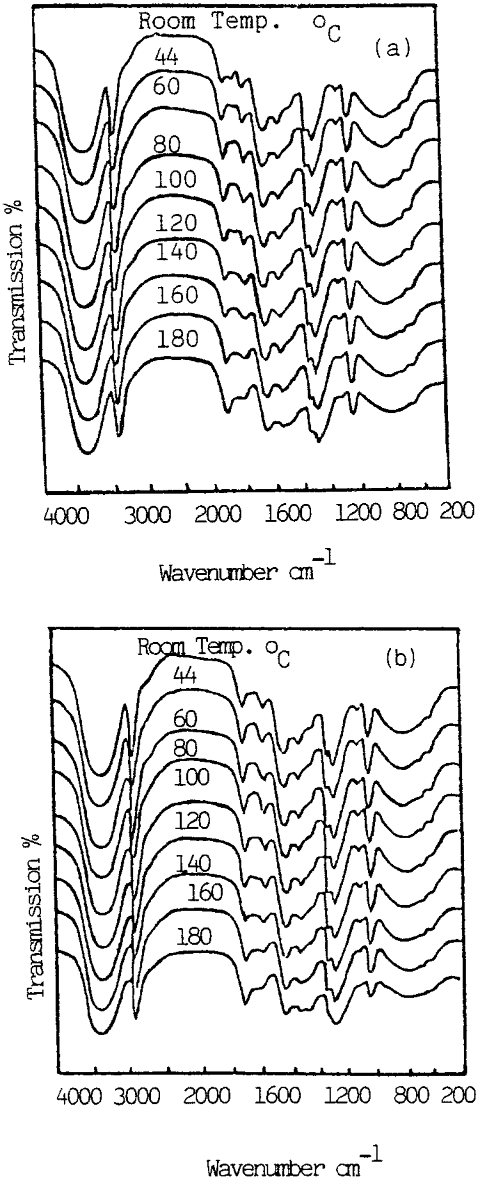

Fig.(5) IR spectra of thermally treated
γ -irradiated PVA
(a) 10 M Rad.
(b) 15 M Rad.

band. Furthermore heating PVA above 140°C results in the appearance of a band at 1580 cm^{-1} corresponds to the absorption of ß-dikitone groups and in an increase in the intensity of the 1710 cm^{-1} band.

The relationship between the temperature and crystallinity is represented in Fig. (6). It appears from this figure that the temperature induced changes depend on the applied dosage. Also heat treatment above 140°C for 3 hrs produces considerable decreases in the crystallinity of the original and γ-exposed PVA samples. However at any given temperature the crystallinity of the γ-irradiated samples (except few readings) is lower than that of the unirradiated samples.

The unirradiated samples of PVA as well as the samples irradiated with 3 M rad were heated in atmosphere of air at 60°C and 120°C for different periods up to 300 minutes. The spectra of these samples are shown in Fig. (7).

The variation of percent crystallinity with time of heating is represented graphically in Fig. (8).

Fig. (8) indicates that the relations between crystallinity and time of heating for the original samples heated at 60 or 120°C have similar behaviour. Also, the behaviour of these relations for the irradiated samples heated at 60 or 120°C are similar. The percent crystallinity of the samples heated at 60 or 120°C suggests two maxima after 30 and 300 minutes for the original samples and after 60 and 240 minutes for the irradiated one.

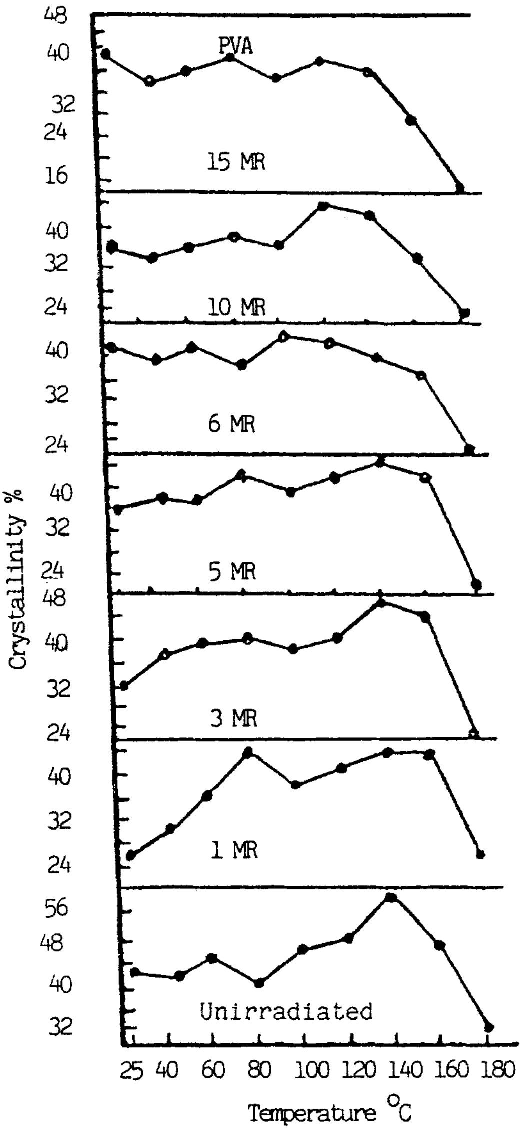

Fig.(6) Effect of heat on the crystallinity of γ-irradiated PVA

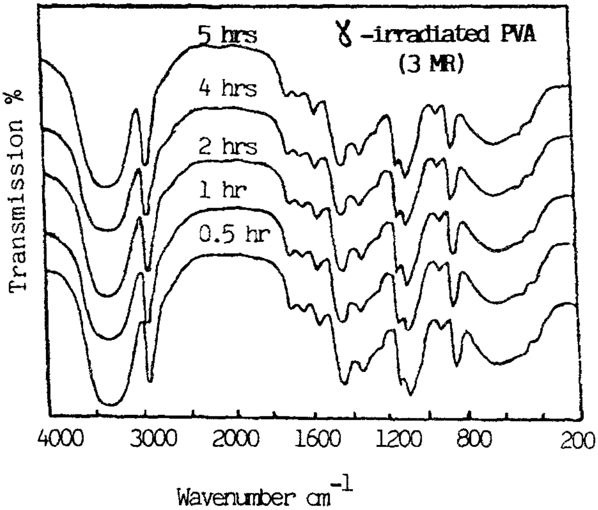

Fig. (7) IR spectra of γ -irradiated PVA heated at 120°C for different times.

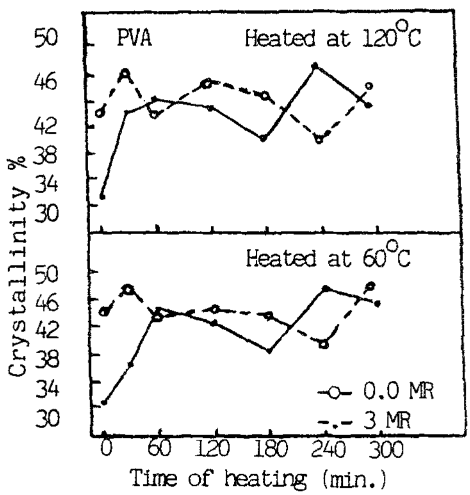

Fig.(8) Variation of percent crystallinity with time of heating

The unirradiated samples of PVA and samples irradiated with 1,3 and 5 M rad were heated in air and in vacuum ($1x10^{-1}$ mm Hg) at 140 and 180°C. One part of the heated samples was kept to cool slowly and the other was quenched at -40°C Figs (9&10).

The crystallinities of the samples heated at 140°C and 180°C were determined. The determined values are plotted against γ-dosages in Figs. ($11_{a,b}$). Fig. (11_a) indicates that the percent crystallinities of unirradiated samples heated in air at 140°C and left to cool slowly or quenched at -40°C nearly equal 55%. The samples heated in vacuum and cooled either slowly or quenched at -40°C have equal crystallinities ≈ 51%.

Fig. (11_b) indicates the following order of crystallinity for the irradiated samples: heated in vacuum and quenched > heated in air and quenched > heated in vacuum and cooled slowly > heated in air and cooled slowly. In other words for any given dosage, the highest crystallinity is obtained by heating in vacuum and quenching, whereas the lowest one is obtained by heating in air and cooling slowly.

From the above mentioned data, one can come to the conclusion that the temperature induced changes depend on the time of heating. The highest crystallinity is obtained by heating in air the sample irradiated at 3 M rad at 120°C for 240 min. Also, the induced changes depend on the atmosphere of heating (air or vacuum). In all cases the samples heated in vacuum show the highest crystallinity. In case of unirradiated samples, the rate of cooling has no effect on the crystallinity of sample heated at 140°C and has considerable effects on the crystallinity of samples heated at

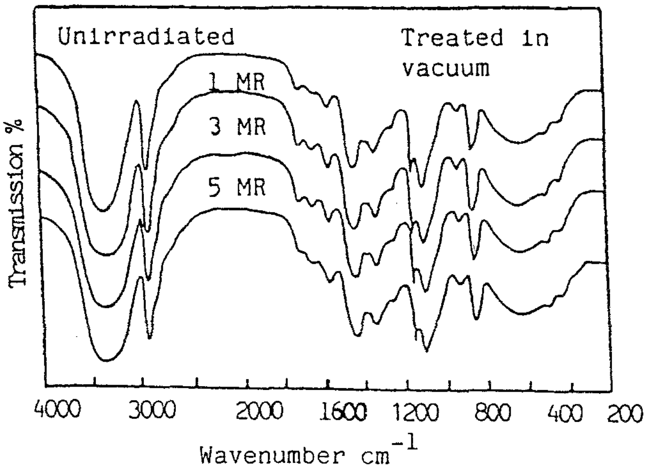

Fig. (9) IR spectra of γ - irradiated PVA heated at 140^{o}C and quenched to - 40^{o}C.

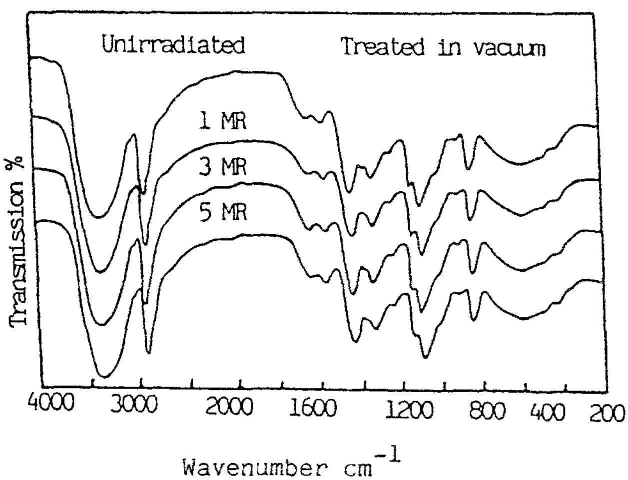

Fig. (10) IR spectra of γ -irradiated PVA heated at 180^{o}C and quenched to - 40^{o}C.

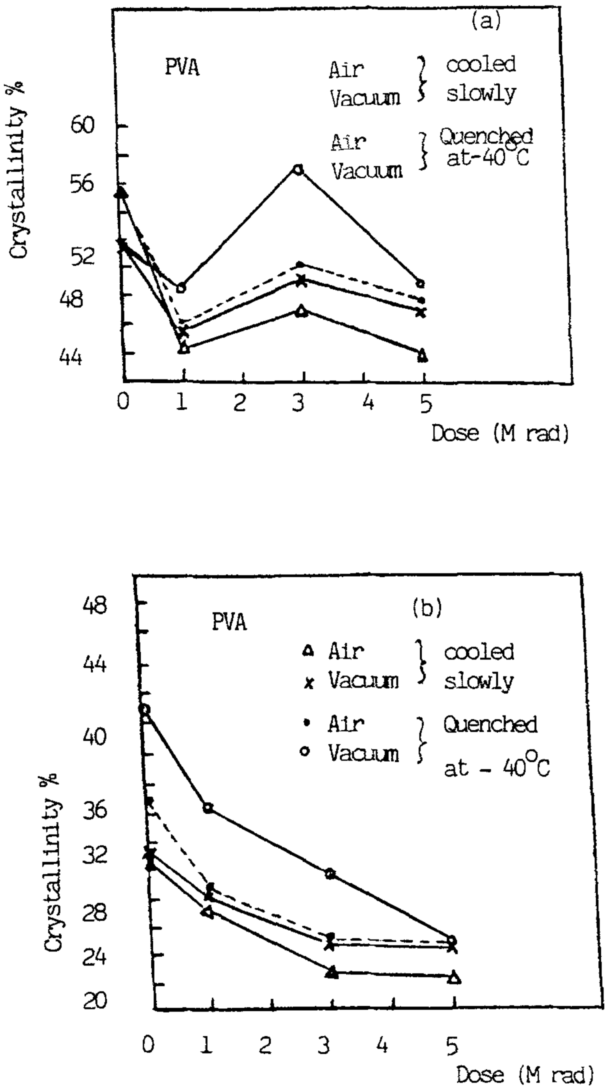

Fig.(11) Relationship between the crystallinity of the samples heated at 140°C (a) and heated at 180°C (b) and dosages.

180°C. The crystallinities of γ -irradiated samples heated either at 140 or 180°C depend on the rate of cooling.

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