

IR Spectroscopic Study on the Thermal Degradation of Plastic Security Cover Sheets of Some Documents

NABIL MOHAMED SAFY EL-DIN

National Center for Social and Criminological Research, Awkaf City, Zamalek, Cairo, Egypt

SYNOPSIS

The change in IR spectra of plastic security cover sheets of ethylene vinylacetate copolymer during thermal treatment was investigated. The results obtained revealed that the temperature reduced the concentration of the ester group; moreover, the carbonyl band disappeared at high temperatures from 200 to 220°C, as well as broadening of the absorption aliphatic-CH band. The change in the mechanical properties, degree of swelling in water, and refractive index of the samples during thermal treatment were also investigated.

© 1993 John Wiley & Sons, Inc.

INTRODUCTION

A significant amount of research has been carried out on the thermal behavior of polymers, since it exercises a significant influence upon phenomena related to thermal deformation, thermal degradation, thermal decomposition, and other heat-resisting properties of polymers.¹⁻⁹

Infrared (IR) absorption spectroscopy has been used to determine the composition of many copolymers and also to provide some limited sequence information.^{10,11} On the other hand some polymers can be used as hot-melt adhesives or thermoplastic powder coatings in the temperature range of about 100 to 200°C.¹² Hot-melt adhesion and wettability between polyethylene and vinylacetate or other polymers in the vicinity of the adherend melting point was investigated.¹³

The present investigation was conducted to obtain information about the change in the IR spectrum of plastic cover sheet of ethylene vinylacetate copolymer of some documents that resulted from different thermal treatments. The mechanical properties, degree of swelling in water, and refractive index of the original and thermal-treated samples were determined.

This study is important in the field of forensic science, as in some falsification processes when the

criminal tries to remove the plastic cover sheet of some documents by thermal treatment to make a change in the information on the document, as well as to exchange the photographic picture before adhering the plastic again. So, the aim of this study is to throw light on the effect of thermal treatment on the properties of the plastic sheet.

EXPERIMENTAL

Materials

Three different samples of plastic security cover sheets were used.

Moisture Content Determination

Moisture content of the three initial samples was determined according to ASTM procedure,¹⁴ and the moisture content of each specimen was calculated to the nearest 0.01 percentage point. The relative humidity (RH) of the ambient air was 65% ± 2%.

Thermal Treatment

Specimens were exposed at 180, 190, 200, 210, and 220°C in an air-circulating oven for 2 h. Each specimen was removed after the required temperature and placed for 1 h at room temperature before investigation.

Table I Elemental Analysis of Untreated (Original Samples)

Sample	Weight of Sample (mg)	Weight of CO ₂ (mg)	C%	Weight of H ₂ O (mg)	H%	N%	Cl%	S%
1	4.430	12.050	75.5	3.170	9.0	—	—	—
2	3.115	8.445	75.0	2.195	8.6	—	—	—
3	4.060	10.630	76.1	3.280	9.1	—	—	—

IR Spectroscopic Study

The infrared absorption spectrum of the samples were measured by means of an infrared spectrophotometer (model Perkin-Elmer 580). Elemental analysis of C, H, N, S, and Cl of the initial samples were determined in the analytical unit in the Faculty of Science, Cairo University.

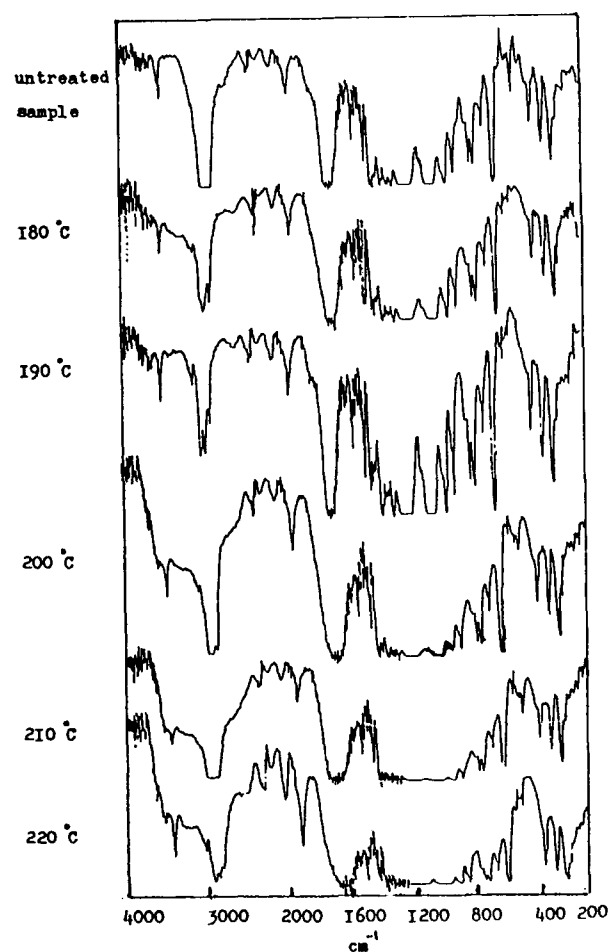


Figure 1 Infrared spectra obtained during thermal treatment.

Mechanical Properties Determination

The tensile strength and percent elongation were determined according to ASTM D42 procedure.¹⁵

Degree of Swelling in Water

Samples were immersed in deionized water at 37°C for 1 week. Excess water droplets were wiped off before the samples were weighed. The same samples were placed in a vacuum oven at 80°C for 3 days and the dry samples were weighed. A measure of the degree of swelling was the ratio of the wet weight over the dry weight.¹⁶

Index of Refraction

The apparatus for the preferred method consists of an Abbé refractometer,¹⁷ a suitable source of a white light, and a small quantity of a suitable contacting liquid. The temperature is accurately controlled to remain at $23 \pm 1.1^\circ\text{C}$.

RESULTS AND DISCUSSIONS

Identification of IR Spectra of Plastic Security Cover Sheets

IR spectra of plastic security cover sheets were identified by matching with different types of IR

Table II Mechanical Properties of the Samples

Thermal-Treated Samples (°C)	Tensile Strength (kg/cm ²)	Elongation (%)
—	3.5	28.0
180	5.0	26.5
190	5.3	30.0
200	3.1	22.0
210	2.4	15.0
220	2.0	10.0

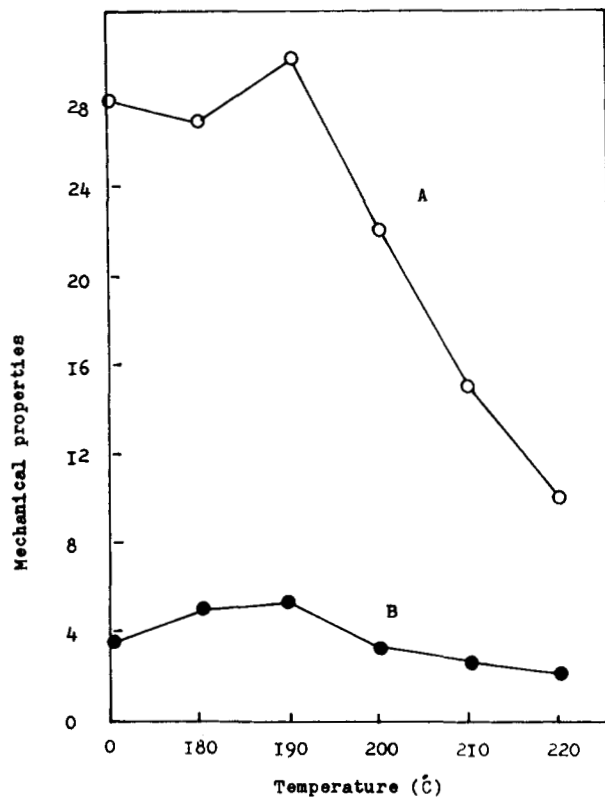


Figure 2 Mechanical properties of untreated and thermal treated samples. (A) Elongation %, (B) tensile strength.

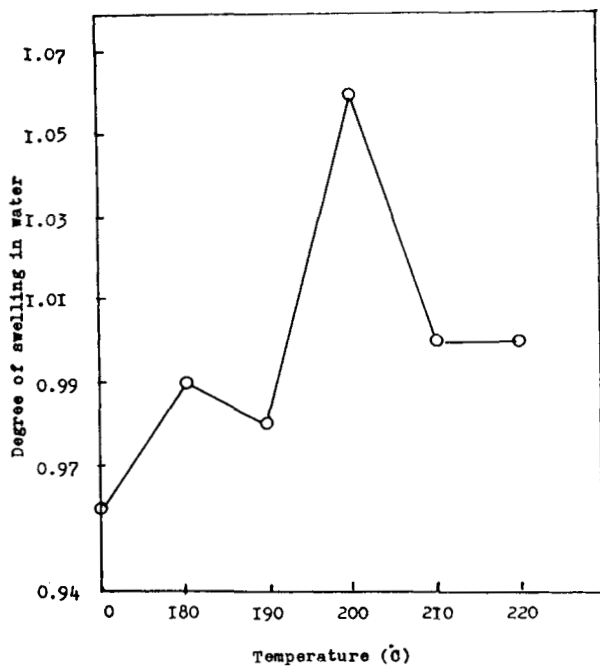


Figure 3 Degree of swelling of untreated and thermal-treated samples in water.

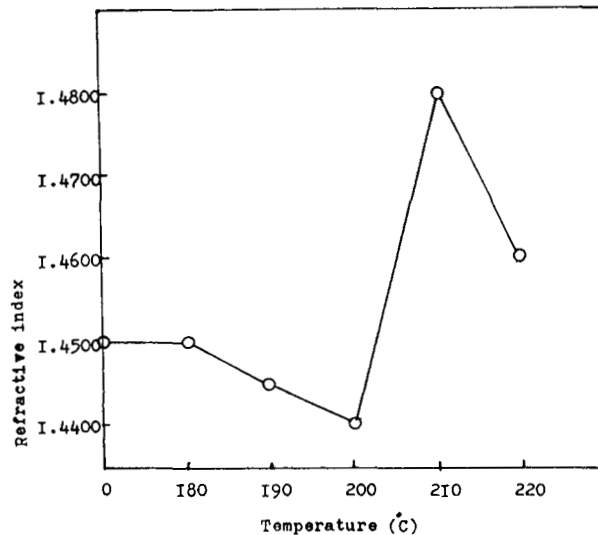


Figure 4 Refractive index of untreated and thermal-treated samples.

spectra of polymers, taking into consideration the results of elemental analysis (Table I). All the unknown plastic spectra were exactly identical to the IR spectra of ethylene vinylacetate copolymer.

The moisture content of the three initial samples was nearly the same value (0.4 wt %) at relative humidity of the ambient air (65% ± 2%).

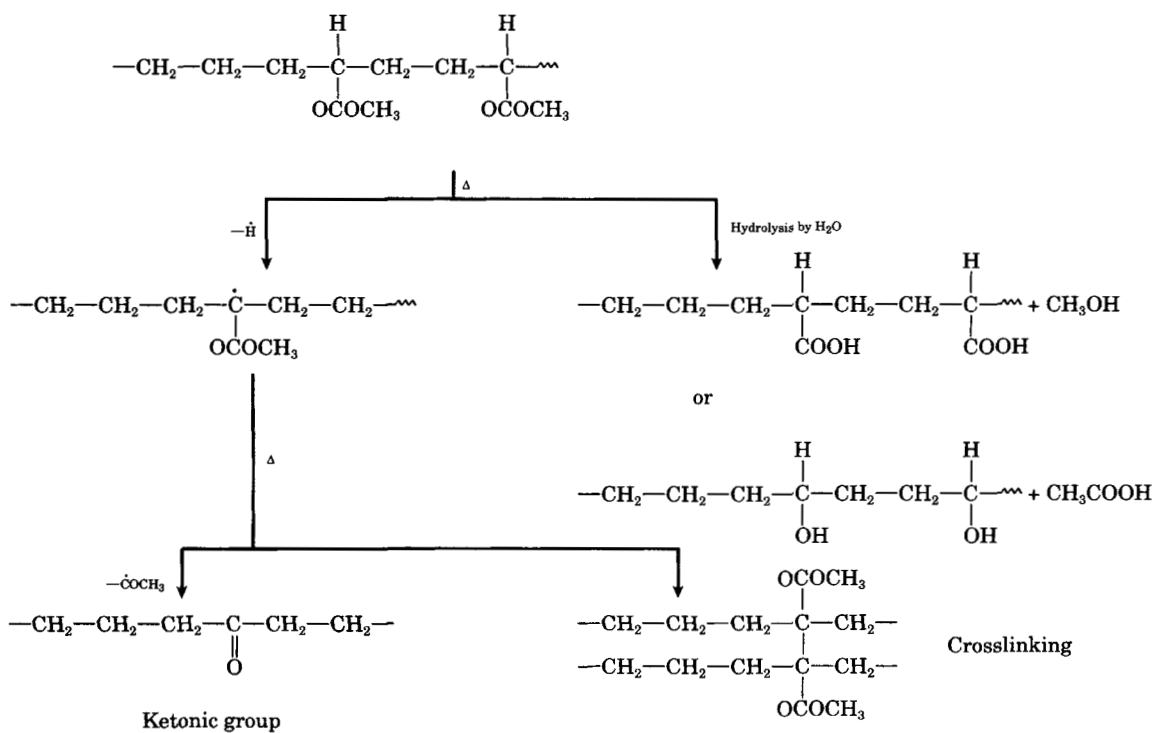
Thermal Treatments

Figure 1 represents the IR spectra of ethylene vinylacetate copolymer degraded at various temperatures ranging from 180 to 220°C.

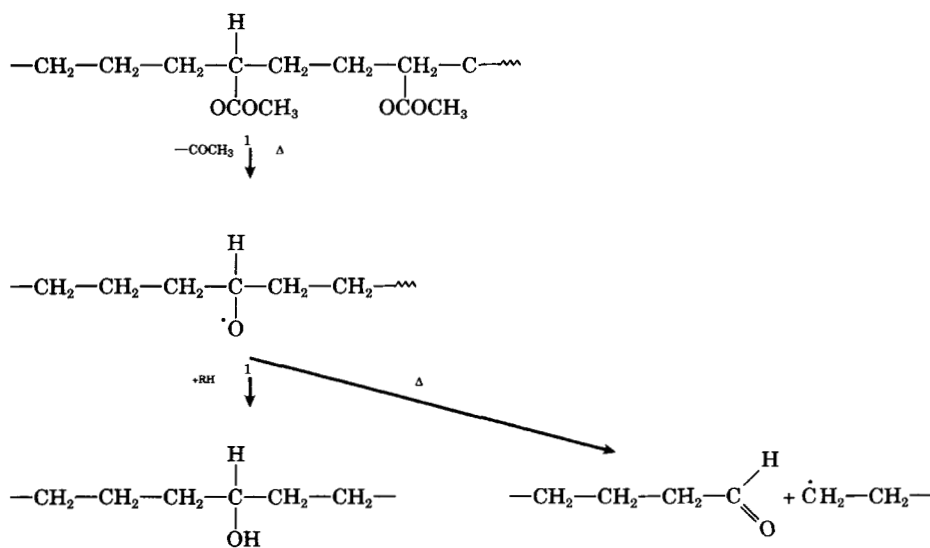
The initial samples have a moisture content of about 0.4 wt %. After heat treatment up to 200°C, the broad bands were located in the region around 3200 cm⁻¹ as well as at 1740–1700 cm⁻¹ corresponding to the hydroxyl and carbonyl of the obtained carboxylic acid groups, respectively. This can be explained by the hydrolysis of the ester by water at elevated temperatures. The results clearly reveal the reduction in the concentration of the ester group as a function of temperature rise; moreover, disappearance of the absorption bands between 1470 and 1000 cm⁻¹ was noticed at high temperature from 200 to 220°C. This resulted from degradation of carbonyl groups by oxidation process, indicating that the ester group in the copolymer is the predominant center for the degradation. On the other hand, the broadening of the absorption band at 2900 cm⁻¹ of the aliphatic-CH also indicates that the tertiary hydrogen in the

copolymer is a weak point for the thermal degradation of the mentioned copolymer.

A probable mechanism illustrating the experimental findings can be represented as follows:



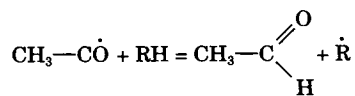
(A)



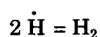
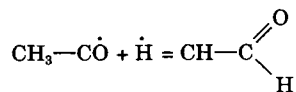
RH = polymeric chain

Chain scission

(B)



or



According to the suggested mechanism, as the temperature increases the ester group hydrolyzed by water to obtain either carboxylic group or hydroxy group. On the other hand the hydrogen atom is split from the copolymer leading to the formation of a polymeric radical (A). The latter can either recombine with another polymeric radical to give a stable crosslinking or it can be stabilized by the formation of a ketonic group with the detachment of a ketyl radical (COCH_3). An alternating mechanism (B) is also possible through the detachment of a ketyl radical from the copolymer as a result of thermal degradation. The formed polymeric alkoxy radical can be stabilized by chain scission with the formation of polymer with thermal aldehydic group or the formation of an hydroxy group.

Mechanical Properties

Table I shows the tensile strength and elongation of untreated and thermal-treated copolymer. It is obvious that elongation decreased with increase in the temperature up to 220°C except at 190°C . This is due to degradation as a result of chain scission. Higher temperature resulted in stronger degradation and consequently lower elongation. The only exception is at 190°C at which elongation increased, probably due to recombination of some obtained free radicals. The increase in tensile strength with temperature up to 190°C could be explained by the increase in the degree of crosslinking. At higher tem-

perature the tensile strength decreased steadily with temperature due to degradation, which affected also the crosslinking groups (Fig. 2).

Degree of Swelling in Water

Figure 3 shows the result of degree of swelling of samples in water. It can be seen from Table III that the degree of swelling in water for all thermally treated samples was found to be slightly higher than the untreated one. This is due to the hydrolysis of the hydrophobic ester groups. It can be concluded that the samples treated at higher temperature ($200\text{--}220^\circ\text{C}$) mean higher degradation and consequently higher degree of swelling.

Refractive Index

Figure 4 shows the refractive index of thermal-treated samples. The refractive index is considerably slightly reduced with an increase in temperature and then increased for the sample treated with 210°C and then decreased again at 220°C . This variation could be ascribed to the vinylacetate polymer used as hot-melt adhesives or thermoplastic powder coating material, so the transparency of the copolymer was changed with an increase in temperature. At 220°C the sample became brittle and dark yellow in color, thus the refractive index was decreased again.

Table III Degree of Swelling in Water and Refractive Index of the Samples

Thermal-Treated Samples		180°C	190°C	200°C	210°C	220°C
Degree of swelling	0.96	0.99	0.98	1.06	1.00	1.00
Refractive index	1.4500	1.4500	1.4450	1.4400	1.4800	1.4600

REFERENCES

1. D. A. Anderson and E. S. Freeman, *J. Polym. Sci.*, **54**, 253 (1961).
2. S. Igarashi and H. Kambe, *Bull. Chem. Soc. Jpn.*, **37**, 176 (1964).
3. B. Kaesche-Krischer, *Chem. Ingr. Tech.*, **37**, 944 (1965).
4. I. C. McNeill, in *Developments in Polymer Degradation, Vol. 1*, N. Grassie, Ed., Applied Science Publishers, 1977, p. 171.
5. D. W. Brazier and N. V. Schwartz, *J. Appl. Polym. Sci.*, **22**, 113 (1978).
6. R. D. Patel, M. R. Patel, and I. S. Bhardwaj, *Thermochim. Acta*, **48**, 111 (1981).
7. R. D. Patel, M. R. Patel, and I. S. Bhardwaj, *Thermochim. Acta*, **53**, 163 (1982).
8. W. W. Wright, in *Developments in Polymer Degradation, Vol. 3*, N. Grassie, Ed., Applied Science Publishers, 1981, p. 1.
9. M. Kryszewski and J. Jaachowicz, in *Developments in Polymer Degradation, Vol. 4*, N. Grassie, Ed., Applied Science Publishers, 1982, p. 1.
10. D. N. Kendall, Ed., *Applied Infrared Spectroscopy*. Chapman and Hall, London, 1966, Chapter 8.
11. I. V. Kunpanenko and K. S. Kanzanskii, *J. Polym. Sci. Polym. Symp.*, **43**, 973 (1973).
12. H. Zimmermann and E. Schaaf, Institute of Polymer Chemistry, "Erich Correns," Kantstr. 55, D-1530, Teltow-Seehof, Ger., 33rd IUPAC Congress, Budapest, 17-22 Aug. (1991).
13. Maski Imachi, *J. Appl. Polym. Sci.*, **34**, 2485-2491 (1987).
14. ASTM Standards D2654, Part 25 (1967).
15. ASTM Standards D412, Part 37 (1982).
16. S. H. Ou, H. Ishida and J. B. Lando, *J. Polym. Sci. Part B, Polym. Phys.*, **29**, 67-73 (1991).
17. ASTM Designation: D542-50 (1963).

Received November 4, 1991

Accepted April 3, 1992