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**DIFFUSION OF BUTYLATED HYDROXY
TOLUOL (BHT) IN PVC FILMS**

Key words diffusion, antioxidant,
dehydrochlorination, BHT, PVC

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ABSTRACT

The diffusion coefficient of butylated hydroxy toluol (BHT) in solvent casted PVC films from tetrahydrofurane (THF) was studied by UV spectroscopy. Diffusion coefficient of BHT in PVC at 140, 160 and 180°C were determined as 1.0×10^{-12} , 3.0×10^{-12} and 6.0×10^{-12} m²/s. The activation energy of diffusion (E_a) was 66 kJ/mol.

IR spectroscopic work showed that the complete removal of THF was possible by heating films 15 minutes at 140 °C, but that caused formation of C=O groups in PVC. No dehydrochlorination of films was observed even for heating them at 180 °C for 60 minutes.

Antioxidant BHT is volatile at high temperatures, so it is not advisable to use it for high temperature applications.

INTRODUCTION

PVC undergoes dehydrochlorination reaction by heat resulting in the formation of conjugated double bonds. If oxygen is present in heating medium, oxidation to carbonyl compounds on PVC macromolecules take place. Presence of antioxidants prevents thermooxidative degradation of polymers. Butylated hydroxytoluol (BHT) is a widely used antioxidant. It is added to plastic wrapping in contact with food products ¹. Volatility of antioxidants must be considered when they are utilized at high temperatures ². Antioxidants evaporate from the surface of the plastic and they are carried to the surface from the interiors of the solid by diffusion. Diffusion of additives and plasticizers in poly (vinyl chloride) was studied by Park and Hoang ^{3,4}, Griffiths et. al ^{5,6}, Park and Saleem ⁷. They used β -emitting diffusants to determine the diffusion coefficients of additives and plasticizers. Görnitz et.al ⁸ studied the diffusion of DOP in PVC, by viscosimetric studies on PVC plastisols. Diffusion coefficient of a molecule in a plastic film can be determined using equation 1 ⁹ for $M_t/M_\infty > 1/2$.

$$\ln(1-M_t/M_\infty) = \ln(8/\pi^2) - (\pi^2 D t / l^2) \quad 1$$

where M_t is the amount diffused at time t , M_∞ is the amount diffused when equilibrium is reached. l is the half thickness of the film, and t is time.

The measurement of concentration of an additive in a film can be made by spectroscopic methods. Braun and Bezdadea ¹⁰ used ultraviolet and IR spectroscopy to detect conjugated double bonds and carbonyl groups in UV light irradiated films. Vymazal et al ¹¹ studied effect of thermal stabilizers in the thermal treatment

of PVC by IR spectroscopy. Davidson and Meek¹² showed by IR spectroscopy that carbonyl compounds formed in PVC irradiated with light having wavelength smaller than 300 nm.

BHT has four characteristic peaks in $1650\text{--}1450\text{ cm}^{-1}$ region due to aromatic C=C stretching vibration in its IR spectrum¹³ and has a characteristic peak at 280 nm in UV region¹⁴.

The purpose of this work is to study the effect of temperature on diffusion of BHT in PVC films using IR and UV spectroscopy.

MATERIALS AND THE METHOD

Suspension polymerized PVC PETVINIL S-39/71 (Petkim-izmir) with M_v of 88000 g/mol was used in preparation of films. PVC was dissolved in THF containing 0.025 % BHT to get a solution containing 40 g PVC/L. 15 ml each of this solution was placed in petri dishes of 9 cm diameter. THF evaporated in one day and rigid PVC films containing 0.6 % BHT were obtained. The thickness of the films was 0.062 ± 0.002 mm.

PVC films were heated in Fisher air circulating oven at 80, 100, 140, 160 and 180 °C. Samples of heated films were removed at certain time intervals and cooled to room temperature on glass dishes.

The IR spectra of the films were taken by using a Perkin Elmer 566 grating spectrometer. Spectronic 800 UV spectrometer was used in obtaining UV spectrum of the films.

EXPERIMENTAL RESULTS AND DISCUSSION

Removal of THF From Films:

THF has a very high vapor pressure at room temperature and evaporates in a very short time in preparation

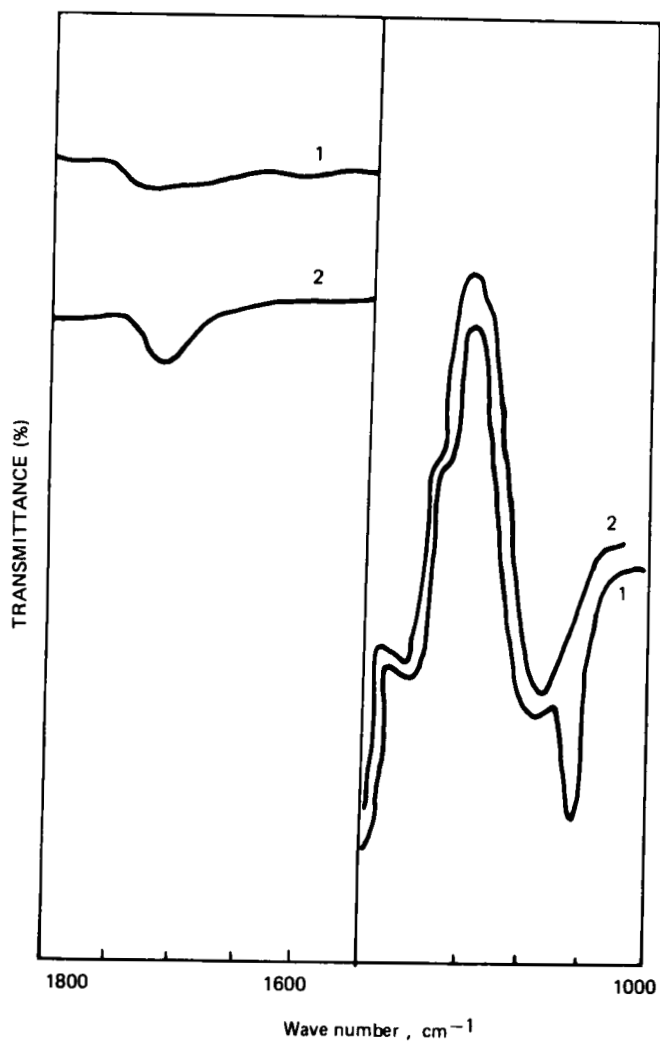


FIG. 1. IR spectrum of (1) unheated film (2) of film heated at 140 °C for 15 minutes

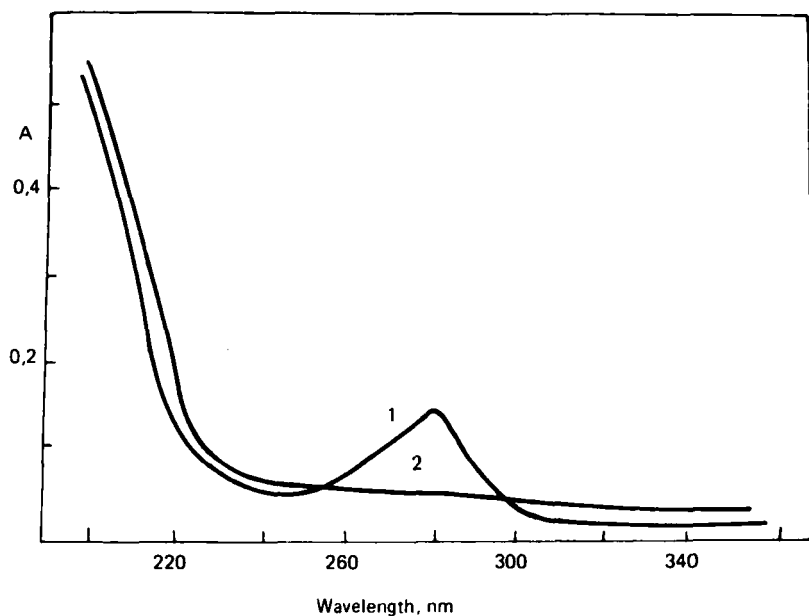


FIG. 2. UV spectrum of (1) unheated film (2) PVC film heated at 160 °C for 60 minutes

of the films. However, removal of the last traces of THF is difficult at room temperature. Park and Hoang³ kept films over silicagel at room temperature to remove THF. Heating films above glass transition temperature of PVC is required to achieve complete removal of THF. No change in intensity of absorption band of THF at 1100 cm^{-1} ¹³, in IR spectra of films heated at 80 °C up to 60 minutes heating time was observed. At 100 °C heating temperature absorption intensity at 1100 cm^{-1} was decreased with heating time. Films heated at 100 °C for 60 minutes had no THF as indicated by complete disappearance of 1100 cm^{-1} band. Complete removal of THF was obtained in 15 minutes by heating films at

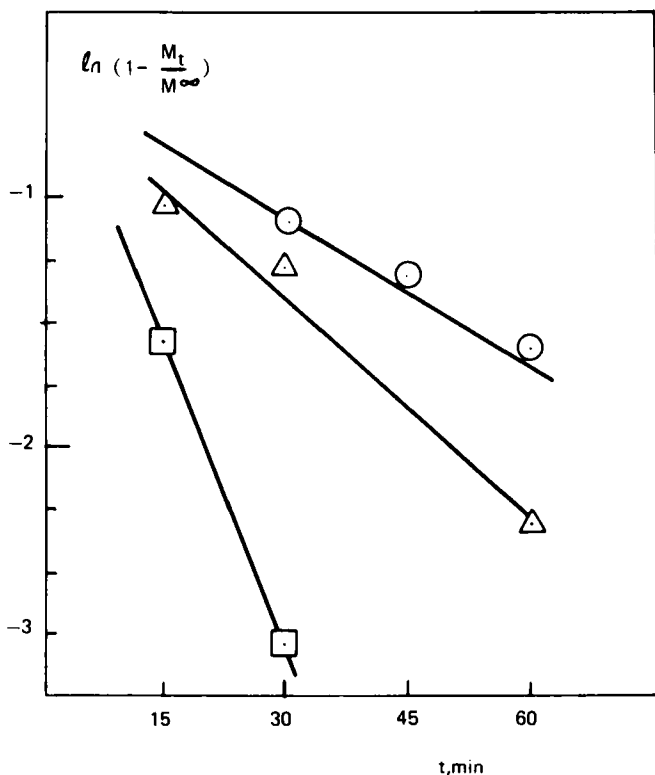


FIG. 3. $\ln (1 - M_t/M_\infty)$ versus t at (○) 140 °C, (Δ) 160 °C, (□) 180 °C

140 °C (Fig. 1). The band observed at 1720 cm^{-1} for film heated 140 °C for 15 minutes indicate the formation of C=O groups on PVC molecules ¹⁰ (Fig. 1).

The Fate of BHT in Heated Films:

BHT in freshly prepared films was detected by UV spectroscopy. The band observed at 280 nm in UV spectra of films indicated the presence of BHT in PVC films

TABLE 1. Diffusion Coefficient of BHT in PVC at Different Temperatures

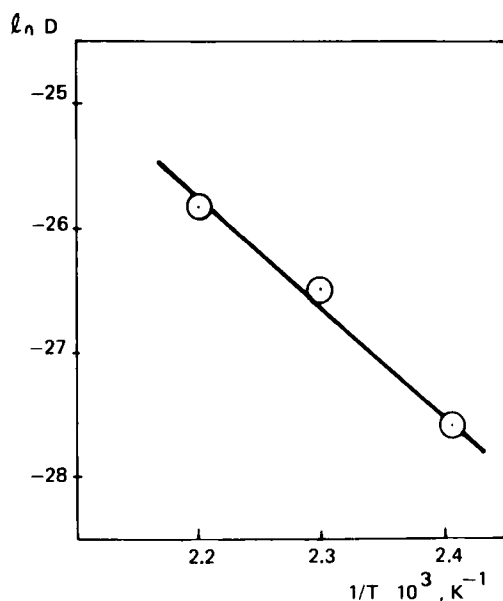
T °K	D x 10 ¹² m ² /s
140	1.0
160	3.0
180	6.0

(Fig. 2). Heating films at 80 °C and 100 °C did not cause any change in the intensity of this band. The absorbance at 280 nm decreased with time of heating at 140 °C, 160 °C and 180 °C. For example, this band is absent in the UV spectra of the film heated for 60 minutes at 160 °C (Fig. 2).

BHT may be decomposed by heat and may evaporate from the film at high temperatures. Assuming decomposition is negligible, the diffusion coefficient of BHT in films can be calculated. If the intensity of the band at 280 nm is A_0 for unheated films and A_t for films heated for t minutes

$$\frac{M_t}{M_\infty} = \frac{A_0 - A_t}{A_0} \quad 2$$

From experimental data M_t/M_∞ can be calculated for each time of heating at different temperatures. Straight lines were obtained when $\ln(1-M_t/M_\infty)$ versus t was plotted (Fig. 3). From the slopes of the lines and equation 1, diffusion coefficient of BHT in PVC at 140 °C, 160 °C and 180 °C was calculated and shown in Table 1.

FIG. 4. $\ln D$ versus T^{-1}

Activation energy of diffusion, E_a , was calculated as 66 kJ/mol from the slope of the line obtained from the plot of $\ln D$ versus T^{-1} (Fig.4) and Arrhenius relationship

$$D = D_0 \exp (-E_a/RT)$$

3

Dehydrochlorination of PVC

UV spectra of the PVC films did not indicate the presence of dien, trien, tetraens and higher conjugated diens at 160 °C (Fig. 2) and at 180 °C.

CONCLUSION

This work showed the importance of spectroscopic methods in determination of small concentration

of substances in PVC. The complete removal of THF from films was checked by IR spectroscopy. On the other hand the diffusion of BHT was followed by UV spectroscopy. Higher BHT concentrations are required to use IR spectroscopy for the same purpose, since the extinction coefficients of characteristic bands in IR spectrum of BHT are small.

The only shortcoming of this method that it can not be applied to determination of diffusion coefficient of BHT in plasticized PVC due to strong absorbance of plasticizers both in UV and IR regions.

BHT is a volatile antioxidant and it must be used with care for high temperature applications of PVC such as cable insulations. The determination of diffusion coefficient of BHT in PVC is usefull in prediction of the time for whic there is sufficient BHT concentration in PVC products. Diffusion coefficient of BHT at different temperatures can be calculated from activation energy.

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