The Effect of Solvent Traces on the Ultraviolet Degradation of Poly(vinyl Chloride)

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Synopsis

The ultraviolet degradation of poly(vinyl chloride) films was studied in a photo-reactor which supplied energy near 3000 Å. It was noted that the rate of degradation and color development was increased when the level of residual solvent in the cast films was increased. Two solvents were employed in the study: tetrahydrofuran and di-chloroethane. The amount of residual solvent was correlated with the height of a characteristic peak at 2800 Å for tetrahydrofuran and 1900 Å for dichloroethane. Films which had very small traces of solvent showed excellent resistance to ultraviolet degradation, even in the absence of ultraviolet stabilizers. The analyis of solubility data showed that chain scission was controlling in the early stages of exposure, while cross-linking was controlling at later stages. As a result, it was not possible to apply Char-lesby's treatment of radiation-induced degradation. Comparison with the results obtained by other workers for degradation at 2537 Å showed that degradation at this wavelength was much faster than degradation at 3000 Å. Furthermore, degradation at 2537 Å appeared to be controlled by crosslinking at all stages of exposure.

INTRODUCTION

As early as 1939, Marvel and co-workers[1] speculated that discoloration which accompanied the thermal and light degradation of poly(vinyl chloride) (PVC) might be related to the development of long sequences of double bonds as a result of the dehydrochlorination reaction. More recently, Winkler[2] proposed a free-radical mechanism for both the thermal and ultraviolet degradations of PVC. Now, it is generally agreed that dehydrochlorination is a zipper-type reaction and that discoloration requires a minimum of seven conjugated double bonds in sequence.[3,4] In addition to causing discoloration, conjugated double bonds may result in crosslinking and the development of stiff, insoluble polymer structures. Many of the above concepts have been substantiated for both thermal degradation[5−8] and degradation of PVC by high-energy radiation.[9−11]

Severe discoloration and dehydrochlorination were observed upon exposure of PVC to radiation above 2800 Å.[12−14] Studies on the degrada-

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tion products and absorption spectra of PVC samples which were exposed to ultraviolet radiation in a variety of atmospheres showed that dehydrochlorination and oxidation occur simultaneously during the degradation process.[15-17] Significant changes were noted in the ultraviolet absorption spectra mainly due to the newly formed conjugated double bond structures and oxidation products.[17] The effect of ultraviolet exposure on molecular weight and crosslinking was also considered both in the presence and absence of oxygen.[13,18,19]

The fact that PVC shows substantial degradation upon exposure to ultraviolet radiation above 2800 Å appears to be in contradiction with the fact that PVC is essentially transparent to ultraviolet radiation in that wavelength range. Some of the proposed mechanisms assume that structural abnormalities in the polymer or the presence of impurities might be responsible for degradation and color development. Poly(vinyl chloride) is usually exposed to contact with a variety of solvents during polymerization and postpolymerization operations. Traces of these solvents remain in the polymer matrix even after the severe drying conditions. Since it is known that some of these solvents are susceptible to ultraviolet degradation themselves[20] or tend to enhance the ultraviolet degradation of PVC in solution,[13,21,22] it would be desirable to determine the effects, if any, of traces of these solvents on the ultraviolet degradation behavior of PVC. The knowledge of these effects is also important since many of the kinetic studies on PVC degradation employ films that have been cast from solutions in some of these solvents.

In this paper, we summarize the results of work that has been conducted to determine the effects of traces of solvents on the ultraviolet degradation of PVC and to elucidate some aspects of the kinetics of PVC degradation. Two common solvents representing different classes of compounds have been selected for this study: tetrahydrofuran (THF) and dichloroethane (DCE). The former is one of the most commonly used solvents in the casting of PVC films, while the latter represents chlorinated solvents which are commonly used at different stages of processing and application of PVC.

EXPERIMENTAL

Materials

Virgin poly(vinyl chloride) resin Q-1812 was obtained from Gulf Chemicals of Canada. The resin is of the medium-high molecular weight type that is usually used for calendering and extrusion purposes. It was in the form of a white powder and met the following specifications by the manufacturer: Fikentscher K-value, 67; inherent viscosity, ASTM D-1755 Method A, 0.9; specific viscosity, ASTM D-1755 Method B, 0.36.

Tetrahydrofuran Certified Grade was obtained from Fisher Scientific, and dichloroethane Spectroquality was obtained from Matheson, Coleman, and Bell.

Preparation of Films

Spectroscopic analysis of the films requires the samples to be of high gloss and less than 1 mil in thickness.

Films were cast from a 4%-by-weight solution of PVC in THF by pipetting 5.0 ml of the solution into a Petric dish. The dish was then covered with three sheets of thin tissue paper which were securely fastened to the top. The solution was then allowed to dry for 6 hr in a closed fume hood.

The best films from DCE solutions were obtained by casting from a 1 wt-% solution. After casting, the Petrie dish, which was covered with tissue paper in the same manner as above, was placed in a covered desiccator to allow drying at a very slow rate in a solvent atmosphere. The desiccator lid was not sealed in order to allow the solvent to escape from the chamber at a controlled rate. The desiccator was placed in a closed fume hood, and drying under these conditions was continued for 24 hr.

The solution-cast films obtained in the above manner were removed from the Petrie dish. Then, they were mounted gently in circular, Teflon-lined holders. The sample holders, with the films, were subsequently placed in a desiccator under high vacuum for 24 hr to remove the remaining available solvent. In some cases, vacuum drying was continued for longer times to determine the feasibility of removing all traces of solvent. However, this procedure was not successful. Films which were prepared according to the above procedure were glossy, clear, and uniform, with a thickness of less than 1.0 mil.

Ultraviolet Exposure

Irradiation was achieved in a Rayonet RS preparative photochemica reactor Model RPR-208. Eight lamps, RUL-3000 Å, with approximately 85 watts of ultraviolet-simulating sunlight phosphor were used in the reactor. The spectral energy distribution of the lamps, as supplied by the manufacturer, is shown in Figure 1. The photoreactor was equipped with a merry-go-round rotating at 8 rpm to ensure uniform exposure of the films to the lamps.

After drying, the films, which were already mounted on sample holders, were placed in the photoreactor. Films cast from both THF and DCE were irradiated simultaneously in order to obtain a direct comparison between the two solvent systems. At the beginning of irradiation, eight specimens from each solvent system were placed in the reactor. The specimens were removed from the reactor at frequent intervals for spectral analysis. They were subsequently returned to the reactor for further irradiation. Care was taken to avoid exposure to light from any source outside the reactor.

Another series of irradiation experiments was conducted to supply material for the solubility tests. Five specimens from each solvent system were needed to supply enough material for solvent extraction after each irradiation interval. Spectral analysis was also conducted on these samples to
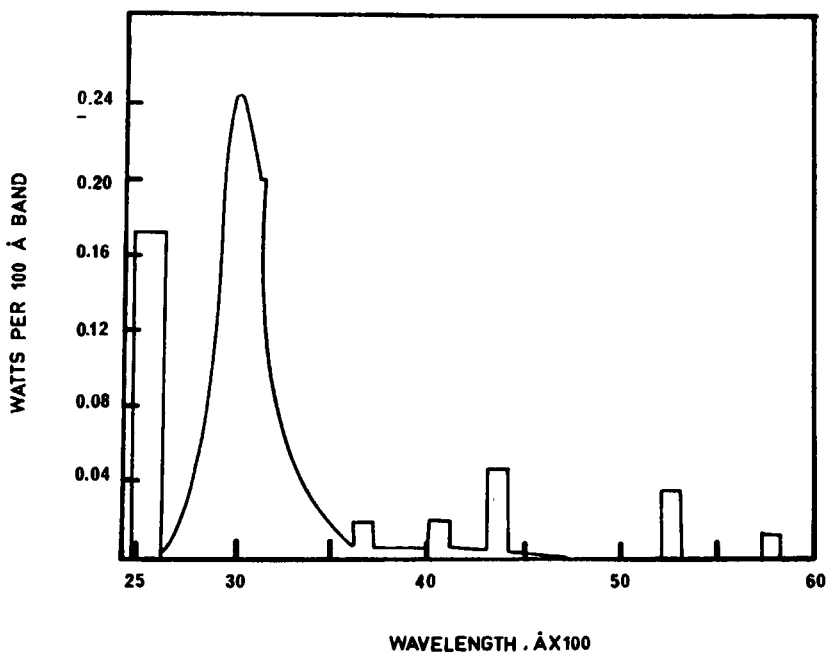
WAVELENGTH , Å X100

Fig. 1. Spectral energy distribution of RPR-3000 Å lamps.

supply ultraviolet absorbence data.   This provided a good means of check-
ing reproducibility of results which appeared quite satisfactory.

Analysis of Samples

Degradation was followed by recording the ultraviolet and visible ab-
sorption spectra corresponding to different exposure times.   A Unicam
S.P. 800 continuous scanning spectrophotometer was used to yield the
absorption spectra of the thin films from 2000 to 7000 Å.   The sample
holders were specifically designed so that they could be fitted in the sample
cell of the spectrophotometer without the need to dismantle the films.

The sol and gel fractions of the degraded films were determined by reflux
extraction in THF for 8.0 hr.   The thimble containing the gel portion was
dried in an oven at 80°C for 15 min.   The soluble fraction was obtained
by subtracting the mass of the gel fraction from the total mass of the sample.

THEORY

Two types of processes are commonly observed during the degradation of
vinyl polymers: chain scission and crosslinking of the polymer structure.
It has been observed that both of these processes occur simultaneously dur-
ing the irradiation of PVC.[13,18,19,22]   Charlesby and co-workers[23-25] have
developed the following equations to deal with simultaneous chain scission

and crosslinking of polymers with random initial molecular weight distribution:

$$s + \sqrt{s} = \frac{\alpha}{\beta} + \frac{1}{\beta P_0 E_{at}} \tag{1}$$

where P_0 is the initial number-average degree of polymerization; α and β are the numbers of scissions and crosslinks, respectively, per mer per unit dose; E_{at} is the energy absorbed by the sample during time t; and s is the weight fraction of the soluble part of the sample at time t. In the derivation of eq. (1), it was assumed that the quantum yields α and β are constant.

A number of workers have employed eq. (1) by assuming that the intensity of absorbed light is constant with time, thus:

$$s + \sqrt{s} = \frac{\alpha}{\beta} + \frac{1}{\beta P_0 I_a t} \tag{2}$$

where I_a is the intensity of absorbed light, which is assumed to be constant. Under these conditions, a plot of $(s + \sqrt{s})$ versus $(1/t)$ should yield a straight line. The slope and intercept of the line may be coupled with known values of P_0 and I_a to yield the values of α and β.

In many cases involving ultraviolet radiation, the intensity of absorbed light varies with time of exposure even when the intensity of incident light is constant. This is mainly due to the continuous change in the absorbence spectra of the exposed sample as a result of degradation. It will be shown later that PVC degradation leads to a substantial change in the ultraviolet absorbence spectra under the conditions of the present study. Therefore, the application of eq. (2) is not valid, and eq. (1) must be employed in this case. Furthermore, it is necessary to recognize that E_{at} consists of polychromatic components in the ultraviolet region between 2800 Å and 3300 Å.

From the definition of the absorbence $A_{\lambda t}$, at a given wavelength λ and time t, the increment of energy, $dE_{a\lambda t}$, which is absorbed by the film at wavelength λ between times t and $t + dt$ after the beginning of exposure is given by

$$dE_{a\lambda t} = I_{0\lambda}(1 - 10^{-A_{\lambda t}})dt \tag{3}$$

where $I_{0\lambda}$ is the intensity of incident light at wavelength λ, which is assumed to be constant. The total energy of wavelength λ that is absorbed between the beginning of exposure and time t is obtained by integrating eq. (3):

$$E_{a\lambda t} = I_{0\lambda} \int_0^t (1 - 10^{-A_{\lambda t}})dt. \tag{4}$$

By definition, the fractional transmittance $T_{\lambda t}$ at wavelength λ and time t is given by

$$T_{\lambda t} = 10^{-A_{\lambda t}}. \tag{5}$$

Then, eq. (4) may be rewritten as follows:

$$E_{a\lambda t} = I_{0\lambda} \int_0^t (1 - T_{\lambda t}) \, dt. \tag{6}$$

The value of $I_{0\lambda}$ is known from the spectral energy distribution of the light source at the sample position. For simplicity, the cumulative energy is normalized by assigning to $I_{0\lambda}$ a value of unity at 3000 Å since the light source peaks at that wavelength. Thus, the cumulative amount of energy absorbed by the sample at wavelength λ in time t may be calculated from a knowledge of the absorption or transmission spectra as a function of time. The total amount of cumulative energy which is absorbed by the sample at all wavelengths, E_{at}, is given by

$$E_{at} = \sum_\lambda E_{a\lambda t} \tag{7}$$

or

$$E_{at} = \sum_\lambda \left(I_{0\lambda} \int_0^t (1 - T_{\lambda t}) dt \right) \tag{8}$$

where summation is carried over values of λ between 2800 Å and 3300 Å to cover the range of emission by the light source. Integration and summation were carried out by means of the trapezoidal rule on the digital computer.

RESULTS AND DISCUSSION

Spectral Analysis

Poly(vinyl chloride) is essentially transparent to ultraviolet radiation above 2800 Å. However, it is known to exhibit severe yellowing to ultraviolet light in this wavelength range. Some of the proposed mechanisms assume that structural abnormalities in the polymer or the presence of impurities might be responsible for degradation and color development. It appears from the present study that traces of solvent may contribute significantly to the degradation and yellowing of PVC.

Figures 2 and 3 show the ultraviolet absorption spectra of PVC films cast from THF and DCE, respectively. These spectra are compared to the absorption spectra of the corresponding pure solvent in each case. Films cast from THF exhibit a characteristic peak at 2800 Å which is also associated with THF. Further studies on infrared spectra, which are not shown here, confirm the presence of traces of THF in these films. In the case of DCE, Figure 3 shows that films cast from DCE have a characteristic peak at 1900 Å which appears to be associated with the high absorbance of the solvent in that wavelength range. It was possible to adjust the level of the characteristic peak in each film type by controlling the drying conditions, but it was not possible to eliminate either of the two peaks completely. A comparion between Figures 2 and 3 on one hand and Figures

4 and 5 on the other shows the effects of varying solvent levels on the height of the characteristic peak for each film type.

In order to determine the effect of residual solvent on the rate and magnitude of degradation of films, studies were conducted on films of varying residual solvent levels, as indicated by the height of the characteristic peak for each solvent system. Typical spectral data before and after degradation are shown in Figures 4 and 5. The effect of THF on degradation, as measured by changes in absorption spectra, is shown in Figures 6, 7, and 8,
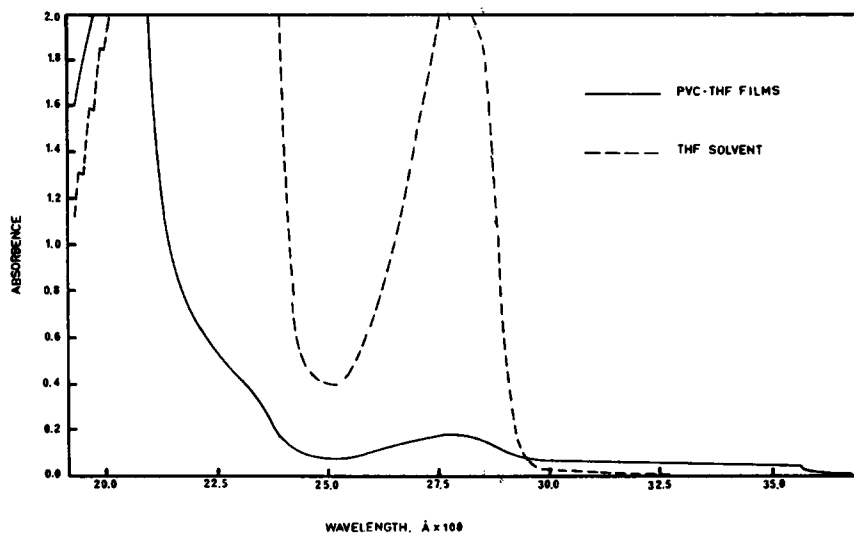
Fig. 2. Ultraviolet absorption spectra for PVC–THF films and THF.
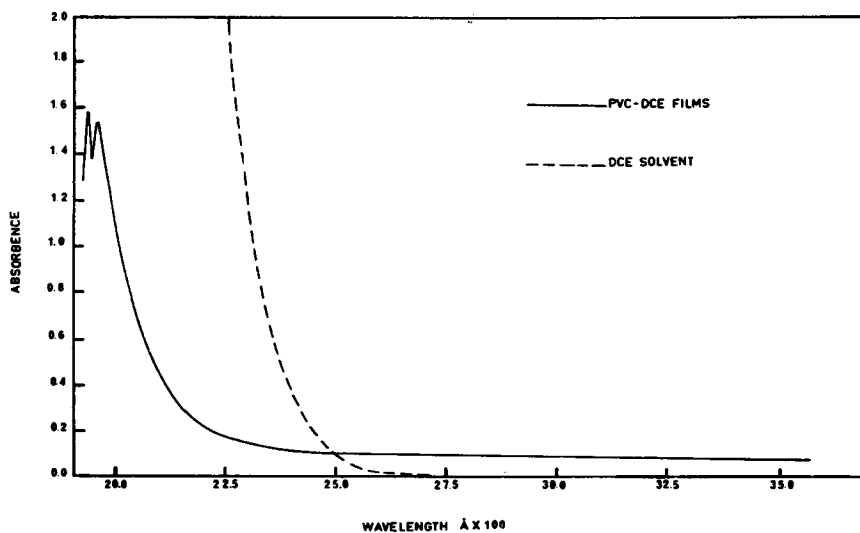
Fig. 3. Ultraviolet absorption spectra for PVC–DCE films and DCE.

while the effect of DCE is shown in Figures 9, 10, and 11.   In each case, it is obvious that the rate of degradation increases with an increase in the level of residual solvent.   Degradation is largest and fastest at the short wavelength end, but changes in absorption at the long-ultraviolet and vis-
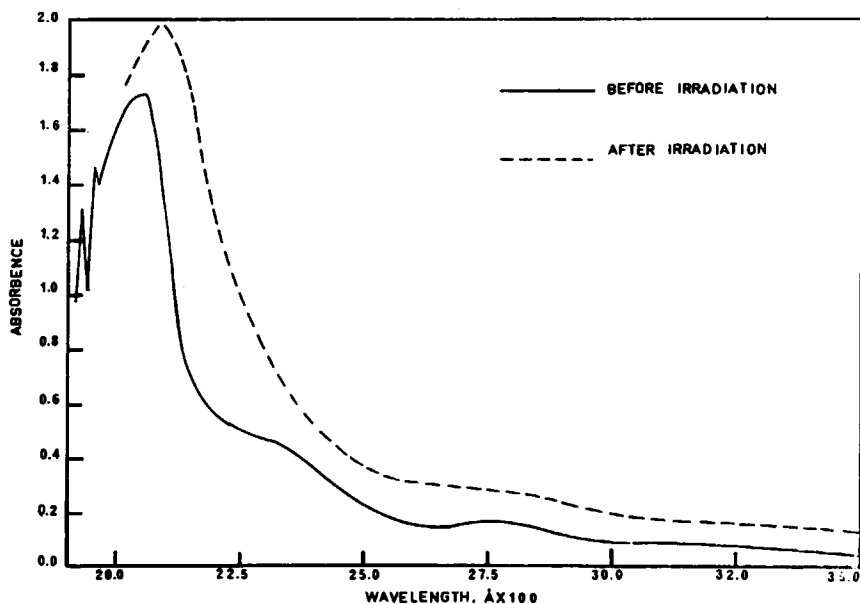

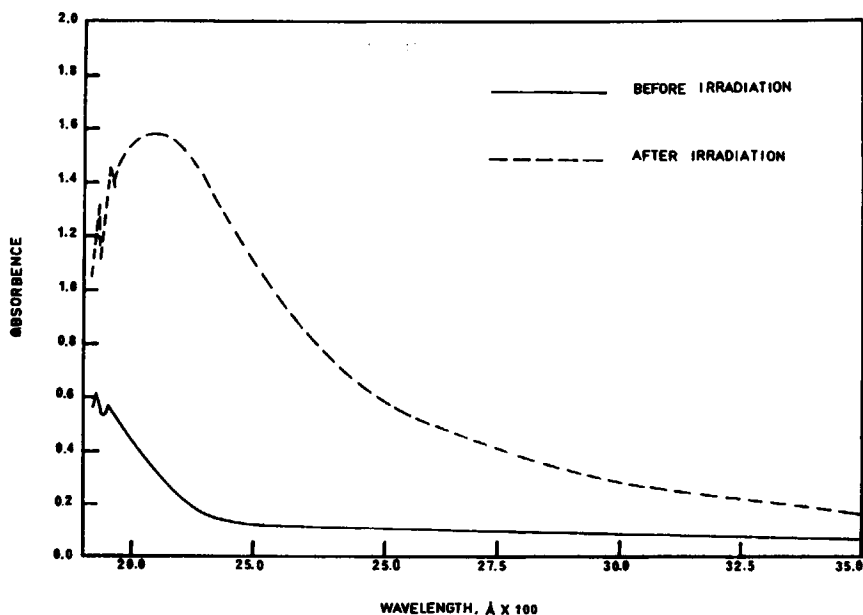Fig. 4. Typical absorption spectra for PVC–THF films before and after irradiation.

Fig. 5. Typical absorption spectra for PVC–DCE films before and after irradiation.

ible ends of the spectra become more evident after long exposure times. This is in agreement with experience on the ultraviolet degradation of many polymers.[26]   It is interesting to compare the rates of degradation, as measured by the rates of change in absorption spectra, for a short wavelength (3000 Å) and a long wavelength (5000 Å).   For the bulk of samples covered
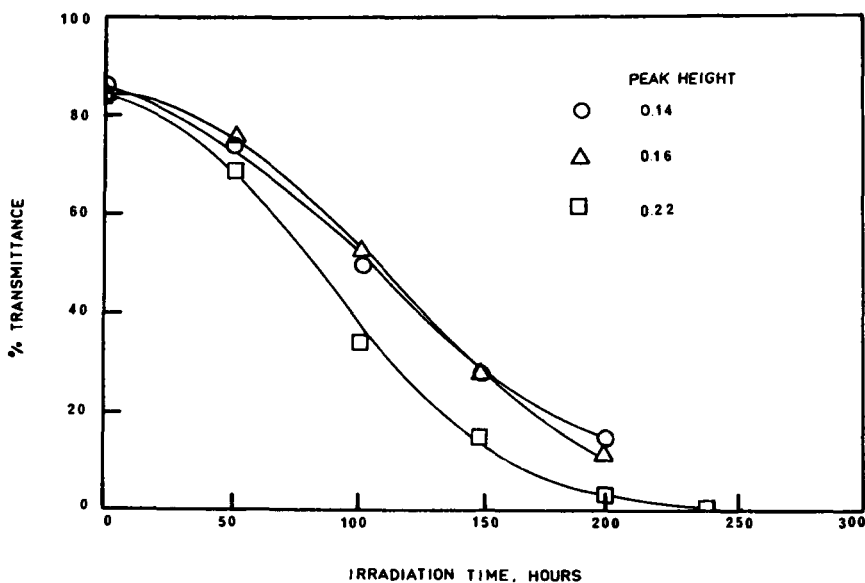

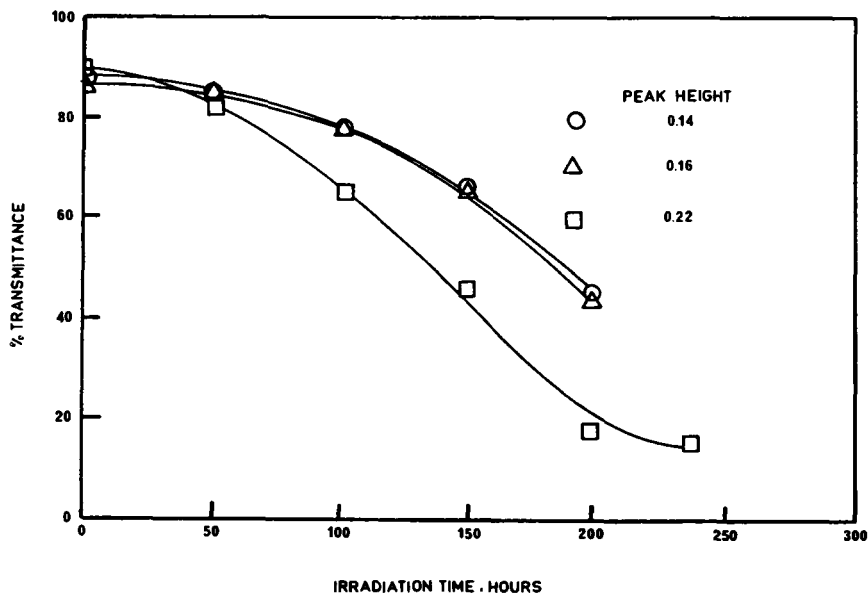Fig. 6. Changes of transmittance for PVC–THF films at 3000 Å.

Fig. 7. Changes of transmittance for PVC–THF films at 4000 Å.

in this study, the rates of change of absorbence at 3000 Å during the first
100 hr of exposure are 5–15 times the rates of change of absorbence at
5000 Å. This is in general agreement with the observation that long se-
quences of conjugated double bonds are required for color development.
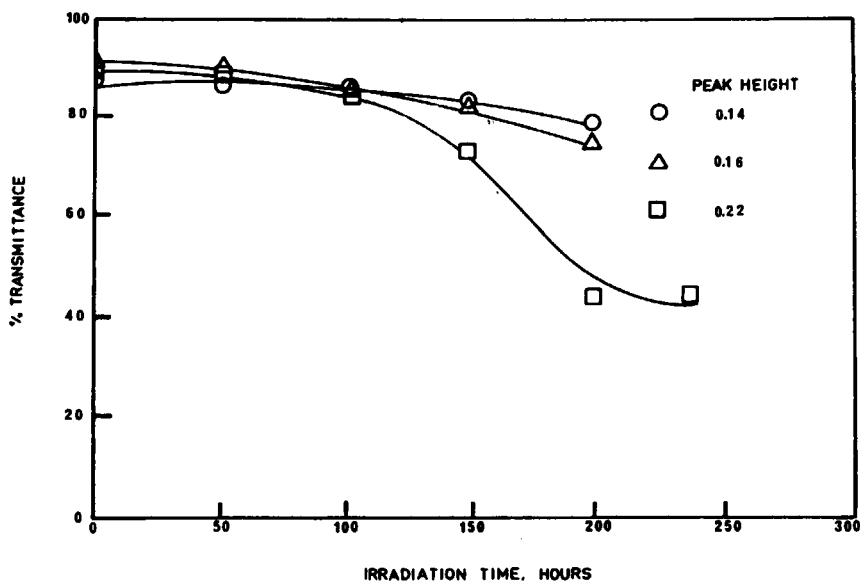Absorption at the 3000 Å may be associated with short doulbe-bond struc-

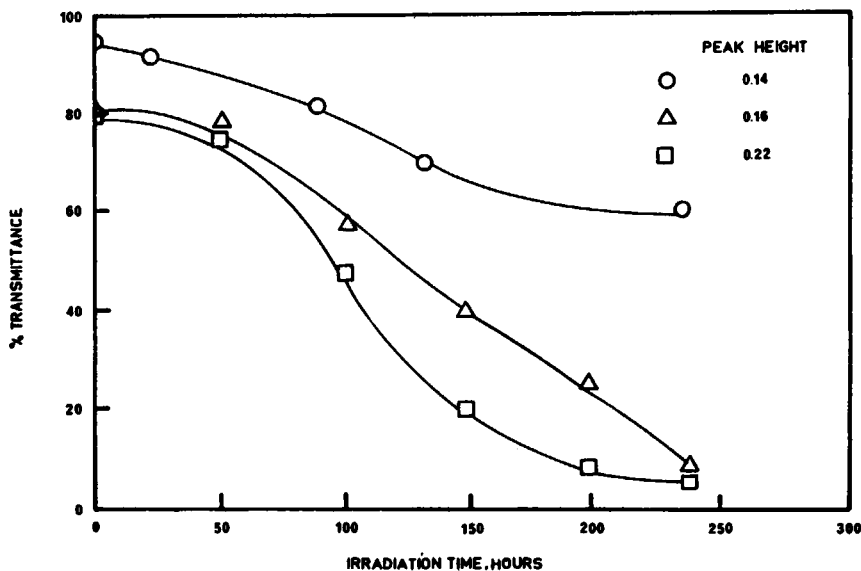Fig. 8. Changes of transmittance for PVC–THF films at 5000 Å.

Fig. 9. Changes of transmittance for PVC–DCE films at 3000 Å.

tures,[27] while absorption at 5000 Å may be related to the longer sequences. The fact that the ratio varies in the range of 5–15 may reflect the influence of factors like oxidation and solvent type.[7,28]

The above evidence suggests that color development and changes in the ultraviolet spectra of PVC upon ultraviolet irradiation are enhanced consid-
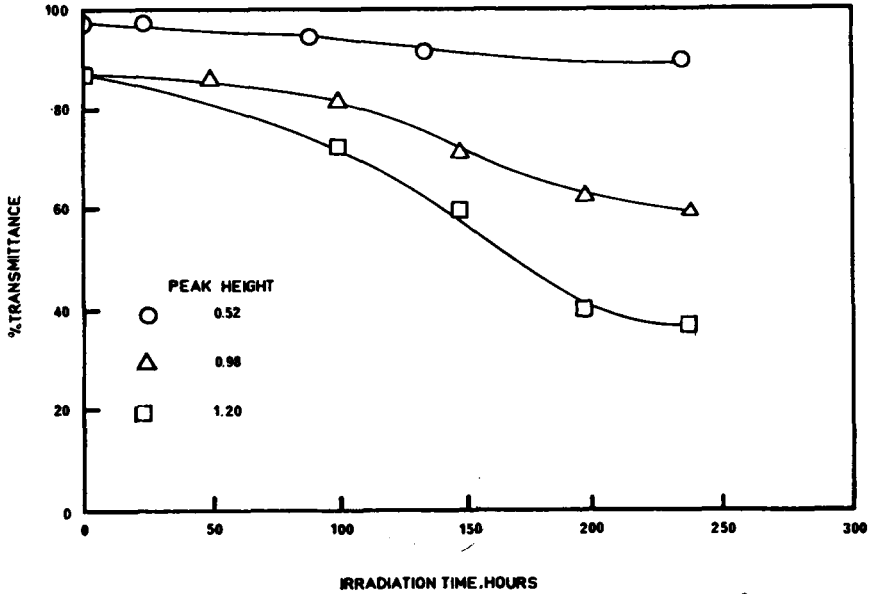

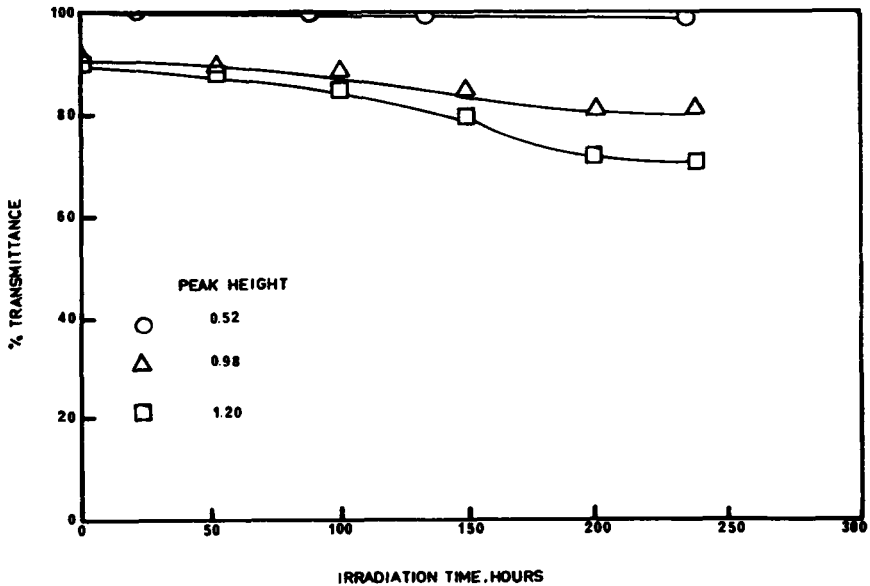Fig. 10. Changes of transmittance for PVC–DCE films at 4000 Å.

Fig. 11. Changes of transmittance for PVC–DCE films at 5000 Å.

erably by residual traces of THF and DCE. The stability of films with the smallest traces, as indicated by the lowest characteristic absorption peaks, is very good and appears to be substantially better than the ultraviolet stability heretofore reported for virgin, unstabilized PVC. In fact, some of the most stable films were the thinnest, and many of them were in the range of 0.1–0.2 mil in thickness. Thus it is possible to deduce that PVC in itself is rather stable to ultraviolet radiation, as one would expect from a material which is transparent to ultraviolet radiation. These results also indicate the importance of removing traces of solvents from PVC in order to ensure good outdoor weatherability characteristics. Moreover, ultra-violet spectral analysis may be used as a useful quality control technique in the production of outdoor-grade PVC.

Solubility Analysis

As shown in the above discussion, the ultraviolet absorbence of PVC films changed substantially over a wide range of wavelengths during irradiation. Accordingly, it would be wrong to employ eq. (2), and the application of Charlesby's analysis would require the coupling of eqs. (1), (6), and (8). Kwei[19] reported success in employing eq. (2) for the degradation of PVC formulations under the influence of 2537-Å radiation. Possibly, Kwei's samples possessed very high absorbence at this wavelength leading to the eventual absorption of all incident radiation at all stages of exposure. Under these conditions, the application of eq. (2) would be valid. It is
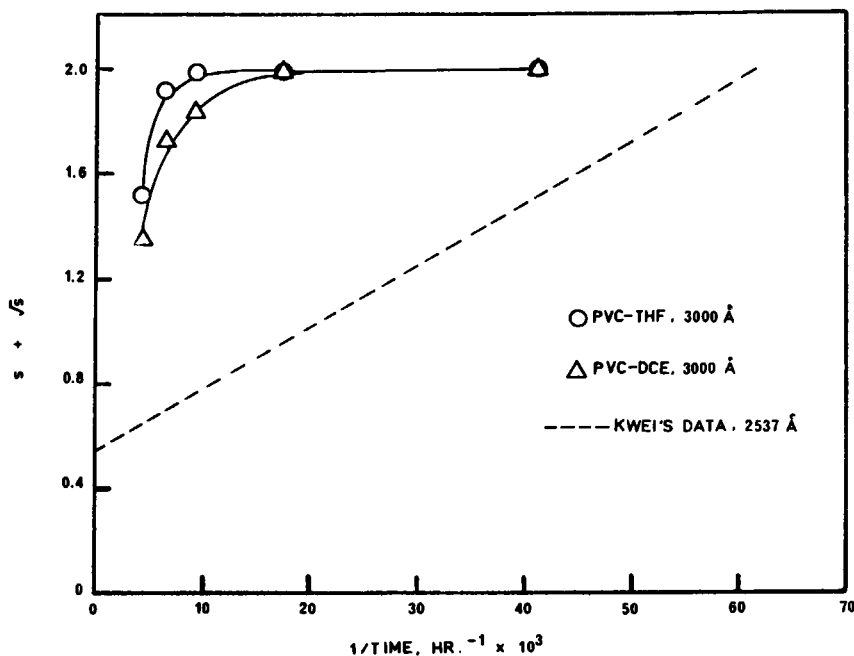

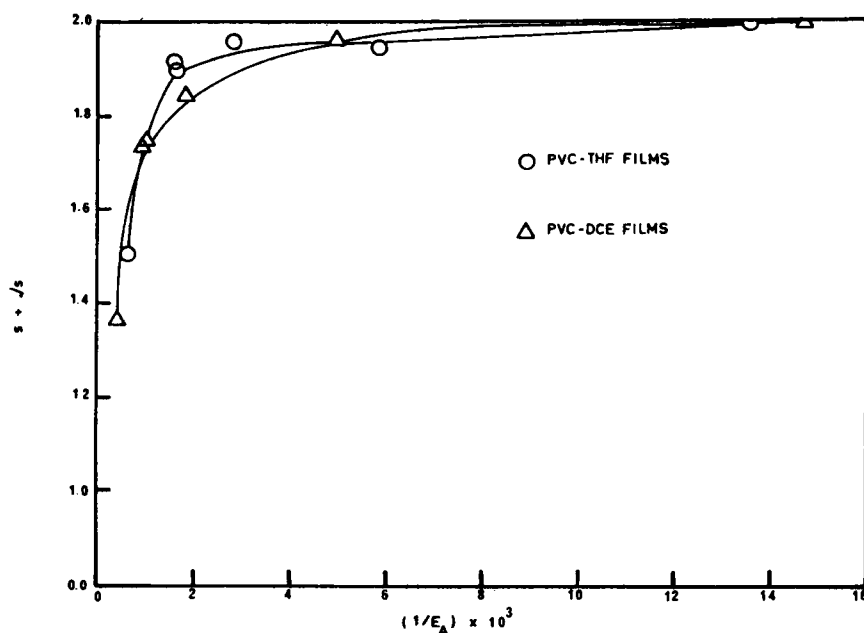Fig. 12. Comparison of irradiation results at 2537 Å and 3000 Å.

Fig. 13. Variation of sol fraction with normalized cumulative absorbed energy.

interesting to note that Kwei observed a small absorption peak at 2800 Å for the films that were cast from THF solutions. This is in agreement with our observations, although Kwei did not attempt to relate degradation rates to the magnitude of the peak.

Figure 12 shows a plot of $(s + \sqrt{s})$ versus $(1/t)$ for comparison with Kwei's data. It is obvious that irradiation at 2537 Å causes more severe degradation than exposure at 3000 Å. It also appears that crosslinking is predominant from the start under 2537 Å, whereas there is a gradual shifting from chain scission to crosslinking-controlled degradation at 3000 Å.

A plot of $(s + \sqrt{s})$ versus $(1/E_{at})$ is shown in Figure 13. The results show that there is only a small difference between samples prepared from THF and DCE solutions. The nonlinearity of the curves suggests that Charlesby's model for simultaneous random crosslinking and chain scission does not adequately describe the degradation process of PVC under the conditions of this study. This is mainly due to the apparent shift in the mechanism of degradation from a situation where chain scission is controlling in the early stages of irradiation to one in which crosslinking is controlling. Thus, the assumption of constant α and β, and consequently a constant value of α/β, is not valid in this study. A comparison between Figures 12 and 13 suggests that the effect of irradiation dose on solubility is not as abrupt as indicated by a plot of $(s + \sqrt{s})$ versus $(1/t)$ as in Figure 12. Furthermore, Figure 13 indicates that the effect of solvent type on changes in solubility is less significant than that indicated in Figure 12. In fact, it

appears that solubility changes are independent of the type of residual solvent during irradiation. The nature of the above conclusions was generally unchanged by changing the breadth of the wavelength band over which the summation in eq. (8) was carried out.

CONCLUSIONS

It has been shown in this study that the presence of traces of solvents like tetrahydrofuran and dichloroethane enhances the ultraviolet degradation of PVC films. This is manifested by more rapid changes in the UV absorption spectra and color as the level of solvent is increased. Thin films of PVC that have very small traces of residual solvent possess very good ultraviolet stability, even when no ultraviolet stabilizers are employed. The analysis of the ultraviolet absorption spectra of PVC offers a useful technique for the early detection of degradation, especially in connection with color development. An attempt to apply Charlesby's analysis to the ultraviolet degradation of PVC films at 3000 Å has not been successful due to the shifting from chain scission-controlled degradation in the early stages of exposure to crosslinking-controlled degradation at later stages. Ultraviolet degradation of films at 2537 Å appears to be much faster than degradation caused by 3000 Å irradiation. The former also appears to be mainly controlled by crosslinking from the start of degradation.

List of Symbols and Abbreviations

$A_{\lambda t}$ absorbence of sample at wavelength λ and exposure time t
DCE   dichloroethane
E_{at} cumulative energy absorbed by the sample at exposure time t
$E_{a\lambda t}$ cumulative energy absorbed by the sample at wavelength λ and exposure time t
I_a intensity of absorbed light
$I_{0\lambda}$ intensity of incident light with wavelength λ
P_0 number-average degree of polymerization before exposure
PVC   poly(vinyl chloride)
s weight fraction of the soluble portion of the degraded sample
t time of exposure
$T_{\lambda t}$ transmittance of the sample at wavelength λ and time t
THF   tetrahydrofuran

Greek Symbols

α number of scissions per mer per unit dose
β number of crosslinks per mer per unit dose
λ wavelength

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