The Photo-Oxidation of Poly(Vinyl Chloride) Investigated by a Stress Relaxation Technique

W. C. COX, D. J. CRAWFORD, and P. L. D. PEILL, *Polymers Section, Chemical Research Division, British Railways' Technical Centre, London Road, Derby, England*

Synopsis

A stress relaxation technique was used to study the kinetics of the photo-oxidation of plasticized poly(vinyl chloride) film.   The effects of ultraviolet irradiation were characterized by the slope of a difference line between the stress relaxation curve of an irradiated test sample and that of a nonirradiated control.   An activation energy of 12 kcal/-mole was obtained for the rate-controlling reaction, which was postulated to be hydrogen abstraction from the substrate by peroxy radicals.   The rate of relaxation was dependent on the radiation energy, being greater at lower energies.   It was also independent of oxygen pressure at "high" pressures and dependent at "low" pressure.   The nature of the plasticizer and the presence of stabilizers and ultraviolet absorbers all affected the relaxation behavior.

INTRODUCTION

It has been stated by Mack[1] that "the effect of light on vinyl resins is quite different from that of heat.   In the latter case there is considerable discoloration but very little loss of mechanical properties.   However, when a vinyl film is exposed to light, loss in tensile strength and embrittlement on prolonged exposure are quite pronounced."   Nevertheless, few attempts have hitherto been made to measure the changes in the mechanical properties of such materials brought about by photoinduced reactions and even fewer have been made in a manner capable of interpretation in terms of chemical reaction mechanisms and their kinetics.   Changes in the tensile properties of several polymers exposed to ultraviolet irradiation have been studied by Stephenson et al.[2,3] and, more recently, accounts have appeared of the effects of such irradiation on the creep rate of polymers.[4]

The oxidative aging of a natural rubber vulcanizate under ultraviolet irradiation has been investigated by Dunn[5] using a stress relaxometer described by Dunn and Scanlan.[6]   It seemed probable that a similar technique could be used to investigate the photodegradation of an extensible polymer such as plasticized PVC.   The present paper describes the work carried out to verify this assumption.

Because of the viscoelastic nature of PVC, it was not possible directly to interpret the stress relaxation curves as were those of rubber by Dunn et al.[7]

Neither did analysis of plasticized PVC stress relaxation data using the seven-parameter Maxwell representation employed by Sabia and Eirich[8] seem likely to provide the desired information.

Resort was therefore made to the direct subtraction of the curve obtained for an irradiated sample from that of an unirradiated control relaxed at the same temperature. It was hoped that this would eliminate the complexities of the response of PVC to stress relaxation and so isolate, in some degree, the effects of ultraviolet irradiation. In fact, a linear difference curve was obtained and the procedure was consequently adopted as standard practice in the work here reported.

EXPERIMENTAL

Materials

The materials used are listed in Table I below.

TABLE I
Materials Used

Name	Proportion used	Supplier
PVC:Corvic P.65/50	100 parts	ICI Ltd.
Plasticizers		
TTP (tritolyl phosphate)	70 parts	Lankro Chemicals Ltd.
D79P (dialkyl phthalate)	60 parts	Lankro Chemicals Ltd.
Stabilizers		
Lankroflex ED6 (an octyl epoxy stearate)	5.0	Lankro Chemicals Ltd.
Lankro Mark LL (liquid barium-cadmium system)	1.5	Lankro Chemicals Ltd.
Ultraviolet Absorbers		
UV 9 (2-hydroxy-4-methoxy-benzophenone)		Cyanamid International
UV 24 (2,2'-dihydroxy-4-methoxy-benzophenone)		Cyanamid International

Preparation of Film

A plastisol technique was employed, in which the compounds were thoroughly mixed on a triple-roll mill to ensure complete dispersion and then subjected to a partial vacuum to remove entrapped air. Specimens were prepared on a thin glass sheet using a hand-operated spreader, giving films of "dry" thickness 0.005 in. (0.13 mm) after curing. Optimum curing

times were determined empirically, using tensile strength as the criterion. TTP-plasticized films were cured for 9 min and D79P-plasticized films for 7 min, both at 200°C. The films were cut into strips of 0.5-cm width and marked at 4-cm length. The test and control samples were taken from the same cured sheet.

Apparatus and Procedure

Two automatically operating helical spring relaxometers were employed.[6] The sample was mounted between two clamps, the lower one fixed and the upper attached to a calibrated spring, via a stirrup. On stretching (usually 50%), the stress in the sample was balanced by extending the spring until electrical contacts on the stirrup and on the body of the relaxometer nearly touched. Reduction in the stress in the PVC strip as it relaxed allowed the stirrup to move slightly, thereby closing the contacts, completing an electrical circuit and operating a device which reduced the spring extension by a definite amount. The closing of the contacts also actuated a timeprinter. In this way were obtained a measured series of time intervals during each of which a constant decrement in the tension had occurred. From these measurements a complete stress–time curve of considerable accuracy was constructed.[6]

The springs were calibrated by means of load–extension curves, determined on a Cambridge Extensometer. The ratio of extension to number of turns of the screw to which the spring was attached was found with the aid of a travelling microscope. From these relationships, the absolute values of stress could be calculated.

The relaxometers were mounted in quartz tubes, through which oxygen or nitrogen could be passed at a constant flow rate sufficient to remove degradation products or which could be left open to the atmosphere.

Each stage in the mounting of the films in the relaxometer, their extension, the insertion of the relaxometers into their tubes, and final assembly in the bath was carried out to a rigid time schedule in order to ensure reproducible conditions.

The whole assembly is illustrated in Figure 1. The ultraviolet source was a 250-watt ME/D medium pressure mercury arc lamp from which the Pyrex window had been removed and replaced by a quartz disc of equal thickness. In a few experiments a low pressure (monochromatic) mercury lamp was used. The geometry of the irradiation system was kept constant and the intensity of the light received by the test sample was monitored at periodic intervals by means of a selenium photocell. Data were collected from new lamps only after their intensity had become stable (approx. three weeks).

THEORY

Two sets of data were obtained, one relating to the stress decay in the sample subjected to thermal effects only, and the other to the superimposed
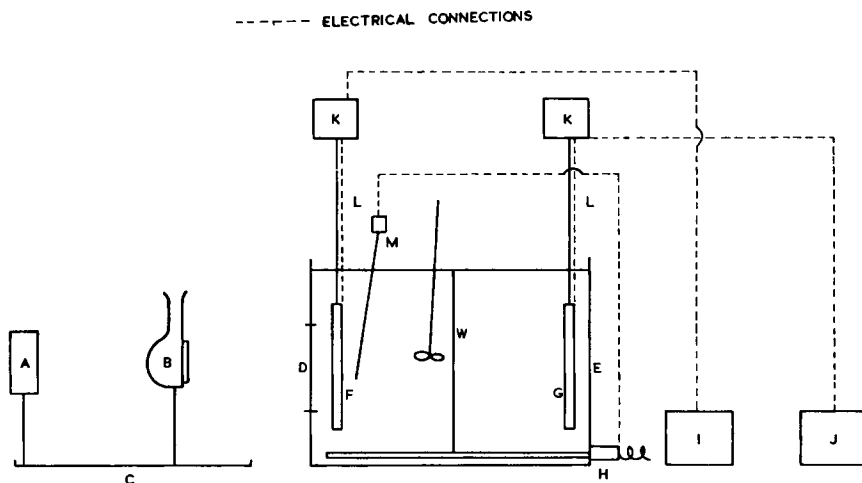
Fig. 1. Diagrammatic drawing of apparatus: (A) ultraviolet source (see text); (B) lens (quartz flask, water-filled, and 'frosted' quartz disc); (C) optical bench; (D) quartz window; (E) bath containing silicone fluid (MS 200); (F,G) quartz relaxometer tubes, test and control; (H) heater; (I,J) timeprinters, test and control; (K) motor units; (L) rotor shafts; (M) thermostat; (W) shield.

effects of ultraviolet irradiation. Plots of the data revealed that the decay curves became approximately Maxwellian[9] after about 4 hr and both could be represented by decreasing exponentials.

For the control sample,

$$S_1 = S_{01}e^{-k_1 t} \qquad (1)$$

and for the test sample,

$$S_2 = S_{02}e^{-k_2 t} \qquad (2)$$

where S_1 and S_2 are stress at time t, and S_{01} and S_{02} are stress when $t = 0$.

Since the difference between the test and control curves was slight, the assumption that both sets of data could be represented by the same function was held to be justified.

Plots of $\ln(S/S_0)$ against t gave nearly straight lines of nominal slope k, over the time considered. Subtraction of the control from the test curve in this equilibrium region resulted in a straight line of slope K, which was found to be reproducible for and characteristic of the system:

$$\ln \frac{S_1}{S_{01}} - \ln \frac{S_2}{S_{02}} = (k_2 - k_1)t = Kt. \qquad (3)$$

The slope K, indicative of the effects of irradiation, has the dimensions of a rate constant; its value is determined by (i) PVC formulation; (ii) temperature; (iii) radiation (inherent intensity, energy distribution, and ge-

ometry of layout, i.e., number of photons above a certain minimum energy incident on sample), and (iv) atmosphere.

The variation of K with absolute temperature T may be represented by an Arrhenius equation:

$$K = A\ e^{-Es/RT}$$

where A is equivalent to the collision number for simple molecular reactions and E is the energy of activation characteristic of the stress relaxation system.

We have assumed that the stress ratio is numerically equal to the relative concentration of elastically active network chains, C/C_0. The stress in the sample will normally be evenly distributed over the total number of chains and so the stress through a small rectangular segment will be proportional to the number of polymer chains passing through the segment. Under our exposure conditions, the stress is assumed to decay by main chain breakages, which cause a proportional decrease in the concentration of network chains. It follows that the stress and chain concentration ratios are equal for a macroscopic sample, i.e., a large population of chains, and hence the stress relaxation activation energy is equivalent to an activation energy corresponding to chemical changes.

The rate of change of chemical concentration is also a function of the rate of diffusion of broken chains from the unit volume considered. For a given temperature, however, the diffusion rate will be approximately constant, providing, as in the present case, that degradation is not so extensive as to give rise to mutual interference between the diffusing chains.

When a polymer undergoes stress relaxation at constant strain, it has been assumed[10] that any crosslinkages formed are in a relaxed state with respect to the network under tension and are, therefore, not revealed in the stress relaxation data.

Scission processes were found to predominate over crosslinkage processes while the PVC was under irradiation from the ME/D lamp. However, 254 nm irradiation caused such a high rate of crosslinkage that the test specimen actually relaxed more slowly than the control sample, even under continuous stress relaxation conditions. Presumably volume shrinkage occurs, as suggested by Tobolsky.[10] Nevertheless, the effects of 254 nm irradiation have not been fully investigated and are not further discussed here.

If we take the usual chemical rate expression

$$-\frac{dc}{dt} = KC^n, \tag{4}$$

then, for a first-order reaction, we have

$$\ln \frac{C}{C_0} = -Kt. \tag{5}$$

In deriving the generalized logarithmic form of eqs. (1) and (2),

$$\ln \frac{S}{S_0} = -kt, \tag{6}$$

and then assuming the equivalence of stress and concentration, it is implied that the chemical degradation reaction is first order.

A simplified method of presenting the data was also investigated. As before,

$$\frac{S_1}{S_0} = e^{-k_1 t} \tag{1}$$

$$\frac{S_2}{S_0} = e^{-k_2 t} \tag{2}$$

Subtracting eq. (2) from eq. (1) we obtain

$$\frac{S_1 - S_2}{S_0} = e^{-k_1 t} - e^{-k_2 t} \tag{7}$$

Expanding the exponentials yields

$$\frac{S_1 - S_2}{S_0} = (1 - (k_1 t) + \frac{(k_1 t)^2}{(2!)} + \ldots) - (1 - (k_2 t) + \frac{(k_2 t)^2}{2!} + \ldots) \tag{8}$$

i.e., $$\frac{S_1 - S_2}{S_0} = (k_2 - k_1)t + \frac{1}{2}(k_1^2 - k_2^2)t^2 + \text{higher terms} \tag{9}$$

As plots of S/S_0 against t gave difference lines that were straight in the equilibrium region, it appears that terms above the first order may be neglected, giving the approximation

$$\frac{S_1 - S_2}{S_0} = Kt. \tag{10}$$

Calculations of activation energy based on this equation gave slightly different values from those obtained by the more rigorous method, eq. (3), and so the simplified method is not recommended for this purpose. It can be used, however, to characterize the effects of light on a PVC formulation and to evaluate stabilizers, ultraviolet absorbers, etc.

RESULTS AND DISCUSSION

General

Typical stress relaxation curves for irradiated (test) films and shielded (control) films of plasticized PVC are shown in Figure 2. Both samples were subjected to the same temperature. The initial steeply curved portions are due largely to viscous flow characteristic of viscoelastic materials.

After about 4 hr of relaxation, the curves became almost straight and it was usually possible to take readings for a further 6 to 12 hr before the films
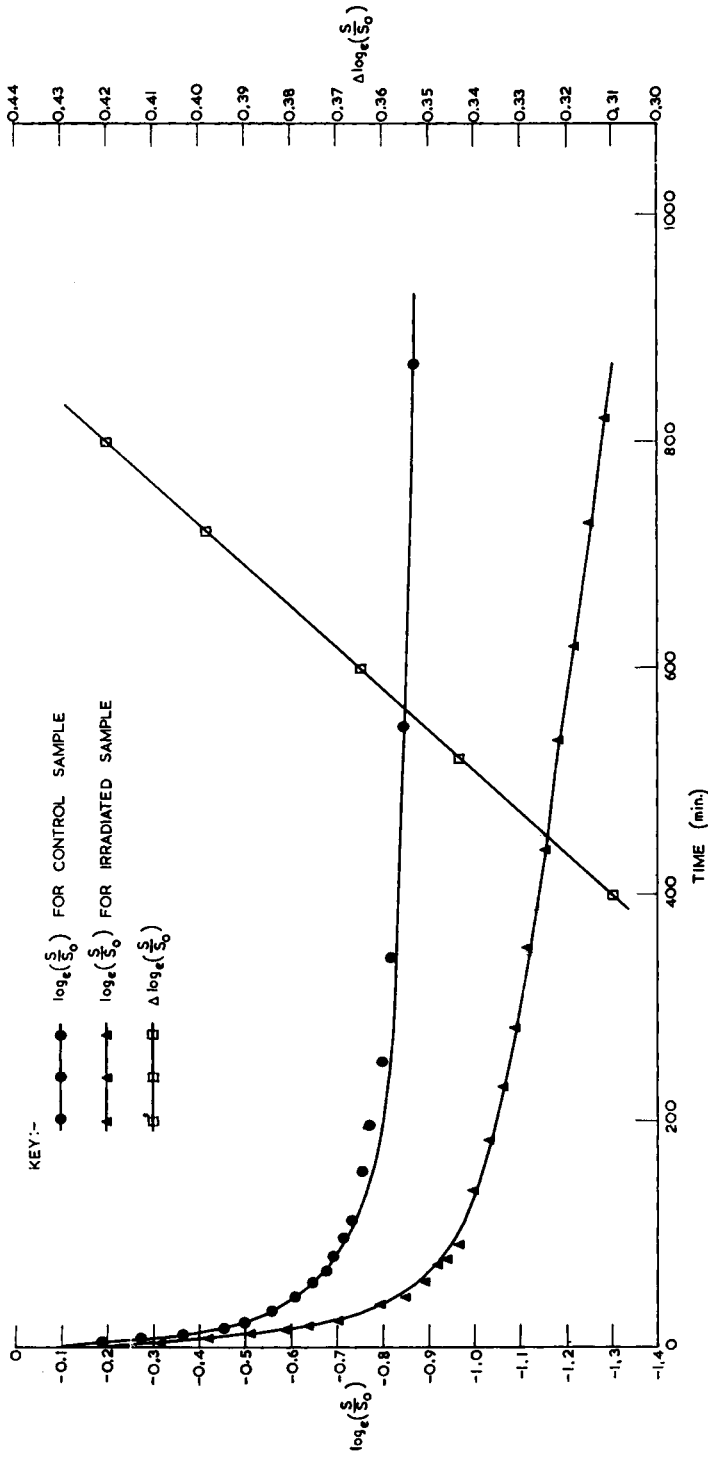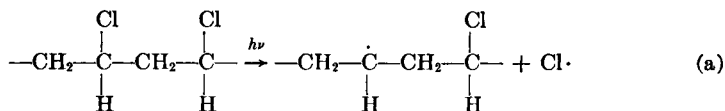
Fig. 2. PVC stress relaxation curves: plasticizer D79P; temperature 82°C.

broke. Difference curves were obtained in this interval, and Figures 2 and 3 show that they were substantially linear.
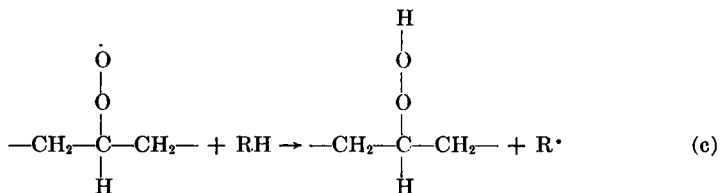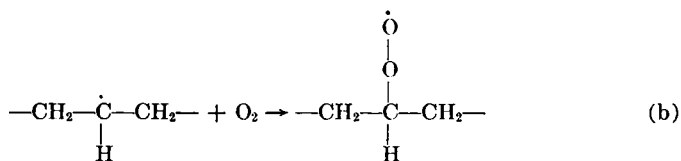
Reproducibility was assessed by making five successive tests on D79P plasticized film at 92°C under identical conditions. The gradients of the difference lines (calculated by the simplified procedure) were within the range $1.90 \times 10^{-3} \pm 2.4 \times 10^{-4}$, for the 95% confidence interval (i.e., coefficient of variation = 10%).

The increased rate of relaxation of the irradiated specimens is believed to be due to scission of the PVC main chains brought about by a photo-initiated first-order reaction. A generally accepted mechanism which results in scission is the photo-oxidative free radical process suggested by Winkler[11]; it is based on the well-known Bolland hydroperoxidation reaction.[12,13]
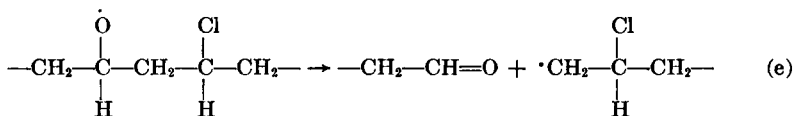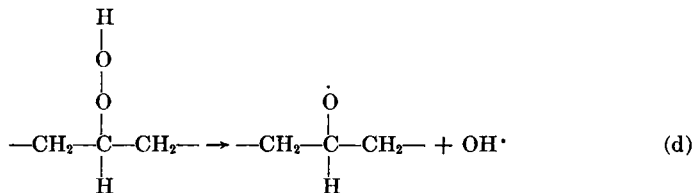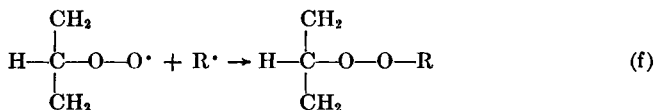
INITIATION

$$\begin{array}{ccc} & \text{Cl} & \text{Cl} \\ & | & | \\ -\text{CH}_2-\text{C}-\text{CH}_2-\text{C}- & \xrightarrow{h\nu} & -\text{CH}_2-\overset{\cdot}{\text{C}}-\text{CH}_2-\text{C}- + \text{Cl}\cdot \\ & | \quad\quad | & | \quad\quad | \\ & \text{H} \quad\quad \text{H} & \text{H} \quad\quad \text{H} \end{array} \qquad (a)$$

OXIDATION—PROPAGATION

$$-\text{CH}_2-\overset{\cdot}{\underset{\text{H}}{\text{C}}}-\text{CH}_2- + \text{O}_2 \rightarrow -\text{CH}_2-\overset{\overset{\displaystyle \cdot\text{O}}{\overset{|}{\text{O}}}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2- \qquad (b)$$

$$-\text{CH}_2-\overset{\overset{\displaystyle \cdot\text{O}}{\overset{|}{\text{O}}}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2- + \text{RH} \rightarrow -\text{CH}_2-\overset{\overset{\displaystyle \text{H-O}}{\overset{|}{\text{O}}}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2- + \text{R}\cdot \qquad (c)$$

SCISSION

$$-\text{CH}_2-\overset{\overset{\displaystyle \text{H-O}}{\overset{|}{\text{O}}}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2- \rightarrow -\text{CH}_2-\overset{\overset{\displaystyle \cdot\text{O}}{}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2- + \text{OH}\cdot \qquad (d)$$

$$-\text{CH}_2-\overset{\overset{\displaystyle \cdot\text{O}}{}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{Cl}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2- \rightarrow -\text{CH}_2-\text{CH}{=}\text{O} + \cdot\text{CH}_2-\overset{\text{Cl}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2- \qquad (e)$$

CROSSLINKING

$$\text{H}-\overset{\overset{\displaystyle \text{CH}_2}{|}}{\underset{\underset{\displaystyle \text{CH}_2}{|}}{\text{C}}}-\text{O}-\text{O}\cdot + \text{R}\cdot \rightarrow \text{H}-\overset{\overset{\displaystyle \text{CH}_2}{|}}{\underset{\underset{\displaystyle \text{CH}_2}{|}}{\text{C}}}-\text{O}-\text{O}-\text{R} \qquad (f)$$
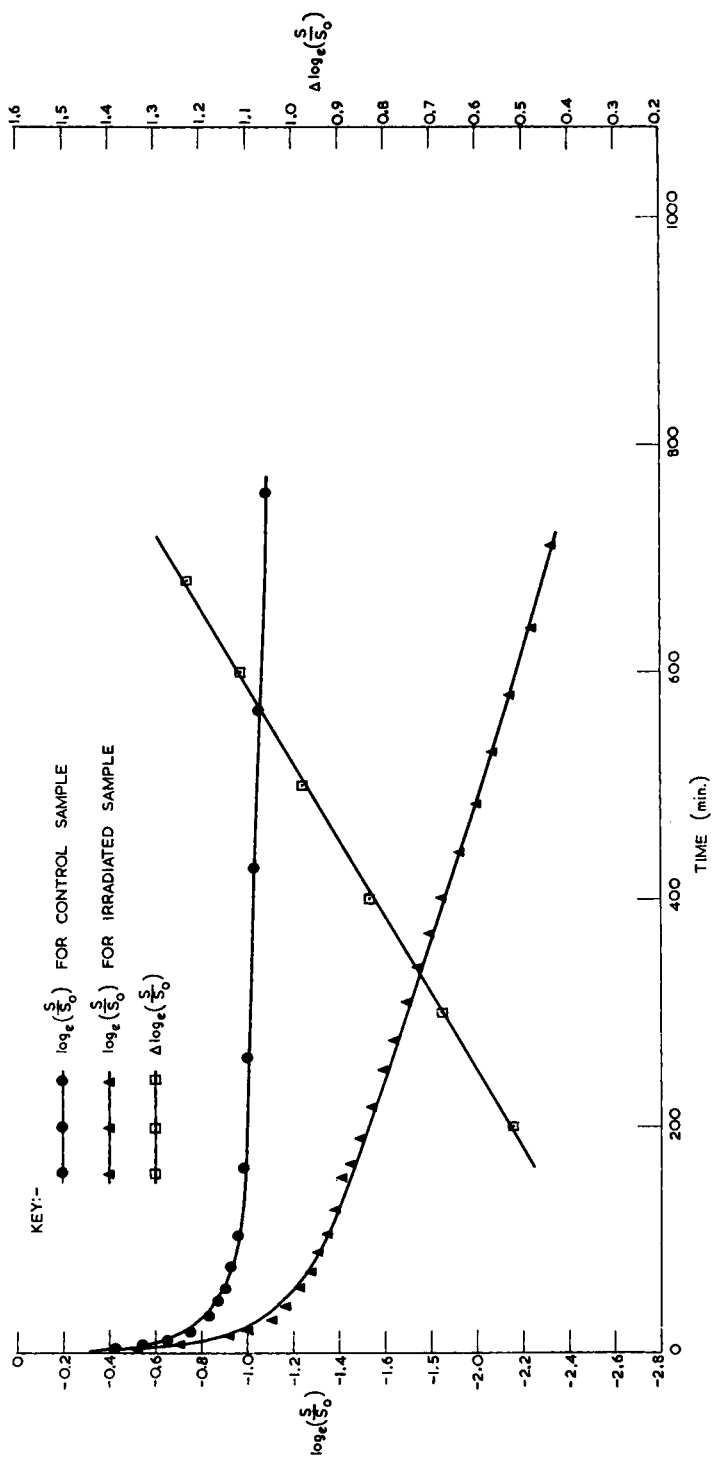
Fig. 3. PVC stress relaxation curves: plasticizer D79P; temperature 118°C.

Activation Energies

Families of difference curves over a range of temperatures were obtained and their slopes were plotted against $1/T$, for D79P and for TTP-plasticized film in air (Fig. 4, calculated by rigorous method), and for D79P film in air and in nitrogen (Fig. 5, calculated by simplified method). In every case, the Arrhenius plot yielded an apparent activation energy of 12 kcal/mole, within the limits of experimental error.

It is interesting to note that Loy[14] obtained an identical figure for the activation energy of the decay of peroxy radicals produced by the irradiation of poly(vinyl chloride). In this work, PVC was irradiated with cobalt 60 at liquid nitrogen temperatures in vacuo, warmed to the desired temperature, and then opened to air. Radical formation and decay were followed by recording their electron spin resonance spectra. Loy found that, at 25°C, the formation of the peroxy radical was virtually complete when the first spectrum was recorded after 24 sec of air exposure. Subsequent spectra, taken over a 45-min period, indicated the exponential decay of the radical. An Arrhenius plot of the apparent rate constants yielded an activation energy of 12 kcal/mole. Similar behavior was observed if the cavity containing the PVC was reevacuated after $3^1/_2$ min of air exposure, indicating that the rate-controlling step does not require oxygen.

The peroxy radical decay was interpreted as a pseudo first-order reaction between the peroxy radicals and the PVC substrate, by hydrogen abstraction from the latter, to form a hydroperoxide and an alkyl radical. Such reactions are known to be strongly influenced by steric factors.[15,16]

Our own observations are also in accordance with Loy's suggested mechanism, the rate-controlling step being reaction (c); and the others, including scission, reactions (d) and (e), and crosslinking, reaction (f), being fast reactions. Crosslinking might well occur by reaction between peroxy and alkyl radicals but this would not normally be detected by the continuous stress relaxation method. It was, however, noted that the irradiated specimens had become stiffer than those which had not been exposed to ultraviolet light, the latter remaining apparently unchanged.

During studies on the benzoyl peroxide-initiated oxidation of thin sheets of various elastomers, by measurement of initial rates of oxygen uptake in the temperature range 60°–100°C, Norling et al.[17] found the activation energy for the formation of hydroperoxide to be 14 kcal/mole in the case of natural rubber and synthetic cis-1,4-polyisoprene and 16 kcal/mole for polypropylene, SBR, ethylene–propylene rubber, ethylene–propylene terpolymer, and other polymers. For squalene, a liquid olefin chemically similar to natural rubber, Bolland[12] reported an activation energy of 11 kcal/mole. By comparison with these figures, 12 kcal/mole would not seem unlikely for the activation energy of hydroperoxide formation in the photo-oxidation of PVC.
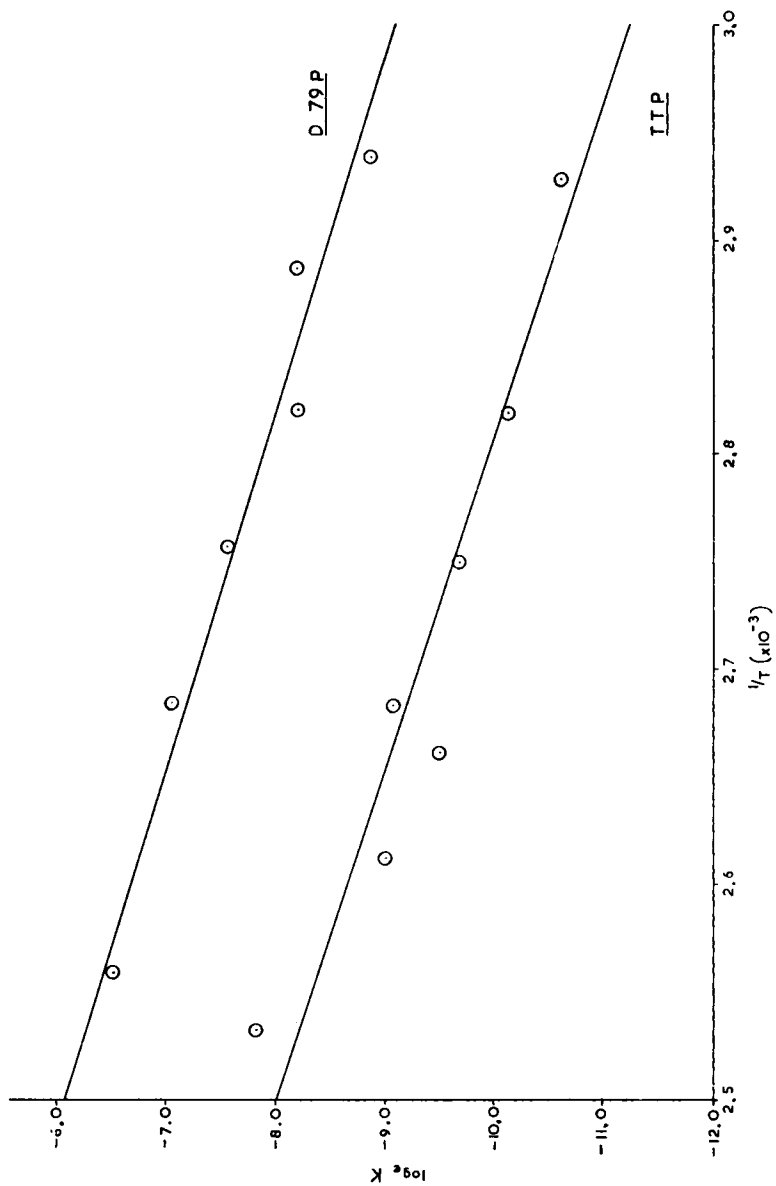
Fig. 4. Arrhenius plot: plasticizers D79P and TTP; $\log_e K \times 1/T$.

Influence of Plasticizers

TTP-plasticized films gave difference lines whose slopes, at a given temperature, were about one-seventh of those given by D79P; their activation energies were however identical (Fig. 4). Ultraviolet absorption spectra of the two plasticizers, between 250 and 290 nm, showed that D79P had an absorbance of about one order of magnitude greater than TTP.

Samples of the D79P and of the TTP plasticizers were exposed to ultraviolet radiation for four days at room temperature. There were no detectable differences between the infrared spectra of these and of the corresponding unexposed samples.

Wippler[18] has reported the marked effect of the presence of TTP, by comparison with dioctyl phthalate, on the mechanical properties of plasticized PVC strips that had been irradiated with gamma rays; he noted a a distinct hardening and increase in rigidity. However, greater extensibility and inhibition of crosslinking (retention of solubility in tetrahydrofuran) were also reported and no explanation could be offered for the observations.

The effects of intense gamma irradiation on plasticized PVC compositions have been investigated by Wells and Williamson.[19] For unpigmented, dioctylphthalate (DOP)-plasticized PVC, they reported an 8% retention of tensile product (tensile strength times elongation) after exposure to 10^8 rads, while for TTP-plasticized PVC the retention was 36%.

During an extensive investigation into the weathering behavior of plasticized PVC compositions, DeCoste and co-workers[20] have reported a 26% retention of tensile strength and a 4% retention of elongation in unpigmented PVC plasticized with DOP, after four years of outdoor exposure, compared with 101% and 57%, respectively, in TTP-plasticized PVC. The explanation was thought to lie in the relative stability to oxidation of the two plasticizers; on heating the two liquids in air at 105°C for 100 hr, it was found that various samples of DOP had absorbed between 25 and 50 times as much oxygen as had been taken up by TTP.

Effects of Atmosphere

D79P-plasticized films were relaxed in oxygen, air, and nitrogen (white spot). No variation could be detected in the gradients of the difference curves for oxygen and air, but those for nitrogen were distinctly lower (Fig. 5, simplified calculation). The activation energies obtained in air and nitrogen were, however, identical (12 kcal/mole). As the nitrogen was not specially purified, it may be assumed that a very low partial pressure of oxygen would be present.

These results are entirely in accordance with the kinetics of the Bolland hydroperoxidation radical chain process, which requires that the reaction rate is independent of or proportional to the oxygen pressure at "high" and "low" (not more than a few millimeters) pressures.[13,16] (For detailed discussion, see Appendix.)
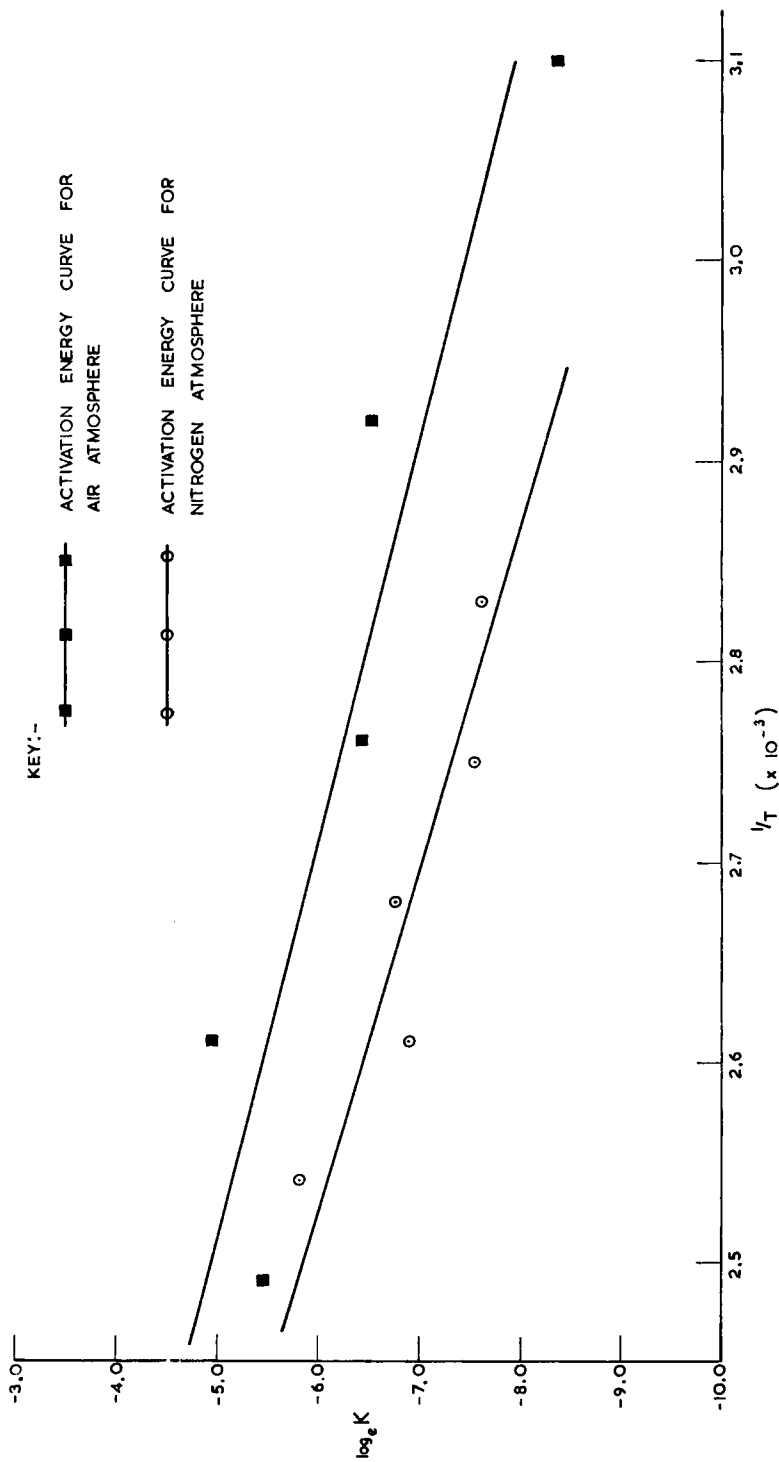
Fig. 5. Arrhenius plot: plasticizer D79P; air and nitrogen atmospheres; $\log_e K \times 1/T$ (simplified method).

Induction Time of Photodegradation

Experiments were carried out in which a film was allowed to relax in the absence of irradiation for about 2 hr and was then suddenly exposed to the ultraviolet source. Conversely, the effect on the relaxation curve of suddenly shielding the test sample from exposure was ascertained. In three PVC systems tested at different temperatures, the introduction or removal of the light source resulted in a sharp change in the slope of the curve; the change appeared to occur in not more than a few minutes. This observation is in agreement with the findings of Loy[14] concerning the rate of formation of peroxy radicals at room temperature and above in γ-irradiated PVC. It also confirms the findings of Regel et al.[4] about the effect of ultraviolet radiation on the creep behavior of polymers.

Effects of Wavelength

Some plasticized PVC films were exposed during stress relaxation to a low-pressure mercury vapor discharge lamp, which gave an intensity of 121 microwatts at 100 cm horizontal distance, of which over 99% is concentrated into the 253.7-nm line. In every instance, although the gradient was small (the test and control curves nearly coincided), the test specimens showed a lower rate of stress relaxation than the controls, i.e., the difference lines possessed a negative slope.

Clearly, crosslinking must have been predominating over scission to such an extent that it was revealed even by the constant strain stress relaxation method; an extremely high rate of crosslinkage must, therefore, have been initiated by the high energy portion of the ultraviolet spectrum. It has been shown by Stephenson et al.[2] that only photons above a certain threshold energy will initiate reactions resulting in scission, and by Grassie[21] that photons of even higher energy are necessary to promote the reactions resulting in crosslinkage.

The profound effects of small differences of wavelength, within the ultraviolet range, on both the rate of stress relaxation and also on the rate of oxygen absorption of natural rubber, have been clearly demonstrated by the work of Morand[22] and her colleagues at the Institut Français du Caoutchouc. It would be surprising if similar effects could not be shown to occur in PVC.

Much more energetic radiation was, of course, used by Loy[14] in his study of the effects of gamma rays on poly(vinyl chloride). No indication was given as to the extent of scission or crosslinking in the resultant polymer, yet the rate-controlling step in the degradation appears to be identical with that occurring on irradiation with ultraviolet rays.

As already mentioned, crosslinking is likely to be brought about by reactions between peroxy and alkyl radicals:

$$R-O-O. + R' \rightarrow R-O-O-R'$$
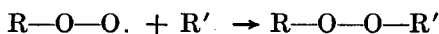
It was not possible to study the effects of the low pressure lamp further as there was no means at that time for removing the considerable amount of ozone produced.

Evolution of Hydrogen Chloride

Hydrogen chloride evolution was measured by a titrimetric method and was found to be small under the conditions obtained in our stress relaxation measurements. During irradiation with the ME/D lamp at 100°C, the quantities evolved were less than 2×10^{-2} mmole/g per hour over a period of 24 hr. On raising the temperature to 180°C, however, the rate of evolution became comparable with that reported by Geddes,[23] namely approximately 8×10^{-2} mmole/g per hour.

When Kenyon[24] irradiated PVC powder with bands of minimum wavelength decreasing from 300 to 235 nm, using an S-4 lamp, he obtained yields of HCl increasing from 1.0×10^{-4} to 1.1×10^{-3} mEq/g per hour. Taken in conjunction with our own results on the effect of wavelength on rates of stress relaxation, it might be surmised that crosslinking in irradiated PVC is a direct consequence of HCl evolution, e.g., by intermolecular dehydrochlorination.

However, Zaitoun[25] has investigated the changes in composition occurring in PVC film as a result of exposure to monochromatic radiation varying from 435 to 302 nm. The latter caused the most drastic changes and it is noteworthy that the proportional increase in oxygen uptake greatly exceeded the loss of chlorine. This tendency was particularly evident in the gel fraction obtained by solvent treatment of 302 nm-irradiated film, which was found to contain as many oxygen as carbon atoms in its empirical formula. This finding is consistent with the postulate that crosslinking in irradiated PVC is brought about by reaction between peroxy and alkyl radicals to form R—O—O—R' bonds, reaction (f), rather than by cross-dehydrochlorination.

It is concluded that the so-called "zipper" dehydrochlorination reaction plays little part in those reactions occurring on exposure to ultraviolet light at temperatures below 150°C, which affect the mechanical properties of the polymer.

Although it has not hitherto been mentioned, the usual discoloration accompanying degradation of PVC was observed in the stress relaxation work. Samples irradiated in nitrogen became a mottled, deep reddish-brown color, whereas those exposed in air or oxygen turned a pale yellow shade. The color obtained by treatment in nitrogen could readily be bleached by exposure to ultraviolet light in air and the effect was more noticeable with specimens which had only been heated in nitrogen, i.e., the control specimens.

Infrared Spectra

No difference could be detected between the infrared spectra of ultraviolet exposed and unexposed stress relaxed samples.

Effects of Stabilizers and Ultraviolet Absorbers

Of the ultraviolet absorbers examined, Cyanamid UV 24 proved to be completely effective, insofar as a difference line of zero gradient was obtained.   Judged by the same criterion, UV 9 was less efficient.

Systems plasticized with D79P and stabilized with Lankroflex ED 6 and Lankro Mark LL gave the relaxation curves illustrated in Figures 6 to 8, which show the effects of progressively increasing the temperature.   At lower temperatures (70°C) the stabilizer was highly effective, giving difference lines of approximately zero slope.   At higher temperatures, a sudden dip occurred in the test curve after a certain time; with increasing temperature more kinks appeared, which started at progressively earlier times.

The effect was attributed to a limited rate of diffusion of the stabilizer to zones of maximum degradation in the film.   When the stabilizer at a particular zone was exhausted, there was a corresponding rise in the rate of relaxation (drop in the curve) followed in due course by a further period of decreased relaxation rate as fresh stabilizer diffused to the depleted site. Increase in temperature, presumably, enhances the rate of polymer degradation more than it increases the diffusion rate of the stabilizer.

CONCLUSIONS

It has been demonstrated that the technique of differential stress relaxation may be used to investigate the kinetics of the photo-oxidation of viscoelastic materials not hitherto considered amenable to such methods. For the routine study of the effects of changes of formulation on the photodegradation of extensible materials, such as plasticized PVC, this technique would appear eminently suitable.

It is postulated that, between ambient temperatures and 130°C, the photo-oxidation of poly(vinyl chloride) proceeds by the rapid formation of peroxy radicals whose subsequent decay provides the rate-controlling step.   This consists in hydrogen abstraction from the poly(vinyl chloride) substrate to give hydroperoxy groups and alkyl radicals.   The activation energy of this reaction is 12 kcal/mole.

The relative importance of crosslinking and scission in the subsequent reactions is sensitive to the wavelength of the incident radiation.   Crosslinking is favored by increase in photon energy and is thought to be due to the formation of R—O—O—R bonds.

Although a contribution has been made to an understanding of the photooxidation of poly(vinyl chloride), it is quite clear that further work along the same lines, making provision for the measurement and control of light intensity and studying in greater detail the effects of changes in wavelength and oxygen pressure, for instance, could add materially to the knowledge already gained.
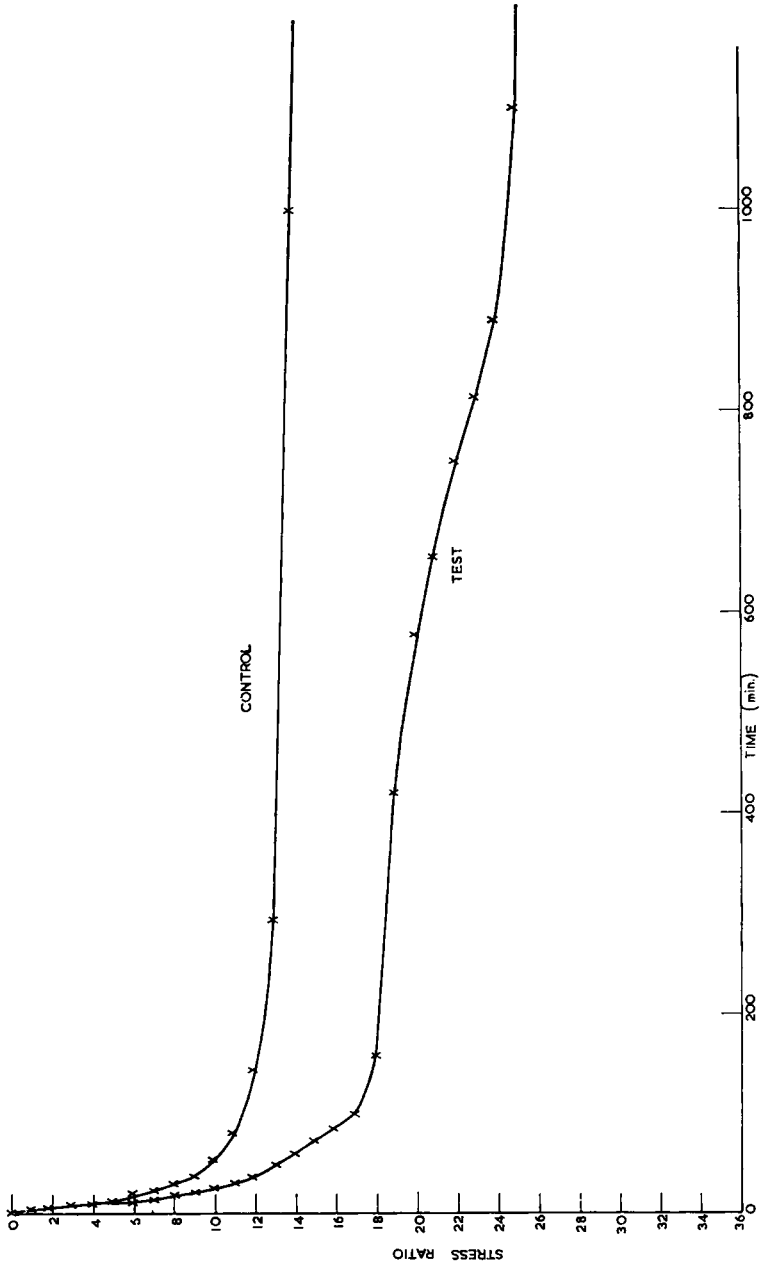
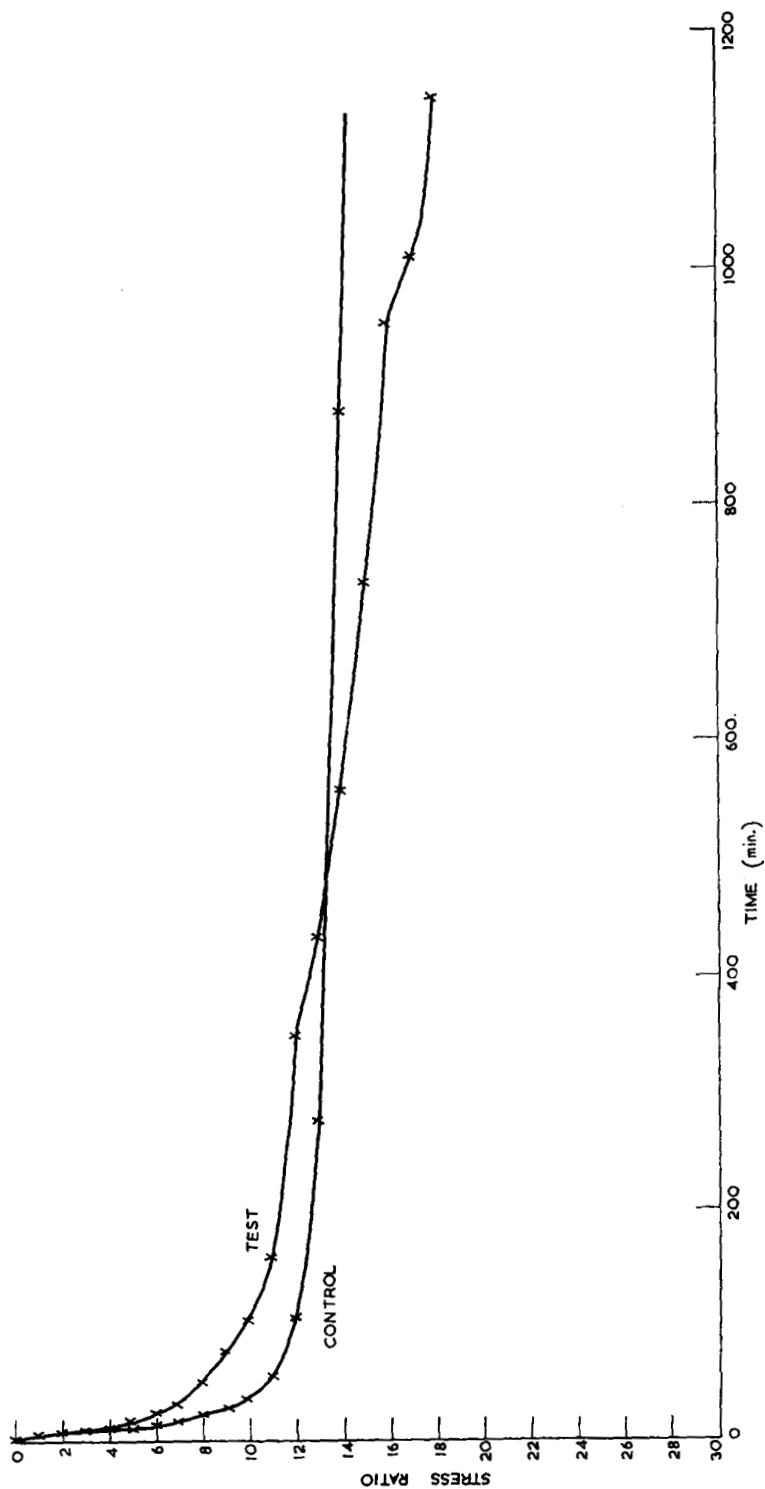Fig. 6. PVC stress relaxation curves: stabilized system; temperature 100°C.

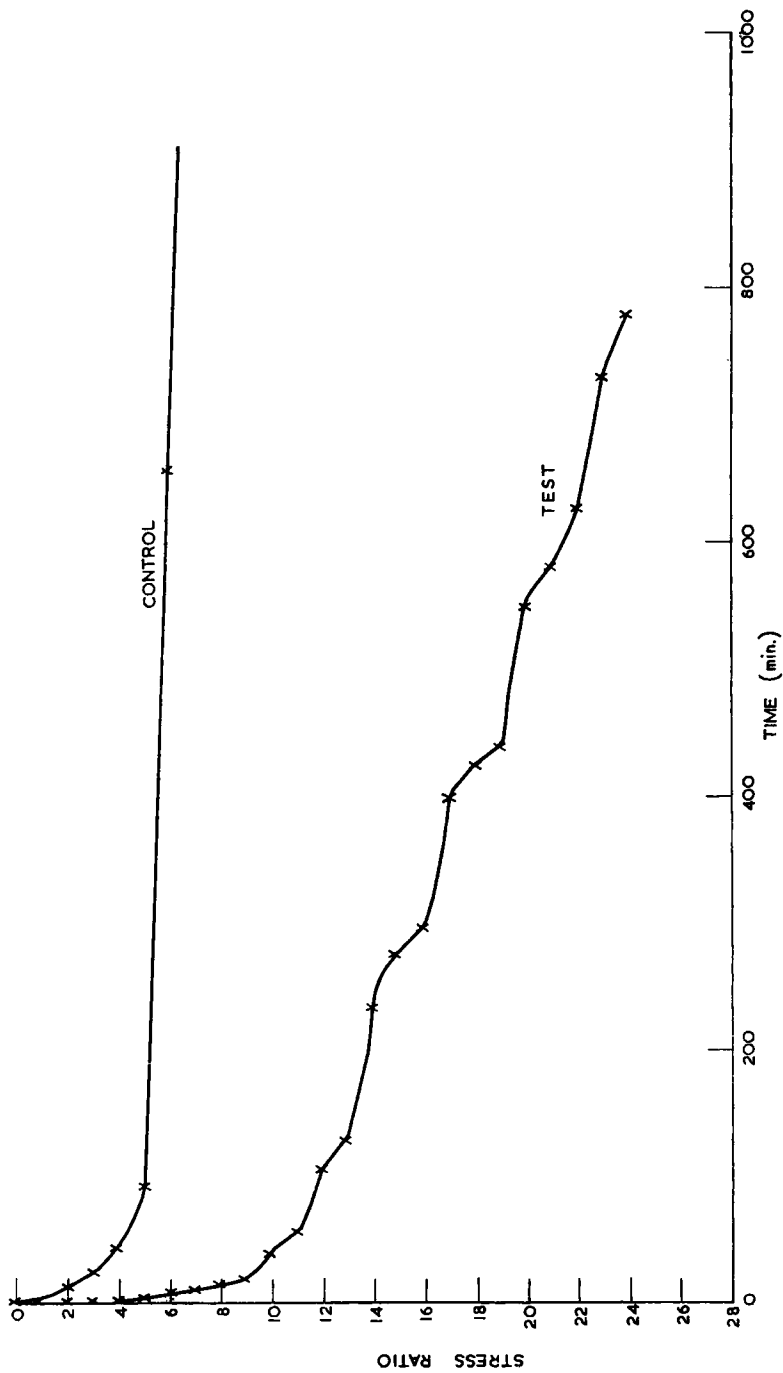Fig. 7. PVC stress relaxation curves: stabilized system; temperature 113°C.

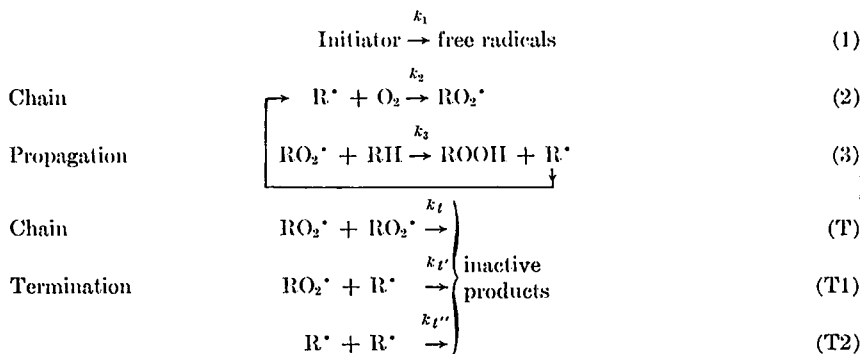Fig. 8. PVC stress relaxation curves: stabilized system; temperature 123°C.

APPENDIX

Effects of Oxygen Pressure–Kinetics of Olefin Oxidation

If the photo-oxidation of PVC is assumed to occur by mechanisms closely similar to those occurring in the autoxidation of olefins, the kinetics used in the interpretation of the olefin oxidation reactions may be taken to apply equally well to PVC.

Olefin oxidation under normal temperature conditions is a free-radical chain reaction and stationary state conditions may be taken to apply. It may be assumed, therefore, that the concentration of free radicals in the system is stationary at any given time, i.e.,

$$\frac{d\,[\text{radical}]}{dt} = 0.$$

The kinetic scheme which emerged from the detailed study of the autoxidation of ethyl linoleate and other olefins by Farmer, Bolland,[12] Gee, Bateman,[13] and their co-workers is

$$\text{Initiator} \xrightarrow{k_1} \text{free radicals} \tag{1}$$

Chain $\qquad \text{R}^\bullet + \text{O}_2 \xrightarrow{k_2} \text{RO}_2^\bullet \tag{2}$

Propagation $\qquad \text{RO}_2^\bullet + \text{RH} \xrightarrow{k_3} \text{ROOH} + \text{R}^\bullet \tag{3}$

Chain $\qquad \text{RO}_2^\bullet + \text{RO}_2^\bullet \xrightarrow{k_t} \tag{T}$

Termination $\qquad \text{RO}_2^\bullet + \text{R}^\bullet \xrightarrow{k_{t'}} \begin{cases} \text{inactive} \\ \text{products} \end{cases} \tag{T1}$

$\qquad \text{R}^\bullet + \text{R}^\bullet \xrightarrow{k_{t''}} \tag{T2}$

For the chain termination reactions, the nomenclature adopted by Uri[26] has been used in order to differentiate the reactions from those indicated on page 618. The same reference[26] has provided most of the following material.

Since the reaction $\text{R}^\bullet + \text{O}_2 \to \text{RO}_2^\bullet$ is very fast, one is justified in neglecting the termination reactions (T1) and (T2) at high pressures of oxygen because $[\text{RO}_2^\bullet]$ is much greater than $[\text{R}^\bullet]$. This was found to be the case with most olefins at oxygen pressures above 100 mm Hg. Applying stationary state conditions, one obtains

$$d[\text{R}^\bullet]/dt = r_1 - k_2[\text{R}^\bullet][\text{O}_2] + k_3[\text{RO}_2^\bullet][\text{RH}] \tag{i}$$

where r_1 is the rate of free radical production. Similarly,

$$d[\text{RO}_2^\bullet]/dt = k_2[\text{R}^\bullet][\text{O}_2] - k_3[\text{RO}_2^\bullet][\text{RH}] - k_t[\text{RO}_2^\bullet]^2. \tag{ii}$$

The stationary state implies that

$$d[\text{R}^\bullet]/dt = d[\text{RO}_2^\bullet]/dt = 0.$$

Hence, addition of the above eqs. (i) and (ii) leads to

$$r_1 - k_t[\text{RO}_2^\bullet]^2 = 0$$

and

$$[\text{RO}_2^\bullet] = (r_1/k_t)^{1/2}.$$

Since
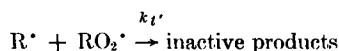
$$d[ROOH]/dt = k_3[RO_2{}^\cdot][RH],$$

we obtain for the rate of hydroperoxide formation

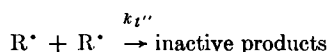$$d[ROOH]/dt = (r_1/k_t)^{1/2} \times (k_3[RH]).$$

In other words, at "high" oxygen pressures, the rate of hydroperoxide formation (the rate-controlling step in the reaction) is independent of oxygen pressure and is first order with respect to the substrate [RH].

Below the levels of oxygen saturation one has also to take into account termination by

$$R^\cdot + RO_2{}^\cdot \xrightarrow{k_t{}'} \text{inactive products}$$

and

$$R^\cdot + R^\cdot \xrightarrow{k_t{}''} \text{inactive products}$$

Analogous treatment to the one outlined above, based on the assumption of the stationary state, i.e.,

$$\frac{d[R^\cdot]}{dt} = \frac{d[RO_2{}^\cdot]}{dt} = 0$$

and

$$\frac{[R^\cdot]}{[RO_2{}^\cdot]} = \frac{k_3[RH]}{k_2[O_2]}$$

and a further simplification by postulating $(k_t{}')^2 = k_t k_t{}''$ leads to the more general rate equation

$$\frac{d[ROOH]}{dt} = (r_1/k_t)^{1/2}k_3[RH]\, \frac{k_2(k_t)^{1/2}[O_2]}{k_3(k_t{}'')^{1/2}[RH] + k_2(k_t)^{1/2}[O_2]}.$$

This equation could be further simplified by assuming $k_t{}'' = k_t$. One then obtains

$$\frac{d[ROOH]}{dt} = (r_1/k_t)^{1/2}k_3[RH]\, \frac{k_2[O_2]}{k_3[RH] + k_2[O_2]}.$$

In other words, at "low" oxygen pressures, the rate of hydroperoxide formation is proportional to the pressure of oxygen, provided [O_2] is small compared with [RH].

In our experiments, the rate of stress relaxation (photo-oxidation) in air was compared with that in white spot nitrogen, containing not more than 10^{-3} vol-% of oxygen. So great a reduction in oxygen concentration would clearly be expected to have a marked effect on the relative proportions of $R^\cdot$ and $RO_2{}^\cdot$ radicals present in the system, with consequent effects on the nature of the termination reactions and so on the kinetics of the formation of hydroperoxide.

Comparison was also made between the behavior in air and in pure oxygen. Here, the oxygen content of air (21 vol-%) is well within the tolerable limits of oxygen deficiency (down to 13 vol-%) where no change in the nature of the termination reaction would be anticipated, except in the case of the most highly reactive olefinic compounds which could by no means be taken as typical of PVC.

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