

A Kinetic Investigation of Thermal Degradation of Poly(vinyl Formals)

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Synopsis

Several samples of poly(vinyl formal) having the same vinyl alcohol content (8–9%) but varying contents of vinyl acetate (6–22%) and vinyl formol (70–85%) were prepared and subjected to thermogravimetric analysis, in air and nitrogen atmospheres, employing both isothermal and dynamic methods. Kinetic parameters determined from both the isothermal and dynamic TGA data are compared. The activation energy is seen to be largely dependent on the degree of conversion, implying a complex degradation reaction. The activation energy is also much less for degradation in air than in nitrogen, which can be explained by a reaction with oxygen-producing structures favoring degradation. The activation energy is less sensitive to variation in polymer composition for degradation in air than in nitrogen. Thus, in the dynamic process, the activation energy value decreases (from 36 to 23 kcal/mole) with increasing acetate content (from 6 to 22%) in nitrogen atmosphere, while in air the activation energy value increases only moderately (from 21 to 27 kcal/mole) with increasing acetate content (from 6 to 22%). The order of reaction is nearly unity, irrespective of the composition of the polymer, both in air and nitrogen.

INTRODUCTION

Poly(vinyl formals), which are thermoplastic resins classified under the general heading of poly(vinyl acetals), possesses a unique combination of properties¹ such as high tensile strength, impact resistance, and elasticity not generally available in other polymers. Poly(vinyl formals) have a high heat distortion temperature of about 90°C and have higher shear strength values at temperatures up to 250°C, coupled with peel strength at low temperatures.¹ These polymers possess flexibility, toughness, resistance to aging, moisture resistance, dielectric strength, and high bonding strength and have outstanding resistance to heat shock, solvents, greases, and oils. These properties are however influenced² by the composition of the polymer determined by its contents of formal, hydroxyl, and residual acetate groups.

Thermal degradation studies on poly(vinyl formals) is helpful in determining the service capability of the polymer in hot environments. The studies are especially important since the polymer is used in a number of applications, e.g., coatings and adhesives, where high temperature conditions are frequently encountered. Poly(vinyl formals) of different compositions can be ranked in order of increasing thermal stability under different environments in order to identify the optimum composition with regard to thermal stability. However, very little has been reported in the literature on the thermal degradation of poly(vinyl formals) and especially on the kinetic aspects of the degradation reaction.

Beachell et al.³ studied the weight loss, coloration, and infrared spectral changes on oxidative degradation of poly(vinyl formals) of different compositions.

In general, it was found that the higher the content of formal groups, the lower the weight loss, implying greater stability. The major organic components of the product mixture were found to be formaldehyde, paraformaldehyde, and low molecular weight poly(vinyl formals).

In the present work, the thermal degradation behavior and the kinetics of degradation of poly(vinyl formals) of different compositions were studied. To determine the influence of oxidizing and inert atmospheres, degradation studies were made both in air and nitrogen.

EXPERIMENTAL

Materials

Poly(vinyl formals) of different compositions were prepared by formalization⁴ of poly(vinyl acetate) with formaldehyde in acetic acid solution. Poly(vinyl acetate) supplied by BDH Chemicals Ltd., England, was used. It had a viscosity-average molecular weight of 45,000.

Poly(vinyl acetate), 100 g, was added to a mixture of 384 g glacial acetic acid and 40 g distilled water in a three-necked round-bottomed flask. The mixture was heated on a water bath at about 70°C with constant stirring until the poly(vinyl acetate) dissolved completely. To this solution was added a solution of 10.4 ml concentrated H₂SO₄ in 30 ml distilled water. Then, 67.5 g formalin solution was added to the flask. A thermostatic control was used to keep the temperature constant at 70°C. The reaction was conducted for a definite period of time as required⁴ for the desired composition of the final polymer product.

The polymer was precipitated from the reaction mixture by adding it dropwise, under vigorous stirring, to a large volume of distilled water. The washed material was dried in a current of air at 30°C in a dryer. The chemical composition of the dried polymer was determined by the spectroscopic method of Chanda and Kumar.⁴

The compositions of the poly(vinyl formal) samples used in the present study are recorded in Table I. The polymer samples were sieved to -35 +45 for TG runs.

Apparatus and Procedure

TG experiments were carried out on a conventional McBain-Baer⁵-type quartz spring balance. Quartz springs supplied by Thermal Syndicate Limited, England, were used. For the isothermal runs the temperature of the furnace was kept within $\pm 2^\circ\text{C}$ of the required temperature. The weight of the sample taken in each run was about 50 mg. Weight fraction-versus-time plots were obtained for the different samples of poly(vinyl formals) at various temperatures (225-

TABLE I
Composition of Poly(vinyl Formal) Samples Used

| Sample | Composition, wt-% | | |
|--------|-------------------|---------------|---------------|
| | Vinyl formal | Vinyl acetate | Vinyl alcohol |
| A | 85.1 | 6.1 | 8.8 |
| B | 75.3 | 15.5 | 9.2 |
| C | 69.4 | 22.1 | 8.5 |

350°C). The experiments were performed at atmospheric pressure and in the presence of air or nitrogen. The results are presented in Figures 1 and 2. For the dynamic TG runs the furnace was heated at a predetermined rate to obtain a constant temperature rise of 4°C/min, as measured with a thermocouple placed near the sample bucket. The weight fraction-versus-temperature plots for the different samples of poly(vinyl formals) are shown in Figures 3 and 4.

RESULTS

Isothermal TGA

For a solid material decomposing to give a gaseous product and a solid residue, the rate of decomposition reaction can be written as

$$-dw/dt = R_t = kw^n \tag{1}$$

where w is the weight fraction of the material undergoing degradation at time t , k is the rate constant, and n is the order of reaction.

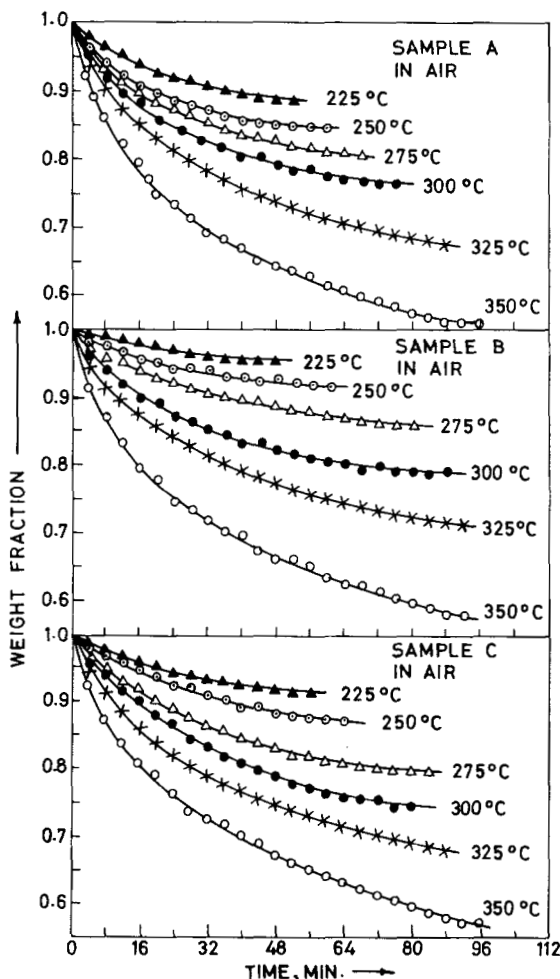


Fig. 1. Plots of isothermal TG data for poly(vinyl formal) samples A, B, and C in air at different temperatures.

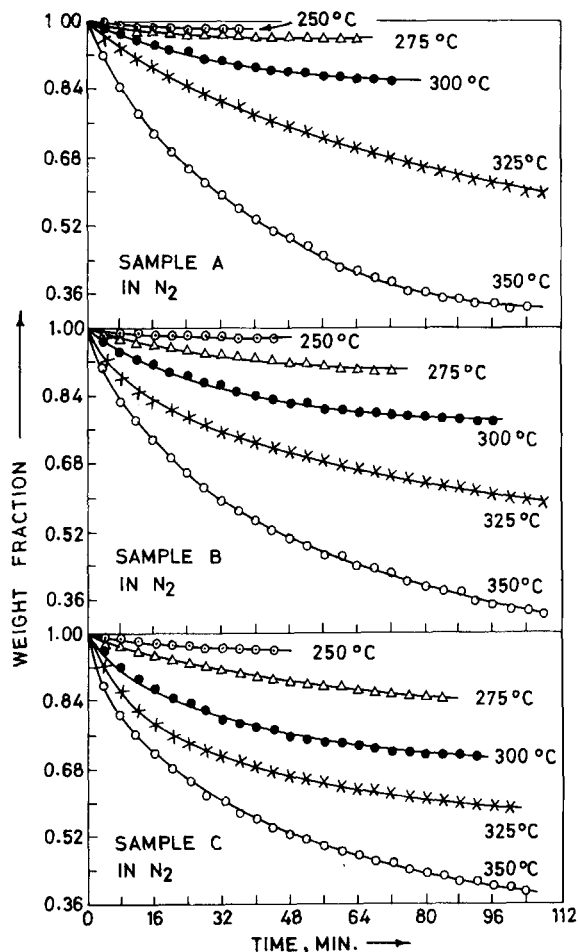


Fig. 2. Plots of isothermal TG data for poly(vinyl formal) samples A, B, and C in nitrogen at different temperatures.

Using the Arrhenius expression for k in eq. (1) and taking logarithms,

$$\log R_t = \log A + n \log w - (E/2.3R)(1/T) \quad (2)$$

At $t = 0, w = 1.0$. Hence, eq. (2) becomes

$$\log R_{t_0} = \log A - (E/2.3R)(1/T) \quad (3)$$

where R_{t_0} is the initial rate of degradation.

Thus, a plot of $\log R_{t_0}$ versus $1/T$ should afford, irrespective of the order of reaction, a linear relationship whose slope yields the value of activation energy E and its intercept, the value of the frequency factor A .

A polynomial equation of the form $w = a + bt + ct^2 + \dots$ was fitted to the curves in Figures 1 and 2 at each temperature and was differentiated to obtain $R_{t_0} = b$. The plots of $\log R_{t_0}$ versus $1/T$ are shown in Figure 5. The values of E and A obtained from the slopes and intercepts are given in Table II.

Activation energy values were also calculated by using the method of Jacobs and Kureishy⁶ which involves data for finite decomposition and depends on the applicability of a single kinetic equation over the chosen range of decomposition.

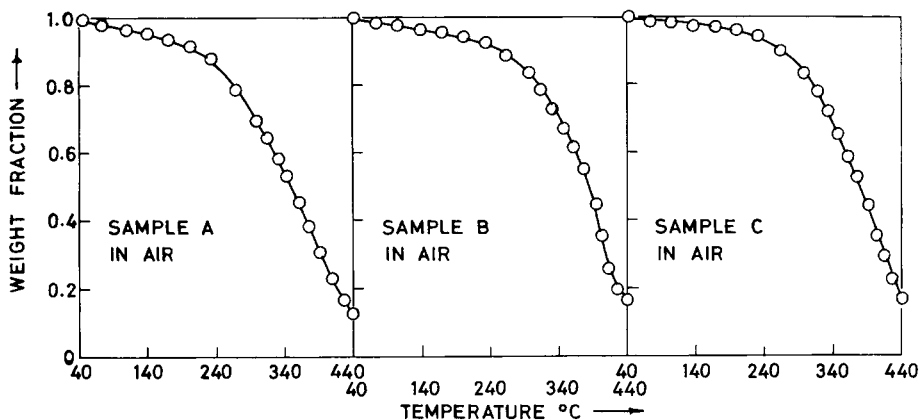


Fig. 3. Plots of dynamic TG data for poly(vinyl formal) samples A, B, and C in air.

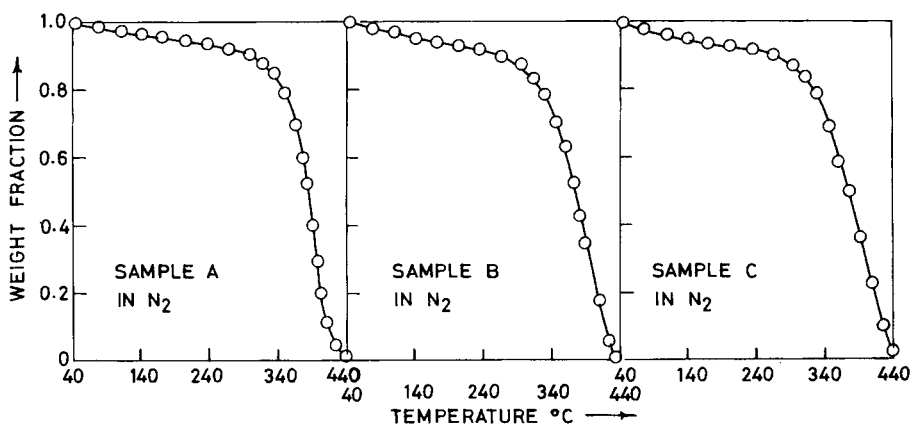


Fig. 4. Plots of dynamic TG data for poly(vinyl formal) samples A, B, and C in nitrogen.

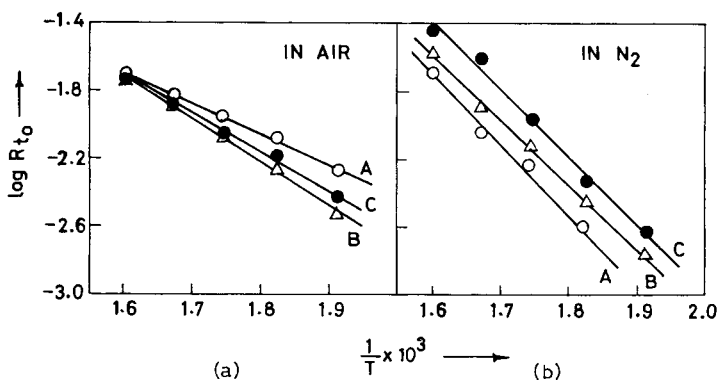


Fig. 5. Plots for determination of kinetic parameters from eq. (3): (a) in air; (b) in nitrogen.

The form of the kinetic equation need not be known, however. The method deals with the time (Δt) taken for the extent of thermal degradation to proceed from one value to another. E is obtained from the plot of $\log \Delta t$ versus $1/T$, which is linear with a slope of $E/2.3R$. E values corresponding to different ranges of decomposition (weight loss), in air and nitrogen, calculated by this method are given in Table III. The calculations were limited to 20% weight loss because of

TABLE II
 Kinetic Parameters for Initial Degradation

| Atmosphere | Kinetic parameters | Sample | | |
|------------|-------------------------|---------------------|---------------------|---------------------|
| | | A | B | C |
| Air | E , kcal/mole | 9.1 | 12.2 | 11.1 |
| | A , min ⁻¹ | 3.685×10 | 4.127×10^2 | 1.754×10^2 |
| Nitrogen | E , kcal/mole | 21.2 | 19.1 | 19.7 |
| | A , min ⁻¹ | 6.998×10^5 | 1.560×10^5 | 4.253×10^5 |

 TABLE III
 Conversion Dependence of Activation Energy

| Fractional weight loss range | E , kcal/mole | | | | | |
|------------------------------|-----------------|----------------|----------|----------------|----------|----------------|
| | Sample A | | Sample B | | Sample C | |
| | Air | N ₂ | Air | N ₂ | Air | N ₂ |
| 0-0.1 | 13.7 | 28.8 | 18.3 | 22.9 | 17.1 | 20.6 |
| 0.1-0.2 | 18.3 | 39.8 | 20.1 | 27.4 | 17.7 | 22.0 |
| 0-0.2 | 16.7 | 35.2 | 18.8 | 24.8 | 17.5 | 20.9 |

a very low rate of weight loss particularly at relatively lower temperatures (Figs. 1 and 2). The significance of the results in Table III is discussed later.

Dynamic TGA

The difference-differential method of Freeman and Carroll⁷ was used for the kinetic analysis of the dynamic TGA data. From the general expression for the rate of decomposition

$$-dw/dt = R_T = (A/RH) e^{-E/RT} w^n \quad (4)$$

where RH is the constant heating rate. The difference form for a single trace is derived as

$$\Delta \log R_T = n \Delta \log w - (E/2.3R) [\Delta(1/T)] \quad (5)$$

Another form in which eq. (4) may be written is

$$\frac{\Delta \log R_T}{\Delta \log w} = n - \frac{E}{2.3R} \frac{\Delta(1/T)}{\Delta \log w} \quad (6)$$

From the slopes of TGA curves in Figures 3 and 4, plots of R_T and weight fraction remaining (w) versus reciprocal temperature ($1/T$) were constructed. The values of $\Delta \log R_T$ and $\Delta \log w$ were then calculated corresponding to an arbitrarily chosen $\Delta(1/T)$ interval, and plots were made of $\Delta \log R_T$ versus $\Delta \log w$, as shown in Figure 6. The values of n and E obtained from these plots are presented in Tables IV and V. Also recorded in these tables are the corresponding values obtained from the plots made according to eq. (6), as shown in Figure 7.

DISCUSSION

The activation energy value E varies depending on the polymer composition and the ambient atmosphere and, in addition, is significantly dependent on the extent of decomposition, as shown by the results of Tables II and III. The acti-

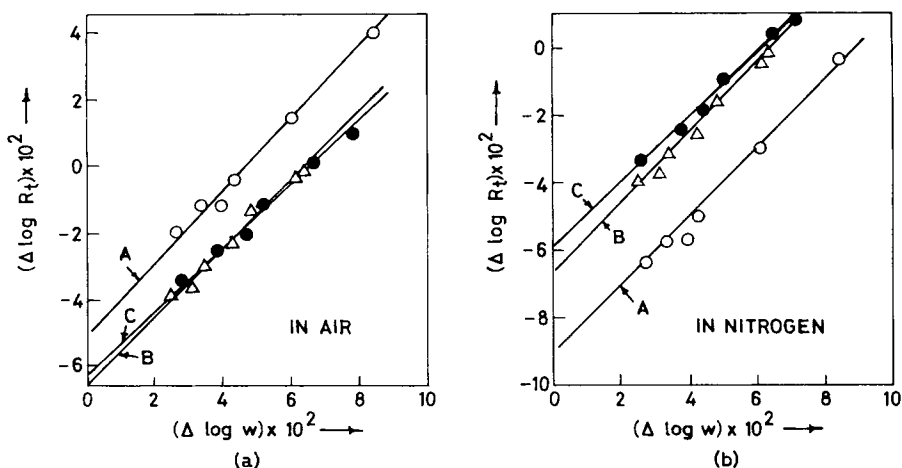


Fig. 6. Plots for determination of kinetic parameters from eq. (5): (a) in air; (b) in nitrogen.

TABLE IV
Order of Reaction (n) and Activation Energy (E) from Dynamic TG Data in Air

| Sample | n | | E , kcal/mole | |
|--------|---------|---------|-----------------|---------|
| | Eq. (5) | Eq. (6) | Eq. (5) | Eq. (6) |
| A | 1.06 | 1.0 | 21.1 | 21.7 |
| B | 0.98 | 1.0 | 27.4 | 27.8 |
| C | 0.95 | 1.0 | 26.6 | 27.2 |

TABLE V
Order of Reaction (n) and Activation Energy (E) from Dynamic TG Data in Nitrogen

| Sample | n | | E , kcal/mole | |
|--------|---------|---------|-----------------|---------|
| | Eq. (5) | Eq. (6) | Eq. (5) | Eq. (6) |
| A | 1.02 | 1.0 | 36.2 | 35.2 |
| B | 1.03 | 1.0 | 26.3 | 25.7 |
| C | 0.98 | 1.0 | 23.3 | 22.6 |

vation energy for initial degradation (Table II) is relatively low and increases with the extent of decomposition of the polymer (Table III). This feature is observed both in air and nitrogen and for all three samples A, B, and C. However, the variation is less pronounced for degradation in air and for a polymer with higher acetate content (sample C, for example). The increase in activation energy with extent of degradation should be attributed to compositional and, possibly, structural changes in the polymer hindering its further degradation.

It is evident from Tables II and III that the thermal degradation in air is associated with a lower activation energy than that in nitrogen. This is suggestive of a reaction of oxygen with the polymer, resulting in structures more favorable for degradation. Beachell et al.³ suggested rupture of the formal ring as the first step in the oxidative degradation of poly(vinyl formal). The rupture occurs by a free-radical mechanism (Fig. 8) involving hydroperoxide formation by an initial attack of molecular oxygen and leads to the formation of carbonyl (C=O) groups and liberation of formaldehyde. The formation of C=O groups was verified in

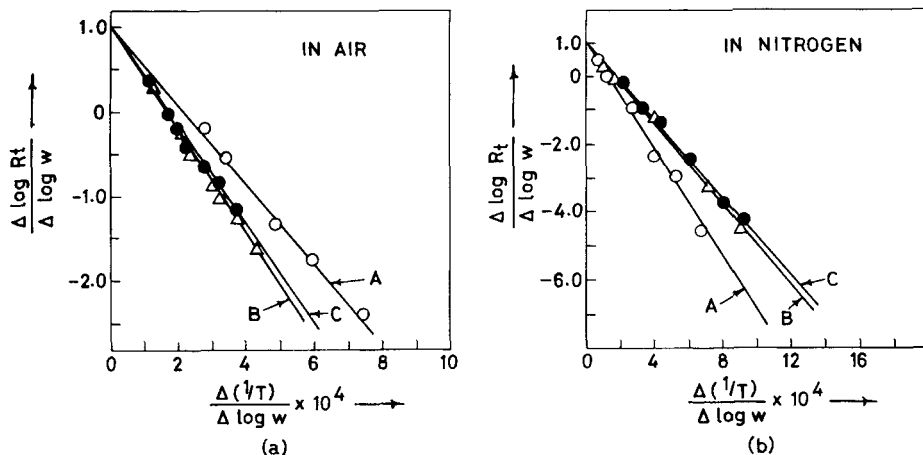


Fig. 7. Plots for determination of kinetic parameters from eq. (6): (a) in air; (b) in nitrogen.

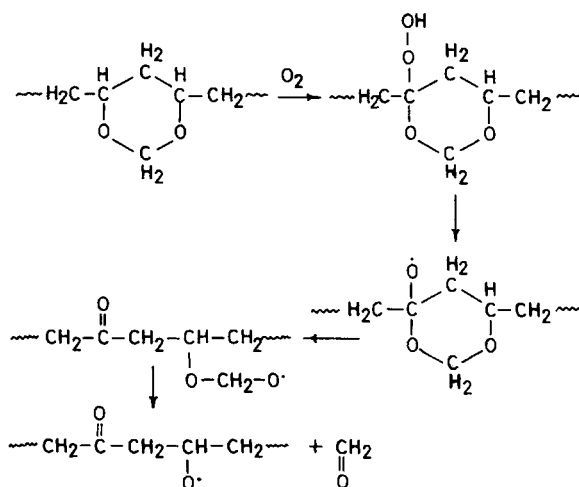


Fig. 8. Initial steps of oxidative degradation mechanism of poly(vinyl formal). From Beachell et al.³

the present work by IR spectroscopy. Figure 9, for example, compares the IR spectra (recorded with a Carl Zeiss Model UR-10 spectrophotometer) in chloroform solution of the poly(vinyl formal) sample A (Table I), before and after oxidative degradation. The absorbance ratio of $C=O$ to $-O-$ is seen to increase from 0.60 for the original sample to 1.85 for the degraded sample.

The mechanism shown in Figure 9 accounts for the role of oxygen and formal rings in the initial degradation process. The presence of oxygen evidently facilitates the initial degradation of the polymer. The activation energy for degradation in the presence of oxygen would therefore be expected to be smaller than in an inert atmosphere. The results presented in Tables II and III are in accord with this view.

Figure 5 allows some conclusions to be drawn regarding the effect of polymer composition on the initial rate of degradation. A definite trend is evident for degradation in nitrogen, and a comparison of curves in Figure 5(b) shows that the polymer with a higher acetate content has a higher initial rate of weight loss. For oxidative degradation, however, as Fig. 5(a) shows, polymer composition has

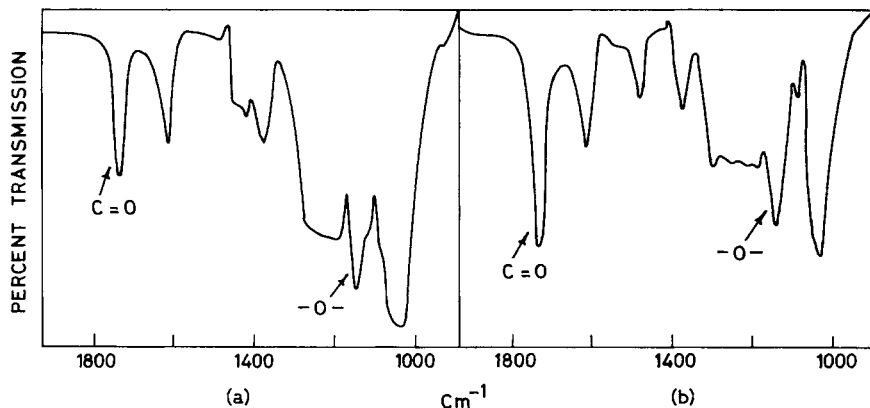


Fig. 9. IR spectra of chloroform solutions of (a) poly(vinyl formal) sample A and (b) the same sample after aging at 280°C for 1/2 hr in a current of air.

little effect on the initial rate of degradation at higher temperatures, while at lower temperatures the polymer with the largest formal content has the maximum rate of initial degradation. This is in agreement with the role of the formal group in the oxidative degradation of the polymer.

The results of Tables IV and V show that the order of reaction is nearly unity irrespective of the composition of poly(vinyl formal) in the range studied and also of the ambient atmosphere in which the thermal degradation is carried out.

The activation energy values obtained from dynamic TG data (Tables IV and V) are, in general, higher than those obtained from isothermal TG data. This is to be expected if the degradation reactions are complex and dependent on the degree of conversion. It is interesting to compare the E values for degradation in nitrogen, given in Table V, with those obtained for isothermal degradation over a finite conversion range (0–0.2), as shown in Table III. The agreement is very good for all the three samples, considering the fact that in dynamic TG experiments the material was degraded to a greater extent than in isothermal studies.

A similar comparison for oxidative degradation, however, shows that the E values derived from dynamic TG data (Table IV) are considerably higher than those obtained from isothermal data over finite conversion range (Table III). This may be taken to signify that the degradation mechanism in the presence of oxygen is more temperature sensitive than in the absence of oxygen.

The effect of polymer composition on the activation energy for thermal degradation is more pronounced in an inert atmosphere than in air. This is revealed by the results of both isothermal and dynamic TG studies (Tables III, IV, and V). Thus in nitrogen atmosphere, the isothermal TG activation energy, for instance, in the 0.1–0.2 conversion range, decreases from 39.8 to 22.0 kcal/mole as the acetate content increases from 6 to 22%, whereas in air the E value increases from 18.3 to 20.1 kcal/mole with an increase in acetate content from 6 to 15% and then drops to 17.7 kcal/mole as the acetate content is increased further to 22%. It may be noted that Beachell et al.,³ from weight loss measurements during isothermal aging of films of commercial poly(vinyl formal) (~12% acetate content) in the temperature range of 150–225°C, derived a value of 21 kcal/mole for the activation energy. It thus compares favorably with the value obtained in the present work.

The authors thank Professor R. Kumar for his interest in the work.

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Received December 8, 1977