

A Study of Thermal Degradation and Oxidation of Polymers by Infrared Spectroscopy. Part I. Experimental Technique and Butylated Melamine Formaldehyde and Urea Formaldehyde

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INTRODUCTION

The purpose of this study was to gain some knowledge of the manner in which polymers undergo thermal degradation and oxidation when heated in the presence of air. Changes in the number or type of functional groups are usually readily detectable by infrared spectroscopy; hence, this method of observation is particularly applicable to a study of this nature. In effect it provides a means of continuously monitoring the decay or generation of functional groups during the course of degradation or oxidation. The experimental conditions are such that the reactions being observed are essentially surface reactions of the polymer exposed to air. This is accomplished by working with very thin films of material; this tends to minimize diffusion effects and hence simplifies reaction conditions. Changes occurring in the major or bulk amount of the polymer are being observed under these conditions; hence, one is observing the polymer as it is at any given stage of oxidation and/or degradation. The method is lacking in that no provisions are made for simultaneous monitoring of the volatile products produced during the reaction. The method has the distinct advantage, however, that it is monitoring the major portion or the bulk of the polymer or its nonvolatile reaction products. Although this study was intended to be primarily a fundamental study of the nature of the oxidation or degradation, a certain amount of information is obtainable concerning the thermal stability of the various polymers or groups within the polymer. The rate of decay of various temperatures gives some indication of the inherent stability of the polymer.

Throughout this study considerable use has been made of the standard reference sources for information concerning absorption bands of various functional groups. These include the *Sadtler Reference*

Spectra,¹ The National Research Council² and the American Petroleum Institute Spectra³ as well as the works of Bellamy⁴ and Randall.⁵ Bellamy's book has been a particularly valuable aid in interpreting the spectra. Most of the characteristic frequencies encountered in the study have been well established and confirmed by many workers in the field of infrared; hence, individual references will not be made for these frequencies except in special cases where unusual circumstances warrant more specific information than is included in the general references listed above.

EXPERIMENTAL TECHNIQUES

Two techniques are used for observing the change in the spectra as a function of time at a particular temperature. For the more stable compounds, such as the silicones, a thin layer or smear of the polymer is placed on either side of a sodium chloride plate, and the plate is placed in a sample holder which maintains the sample in a fixed position with respect to the spectrophotometer. The specimen and sample holder are placed in an oven of the desired temperature and removed at various intervals of time to obtain the spectra. The second technique used employs a heated stage which permits the spectra to be obtained while the specimen is maintained at the desired temperature. Figure 1 shows the heated stage and temperature regulating device. The sodium chloride plate (1 in. diameter, 1/4 in. thick) has two small holes bored approximately halfway through the plate on either side of the region through which the infrared beam passes. Thermocouples are placed in the holes, one of which controls the thermoregulator; the other thermocouple is used to check the temperature of the plate. A Model 21 Perkin-Elmer spectrophotometer is used to obtain the spectra. This instrument can be made to scan repetitively any desired

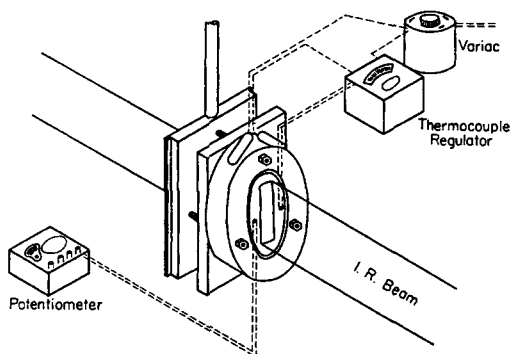


Fig. 1. Regulated heated stage.

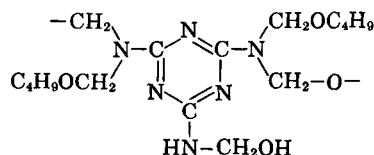
portion of the spectra automatically; hence, the data may be collected rather conveniently.

We are not aware of any other infrared studies employing continuous or repetitive scanning of the specimen while it is maintained at the desired temperature. Some workers have used successive heating periods and obtained the spectra between heating periods. This technique has also been used in this study in some cases in which the polymers are particularly resistant and undergo change very slowly.

Such a technique has been used by others to compare silicones with phthalic alkyds,⁶ and to study degradation of polystyrene,⁷ polyvinyl formal,⁸ and cellophane.⁹

BUTYLATED MELAMINE-FORMALDEHYDE RESIN

A typical structural unit of a butylated melamine-formaldehyde resin may be represented as



(At least this represents the various groups and linkages possible in the polymer.) Table I lists the characteristic absorptions of the functional groups occurring in the polymer.

TABLE I
Characteristic Absorptions of Butylated Melamine Resin

Wavelength, μ	Functional group
2.9-3.05	—OH and —NH
3.4	—C—H (primarily in —CH ₂ OCH ₂ CH ₂ CH ₂ CH ₂ CH ₂)
9.3	—C—O—C—
12.3	Triazene ring

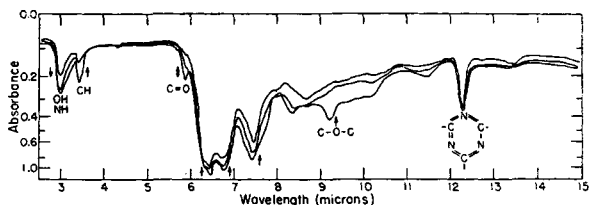


Fig. 2. Initial stage of thermal degradation of butylated melamine-formaldehyde resin.

The heating technique used in this resin was that of placing the sample in an oven, removing it, and then obtaining the spectra. Figure 2 shows a few of the runs made. The arrows indicate the direction of progress of the absorption bands with time. Arrows pointing down indicate an increase in absorption or band intensity; hence, a generation of that specific group and the arrows pointing upward indicate a decrease of absorption intensity hence a reduction of the particular functional group. The course of decay and growth of the various groups are shown more clearly in Figure 3, in which the percentage of each individual group (either remaining or being generated) is plotted as a function of time. The temperature treatments were consecutive, beginning at 140°C. and subsequently being raised to 200 and finally to 300°C. The temperatures are labeled on the graph showing the time that each temperature was in effect.

The following observations from Figure 3 indicate the course of the degradation.

(1) There is little degradation at 140°C.; however, some loss of butoxy and ether groups occurs, as indicated by the decrease in the CH₂ and ether group bands.

(2) The melamine ring remains fairly stable throughout the 200°C. range, as indicated by the fact that only about 10% of the triazene ring is lost.

(3) The butoxy group is split off at a fairly rapid rate at 200°C. This is shown by the parallel loss of —C—O—C— and —CH₂— and the corresponding increase in the percentage of —NH and/or —OH groups. The close proximity of the —NH and —OH bands and the possibility of variations in the degrees of hydrogen bonding make it impossible to say specifically whether the —OH or —NH preponderates. The splitting of the carbon-nitrogen bond with the subsequent formation of an —NH group, the splitting of the —C—O— bond with the subsequent formation of a —NCH₂OH group, or a combination of these two processes would account for the observed data, at least up to 300°C. At 300°C. a second band becomes apparent near 3.2

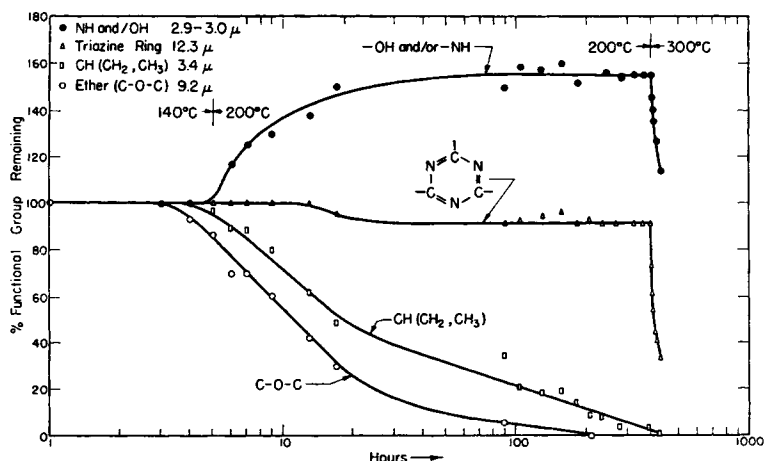


Fig. 3. Thermal degradation of a butylated melamine-formaldehyde resin.

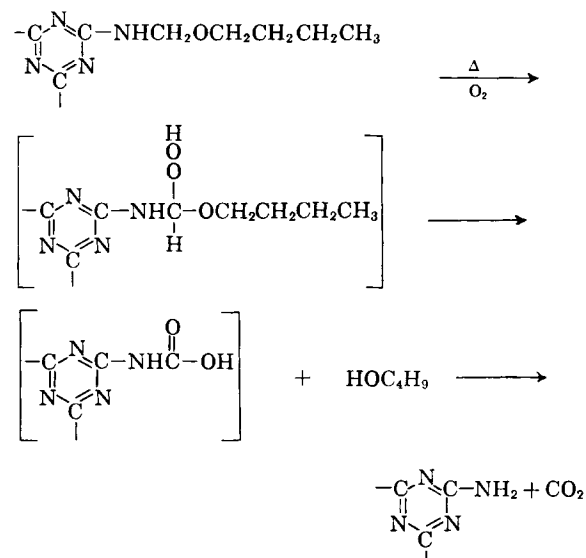
microns. Two bands of this type are somewhat characteristic of primary amines. This might be produced either by splitting of the —N—C— bonds or the possible decomposition of the methylol group ($\text{—NCH}_2\text{OH}$) which may have been generated at lower temperatures.

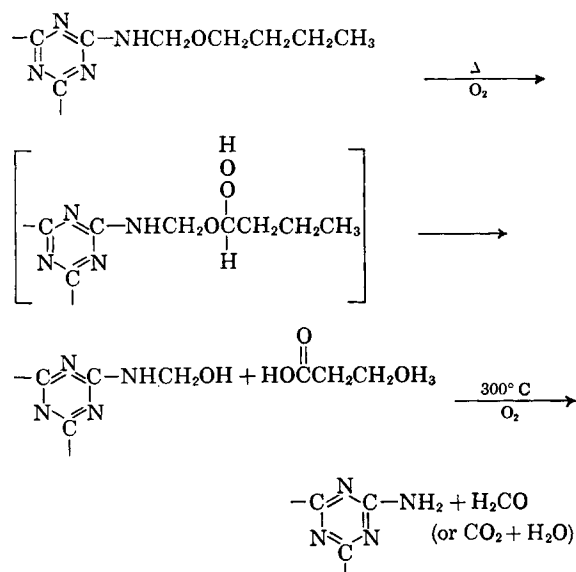
(4) At 300°C . the residual structure is broken down rapidly as indicated by the rapid decrease of all bands.

An examination of the spectra (Fig. 2) indicated that, in addition to the increase in —OH and/or —NH group near 3 microns, there is only one other band observed to increase, namely a —C=O band at 5.9 microns which forms and then disappears. This band could possibly arise from a keto, an aldehyde, or carboxyl group. There is no indication that this is an intermediate in the degradation process. The primary degradation process is well underway prior to its appearance. Also the —C=O bands are of high intensity; hence, the small band formed actually represents a very small amount of this group. The general lack of bands occurring in the 5–6 micron region indicates that appreciable amounts of nonvolatile oxidation products, such as ketones, aldehydes, carboxyls, or anhydrides, are not formed.

From the information derived from the spectral data, the following conclusion can be drawn regarding the degradation of the polymer. The initial step constitutes the loss of the butoxy group by fracture of the —C—O— or —C—N— bond and the simultaneous formation of an —OH or —NH group. In the earlier stages of degradation the position of the band slightly favors the formation of the methylol group. The loss of butoxy occurs fairly rapidly at 200°C . The melamine

ring undergoes little degradation at 200°C . At 300°C . all bands, and hence, all groups decrease rapidly; this indicates the presence of chain fracture resulting in volatilization of the polymer. The —OH and/or —NH band decreases and then shifts somewhat to longer wavelengths, and two bands become apparent. The portion of the band near 3.0 microns decreases more rapidly, thus bringing out the band at 2.9. As indicated above, this combination of bands is somewhat indicative of primary amines; hence, it seems feasible that the methylol groups are undergoing decomposition, the —NH_2 group being left formaldehyde being formed. The melamine ring undergoes fairly rapid oxidation or degradation at 300°C . Two possible mechanisms which might account for the data follow:





Both mechanisms are based on the formation of hydroperoxide intermediates. By the use of a free radical mechanism a number of other possible mechanisms producing the same final products could probably also be written.

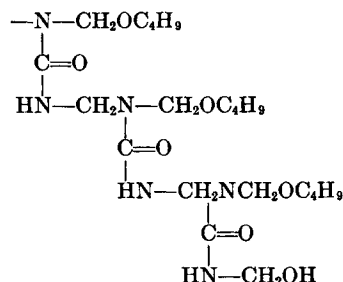
Unfortunately, we are unable to observe the unstable intermediates because they are, in all probability, not present in detectable amounts. Hence, any mechanism proposed at this time is for the most part speculation.

It should be noted that, even though the melamine ring is stable and resistant to oxidation at 200°C., it could not be considered a desirable resin for this temperature because it becomes cracked almost to the point of being pulverized, hence demonstrating poor mechanical strength.

BUTYLATED UREA-FORMALDEHYDE RESIN

The interpretation of changes occurring in the spectrum of urea-formaldehyde resin is complicated by a number of factors; namely, (1) oxidation products are generated which have ---C=O bands which overlap the normal amide ---C=O region; and (2) the possible formation of cyclic compounds such as cyclic amides would result in a shift of the amide ---C=O frequency into the ---C=O region normally associated with oxidation products. In spite of these limitations, a number of interesting conclusions are nevertheless forthcoming from the data on this particular type polymer.

The structural unit of butylated urea formaldehyde may be represented as



This is at least representative of the types of possible functional groups present.

Table II gives the characteristic absorptions of the functional groups which are easily monitored by infrared techniques in this polymer.

TABLE II
Functional Groups Present in Butylated Urea-Formaldehyde Polymer

Wavelength, μ	Functional group
3.4, 3.47	---CH--- (---CH_2 and ---CH_3 , primarily from butoxy group)
2.95-3.0	---OH and/or ---NH
6.05 (Amide I Band)	$\begin{array}{c} \text{O} \\ \\ \text{N---C---N} \end{array}$
6.5 (Amide II Band)	$\begin{array}{c} \\ \text{---C---NH---} \end{array}$
9.3	---C---O---C---

The repetitive scanning technique was used for this resin because the degradation takes place rather rapidly. Figure 4 shows a few of the scans made at 200° and Figure 5 shows some of the scans

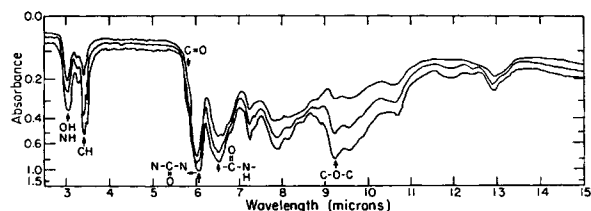


Fig. 4. Thermal degradation of a butylated melamine-formaldehyde resin.

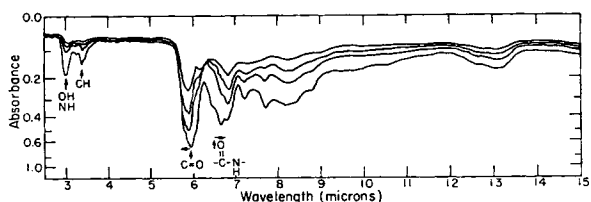


Fig. 5. Thermal degradation of butylated urea-formaldehyde resin at 250°C.

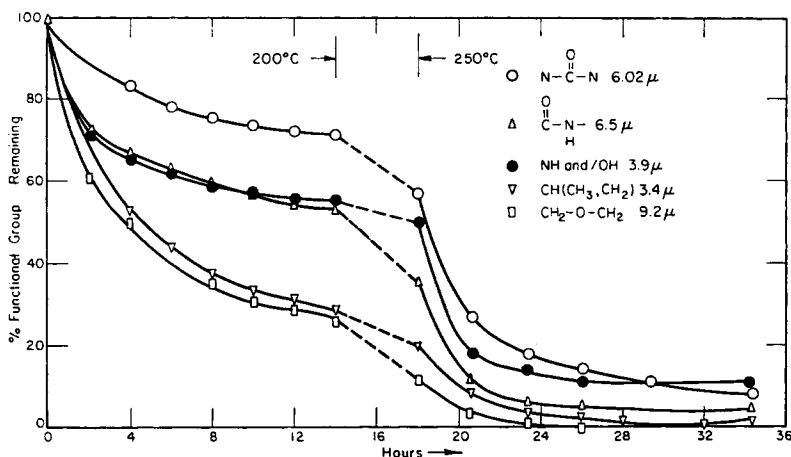


Fig. 6. Thermal degradation of a butylated urea-formaldehyde resins.

at 250°C. It may be noted in Figures 4 and 5 that some of the bands appear to shift to different wavelengths during the course of decay. The amide —C=O appears to shift to lower wavelengths. However, as already noted, this may be entirely due to the simultaneous growth of —C=O bands of oxidation products, as the amide —C=O is decaying, or to a formation of cyclic amide compounds which might produce the same effect. As the amide II band decreases, one or two other bands become apparent between 6.5 and 7.0 microns. They may arise from the formation of some primary amide groups, or may be present in the original polymer, although not at first distinguishable because of the heavy amide II band at 6.5 microns. Figure 6 shows a plot of the decay of the various functional groups. For the initial portion of the degradation at 200°C. a scan time of 2 hr. was used. For the later portion of the degradation, the temperature was raised to 250°C., and a scan time of 2.7 hr. was used. There is a discontinuous region between the temperature change, since appreciable change took place during the interval between runs (during the temperature change).

An examination of the decay rates shown in Figure 6 results in the following conclusions regarding the course of decay and oxidation of polymers.

(1) The decay curves of the —C—H band, the —C—O—C , or ether band parallel each other and exhibit a decay rate considerably greater than that of the other groups. This is in all probability caused by the splitting off of butoxy groups.

(2) The —OH and/or —NH group, represented by the band near 3.0 microns and the amide

II(—C—NH—) band at 6.5 microns are decaying

$$\begin{array}{c} \text{O} \\ || \\ \text{C—N—} \\ | \\ \text{H} \end{array}$$

at approximately one-half the rate of decay of the butoxy groups.

(3) The band at 6.02 microns (Amide I, or N—C=O(N—) group) gives a decay curve which indicates it is decaying at a much slower rate than the other group. However, this curve probably does not accurately represent the actual decay rate. In addition to the decay of this band there is a shift toward lower wavelengths which may indicate either the formation of other oxidation products, with corresponding development of the broad band in the 5.9-micron region due to —C=O or the formation of cyclic amides. There is also evidence of oxidation products by the growth of a side band or shoulder at 5.8 microns. The broad bands in the —C=O region in all probability overlap the 6.02 band of the amide group; hence, the resulting decay rate is smaller than it should be.

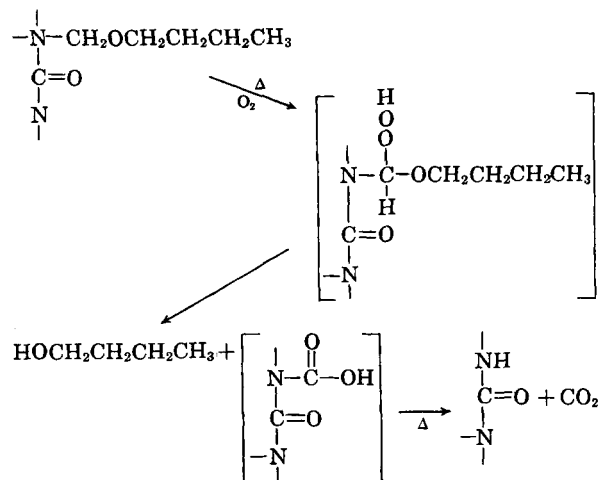
(4) At 250°C. the degradation of all bands occurs at a greatly accelerated rate. The Amide II band decreases rapidly, indicating an increase in all bands indicates an oxidation or degradation of the entire polymer leading to volatile products.

(5) In addition to the above information, the fact that we do not observe the formation of a band near 4.5 microns indicates that isocyanate groups are not being generated in any appreciable quantity nor are carboxyl groups being generated to any great extent, as evidenced by the absence of the acid —OH band near 3.8 microns.

In an attempt to determine whether the butoxy group was split off by fracture of the —C—O— or the —N—C— bond (bond energies of 75 and 53.5

kcal., respectively¹⁰), the volatile components from the thermal degradation of this polymer were trapped in a separate experiment and the infrared spectra taken. At 200°C., the trapped component appeared to be primarily butyl alcohol plus other oxidation products which we were unable to identify.

The data seem to favor the splitting of the —C—O— bond which would, in all probability, result in a very readily oxidizable fragment. One possible mechanism for splitting off the butoxy group through the formation of a hydroperoxide intermediate is as follows:



There is a considerable degree of speculation involved in postulating this or any other mechanism since we cannot observe the intermediates involved. However, the data do seem to favor a reaction which does not produce appreciable quantities of nonvolatile acid or isocyanate groups.

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Synopsis

This is the first of a series of papers concerned with the general problem of thermal degradation and oxidation of polymers. Part I consists of a description of the technique used and the results obtained on butylated melamine-formaldehyde and urea-formaldehyde resins. The course of the degradation and/or oxidation is followed by observing the changes occurring in the infrared absorption bands which are associated with various functional groups present in the polymer or being generated by oxidation. Other polymers which have been studied, or are presently being studied, include: Formvar and urea formaldehyde-epoxy copolymers, polyesters, acrylics, phenols, novolacs, polybenzyl, and various silicon polymers.

Résumé

Ceci est le premier article d'une série ayant pour objet le problème général de la dégradation thermique et de l'oxydation des polymères. La partie I est une description de la technique employée et des résultats obtenus avec des résines, mélamine butylée-formaldéhyde et urée-formaldéhyde. L'allure de la dégradation et/ou de l'oxydation est suivie par l'observation des changements dans les bandes d'absorption infra-rouge associées aux différents groupements fonctionnels présents dans le polymère au produits par oxydation. D'autres polymères ont été étudiés ou sont étudiés à l'heure actuelle, à savoir: le Formvar et copolymères urée formaldéhyde-époxy, polyesters, acryliques, phénols, novolaques, polybenzyle et différents polymères de silicone.

Zusammenfassung

Die vorliegende Mitteilung ist die erste einer Reihe von Arbeiten, die sich mit dem allgemeinen Problem des thermischen Abbaus und der Oxydation von Polymeren befassen. Teil I besteht aus einer Beschreibung der angewendeten Versuchsmethodik sowie der Ergebnisse die an butylierten Melamin und Harnstoff-Formaldehydharzen erhalten wurden. Der Verlauf des Abbaus sowie der Oxydation wird durch Beobachtung der Änderungen verfolgt, die bei den Infrarot-Absorptionsbanden auftreten, welche mit den verschiedenen im Polymeren vorhandenen oder durch die Oxydation erzeugten funktionellen Gruppen verknüpft sind. Zu den Polymeren, die untersucht wurden oder deren Untersuchung noch im Gange ist, gehören: Formvar und Harnstoff-Formaldehyd-Epoxycopolymer, Polyester, Acrylpolymer, phenolische Harze, Novolake, Polybenzyle und verschiedene Silikonpolymer.

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