

The Behavior of Polypyromellitimide Resins at High Temperatures

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Synopsis

Aromatic polyamides and polyimides of high molecular weight are currently under development by many industrial laboratories. Wire enamels, laminating and impregnating resins, and varnishes incorporating this new class of thermally stable polymers withstand higher operational temperatures than do most organic polymeric materials in use today. The thermal and oxidative stability of two of these resins has been investigated in air, in oxygen, and in O¹⁸-enriched oxygen over a temperature range of 300–400°C. The mechanism of degradation is postulated to be that of a unit by unit destruction of the polymer.

I. INTRODUCTION

Aromatic polyamides and polyimides of high molecular weights exhibit certain characteristics which make them attractive for high temperature applications. Wire enamels, bonding agents, varnishes, etc., incorporating these polymers have longer life at higher operational temperatures than do most organic polymeric materials in use today.¹⁻⁴

The thermal stability of this type of resin has been studied in vacuum, in air, in helium, in oxygen-argon atmospheres, and in isotopically enriched oxygen. Experimental temperatures ranged from 300 to 400°C. Reaction rates were measured and mechanisms associated with the oxidation of these resins are proposed on the basis of the fate of the oxygen in the oxidizing atmospheres and of the oxygen originally present in the polymer.

Polymers of this class consist of linear chains of aromatic nuclei linked by various atom groupings of which the imide structure is always a prominent fraction. Two prototype structures were examined. Type one, referred to as (IM), comprises a chain in which the chain linkage alternates between imide and oxa(ether) structures. Such a polymer results from the reaction of 4,4'-diaminophenyl ether and pyromellitic dianhydride. In type two, referred to as (IMAM), the ether linkage is replaced by an amide group. Such a structure results from the reaction of 3,4'-diaminobenzanilide and pyromellitic dianhydride.

II. EXPERIMENTAL

A. Procedure

The oxidation of these resins was carried out in two types of apparatus.

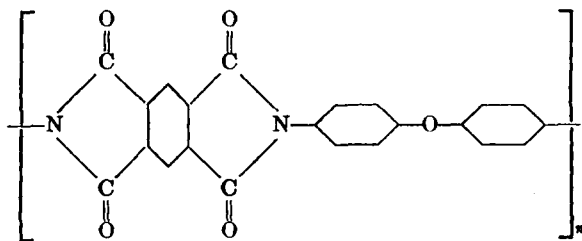
The first consisted of a gas circulating system equipped with a magnetic balance and a quartz reaction chamber.^{5,6} In this system the weight loss of the sample was followed continuously and the gases consumed and evolved were followed manometrically and mass spectrometrically.

The second system was used in the isotopically-enriched oxygen and in the vacuum experiments and consisted of a platinum tube (95 cc.) attached to the mass spectrometer. When the atmosphere used was oxidizing, it consisted of 50% argon and 50% enriched oxygen* made up of 90% of O¹⁸ and 10% of O¹⁶ at a total initial pressure of approximately 1 cm. Hg. The gases consumed and evolved on heating were measured. The platinum tube was cleaned between runs by heating to 600°C. in air for several hours. The use of a Vycor or quartz tube furnace was found to alter the results obtained when using isotopically enriched oxygen because of the exchange of oxygen between the CO₂ generated by the sample and the oxygen in the furnace material. A platinum tube was used in order to eliminate this difficulty.

All the experimental results obtained in this investigation were processed by the Datatron, which made feasible the handling of the large amount of data obtained.⁷

B. Materials

Imide-Linked Polypyromellitic Resin (IM). This resin (I) was made by the reaction of 4,4'-diaminodiphenyl ether (DAPE) with



I

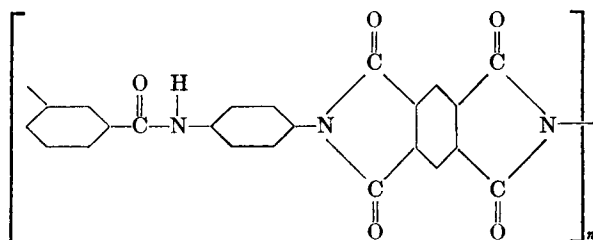
PMDA in 1:1 molar proportion. The resin was obtained in dimethylacetamide (DMA) solution. The solution was poured onto a large aluminum dish to a thickness of a few millimeters, and the solvent evaporated at 150°C. for 3 hr. This treatment not only eliminated the greatest part of the solvent, but also set up the resin to a solid but cracked film. The film surface exposed to the air was lucid, dark, and smooth, while the underside closest to the aluminum tray was dark opaque. The film was

* Obtained from Weizmann Institute of Science, Isotope Department, Rehovoth, Israel.

broken into small pieces and ground in a Wiley mill to a mesh of 35–42 (average particle size 0.010 in.). This ground material was then heated *in vacuo* for 3 hr. at 150°C. The unit weight of this polymer is 382; it contains 29.2% CO groups by weight.

Imide-Amide Linked Polypyromellitic Resin (IMAM). IMAM resin is the product of the condensation of 3,4'-diaminobenzanilide with pyromellitic dianhydride in 1:1 molar proportion, and was supplied as a 20% solids solution in dimethylacetamide. This solution was treated as outlined above to obtain experimental samples. When samples of both resins were heated for 3 hr. at 350°C. in air, no sintering of the discrete particles was observed.

A representation of the basic unit of this polymer, with a unit molecular weight of 409, is shown as structure II.



II

Each unit contains four imide carbonyl groups and one amide carbonyl group for a total of 34.06% CO groups by weight.

III. RESULTS AND DISCUSSION

A. IM Resin

Oxidation in Gas Circulating System. The experiments were conducted with the system at an initial pressure of 1 atm. of air. Resin samples weighing 3.5 g. were heated at a temperature of 300°C. The weight loss as a function of time is given in Figure 1. Within the initial $\frac{1}{2}$ hr. of heating, 95% of the total observed weight loss occurred. After 7 hr. of heating, the weight of the sample had decreased by 7.9%. The observed rate of weight loss in steady state was 0.0002 g./g. polymer/hr. A liquid distillate was collected in the cold traps which were maintained at Dry Ice temperature. This liquid was analyzed by infrared spectroscopy techniques and found to consist of DMA, polymeric material, and traces of water. No change was detected between the structure of the original material and that of the residue by infrared techniques.

Figure 2 shows the moles of gas consumed and evolved per mole of polymer unit as a function of time. It is noted that 55% of the total oxygen consumed is consumed within the first $\frac{1}{2}$ hr. and that 50% of the total CO₂ is evolved during this time. After this initial $\frac{1}{2}$ hr. period the

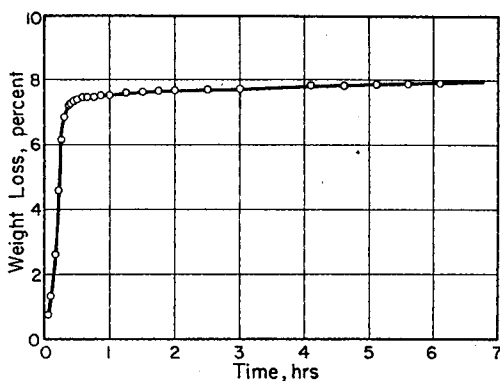


Fig. 1. Weight loss of IM in air using gas circulating system (300°C.).

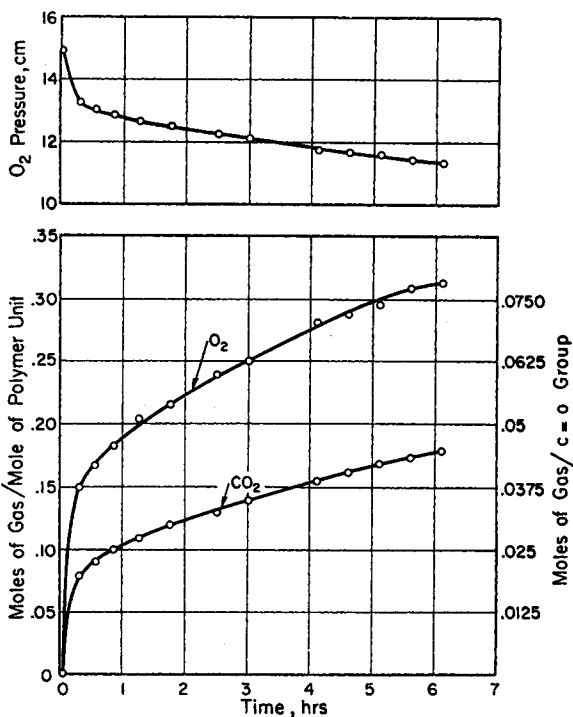


Fig. 2. Consumed and evolved gases during oxidation of IM in air at indicated pressure of oxygen using gas circulating system (300°C.).

rate for oxygen is approximately 0.022 mole/unit mole/hr., and 0.013 mole/unit mole of polymer/hr. for CO₂.

Figure 2 also gives the moles of gas consumed and evolved per carbonyl group as a function of time. These results indicate that the greatest portion of the reaction involves the consumption of oxygen and the parallel formation or liberation of carbon dioxide from the polymer. The gas

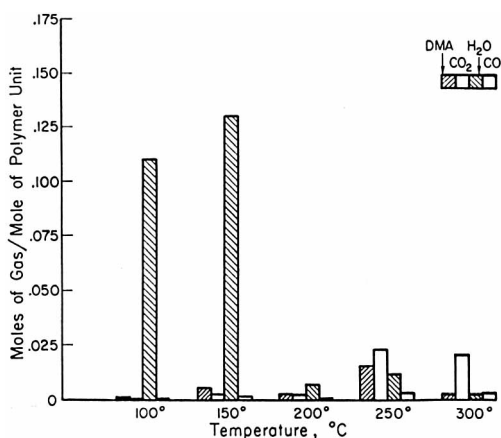


Fig. 3. Gas evolution from a single sample of IM heated in vacuum for 1 hr. at each successive temperature.

curves have a shape similar to the weight loss curve. The final amount of CO₂ evolved corresponds to 58% of the total oxygen consumed. At the end of the run 0.081 mole of O₂ had been consumed and 0.048 mole of CO₂ had evolved per carbonyl group.

Vacuum Degassing in Platinum Tube. A weighed sample of IM (15 mg.) was placed in a platinum tube, which was sealed and evacuated at room temperature. The sample was first heated at 100°C. for 1 hr. and then the temperature raised in 50°C. steps for 1 hr. at each temperature. The gas was removed and measured every half hour. At any given temperature, about 90% of the total gas evolution occurred during the first half hour. The moles of gas per mole of polymer unit evolved for a 1-hr. heating period at each temperature are shown in the bar graph of Figure 3. In addition to the DMA, CO₂, H₂O, and CO shown, traces of acetic acid and of hydrogen were observed. The increased evolution of 150°C. followed by a decrease at 200°C. suggests that the gases evolved in this temperature range were those adsorbed on the sample surface. The increase observed at 250°C. may be associated with a higher rate of diffusion permitting the evolution of gas from the solid sample. The carbon dioxide observed on vacuum degassing can largely account for the CO₂ observed during the first 1/2 hr. in the oxidation experiment for which the results are given in Figure 2.

Oxidation in Platinum Tube Using O¹⁸. In order to follow the identity of the oxygen consumed and of that evolved in the form of CO₂, oxidation experiments were carried out in an O¹⁸ atmosphere. Samples of oxygen¹⁸ were used in which the isotopic concentration of O¹⁸ was 90% and that of O¹⁶ was 10%. The limited quantities of enriched O¹⁸ available necessitated carrying out the oxidation in a small system of approximately 95 cc. volume at a reduced oxygen pressure as distinguished from the previously described circulating system. Oxygen pressures used were of the order

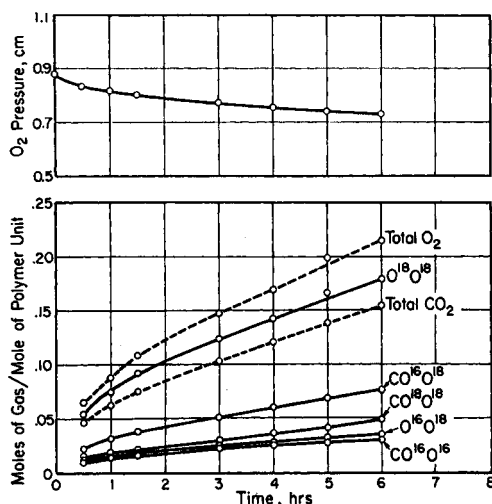


Fig. 4. Consumed and evolved gases during oxidation of vacuum-treated IM at indicated pressures of isotopically enriched oxygen ($300^{\circ}\text{C}.$).

of 15 mm. Hg and polymer samples approximated 3–15 mg. The weighed polymer samples were placed in a platinum tube, and the system was sealed and evacuated to a pressure of less than 10^{-4} mm. Hg. Measured quantities of an isotopically enriched oxygen and argon mixture were admitted to the system using a mercury manometer and standard volumes. The argon served as an internal standard for evaluating the quantities of oxygen consumed and gaseous products evolved. It also permitted following the oxygen pressure in the system similarly to the experiments carried out in the circulating system. In this small system one must not only take into account the oxygen consumed by oxidation but also the oxygen and other products removed by sampling.

The sample of IM, from which the results of Figure 3 were obtained, was heated at $300^{\circ}\text{C}.$ in isotopically enriched oxygen. At no time between the vacuum treatment and heating in oxygen was the sample exposed to air. In Figure 4 are plotted the total moles of each oxygen species consumed and the total moles of each isotopic species of CO_2 evolved per unit of polymer. At the top of the figure is plotted the oxygen pressure throughout the run. After the initial period of 2 hr., the total O_2 and total CO_2 curves are nearly parallel, indicating that about the same rate is associated with the consumption of O_2 and the evolution of CO_2 . The rates for CO_2 evolution are approximately 0.018 mole/mole of polymer unit/hr., or 0.00206 g./g. polymer/hr., and the rates for O_2 consumed are 0.022 mole/mole of polymer unit/hr., or 0.00185 g./g. polymer/hr., in steady state. The difference between the CO_2 and O_2 rates is 0.00021 g./g. polymer/hr., which represents a weight loss.

A sample of IM was degassed in vacuum at $300^{\circ}\text{C}.$ for $2\frac{1}{2}$ hr. and then exposed to atmospheric pressure of air at this same temperature while

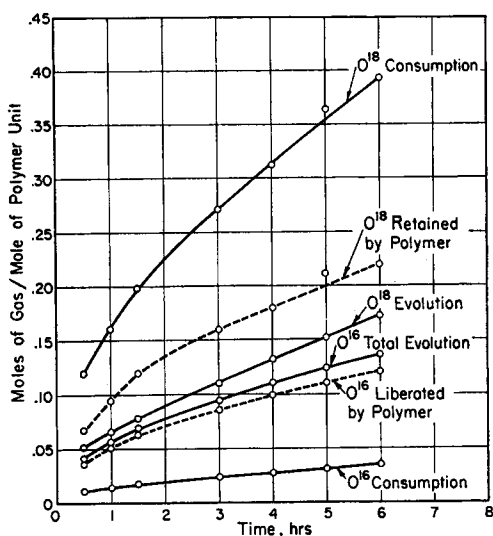


Fig. 5. Atomic oxygen constitution of consumed and evolved gases during oxidation of vacuum-treated IM in isotopically enriched oxygen (300°C.).

the sample weight was continuously measured. The weight loss rate at steady state following the initial 2 hr. of oxidation was 0.000286 g./g. polymer/hr. A comparison of this value with the calculated weight loss rate of 0.00021 g./g. polymer/hr., based on changes in the gaseous atmosphere, shows that at least 75% of the apparent weight loss in steady state is associated with the changes in the gaseous atmosphere. The rate of carbon loss (as CO₂) is 0.00056 g./g. polymer/hr. or approximately twice as large as the observed weight loss rate (0.000286 g./g. polymer/hr.). This carbon rate, the CO₂ rate (0.00206 g./g. polymer/hr.) and the O₂ rate (0.00185 g./g. polymer/hr.) demonstrate that low weight loss rates are not indicative of reduced chemical activity. The fact that the rate of carbon weight loss (as CO₂) alone is twice the observed rate of polymer weight loss during steady state shows that attack by a single oxygen molecule does not result in the splitting out of a heavy volatile fragment from the polymer chain. Although the oxygen consumed is primarily O¹⁸, a high percentage of the CO₂ evolved contains O¹⁶. A second way of displaying the results in Figure 4 is that of Figure 5. Here the oxygen is plotted not in terms of the species observed but in terms of the actual O¹⁶ and O¹⁸ consumed and evolved as carbon dioxide. Approximately 90% of the oxygen consumed consists of O¹⁸ throughout the run. This shows that the molecular oxygen in the system does not undergo isotopic exchange with any oxygen-containing materials in the system at 300°C. The difference between the O¹⁸ consumed and O¹⁸ evolved corresponds to the O¹⁸ retained by the polymer. A part of this difference may be due to the buildup of unreacted O₂ within the polymer or to unknown oxygen-consuming reactions. Throughout the run only a part of the O¹⁸ consumed

is evolved as CO_2 . On the assumption that this same fractional part applies to the O^{16} consumed, one can calculate the O^{16} liberated by the polymer.

No water or DMA was observed, in contrast to the results of the degassing experiment (Fig. 3). It has been found experimentally that the residue of IM is hygroscopic at room temperature. It would be expected that the lower molecular weight film found deposited on the cold walls would behave similarly in regards to water and possible DMA.

In Figure 6 are shown the data obtained from the oxidation of IM without degassing at 300°C . The sample was placed in a platinum tube and evacuated to a pressure of the order of 10^{-5} mm. Hg in a short

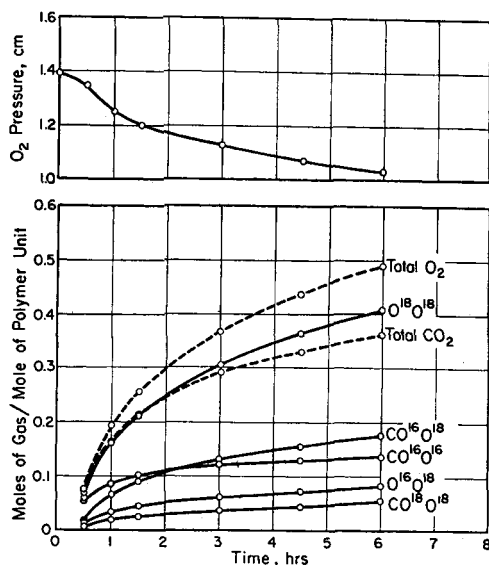


Fig. 6. Consumed and evolved gases during oxidation of undegassed IM at indicated pressure of isotopically enriched oxygen (300°C).

time and the isotopically enriched oxygen plus argon admitted. The results show the oxygen consumption and the carbon dioxide evolution along with the oxygen pressure. The total quantity of oxygen consumed and carbon dioxide evolved is approximately twice that observed for the vacuum-treated sample of Figure 4. A part of the carbon dioxide can be explained in terms of the carbon dioxide lost on degassing, the results of which were given in Figure 3. The initial higher level of $\text{CO}^{16}\text{O}^{16}$ shown in Figure 6 as compared to that of Figure 4 is evidence that the $\text{CO}^{16}\text{O}^{16}$ in Figure 6 arises primarily from thermal effects and not from oxidation. The CO_2 results of degassing, shown in Figure 3, offer further evidence of this point. The remainder, $\text{CO}^{16}\text{O}^{18}$ and $\text{CO}^{18}\text{O}^{18}$, can be traced to the faster oxidation rate of the lower molecular weight resin fragments which are principally responsible for the weight loss. This faster oxidation rate may

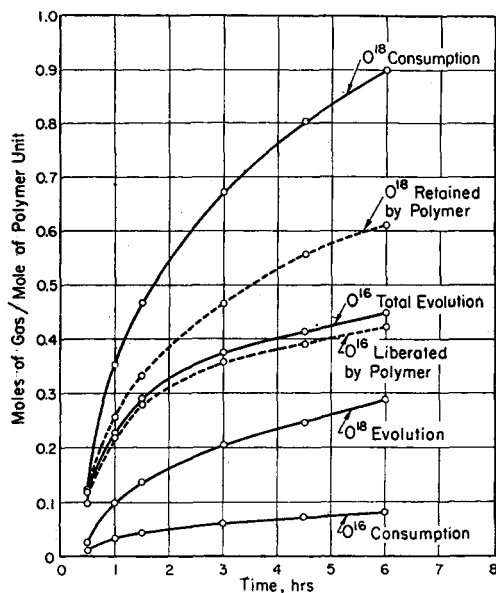


Fig. 7. Atomic oxygen constitution of consumed and evolved gases during oxidation of IM in isotopically enriched oxygen (300° C.).

be explained by the fact that these fragments pass through a liquid and gaseous phase in escaping from the solid resin.

The data in Figure 6 have been plotted in Figure 7 in terms of atomic oxygen. Here again the difference between the O¹⁸ consumed and the O¹⁸ evolved corresponds to the O¹⁸ retained by the polymer. Once the low molecular weight fragments have been largely removed, the ratio of O¹⁸ consumed to O¹⁸ retained by the resin is approximately the same for the initially degassed and initially undegassed samples.

In using enriched oxygen isotopes to follow a chemical reaction, it is possible that the results are influenced by isotopic change. The fact that the isotopic constitution of the molecular oxygen does not change during a run, that CO¹⁶O¹⁶ and O¹⁸O¹⁸ do not exchange in the platinum furnace system at 300°C., and the shapes of the observed curves all suggest that isotopic exchange is a negligible process in the particular system investigated. Pretreating of samples in vacuum results in the removal of more easily oxidizable polymeric material of lower molecular weight. Subsequent oxidation of the vacuum-treated samples in an O¹⁸-enriched atmosphere shows a large reduction in total oxygen consumed and carbon dioxide evolved as compared to corresponding results for undegassed samples. Furthermore, when oxidizing such a vacuum-pretreated sample, a slightly higher reaction rate constant is obtained for oxygen consumption than for carbon dioxide evolution, indicating that there is at least a 1:1 molar correspondence between oxygen consumption and carbon dioxide evolution. In the case of the oxidation of an undegassed sample, the

curves tend to become parallel with time and appear to approach the same 1:1 molar correspondence. A large fraction of the consumed O^{18} is retained by the polymer.

B. IMAM Resin

Oxidation in Platinum Tube Using O^{18} . In order to follow the identity of the oxygen consumed and of that evolved in the form of CO_2 , oxidation experiments were carried out at $300^\circ C$. in an O^{18} atmosphere. In Figure 8 are plotted the total moles of each oxygen species consumed and the total moles of each isotopic species of CO_2 evolved per unit polymer. At the top of the figure is plotted the oxygen pressure throughout the run. After an initial period of 2-3 hr. the total O_2 and total CO_2 curves are nearly parallel, indicating that the same rate is associated with the consumption of O_2 and the evolution of CO_2 . The final amount of CO_2 evolved corresponds to 81% of the total O_2 consumed. Although the consumed oxygen is primarily O^{18} , a high percentage of the evolved CO_2 contains O^{16} , indicating that the polymer itself contributes some of the oxygen evolved as carbon dioxide from its carbonyl groups. The rapidly decreasing oxygen pressure during the last part of the run partly accounts for the leveling off of the gas curves.

The results are similar to the corresponding results obtained from the IM resin (see Fig. 6), except that the total values of O_2 consumed and CO_2 evolved by IMAM are about three times as large as those in the case of IM. The values can be compared almost directly since the unit molecular weight of the IM is 382, and that of IMAM is 409. These results again illustrate the initial high oxidation rates observed with undegassed samples; they are thought to be associated with the faster oxidation rates of the low molecular weight polymeric fragments that distill out of the

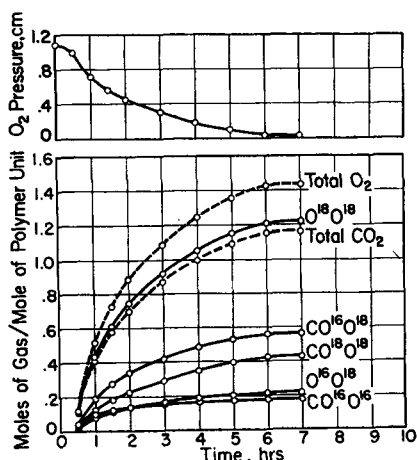


Fig. 8. Gases consumed and evolved during oxidation of untreated IMAM at indicated pressure of isotopically enriched oxygen ($300^\circ C$.).

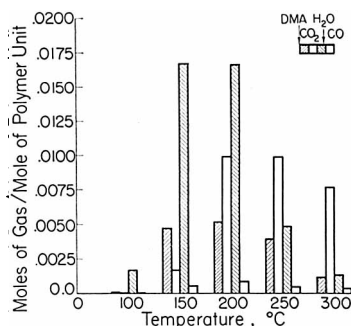


Fig. 9. Gas evolution from a single sample of IMAM heated in vacuum for 1 hr. at each successive temperature.

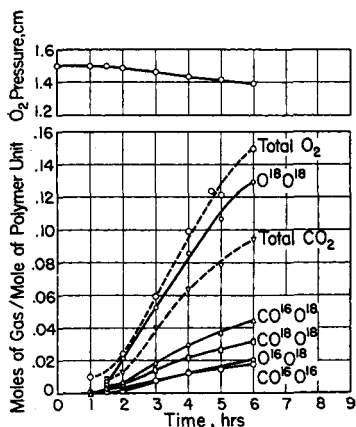


Fig. 10. Gases consumed and evolved during oxidation of vacuum-treated IMAM at indicated pressures of isotopically enriched oxygen (300°C.).

polymer, rather than with the bulk of the polymer itself. This phase of degassing will be discussed later.

Vacuum Degassing in Platinum Tube. A sample of IMAM was degassed in vacuo in order to determine the identities and the amounts of volatiles contained in the set-up, ground polymer. Figure 9 shows the number of moles of volatiles per mole of polymer unit evolved from a single sample in 1 hr. at each successive temperature. Water is the most abundant contaminant and is eliminated almost completely after heating at 200°C. for 1 hr. DMA, the initial solvent, is more difficult to eliminate, a substantial amount still being liberated at 250°C. Carbon dioxide appears at 150°C. and continues to be evolved up to 300°C. On an absolute scale, however, the total amounts of volatiles evolved are very small, in fact smaller by a factor of three than the corresponding values from the degassing of IM when one neglects the water from IM in the 100–150°C. temperature range. The vacuum degassing resulted not only in the evolution of physically bound light-weight volatiles, but also in the dis-

tillation of variable amounts of low molecular weight, higher vapor pressure polymeric materials.

The vacuum-treated sample of IMAM was then heated at 300°C. in O^{18} -enriched oxygen. At no time between the vacuum treatment and the heating in oxygen was the sample exposed to air. In Figure 10 are plotted the total moles of each oxygen species consumed and the total moles of each isotopic species of CO_2 evolved per unit polymer. The oxygen pressure throughout the run is shown at the top of the figure. An induction period is apparent in all the curves; however, after 1 hr. of heating, the curves of CO_2 evolution and O_2 consumption show nearly a constant rate. Because these rate values are 10 times smaller than those obtained before evacuation, it would seem that the vacuum treatment has eliminated the portions of polymer more susceptible to oxidation. These results are quite similar to those previously obtained for IM.

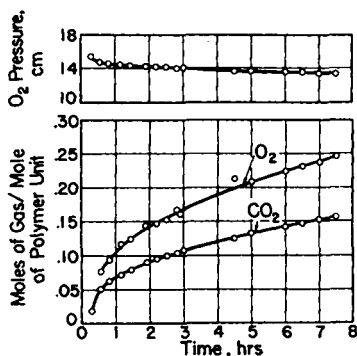


Fig. 11. Gases consumed and evolved during oxidation of undegassed IMAM at indicated pressure of oxygen using circulating system (300°C.).

Here again, while the consumed O_2 was primarily O^{18} , a high percentage of the evolved CO_2 contained O^{16} , an indication that the polymer donates some of its oxygen for the formation of CO_2 . The difference between the consumed O^{18} and O^{16} evolved as CO_2 corresponds to the oxygen retained by the polymer or by the distillates.

Oxidation of IMAM in Gas-Circulating System. The experiments were conducted at an initial pressure of 1 atm. of air. Gas evolution and consumption were followed, together with the weight loss, as functions of time. Figure 11 shows the number of moles of gas consumed and evolved per mole of polymer unit in the case of an untreated sample of IMAM heated at 300°C. In this case the CO_2 and O_2 values are higher than those shown in Figure 8, probably because a large excess of oxygen was present in the circulating system, in contrast to the experiment in the platinum tube where practically all the O_2 had been used in a relatively short time. The same parallelism between the O_2 and CO_2 curves observed previously is apparent here. The final amount of CO_2 evolved corresponds to 62% of the total O_2 consumed.

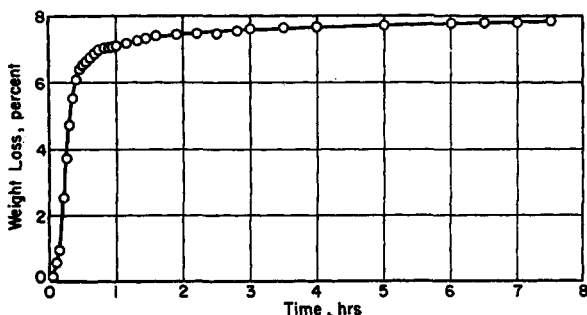


Fig. 12. Weight loss of untreated IMAM in air using gas circulating system (300°C.).

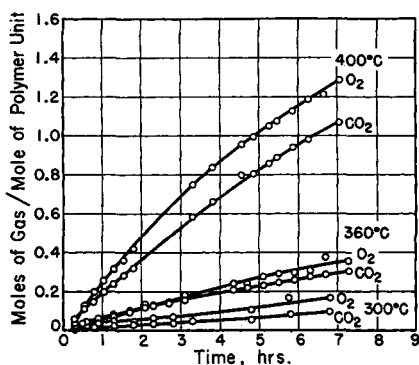


Fig. 13. Gases consumed and evolved during oxidation of IMAM in air at indicated temperatures after degassing in He at 360°C. Gas circulating system was used.

The weight loss as a function of time is shown in Figure 12. About 86% of the total observed weight loss occurs within the initial $\frac{1}{2}$ hr. of heating, after which the weight loss curve approaches a constant rate, a total weight loss of 7.8% being reached after 7.5 hr. of heating. The liquid distillate collected from the cold traps consisted of DMA, traces of water, and a polymeric material whose fundamental structure did not differ appreciably from that of the starting material insofar as it could be identified by infrared technique.

In Figure 13 are shown curves for the oxygen consumption and carbon dioxide evolution at various temperatures for a sample of IMAM which had been previously treated in helium at 360°C. It is observed that all the curves rise almost linearly and pass through the origin. This type of curve has been observed in all degassed samples, not only with regard to gases but also in the case of observed weight loss, whether for IMAM or IM. This is interpreted to mean that approximately 10 wt.-% of the starting material differs drastically in many properties from the remaining 90%, although infrared examination indicates the two fractions to be structurally identical. The curves of Figure 13 show that the CO₂ evolution rate doubles about every 15°C. This is typical of the rate increases frequently observed in chemical reactions.

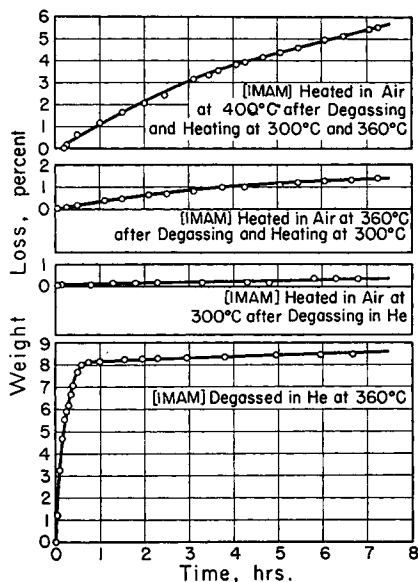


Fig. 14. Weight loss of IMAM at indicated temperatures using gas circulating system.

Figure 14 shows the percentage weight losses at three temperatures based on the original weight of the sample. At 360°C. in helium the bulk of the lower molecular weight polymeric material is lost within the first $\frac{1}{2}$ hr. After the initial 1 hr. period, the weight loss rate in air at 300°C. is approximately the same as in helium at 360°C., but at 360°C. the rate in air rises to about three times that in helium. At 400°C. in air the weight loss rate is approximately four times that at 360°C. in air. The observed weight loss rate is clearly associated with an oxidation process. Approximately the same weight loss rate is observed in the gas-circulating system with helium at one atmosphere pressure as when the system is evacuated. The helium used in the experiment had a measured purity of 99.998% and contained of the order of 1 ppm on a mole basis of oxygen.

C. Long-Term Oxidation of IMAM

Oxidation at 360°C. The oxidation time in all previous work was about 8 hr. As shown in Figure 14, it is only after heating for 8 hr. at 400°C. that the amount of degradation in the sample after degassing becomes appreciable. In order to ascertain the validity of a straight line extrapolation of such short-term results, which might be used in the search for termination of postulated reactions that are taking place, a sample of IMAM was heated in an oxygen-containing atmosphere at 360°C. for approximately 105 hr. During this time the gases consumed and evolved were followed, along with the weight loss. In this long-term experiment, an initial mixture of approximately 60% oxygen and 40% argon was used. Figure 15 shows the O_2 consumption, CO_2 and CO evolution along with the

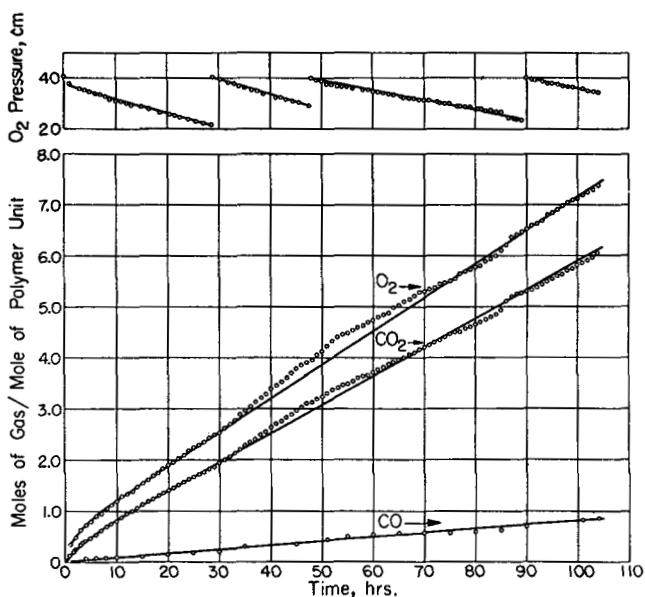


Fig. 15. Gases consumed and evolved in gas circulating system during oxidation of IMAM in oxygen-argon atmosphere at 360°C. after degassing in He at 400°C.

O₂ partial pressure. During the course of the experiment the oxygen-argon mixture was replaced four times. This is shown by the breaks in the O₂ pressure curves. Although previous data indicate that large changes in O₂ pressure influence the reaction rates, the latter do not seem greatly affected by pressure variations within the range presently employed. The O₂ consumption and the CO and CO₂ evolution rates are essentially constant over the 105 hr. period.

Figure 16 shows the observed weight loss $\Delta W/W_0 \times 100$ as a function of time at 360°C. The weight loss rate remains a constant over the entire range. During the course of the experiment a total weight loss of 28% was observed. This loss, however, cannot be uniquely interpreted as a loss only of the original starting material, but rather it is a net value involving both loss and gain. Also given in Figure 16 are the curves for the calculated weight of carbon lost as gaseous CO₂ and CO, and a curve representing the total carbon lost from both species. The loss of carbon from the sample at the end of the 105 hours period amounts to approximately 20% by weight.

The weight per cent of carbon associated with the carbonyl of the four imide groups is 11.7, and that of the single amide carbonyl group is 2.9. The observed total carbon weight loss far exceeds the total of these two (14.6%) and demonstrates that the C=O carbon is not the only carbon involved in the oxidation reaction, if the starting structure of the unit is correct. In fact, the close agreement of the total carbon line and the line expressing 67.5% of the observed weight loss (theoretical weight of carbon

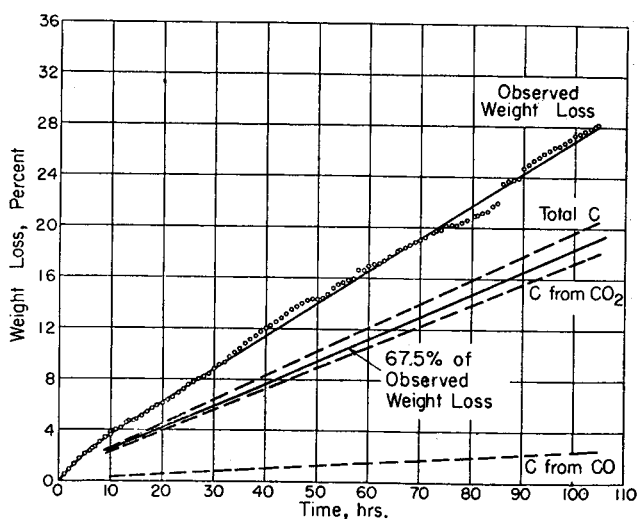


Fig. 16. Observed and computed weight losses ($\Delta W/W_0$) from IMAM at 360°C. in oxygen-argon atmosphere after degassing in He at 400°C.

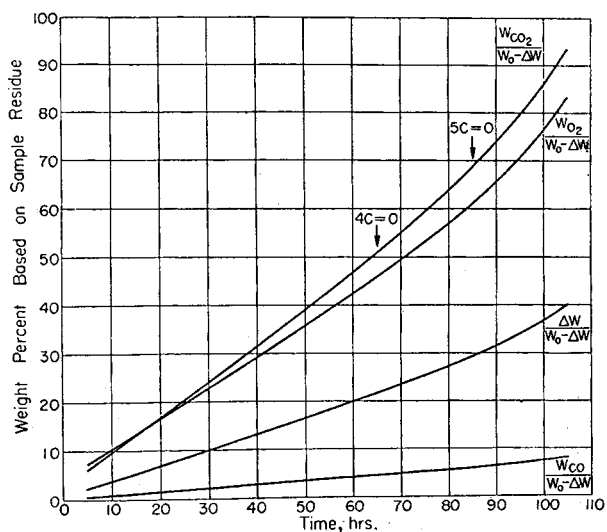


Fig. 17. Gases consumed and evolved from IMAM expressed as weight per cent sample residue. Same conditions as in Fig. 16.

in polymer is 67.5%) suggests that the carbon is not selectively lost from the amide or imide group but rather that a complete degradation of each polymer unit occurs.

If it is assumed that the observed weight loss (ΔW) is a measure of the quantity of polymer destroyed, the remaining polymer being ($W_0 - \Delta W$), curves can be derived such as those shown in Figure 17. The two positions marked 4 C=O and 5 C=O correspond to four and five atoms of carbon

per polymer unit, respectively, lost in the form of carbon dioxide. There are four imide C=O groups in each polymer unit and a total of five imide plus amide C=O groups. The fact that the curve passes smoothly through this region is evidence that these groups are not the primary source of the carbon evolved as carbon dioxide. On the other hand, it is conceivable that the initial attack point of a completely destroyed polymer unit could have been one of the carbonyl group types, probably the amide group (see discussion on infrared results).

The data presented above relate to the oxidized portion of the sample and suggest that the chemical composition of the remaining residue is only slightly different from that of the original sample. In order to examine this point, an elemental analysis was obtained of the original sample and of the residue after 105 hr. of heating in oxygen at 360°C. The results are shown in Table I.

Differences between the theoretical composition and the composition obtained from experimental analysis of the original sample are believed to arise from inherent difficulties in the analytical methods rather than a departure from the theoretical composition. The elemental analysis of the original sample and residue performed by two independent laboratories seem to indicate no large differences in composition. One of the disturbing features of the elemental analyses is that in no case do the individual components total 100%. Although the experimental analyses may reveal the presence of minor differences between the original sample and the residue at 360°C., the significance of such differences becomes clearer after examination of the residue from a sample that has undergone 80% weight loss at 400°C.

TABLE I
Elemental Composition of IMAM Resin Before and After Oxidation at 360°C.

Sample	C, wt.-%	H, wt.-%	N, wt.-%	O, wt.-%
Theoretical	67.5	2.7	10.3	19.6
Original sample				
Commercial lab A	63.44	2.64	8.57	
	63.58	2.67	8.77	
Checks	64.01	3.77	8.52	20.43
	64.17	3.67	8.59	20.45
	64.24	3.57	8.72	
	63.15	3.69	8.72	
Commercial lab B	63.42	3.86	8.35	21.63
	65.86	3.63	8.63	
Residue (105 hr.)				
Commercial lab A	63.44	2.64	8.57	20.27
	63.58	2.67	8.77	20.51
	63.60	2.94	8.78	
	62.86	2.78	8.94	
Commercial lab B	61.09	2.69	7.98	21.70
	64.31	2.64		
	64.55	2.44	8.38	

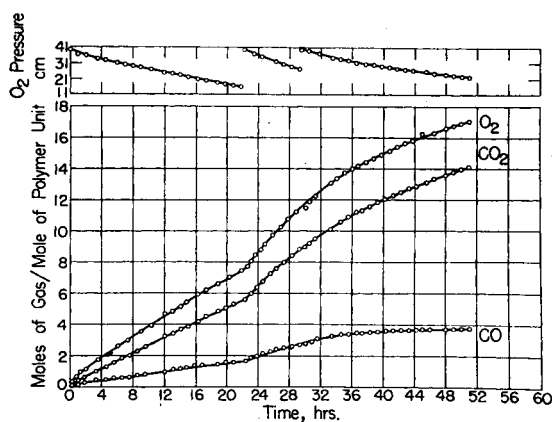


Fig. 18. Gases consumed and evolved in gas circulating system during oxidation of IMAM at 400°C. after vacuum treatment for 3 hr. at 400°C.

Oxidation at 400°C. The long-term oxidation results at 360°C. suggest that the polymer is being primarily destroyed unit by unit. In order to substantiate such a mechanism, it was desirable to oxidize a much higher percentage of the sample than was oxidized at 360°C. To obtain this high degree of reaction within a reasonable time, the polymer was oxidized in a 60:40 (by volume) oxygen-argon mixture at 400°C. Figure 18 shows the oxygen consumed and the CO₂ and CO evolved in the circulating system as functions of time at 400°C., along with the oxygen pressure. In general, the O₂, CO₂ and CO curves approach straight lines. Departures from linearity are believed to result from insufficient control of experimental conditions rather than from a departure from a constant rate. Changes in rates appear to be associated with refilling the system with the oxygen-argon mixture.

The quantity of oxygen evolved in the form of CO and CO₂ accounts for 95% of the oxygen consumed throughout the entire run. The missing 5% of oxygen is equivalent to 0.85 mole per polymer unit. The polymer originally contained 2.5 moles of O₂ per polymer unit, making a total of 3.35 moles of O₂ per polymer unit unaccounted for. The combination of a major portion of this excess O₂ (2.75 mole) with the H₂ contained in the unit (5.5 mole) to form water provides an acceptable material balance even in the absence of nitrogen-containing reaction products.

It is interesting to note that 4 moles of CO per mole of polymer unit are obtained at the termination of the run. During the run 80% weight loss of the sample was observed. The total carbonyls available in the destroyed fraction of the sample is 80% of five carbonyls and this might suggest that the observed CO is primarily associated with the carbonyl groups. The approximately constant rates observed for O₂ consumption and CO₂ and CO evolution during the degradation of 80% of the original sample suggest that throughout this period the number of available reaction sites is the

same at any time on the curve. A logical constant during the degradation reaction is the number of chain ends. If the oxidative attack were a random process, the average molecular weight of a chain would be rapidly reduced. In such a case, the resulting lower molecular weight materials of the same structure would be expected to be much less resistant to oxidation (see initial portion of curves of Figs. 11 and 12).

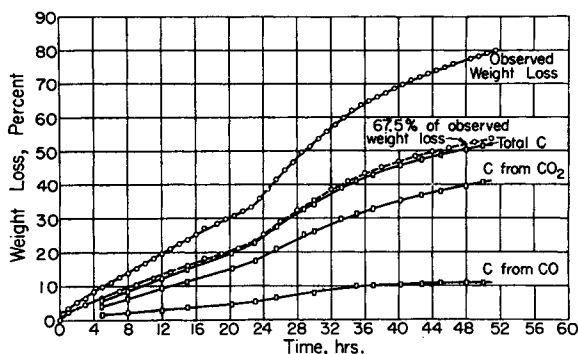


Fig. 19. Observed and computed weight losses ($\Delta W/W_0$) of IMAM at 400°C. after vacuum treatment for 3 hr. at 400°C.

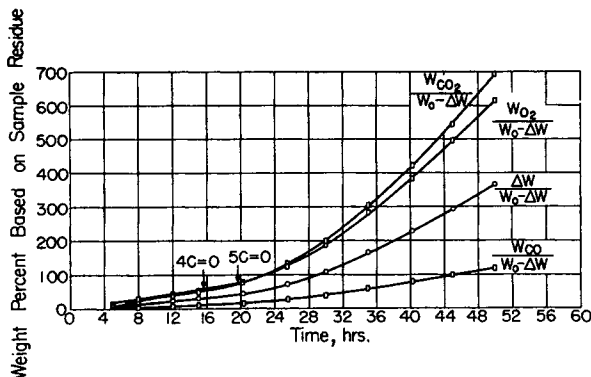


Fig. 20. Gases consumed and evolved from IMAM expressed as weight per cent sample residue. Same condition as in Fig. 19.

In Figure 19 is shown the observed weight loss of the sample at 400°C. along with various curves associated with the carbon behavior. Nearly linear curves are obtained for the weight per cent carbon from the CO and CO₂ evolved. The total carbon curve is merely the sum of the carbon from the evolved CO and CO₂. The dotted line represents 67.5% of the weight loss curve, corresponding to the theoretical carbon content of the starting material. The close agreement of these two curves indicates that the difference between the observed weight loss curve and the measured total C weight loss is accounted for by the O, N, and H loss from the polymer.

The curves shown in Figures 18 and 19 were calculated using the original weight of the sample. Figure 20 shows curves of the weight loss, the weight of O₂ consumed, the weight of CO₂ evolved, and the weight of CO evolved up to any time (T) divided by the weight of the remaining polymer sample. The increasing slope of the curves with time shows the increased activity of the sample residue. This increased activity may be due to the reduction in molecular weight of each chain during oxidation and to the resulting increase in the ratio of the number of chain ends per unit weight of residue, or to the formation of more active intermediates in the polymer.

The above interpretation of the experimental curves is based on the assumption that the residue has, at any time, approximately the same chemical composition as the starting material. Unfortunately, the role of nitrogen is obscure and although traces of HCN and nitric oxide have been observed in the system atmosphere, they are far too small to account for the total nitrogen associated with the degraded polymer. In order to obtain additional information on the role of the hydrogen and the nitrogen, an elemental analysis was obtained of the residue at the end of the 400°C. run in which the original sample had lost 80% of its weight. The analyses obtained from commercial analytical laboratory A are shown in Table II.

Large differences in the carbon, nitrogen, and hydrogen content are found when comparing the above analytical results with those of the starting material in Table I. The carbon and the hydrogen contents are lower in the residue and the nitrogen content is considerably greater. The oxygen content is indicated as slightly lower. The difficulty of such analysis is evidenced by the fact that the results total approximately 93%. However, the changes in composition reported are believed due to chemical changes resulting from the treatment.

A number of samples of the original material, the distillates collected in the traps, and the residues were examined by infrared spectrometric techniques. Since the spectra are difficult to interpret, only tentative conclusions were drawn from the infrared results. The spectrum of the residue after the 360°C. run was quite similar to the spectrum of the original sample. On the other hand, the spectrum of the distillate from the 360°C. run shows considerable change in the chemical structure. The observed disappearance of any vibrational level corresponding to a *para*-substituted structure in the distillate suggests that the initial attack might have occurred at the *p*-phenylenediamine structure. A greater reduction of the amide band intensity than of the imide band intensity was observed.

The infrared analysis also revealed the presence of the C≡N structure in the distillate. This observation, coupled with the observation of HCN

TABLE II

Sample	C, wt.-%	H, wt.-%	N, wt.-%	O, wt.-%
Residue at	56.25	1.65	16.36	18.04
400°C.	56.52	1.85	16.44	18.36

and nitric oxide by mass spectrographic methods and the increased nitrogen content in the residue illustrates the complexity of the chemical reactions involving the nitrogen in the polymer.

In addition, emission spectrographic analyses were made of the starting material and of the residue (400°C.) for metallic constituents. The results obtained are shown in Table III.

TABLE III
Spectrographic Analyses of IMAM Resin

Metallic constituent	Amt. metal, wt.-%	
	Original IMAM	IMAM residue at 400°C.
Ca	0.001	0.002
Al	0.0025	0.02
Cr	<0.0025	<0.0025
Na	<0.025	<0.025
Li	<0.025	<0.025
K	<0.025	<0.025
B	0.0025	0.0025
Si	0.0025	0.025
Fe	0.005	0.02
Mn	<0.0025	<0.0025
Pb	<0.0025	0.0025
Mg	<0.0025	0.0025
Ti	<0.0025	<0.0025
Cu	0.0025	0.005
Ag	<0.0025	<0.0025

These semiquantitative results show that the metal content of the residue is appreciably higher than that of the original sample. The total metal content of the residue approaches 0.1 wt.-%. It is possible that the metals at the reported levels influence the oxidation rates.

IV. CONCLUSIONS

The degradation mechanism of imide and imide-amide-containing polymers is interpreted to be one of unit-by-unit destruction and the rate-controlling factor to be the number of available chain ends. The point of attack of a single polymer unit is probably the carbonyl group, the amide carbonyl possibly being more labile than the imide carbonyl.

The major oxidation products are CO₂, CO, and water, which provide a complete material balance for C, H, and O in the polymer. Nitrogen-containing compounds are observed in the distillates and in the form of gases, and the residue is enriched with nitrogen.

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Résumé

Dans de nombreux laboratoires industriels on étudie actuellement les polyamides et polyimides aromatiques de haut poids moléculaire. Les fils émaillés, les résines et les vernis utilisés pour le laminage et l'imprégnation, qui contiennent cette nouvelle sorte de polymères thermiquement stables, supportent les températures opérationnelles plus élevées que la plupart des substances polymériques organiques en usage aujourd'hui. La résistance à la chaleur et à l'oxydation de deux de ces résines a été étudiée à l'air dans l'oxygène, et dans l'oxygène enrichi en O^{18} pour un domaine de température compris entre 300 et 400°. On suppose que le mécanisme de dégradation est constitué par une destruction du polymère unité par unité.

Zusammenfassung

Aromatische Polyamide und Polyimide mit hohem Molekulargewicht werden gegenwärtig in vielen Industrielaboratorien entwickelt. Drahtemails, Schicht- und Imprägnierungsharze und Firnisse aus dieser neuen Art thermisch stabiler Polymerer halten höhere Anwendungstemperaturen als die meisten organischen heute verwendeten Polymeren aus. Die Wärme- und Oxydationsbeständigkeit zweier dieser Harze wurde in Luft, Sauerstoff und O^{18} -angereichertem Sauerstoff in einem Temperaturbereich von 300–400°C untersucht. Als Abbaumechanismus wird eine schrittweise Zerstörung des Polymeren angenommen.

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