Effects of Interfaces on the Thermal Degradation of Polymer–Metal Composites

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Synopsis

Previous studies by Black and Blomquist on the degradative failure of polymer–metal adhesive bonds have shown that composite failure depends largely on the type of metal substrate employed.   In the work reported herein, metal powders of high surface area have been employed to maximize the metal–polymer interface.   The composite systems studied consisted for aluminum and iron with polycondensates of bisphenol A–diglycidyl ether, phenol–formaldehyde and poly-2,2'-(*m*-phenylene)-5,5'-bibenimidazole.   The composites were prepared in the absence of air and thermally degraded in a time-of-flight mass spectrometer while the degradation products were continuously monitored from mass 1 to 200.   In the polymer and polymer–metal systems investigated, iron accelerated the decomposition of all polymers studied.   This was determined by plotting m/e against degradation temperature for the more common mass peaks such as hydrogen and carbon monoxide for the carbon–hydrogen–oxygen-containing polymer and hydrogen cyanide and ammonia for the carbon–hydrogen–nitrogen-containing polymer.   This technique offers promise in determining the nature of the interface as well as the effect of the interface on polymer degradation.

INTRODUCTION

A knowledge of elementary reactions in the solid and gaseous states at an interface is essential for the understanding of degradative processes in a polymer–metal composite.   The studies of Black and Blomquist[1] on the degradative failure of polymer–metal adhesive bonds have shown that failure depends largely on the type of metal substrate employed.   More specifically, a phenol–epoxy adhesive is resistant to thermal degradation in bonds with aluminum but deteriorates rapidly with stainless and carbon steel, copper, and brass.

The approach used in the present work involved the use of composites consisting of metal powders of high surface area in combination with selected polymers.   The study included the careful characterization of the metal powders as well as purification of the polymers.   Maximizing the interface area by using metal powders of high surface area was complemented by the use of mass spectrometry for determining the composition of degradation products.   With this approach it was found that good correlation could be obtained between the previously demonstrated mechanical properties of polymer–metal plate composites and the chemical behavior of polymers in

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contact with metal powders. The loss of integrity of composites of polymers on metal substrates under thermal and oxidative environments has been ascribed by some to the catalytic effect of the metal substrates. It is generally accepted that, if present, the catalytic effect of the metal substrate should be exhibited in the interfacial region and it is in this region that adhesive failure occurs. The experimental difficulty lies in separating the oxidative, thermal, and catalytic degradative processes. Elimination of oxygen from the interfacial region can be used to minimize the first of these and study of the degradation of bulk polymer can be used to account for the second. Polymer degradation in contact with metal with subsequent analysis of the products so formed then provides information on the third process, namely, the catalytic effect. These products can be detected accurately by mass spectrometry, particularly if the amount of the interfacial region is increased relative to that of the bulk polymer. Continuous monitoring of the degradation process by mass spectrometry over a temperature range yields a temperature profile of the composite degradation.

The present paper describes some data reported previously on an Air Force contract.[2,3] The overall applicability and high sensitivity of the techniques used offer promise and new understanding of the properties and behavior of interfaces in general and of composites under thermal stress in particular.

EXPERIMENTAL

Characterization of Experimental Polymers and Metal Powders

Bisphenol A–Diglycidyl Ether Polycondensate. The epoxy resin used was prepared from a bisphenol A–epichlorohydrin adduct monomer. The epoxy equivalent weight was 174; theoretical 177. The dissolved oxygen in the resin and in the triethylenetetramine curing agent was removed by alternate freezing and thawing in vacuum.[4]

Phenol–Formaldehyde Polycondensate. The phenolic resin used was base-catalyzed and handled in an isopropyl alcohol solution at a concentration of 61.5% by weight. Air was removed from the prepolymer by bubbling helium through the solution.

Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole. The bibenzimidazole prepolymer was supplied by the Air Force Materials Laboratory, Wright Patterson AF Base, Ohio. The material was recystallized from methylene chloride and dissolved in pyridine at a concentration of 52% by weight for composite preparation.

Iron and Aluminum Metal Powders. The metal powders of high surface area were produced by evaporating the metal at reduced pressure in an inert argon atmosphere.* The powders were collected and stored and shipped under argon gas in air-tight containers.

The ultrafine iron powder of high surface area used in this work con-

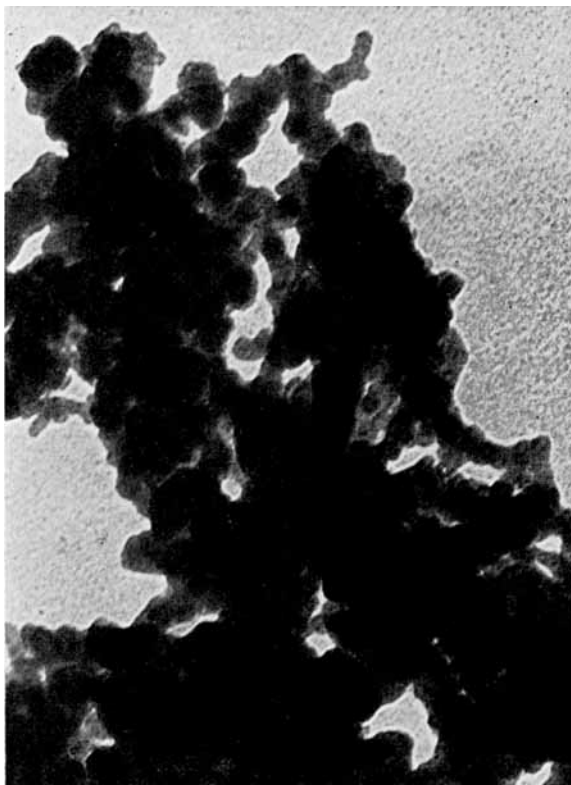* The source of this material was National Research Corporation, Cambridge, Massachusetts.

Fig. 1. Electron photomicrograph of ultrafine iron powder showing agglomerates and bridging between particles. Magnification ×392,000.

tained oxides of Fe_2O_3 and Fe_3O_4. The oxide concentration varied between 3 and 8%. The ultrafine high-surface-area aluminum powder used contained slight impurities of zinc, iron, copper, chromium, and possibly lead. It was assumed that the aluminum was also partially oxidized, since x-ray patterns of unexposed samples were identical to samples exposed to air. The particle sizes of the powders were in an average range of 300 A. The iron powder, in contrast to the aluminum, was highly agglomerated. An electron photomicrograph of the iron powder is shown as Figure 1.

Preparation of Polymer–Metal Composites

To eliminate oxygen from the composite system an inert atmosphere (helium) glove box was used during composite preparation. A glove box capable of being evacuated to 3×10^{-2} torr was equipped with a helium inlet line. To this line was added a train containing a magnesium perchlorate scrubber for the removal of trace water, an external cryosorption trap (a copper coil filled with synthetic zeolite 5 A. pore diameter) operating at liquid nitrogen temperature for the removal of oxygen, and internal to the glove box a NaK (sodium–potassium alloy) bubbler to serve as a final
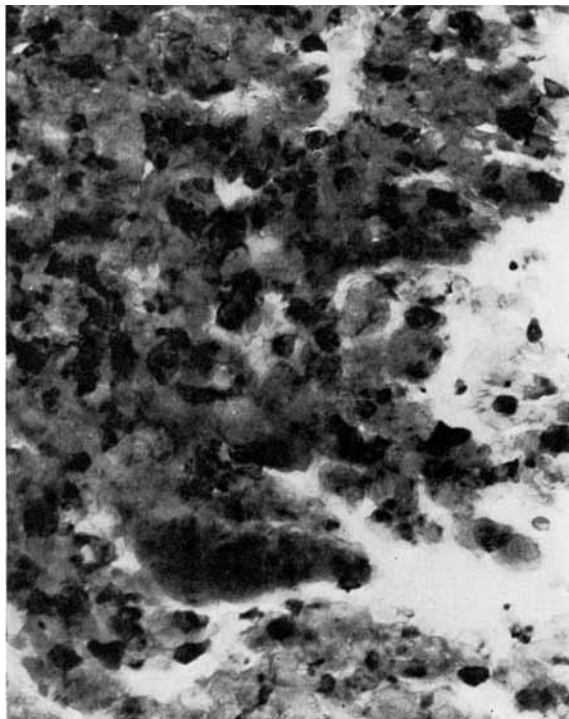
Fig. 2. Electron photomicrograph of a thin section of an epoxy–aluminum (ultrafine powder) composite cured at room temperature. Magnification ×136,000.

getter for traces of O_2 and water. A "cure cell" inside the glove box was used for the preparation of polymer–metal composites and for curing. The products and gas from the cure cell were vented to an external trap. The epoxy and phenolic polymers were cured in a fluorinated ethylene–propylene polymer release cup which was molded at 425°C.

The polymer and metal powders were mixed and cured to yield composites containing approximately 33% by weight metal. The cure temperature for the epoxy–metal composite was 2 hr. at 100°C. An electron photomicrograph of an aluminum–epoxy composite is shown as Figure 2. The phenolic–metal composites were cured for 2 hr. at 100°C. and 1 hr. at 150°C. The polybibenzimidazole (PBI)–metal composites were cured for 2 hr. at 300°C. The composites were cooled, powdered, and stored in a helium atmosphere until degradation.

Mass Spectrometric Thermal Analysis

The finely powdered polymer–metal composites (based on 10 mg. of polymer) were placed in a glass cell containing a thermocouple and heated with a programed resistance heater at a rate of 10°C./50 sec. The decomposition products were allowed to pass continuously into a time-of-flight mass spectrometer by means of a controlled leak. Spectra in the

range 1–200 were determined every 50 sec. for a given polymer–composite degradation series; the quantity of resin and the instrument sensitivity were held constant. No attempt was made to calibrate the instrument to a given concentration of decomposition products. Instead, the ion signal was plotted as a function of decomposition temperature.

DISCUSSION

Product Analysis

The decomposition spectra of all three polymers—epoxy, phenolic, and polybibenzimidazole—were extremely complex. The main products were similar to those reported previously by other workers using this[5–9] and other techniques.[10] The main peaks used to monitor interface degradation were the hydrogen and carbon monoxide peaks for the epoxy and phenolic resin and hydrogen, carbon monoxide, hydrogen cyanide, and ammonia peaks for the polybibenzimidazole resin. The position of the mass peaks with respect to temperature and the area under the curve are both indicative of the influence of the metal substrate on the degradation of the polymer interface.

The addition of metal to the before mentioned polymer system further complicates the spectra. The effects of temperature and metal substrate
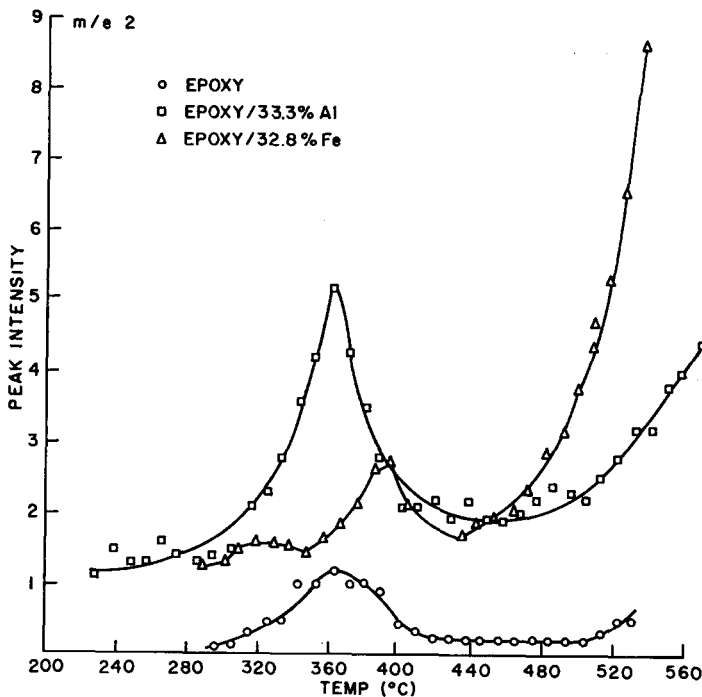

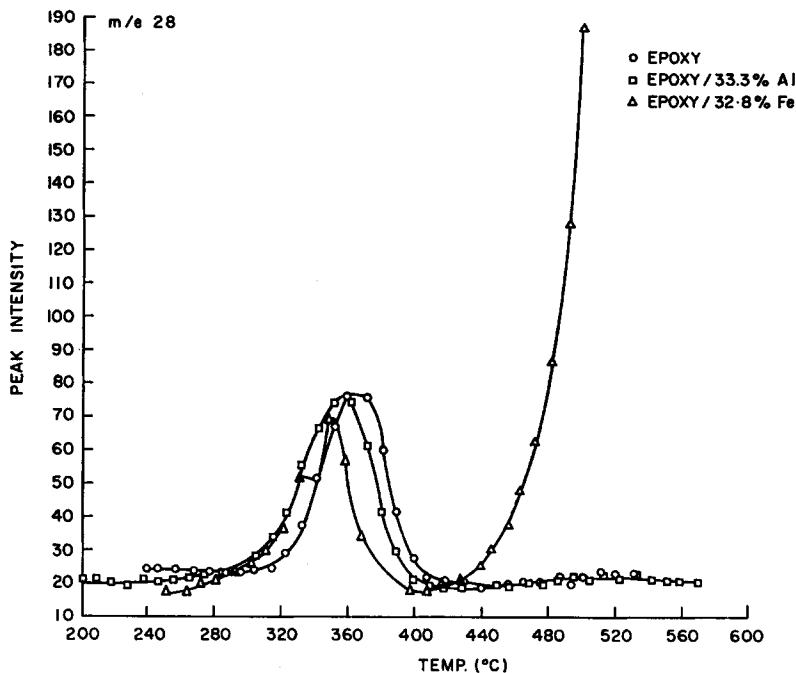Fig. 3. Plot of the yield of m/e 2 vs. temperature.

Fig. 4. Plot of the yield of m/e 28 vs. temperature.

on product distribution from pyrolysis of epoxy resin–metal composite systems are shown as Figures 3 and 4. The yield of the mass 2 peak at lower temperature was proportional to m/e 18 up to 400°C. Above 400°C. the mass 2 peak results from molecular hydrogen. The epoxy–iron composite yields hydrogen at a greater rate and lower temperature than the epoxy and epoxy–aluminum composite. The m/e 28 (CO$^+$) for the epoxy system are plotted as Figure 4. Again, the epoxy–iron composite liberates carbon monoxide at a greater rate and lower temperature than either pure epoxy or epoxy–aluminum composites. The liberation of hydrogen as well as carbon monoxide starts significantly at approximately 440°C. In summary, when epoxy resin was heated with iron: (1) increases in each of the major low molecular weight products occurred, (2) the maximum yield point for each of these products was shifted to a lower temperature, (3) the lower molecular weight products were drastically increased at the high temperatures.

The investigation of the phenolic–metal composite system was complicated by the necessity of using isopropyl alcohol as a solvent carrier for the polymer. The effect of solvent on the composites was only detectable in the phenolic–aluminum system. The effects of temperature and metal substrate on product distribution for the pyrolysis of the phenolic resin–metal composite system are shown as Figures 5 and 6. The hydrogen curves m/e 2 (Fig. 5) reflect the influence of iron at the polymer interface. Again, the catalytic effect of the metal on the polymer interface can be de-
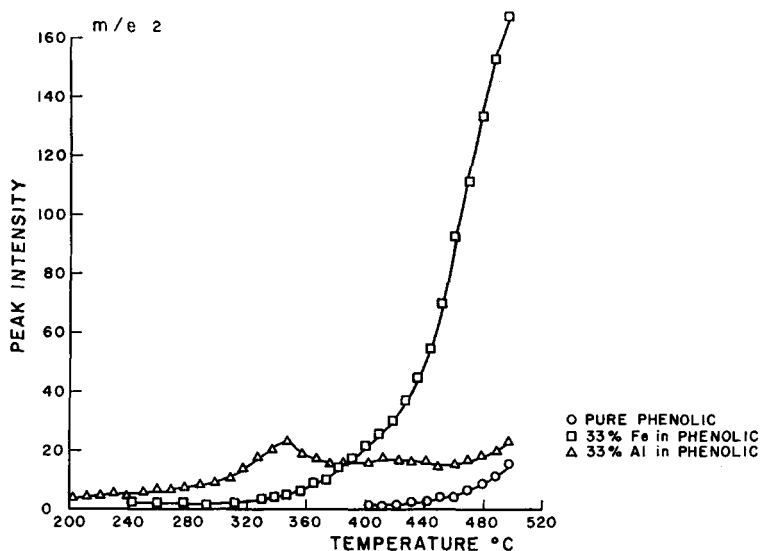
Fig. 5. Plot of the yield of m/e 2 vs. temperature for phenolic–metal composites.
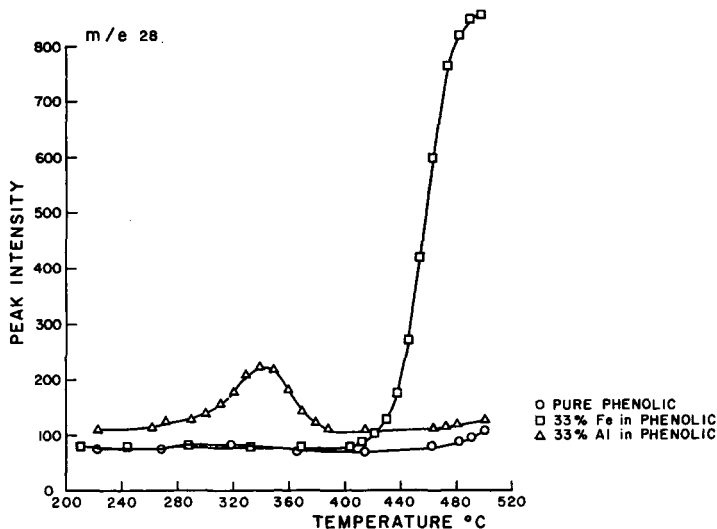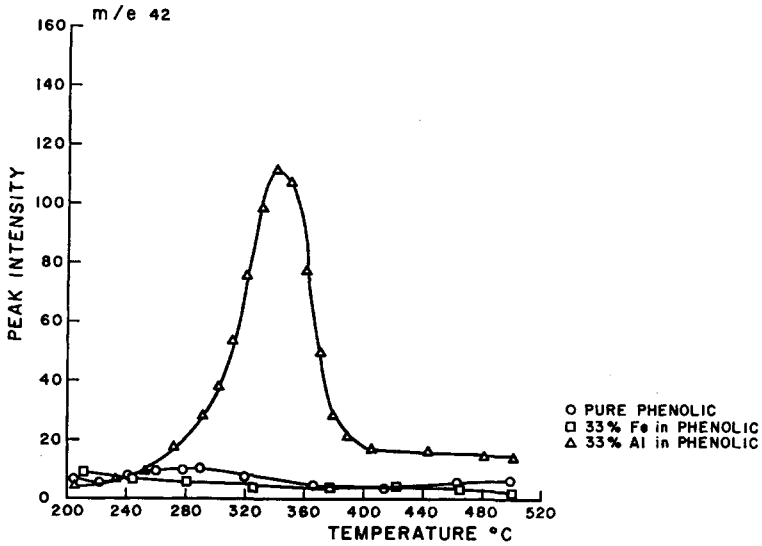

Fig. 6. Plot of the yield of m/e 28 vs. temperature for phenolic–metal composites.

tected. Although the degradation temperature of the phenolic polycondensate was carried only to 500°C. in this work, the degradation of pure phenolic by Shulman and Lochte[7] using a similar technique demonstrated that at higher temperatures the pure phenolic polymer also yields considerable quantities of hydrogen. The hydrogen degradation product of phenolic–aluminum are substantially the same at these temperatures. The m/e 28 (CO$^+$) for the phenolic systems are plotted in Figure 6. The tem-

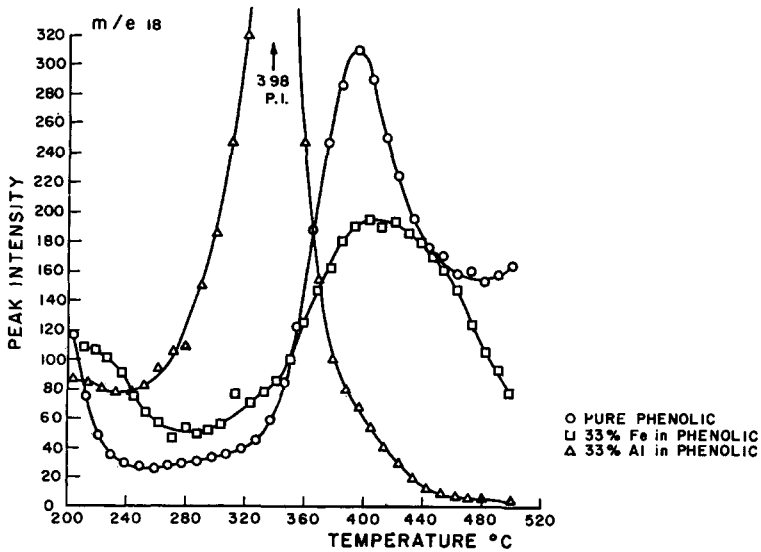Fig. 7. Plot of the yield of m/e 42 vs. temperature for phenolic–metal composites.

Fig. 8. Plot of the yield of m/e 18 vs. temperature for phenolic–metal composites.

peratures of the catalytic degradation of the iron–phenolic composite are the same as for the hydrogen peaks. The isopropyl alcohol solvent in the phenolic resin has reacted with or was absorbed on the aluminum powder during composite preparation. This is shown in Figure 7 in which the m/e 42 peak ($CH_3CH_3=CH_2$) is plotted. In Figure 8 can be seen the m/e 18 (H_2O^+) water peak which results from the dehydration of the iso-propoxide group. In this instance the polymer was protected from any catalytic effect of the metal substrate.
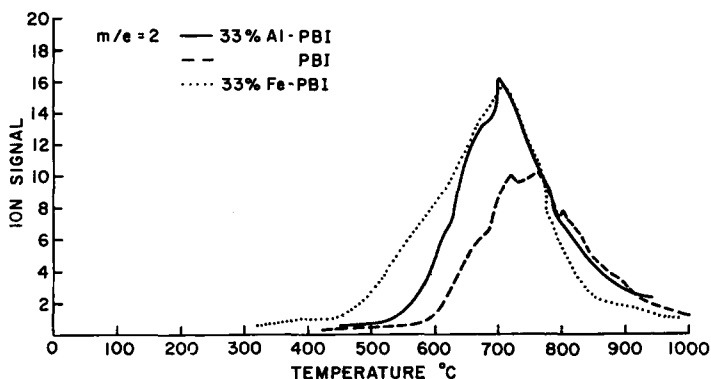
Fig. 9. Plot of the yield of m/e 2 vs. temperature for PBI and PBI–metal composites.
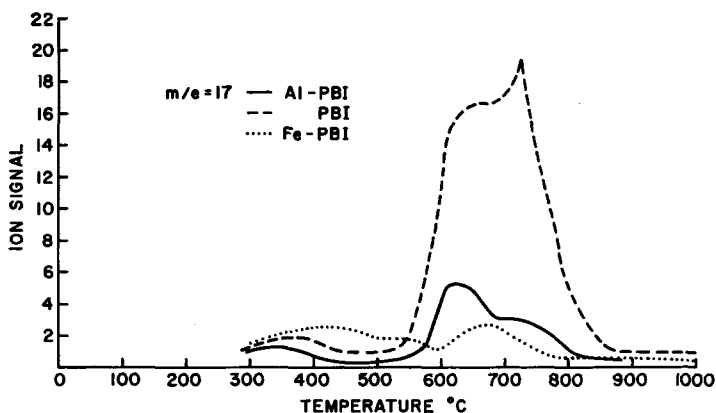

Fig. 10. Plot of the yield of m/e 17 vs. temperature for PBI and PBI–metal composites.

The results on the degradation products of polybibenzimidazole alone at elevated temperatures were in agreement with the findings of other workers;[8,9] notably water and phenol were the only significant products below 550°C., with the latter product probably representing a measure completeness of polymerization. The influence of iron on interfacial degradation of polybibenzimidazole markedly changed these observations. There was little difference in the hydrogen peak obtained from the degradation of the polybibenzimidazole composites (Fig. 9). This indicates that the hydrogen atoms attached to aromatic rings do not appear to be as labile to catalytic effects as those attached to aliphatic carbon chains. Detectable also was the lower temperature of degradation of the polybibenzimidazole–iron composite. The m/e 17 peak, mostly ammonia, is shown as Figure 10. The polybibenzimidazole yields considerably more ammonia than either the iron or aluminum–bibenzimidazole composites. Concerning the hydrogen cyanide peak (m/e 27), the bibenzimidazole–iron composite yields very little HCN as compared to bibenzimidazole and bibenzimidazole–aluminum composite (Fig. 11). The m/e 28 peak (Fig. 12)
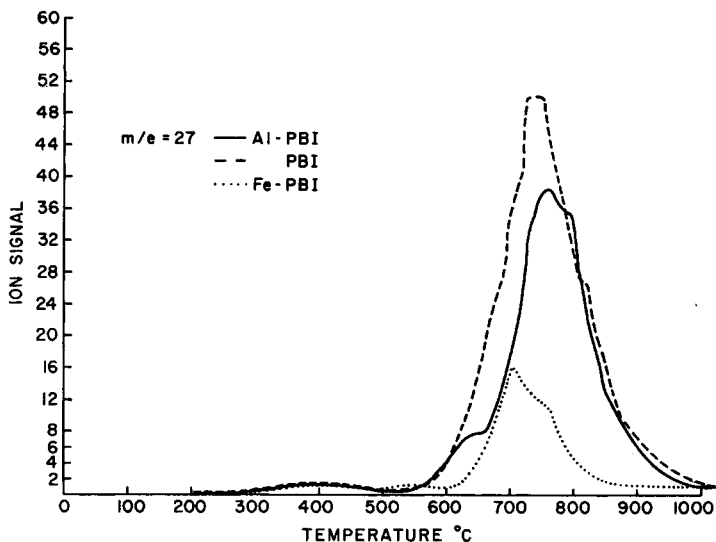
Fig. 11. Plot of the yield of m/e 27 vs. temperature for PBI and PBI–metal composites.
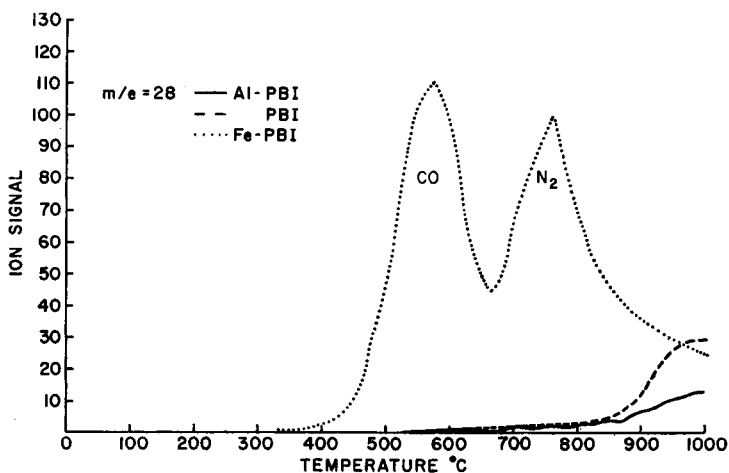

Fig. 12. Plot of the yield of m/e 28 vs. temperature for PBI and PBI–metal composites.

consists mostly of carbon monoxide and nitrogen. The peak at 575°C. in the iron–bibenzimidazole composite was a result of carbon monoxide formation, while the 765°C. peak resulted from nitrogen. These assignments were based not only on the m/e 28 peak but also on the heights of the respective daughter fragments, m/e 16 and m/e 14. It was significant that the bibenzimidazole and the bibenzimidazole–aluminum composites did not yield these products. In these instances not only was the rate of a reaction changed, but completely new reaction products were obtained.

In conclusion, certain metals have a catalytic effect on the thermal degradation of a polymer interface in the absence of oxygen. This effect was

demonstrated for an iron substrate with epoxy, phenolic, and polybibenz-imidazole polymers by means of mass spectrometry. The degradation product analysis of the composites is in agreement with the observed increased rate loss of mechanical integrity of steel–polymer as compared to aluminum–polymer composites.

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Résumé

Les études antérieures de Black et Blomkist sr la dégradation de liens adhésifs polymère-métal ont montré que la cassure dépend fortement du type de substrat métallique utilisé. Dans le présent travail des poudres métalliques à grande surface ont été utilisées pour augmenter au maximum l'interface polymère-métal. Les systèmes composites étudiés consistaient en aluminium et en fer avec des polycondensats à base de bisphénol-A, glycidyl éther, de phénol–formaldéhyde et de poly-2,2'-(m-phénylène)-5,5'-bibenzymidazol. Ces composites étaient préparés en absence d'air et dégradés thermiquement dans un spectromètre de masse Time of Flight tandisque la polydégradation est continuellement enregistrée de la masse 1 à 200. Dans le plymère et les systèmes métal–polymère étudiés, le fer accélère la décomposition de tous les polymères étudiés. Ceci était déterminé en portant graphiquement en fonction de la température de dégradation pour des pics de masse les plus communs, l'hydrogène et l'oxyde de carbone pour les polymères contenant du carbone, de l'hydrogène et de l'oxygène et HCN

et NH$_3$ pour les polymères contenant du carbon–hydrogène–azote. Cette technique permet de déterminer la nature de l'interface aussi bien que l'effet de l'interface sur la dégradation des polymères.

Zusammenfassung

Frühere Untersuchungen von Black und Blomquist über die Abbaubeständigkeit von Polymer-Metallklebeverbindungen haben gezeigt, dass die Beständigkeit des zusammengesetzten Systems weitgehend vom Typ des verwendeten Metallsubstrates abhängt. In der vorliegenden Arbeit wurden Metallpulver mit grosser spezifischer Oberfläche verwendet, um die Metall-Polymergrenzfläche möglichst gross zu machen. Die untersuchten zusammengesetzten Systeme bestanden aus Aluminium und Eisen mit Polykondensaten aus Bisphenol-A-diglycidyläther, Phenol-Formaldehyd und Poly-2,2'-(m-phenylen)-5,5'-bibenzimidazol. Die zusammengesetzten Systeme werden unter Luftausschluss hergestellt und in einem Flugzeit–Massenspektrometer unter kontinuierlicher Registrierung der Abbauprodukte von der Masse 1 bis 200 thermisch abgebaut. Bei den untersuchten Polymer- und Polymer–Metallsystemen beschleunigte Eisen die Zersetzung aller untersuchter Polymerer. Das wurde durch Auftragung von m/e vs. Abbautemperatur für die gewöhnlicheren Massenmaxima, wie Wasserstoff und Kohlenmonoxyd bei dem Kohlenstoff-Sauerstoff-Wasserstoff-hältigen Polymeren und Cyanwasserstoff und Ammoniak bei den Kohlenstoff-Wasserstoff-Stickstoff-hältigen Polymeren, festgestellt. Dieses Verfahren scheint für die Bestimmung der Natur der Grenzfläche und des Einflusses der Grenzfläche auf den Polymerabbau brauchbar zu sein.