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Final Report

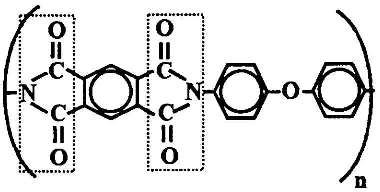
Surface Evaluation by XPS of High Performance Foams After Exposure to Oxygen Plasma

Dr. Michael D. Hampton

Introduction

This report will present the results of a study done during a 10-week summer faculty fellowship during the summer of 2001 working with Ms. Martha Williams of the Testbeds Group at Kennedy Space Center. The work was in a new area for this faculty and was both interesting and enjoyable.

An imide is a in which nitrogen is bonded directly to an R group and to two other R groups through carbonyls. The structure below is that of Kapton, a commercially available polyimide, and the imide groups in the repeating unit of the polymer are indicated by the dashed boxes.



Polyimides have a number of properties that make them highly desirable materials for use on structures that are exposed to extreme conditions. They are strong, fire resistant, minimally outgasing, stable over a large temperature range, resistant to chemical attack, transparent to infrared and microwaves, and have a low density. One polyimide, solimide, commercially available as a foam, retains resiliency from –300°F to +500°F, is highly flame retardant, and decomposes with virtually no smoke or toxic byproduct formation. The density of this product is such that its use in place of fiberglass in the lower lobe of a 747 saves 400 lb. Shipboard applications have resulted in literally tons of weight reduction.

While polyimide films have been used in structures to be placed in low earth orbit (LEO) for many years, polyimide foams have found only minimal application in this realm. NASA Langley Research Center has developed new technology that allows for the processing of new polyimide foams. The resulting increased availability of these materials, along with their highly desirable properties, has prompted a study to determine the suitability of these materials for use in structures to be placed in LEO.

The atmosphere at LEO altitudes has a composition that is essentially the reverse of that in the troposphere, 20% N_2 and 80% O_2. Without the overlying atmosphere to filter short wavelength UV radiation (<243 nm), the molecular oxygen present is largely photodissociated to atomic oxygen (AO). Atomic oxygen is a highly reactive substance and thus is prone to rapidly oxidize materials exposed to it. Making the situation more extreme is the fact that structures in LEO are typically moving rapidly, as fast as 8 km/s, to maintain the orbit. Moving at that speed, it is typical for structures to collide with atomic oxygen with an energy of as much as 5 eV and to encounter 3×10^{24} oxygen atoms per cm^2 of surface area per second.

Before utilizing polyimide films in the aggressive environment of LEO, it is important to understand how they will perform. The purpose of this study was to study the interaction of atomic oxygen with these foams in order to determine their suitability for use in LEO applications. In the study, an oxygen plasma generator was utilized to produce an atmosphere of atomic oxygen that will simulate the atmosphere of LEO.

Experimental

The H, L. and C-series foams were supplied by NASA Langley Research Center. The foam samples supplied by Langley Research Center have labels in which the first letter indicates the series. Solimide was supplied by the manufacturer, Inspec foams, Inc. Kapton tape, Mystic 7362, was purchased from NASA federal stock. Kapton HN films, HN 100 (1 mil thick) and HN 200 (2 ml thick) were provided by the manufacturer.

Surface analysis of samples was done with a Kratos XSAM XPS/AES/ISS/SEM system. Foam samples were typically placed in the sample insertion chamber and allowed to pump down for 1-3 days before analysis. Film samples only required 2-3 hours to pump before analysis. Analyses were done with a Mg anode at 12 kV and 10 mA.

The oxygen plasma was generated with a SP1 Plasma Prep II plasma etcher. The Plasma Prep II was operated with an oxygen atmosphere at a feed pressure of 5 - 25 psi. The etcher was used at full power for cleaning sample pans and for the initial foam exposure. The second trial of atomic oxygen exposures was done at 25% power.

The effective atomic oxygen flux with the cavity of the etcher was determined, using the following procedure, at 100%, 50% and 25% power levels. This procedure was originally worked out by this researched and then was found to conform to that found in ASTM E 2089-00, "Standard Practices for Ground laboratory Atomic Oxygen Interaction Evaluation of Materials for Space Applications". Aluminum sample pans were cleaned by placing in the etcher at full power for 1 hour. Samples of Kapton tape, roughly 1-2cm square, were placed in cleaned aluminum samples pans, mastic side down, and weighed. Samples were then individually placed in the etcher and exposed to oxygen plasma for 30 min periods at the desired power level. After each 30 min period the samples were weighed. Determinations at each power level were run in triplicate. The effective atomic oxygen flux, F, was then calculated according to the following equation in which ΔM is the mass loss of the sample in grams, A is the sample surface area in the cm^2, E is the in-space erosion rate of Kapton, 3x10-24 g/O atom[1] and t is time in seconds.

$$F = \Delta M/(A\ E\ t)$$

The effective atomic oxygen flux determination was repeated using 4 samples of Kapton HN film mounted to the cleaned sample cups with a very small piece of carbon tape. The tape was situated such that the sample covered and protected it. The Kapton HN film samples were placed in the 4 positions within the etcher that were used for foam exposures and the flux determined as above.

For the initial trial of foam studies, samples were mounted to the tabs of a multisample tray from the XPS using carbon tape. Both survey and area scans were done on each sample with the XPS. Then the samples were removed from the XPS and the entire tray containing the samples was placed in the etcher and exposed to oxygen plasma at full power for 2 hr. Following the oxygen plasma exposure photos were taken and the remaining foams were analyzed again with XPS.

The next series of foam studies was done with the samples mounted to the tops of aluminum sample pans using carbon tape. The pans were previously cleaned in the etcher for 1 hr at full power. Samples were placed in reduced pressure, ~10-3 torr for 1 hr and then weighed. They were then placed in the etcher in groups of 4 and exposed to oxygen plasma at 35% power for 30 min increments. Samples were removed from the etcher and weighed, then placed back in the etcher and exposed to oxygen plasma again. This process was repeated until samples exhibited significant weight change. When significant weight change occurred, samples were placed in the XPS for surface analysis and then returned to the oxygen plasma treatment. When samples

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[1] Obtained from: L. E. Bareiss, R. M. Payton, and H. A. Papazian, "Shuttle/Spacelab Contamination Environment and Effects Handbook", NASA Contractor Report 3993, pp 3-26, Sept., 1986.

were removed from the etcher for weighing or for XPS analysis, they were kept in a nitrogen atmosphere to exclude atmosphere oxygen and moisture.

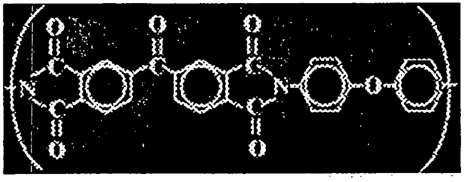
One set of foams was analyzed for nitrate, sulfate, and carbonate ions before and after atomic oxygen exposure (full power, 1 hr). To do this analysis, samples were placed in a small amount of deionized water and placed in the sonicator for 5 min. The resulting extract was analyzed by ion chromatography for nitrate and sulfate ions. Separate portions of the extract were placed in centrifuge tubes and treated with barium nitrate solution to determine the presence of carbonate.

Results and Discussion

At the altitudes of low earth orbit (LEO), the concentration of gas is very low. The gas present at this altitude has a composition that is roughly the inverse of the atmosphere in the troposphere, 20% N_2 and 80% 0_2. The absence of any overlying atmosphere allows short wavelength UV 9<240 nm) to split the majority of the molecular oxygen to individual atoms. This atomic oxygen is extremely reactive and will readily react with anything with which it collides. Structures in LEO are typically moving rapidly, as fast as 8 km/s, to maintain their orbit. At that velocity, these structures will encounter an atomic oxygen flux of 10^{15} oxygen atoms per second per square centimeter and collide with an impact energy of up to 5 eV. This collision energy accelerates the reaction of atomic oxygen with the structure materials and provide energy to drive additional reactions as well. The collision energy also allows atomic oxygen to more deeply penetrate materials and thus exert and even greater influence on the material.

In this study, an oxygen plasma etcher was used to generate an atmosphere that simulates that of LEO. This etcher utilizes radio frequency, 13.56 MHz, to excite an oxygen atmosphere at a pressure of 2-5 torr in to a plasma. This atmosphere will contain some undissociated oxygen molecules, oxygen ions, electrons, and oxygen atoms. For this work, the atmosphere was considered to consist of oxygen atoms only and the terms, oxygen plasma and atomic oxygen will be used synonymously.

In this study, foams based on four different chemistries were studied. One foam, Solimide, is a commercial product and its structure is proprietary. The other foams studied were produced by Langley research Center and they have the structures shown below. The structures are very similar but do have some important differences. Both the C and the L series foams have a carbonyl group between the two dianhydride groups while the H series foams have these groups bonded through and ether linkage. In the L series foams both benzene rings in the diether are linked through oxygen and both show para bonding. In the H series foams, the right most benzene ring is meta bonded. In the C series foams the two phenyl rings in the diether are linked through an SO_2 instead of a simple ether linkage. While these differences are small, they were expected to provide different reactions with atomic oxygen.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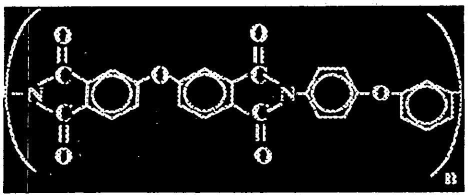
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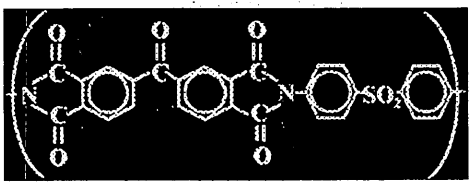

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A significant amount of time in the first part of the fellowship period was devoted to helping the service engineer complete the installation of the XPS upgrade, work out bugs, and to learning the new system. Additional time was used to assemble, repair, and learn the oxygen plasma etcher. Once these tasks were accomplished, data gathering began.

For the initial trial, samples were prepared by cutting them from the larger foam pieces supplied with a razor blade. The samples were each approximately 1 mm thick and 1 cm on edge. They were mounted to the tabs of the XPS sample tray using carbon tape. For each sample, both survey and area scans were run. The sample tray was removed from the XPS and placed in the oxygen plasma etcher and exposed to oxygen plasma with the etcher set at full power for 2 hrs. Most surprisingly, when the sample tray was removed from the etcher, much greater than anticipated changes were observed in the foams. The sample tray that was originally coated with gold, showed a large visible decrease in the gold coating. The tray with the samples was placed back in t he XPS and the survey and area scans repeated.

Figure 1 shows the samples after the 2 hr, full power, oxygen plasma exposure, labeled B in the figure. Along with each of those samples in the figure, is a photo of a price of the original foam that was not exposed to plasma, labeled A in the figure. The figure also lists densities and surface areas of the samples for which those values were known.

The three L series samples show a definite relationship between density and oxygen plasma interaction. The L.5 foam was bleached from yellow to a gray color and only a small amount of material remained after oxygen plasma exposure. The L.H sample, with 10x the density of the L.5 sample showed a core of material remaining with the original color but reduced visual density surrounded by bleached and highly density-reduced material. The still higher density L8 sample showed a slight visible density reduction with the majority of the material remaining the original color and just a slight fringe of bleached material.

Two C series samples were exposed. The CL sample was just a typical foam and it showed total discoloration and a large amount of material loss after oxygen plasma exposure. The CL skin samples was the same foam but produced with a densified layer, the skin, that was oriented upwards. This skin largely protected the sample form the oxygen plasma. The skin showed some discoloration and material loss but largely remained intact. The foam underneath the skin was not affected by the plasma though the edges showed material loss where the foam was not protected by the skin.

The H series sample showed only slight discoloration and a small amount of material loss after oxygen plasma exposure. This was unexpected since this material was low density and had a large surface area.

The Solimide sample was totally decolorized and suffered a very large material loss after oxygen plasma exposure. This response was not totally unexpected, however, since the sample had a very low density and a large surface area.

The changes in the atomic percentages of C, N, and O in the surfaces of these samples, as determined by XPS, are plotted in Figure 2. Density and surface area are also plotted. Each sample showed a large increase in oxygen, a large decrease in carbon, and a small decrease in nitrogen concentration on the surface. For each of the samples, the decrease in the relative to the increase in oxygen is essentially the same and the nitrogen decrease is very small. There does not appear to be any correlation between these compositional changes and the surfaces are of the samples. The sample with the greatest density, the L8, showed the smallest visual changes after oxygen plasma exposure. This sample also showed the smallest oxygen increase and the smallest carbon decrease. In this trial, there also does not appear to be any link between the chemical structure of the foam and the interaction observed with atomic oxygen.

The changes in the binding energies of the C 1s, O 1s, and N 1s peaks in the XPS spectra of the samples after oxygen plasma exposure are shown in Figure 3. No correlation between the density or surface area and the binding energy shifts can be observed. This is as expected since the binding energy shifts indicate chemical changes. It is interesting that co correlation in these shifts and the chemistries of the foams can be detected either.

The first trial data indicate that there is indeed an interaction between oxygen plasma and the foams. The lower the density of the foam, the greater the bleaching and material loss upon exposure to the oxygen plasma at full power. In this trial however, no relationship between the chemical structure of the foam and the interaction with atomic oxygen was observed.

The lack of structure-property correlation is not reasonable and is probably due to several experimental factors. After oxygen plasma exposure, many of the samples were found to contain silver and sulfur. Since only the C series and Solimide sample should contain sulfur and none has silver in their structure, there must be material transfer between the samples and the tray during oxygen plasma exposure. The effects of such a transfer are very difficult to predict. Also, the stability and homogeneity of the oxygen plasma within the etcher cavity were as yet unknown.

In order to characterize the atmosphere in the oxygen plasma etcher, studies were done with Kapton tape and Kapton HN films. The procedure was devised and utilized the Kapton tape samples. Then the standard procedure, ASTM E2089-00, was discovered. It is rewarding that the procedure devised was identical to that of the standard method with the exception of our use of Kapton tape instead of Kapton HN film. Thus, the determination was redone with Kapton HN film to verify the previous work with Kapton tape. The study done with the Kapton HN film was also done to determine the homogeneity of the plasma in the etcher cavity. This was accomplished by suing 4 samples simultaneously, each placed in one of the positions within the etcher caving where foams were placed for the exposure studies.

The parameter determined for the oxygen plasma generator was the effective atomic oxygen flux. This is the number of oxygen atoms striking a square centimeter of a surface per second assuming the same erosion rate as encountered in LEO. The effective atomic oxygen flux was determined for the etcher operating at full power, half power, and at 25% power. The results of these determinations are given below and plotted in Figure 4. The results indicate and the plots support the fact that the etcher is unstable at full power and provides much more reproducible results at 50 and 25% power levels. The plots indicate that, at 25% and 50% power levels, the effective atomic oxygen flux decreases with time but approaches a limiting value. Thus, the final value measured for each trial was taken as the limiting value.

effective atomic oxygen flux, 100% power = 5.10×10^{16} O atoms/cm^2 s
s = 2.81×10^{16} O atoms/cm^2 s

effective atomic oxygen flux, 50% power = 3.44×10^{16} O atoms/cm^2 s
s = 1.86×10^{16} O atoms/cm^2 s

effective atomic oxygen flux, 25% power = 2.16×10^{16} O atoms/cm^2 s
s = 1.20×10^{16} O atoms/cm^2 s

Figure 5 shows the data obtained from the Kapton HN samples. The data from this study corroborate well with those obtained from the Kapton tape studies, yielding an average effective atomic oxygen flux of approximately 2×10^{16} O atoms/cm^2 s. The effective atomic oxygen flux also appears to remain relatively constant throughout the etcher cavity.

Because the full power level of the etcher produces an unstable atmosphere that very rapidly attacks foam samples, a lower power was chosen for the next studies. The 25% power level was chosen because it produced the most reproducible environment and I had the lowest effective atomic oxygen flux to allow determination of changes with time in the foam samples.

The final part of the research done during this fellowship period was a more detailed study of the interaction of oxygen plasma with the foams. The was done by mounting samples on the bottoms of cleaned aluminum sample pans to allow for mass measurements and stable placement in the XPS. The etcher was used at 25% power to allow slower changes to the foams. Foams were placed in a reduced pressure environment to reduce the amount of absorbed moisture before initial weighing. After obtaining XPS survey and area data, they were exposed to oxygen plasma at 25% power for 30 min increments and weighed after each. When significant weight loss occurred, samples were re-analyzed with XPS, and then oxygen plasma exposure continued.

The mass loss data for foam samples during exposure to oxygen plasma at 25% power are shown in Figure 6. The carbon tape is particularly susceptible to the oxygen plasma. Thus, for this study, the carbon tape used to mount the samples was very small and placed up under the sample to protect it from mass loss. All of the samples, except Solimide, showed only a small mass loss for the first hour of oxygen plasma exposure and then began a more rapid mass loss. Solimide resisted weight loss for only 30 min. The CL sample showed the greatest resistance to weight loss. This is the structure with the SO_2 linkage in the diamine and that structural group evidently provides added stability to the polymer in the presence of oxygen plasma.

Figure 7 shows the surface composition data for two samples as a function of oxygen plasma exposure time. Both samples show carbon losses and oxygen gains that mirror each other. However, the H series sample show greater carbon loss and oxygen gain than does the C series sample. The nitrogen content of the C series sample surface continually increases whereas that of the H series sample increases then drops again.

All of the foam samples exposed to oxygen plasma show huge increases of oxygen in the surfaces. The high vacuum of the XPS would cause loss of any oxygen that was just implanted and not bound in the samples. Thus, the oxygen shown to be present must be bound in some way. It was decided to determine if the oxygen plasma was causing oxidation of carbon to carbonate ion, the nitrogen to nitrate ion, and the sulfur to sulfate ion. This was accomplished by placing both virgin and samples that were exposed to 100% power oxygen plasma for 1 hr in separate flasks and sonicating for 5 min with a small amount of water. The aqueous extract of each sample was then analyzed with ion chromatography to determine the presence of sulfate and nitrate. A separate portion of each extract was also treated with aqueous barium nitrate to detect the presence of carbonate.

The following foams were extracted, HL, HLA, CL, Solimide, L8, and LH. The extracts from the unexposed samples showed no significant quantities of nitrate, sulfate, or carbonate for any of the samples. The CL sample showed a large amount of sulfate present after oxygen plasma exposure, indicating that the SO_2 linkage in the polymer backbone was oxidized. The extract from the exposed Slimmed sample also showed a significant amount, though far smaller than that of the CL sample, of sulfate ion. The exposed L8 extract showed a very small amount of sulfate, indicating a possible cross contamination in the etcher.

These studies indicated that the oxygen found in the surfaces of these samples is not in the form of nitrate or carbonate. Foams with structures containing sulfur do have a tendency to form sulfate and it is possible that this sulfate is part of the reason that the C series samples show the greatest resistance to oxygen plasma.

This summer faculty fellowship was highly successful and resulted in a large number of accomplishments. The upgrade and additional techniques were successfully completed on the XPS instrument. Many of the bugs from that installation were worked out and the software was learned. The oxygen plasma etcher was repaired, completed, set up, and characterized. Protocols for foam exposure and analysis were developed. Preliminary studies were done and finer studies begun on the interaction rates and mechanisms due to both physical and chemical parameters.

Most importantly, strong working relationships between this researcher and NASA colleagues have been established and reinforced. These relationships will last long into the future as the collaboration in research continues and grows.

Acknowledgements

The support of the NASA/ASEE Summer Faculty Fellowship program is deeply appreciated. The hard work of Dr. Ramon Hosler, Ms. Cassie Spears, Ms. Cassandra Black, and Mr. Gregg Buckingham to make the fellowship both happen and to be an enjoyable and rewarding experience are also greatly appreciated. My NASA colleague, Ms. Martha Williams was a true pleasure to work with. Thank you also to Dr. Orlando Melendez for his input as a colleague and friend. Mr. Wayne Marshall's help and expertise in doing the ion chromatography is greatly appreciated. Thank you also to the entire chemistry group for support, enthusiasm, professionalism, help and friendship.

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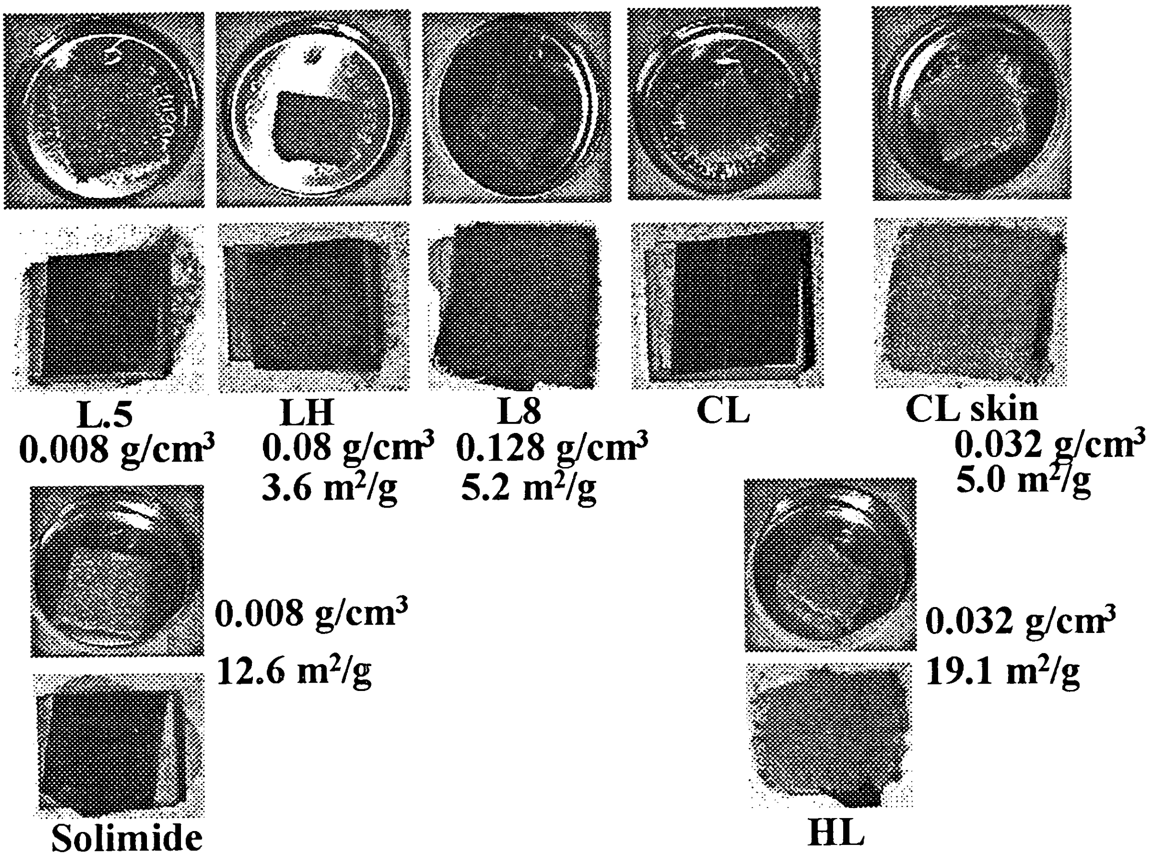
Figure 7. Surface composition data for C series sample and H series sample relative to oxygen plasma exposure time.



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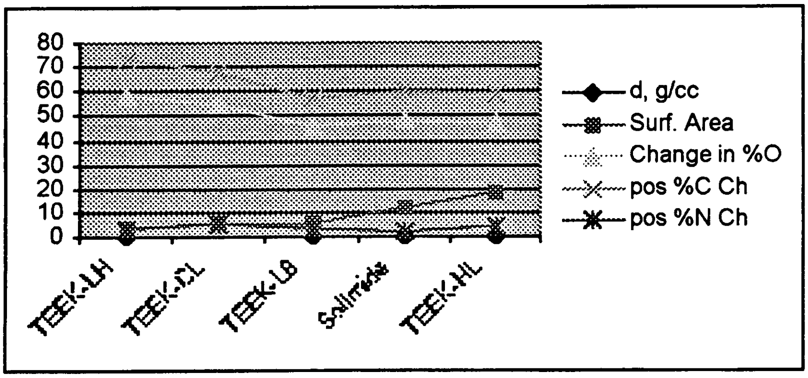

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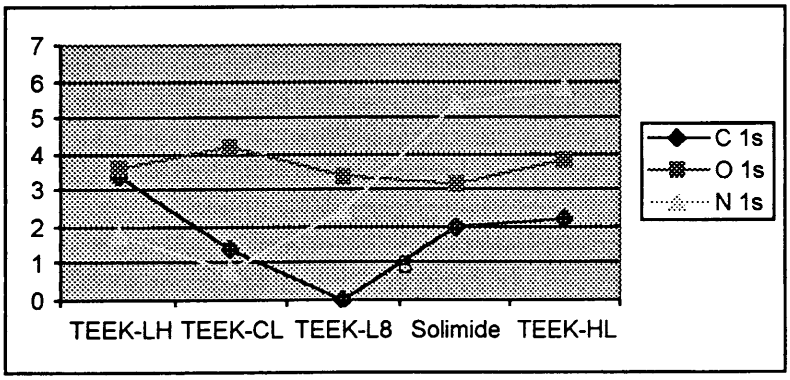

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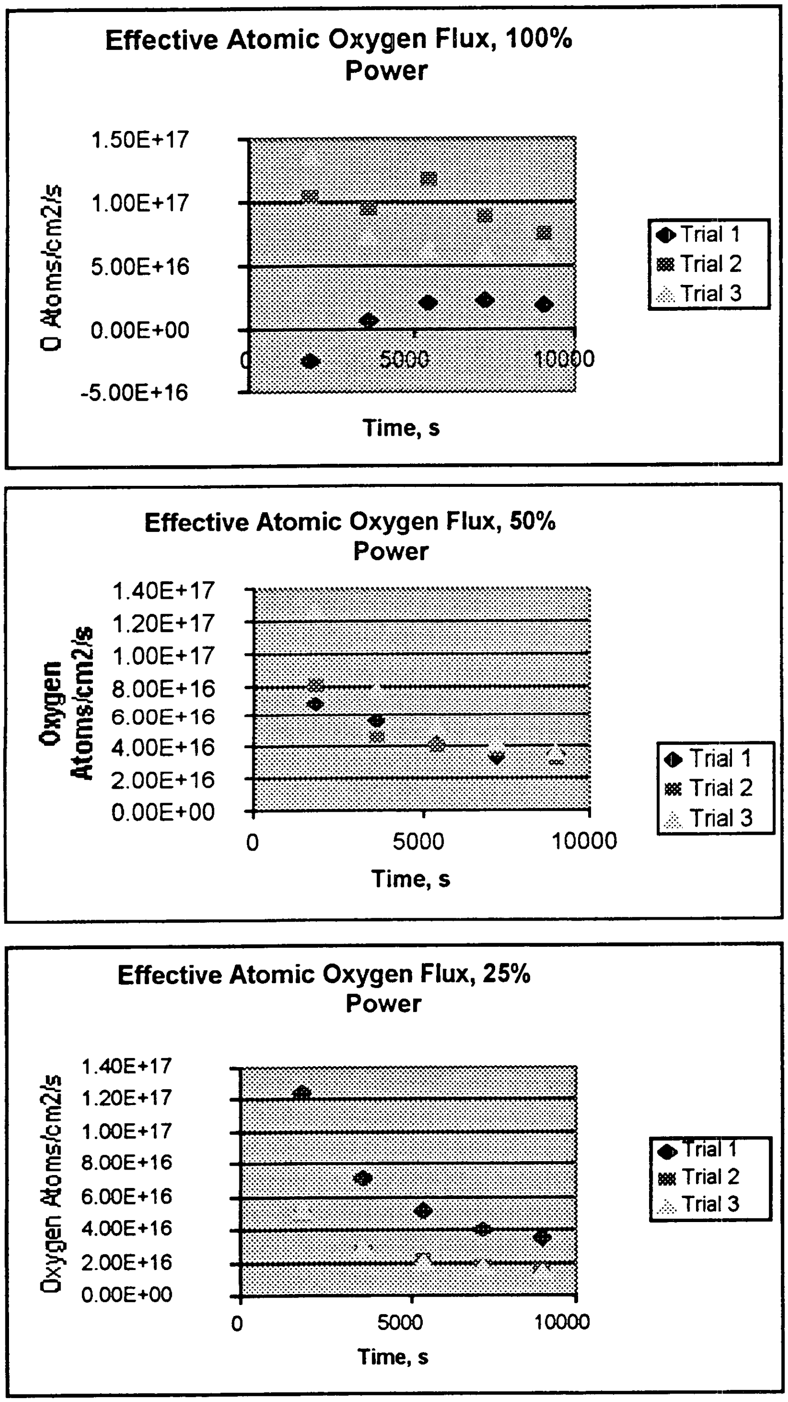

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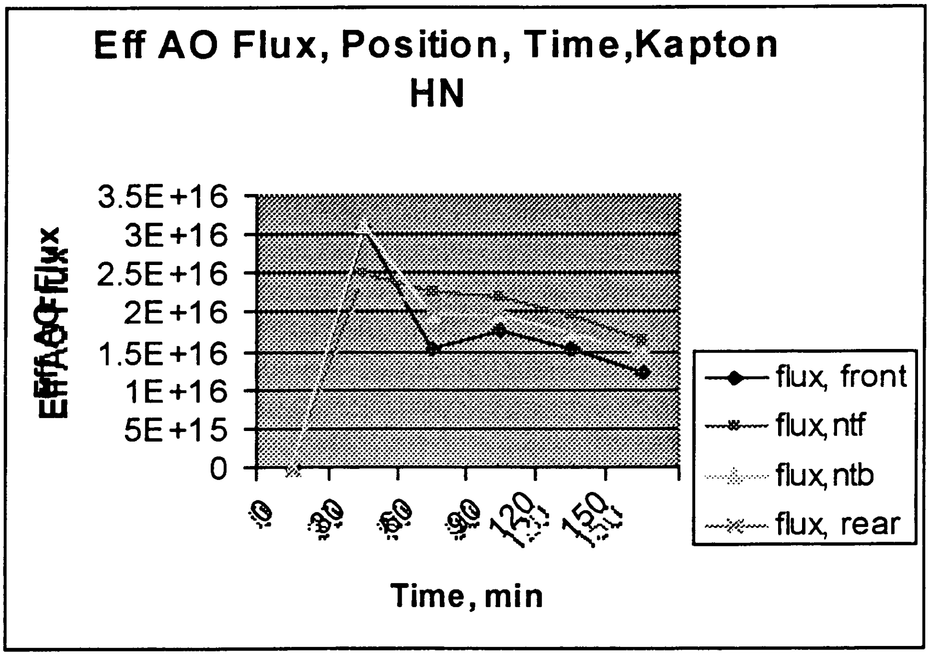

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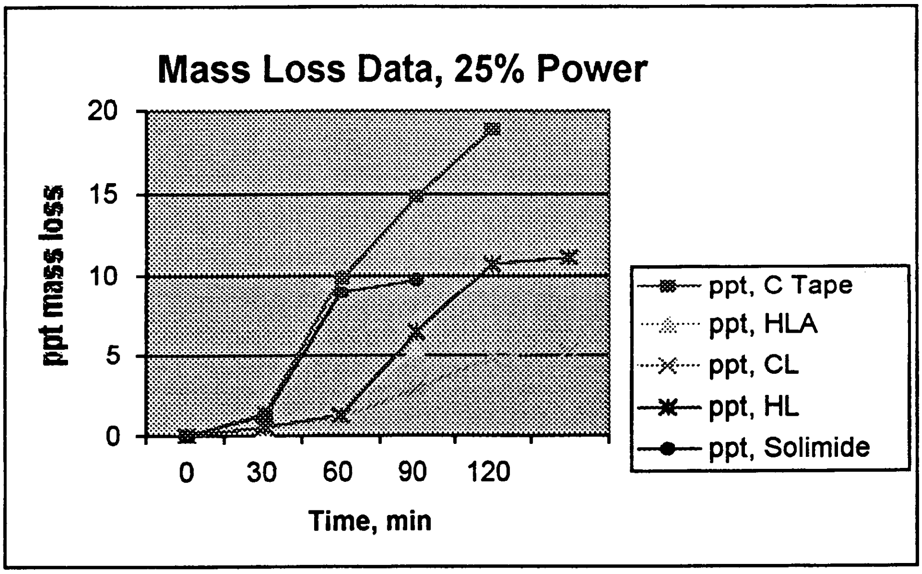

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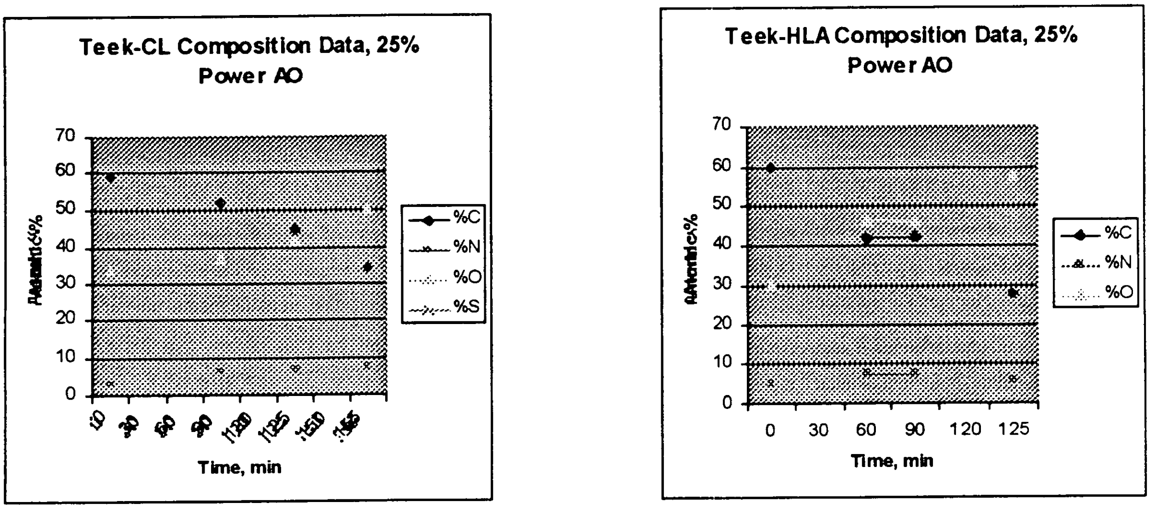

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