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Isothermal Aging Effects on PMR-15 Resin

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by

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ABSTRACT

Specimens of PMR-15 polyimide neat resin were aged in air at temperatures of 288, 316, and 343 °C. Weight losses and dimensional changes were monitored during the course of the exposure time. Physical changes were also observed by optical and electron microscopy. As a result of this study it was found that polyimide polymer degradation occurred within a thin surface layer that developed and grew during thermal aging. The cores of the polymer specimens were protected from oxidative degradation, and they were relatively unchanged by the thermal treatment. Surface cracking was observed at 343 °C and was probably due to an interaction between voids and stresses that developed in the surface layer.

Keywords: Polymers; Oxidation; Polyimides; Thermal aging.

1. INTRODUCTION

Some progress has been made in understanding the geometric effects,(1) the fiber effects,(2,3) and the temperature effects on the thermo-oxidative stability (TOS) of polymer matrix composites. However, the possibility of significant synergistic effects and the mechanism changes that may occur with changing environmental conditions(4) are still not fully understood. These are important areas for study in the development of accelerated environmental testing and the subsequent development of models for predicting the TOS of polymers and polymer matrix composites. In order to gain a clear knowledge of how reinforcement fibers affect the TOS of polymer matrix composites, it is necessary to understand how the neat matrix resin behaves during long periods of aging in air at elevated temperatures.

Weight loss data for polymers, as measured by different investigators, are not always in close agreement. To date, neat resin TOS data have not been successfully used to predict fiber-reinforced composite TOS behavior. With the increased need for accelerated environmental testing methods to describe the long-term behavior of polymers and their composites, a thorough examination of how aging at elevated temperatures affects a state-of-the-art polymer must be undertaken. Once the polymer behavior is understood, it should be easier to distinguish reinforcement fiber effects on the TOS. A program to investigate the TOS of PMR–15 at three elevated temperatures is described herein. PMR–15 was chosen as the resin for study because of the wealth of PMR–15 TOS data that have been published over the last 20 years.

2. MATERIALS

The PMR–15 neat resin specimens were machined from neat resin plates measuring 15.24 by 15.24 cm. They ranged in thickness from 0.25 to 0.64 cm. The plates were cut into 7.5-cm-long by 0.64-cm-wide strips.

The resin plates were fabricated by using tight-fitting, matched metal die molds. Molding powder was prepared commercially by removing the methanol solvent from the PMR–15 monomer solution and then imidizing the solids at 232 °C for 2 hr. The imidized material was then microground to a particle size of 12.5 μm. The molding and curing process was carried out in the following way:

1. The press was preheated to 260 °C.

2. A cold mold with a 0.08-cm stop was placed between the platens of the press.

3. After 10 min, the press temperature was raised to 288 °C.

4. When the polymer temperature reached 232 °C, the stop was removed and a 0.69-MPa pressure was applied to the mold.

5. When the polymer temperature reached 288 °C, the pressure was increased to 1.65 MPa.

6. The polymer was held at 316 °C for 2 hr and then the heat was turned off.

7. In order to prevent cracking of the resin, the resin plates were removed from the mold when the temperature of the mold and the resin was at 316 °C.

8. The plates were given a standing postcure in air at 316 °C for 16 hr.

3. TESTING AND EVALUATION

After being machined into strips the PMR–15 specimens were baked in an air-circulating oven for 24 hr at 122 °C. This procedure was sufficient to remove absorbed moisture from within the specimens. The water absorption-desorption characteristics of PMR–15 were measured in a separate study[5] at the Lewis Research Center.

Weight loss and dimensional measurements were made first after the initial air postcure and then throughout the duration of the isothermal aging. When the specimens were removed from the aging ovens, they were placed in a desiccator and weighed on a Sauter RE–1614 balance after they had cooled to room temperature. In addition to the weight loss data, dimensional changes were monitored by intermittent micrometer and vernier measurements of the thickness, width, and length for each specimen. The measurements were accurate to 2.54×10^{-5} m. Dimensional measurements were made during the aging periods as it was deemed necessary but not during every weighing period.

Initially 15 specimens were aged at each of the three temperatures. As the aging time progressed, specimens were removed for mechanical tests and microscopic examination. All aging was done in air-circulating ovens with an airflow rate of 100 cm^3/min.

Physical changes were monitored with standard metallographic optical microscopy and scanning electron microscopic (SEM) techniques. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy were used as tools to evaluate any chemical changes that occurred during the isothermal aging.

4. RESULTS

4.1 Weight Loss

Weight losses of PMR–15 neat resin at 288, 316, and 343 °C are shown Figure 1. The 288 °C data are shown for specimens of two different thicknesses to illustrate TOS dependence on surface area. The areas corresponding to the thin and thick specimens were 45.5 and 57.2 mm^2, respectively. Only thin specimens were tested at the other two temperatures. The weight loss rate (slope of the curve) was relatively rapid initially and then decreased to a final constant value with a positive linear slope. The data are displayed in Figure 2 on a weight-loss-rate basis. At all three temperatures the curves are characterized by a high initial weight loss rate that decreased as the aging time progressed and then became constant. When the data were normalized for area differences by presenting them on a weight-loss-rate-per-unit-area basis, as shown in Figure 3, the two 288 °C aging curves coincide. The Arrhenius activation energy was calculated from the slopes of the curves at identical times during the initial, nonlinear portions of the curves, and it was found to be 22.7 kcal/g-mole with an R^2 value of 0.99613. Four values were calculated over this range and then averaged. This average value is considerably smaller than the 30.6 kcal/g-mole value calculated in Reference 3. The reason for the discrepancy cannot be explained.

4.2 Dimensional Changes

Dimensional changes in the thickness, width, and length of the specimens at the three different aging temperatures are shown in Figure 4. The initial negative dimensional change may be related to the specimen volume. The initial change in length at all three temperatures was significantly larger than the changes in thickness and width. After the initial change the rates of dimensional change were the same for all three dimensions. When the volume changes were converted to weight changes by using the measured polymer density, the calculated weight losses were equivalent to the measured weight losses.

4.3 Surface Features and Metallography

The specimens that were aged at 343 °C exhibited surface cracking after 362 hr of aging. No surface cracks were observed on the specimens that were aged at the two lower temperatures. Earlier studies resulted in specimen surface cracking at lower temperatures.(2) Figure 5 shows a micrograph of a resin specimen with cracks. The cracks appear to begin at the surface and then extend in distinct stages. Figure 6 shows the surfaces of four specimens, three of which are aged at different times at elevated temperatures. The cracking was in the form of a spiral around the rectangular circumference of the specimen. As the aging time increased, more cracks appeared between the original ones and eventually some began at angles to the earlier ones.

Another interesting observation from Figure 5 is the presence of a distinct layer (light area) that developed and grew on the polymer specimen surface and also on the crack surface. This light area, or surface layer, thickened with aging time. Also, voids began within this layer and increased in size and in number with aging time. The surface layer thickness is plotted as a function of aging time for different aging temperatures in Figures 7 and 8. Data measurement for the 343 °C aged specimens was stopped at about 500 hr because an extreme amount of surface cracking developed. (See Fig. 6.) At all three temperatures the thicknesses appeared to asymptotically approach a constant value of about 0.17 mm as aging time increased. The initial growth is shown in Figure 7 for specimens aged at 288, 316, and 343 °C. The equations for the curves that were obtained by regression analyses are

$$L = 0.00039\ t^{0.35}$$

$$L = 0.000216\ t^{0.49}$$

and

$$L = 0.000473\ t^{0.39}$$

respectively, where L is layer thickness, t is aging time at temperature, and R^2 ranged from 0.952 to 0.998.

Figure 8 shows the data that were measured for aging times up to about 4000 hr at 288 and 316 °C. An Arrhenius plot was constructed by using the data from the initial portions of the curves (up to 600 hr of aging time), and the calculated activation energy is 5.5 kcal/g-mole. Figures 9 and 10 show the surface layers that developed after 1000 hr at 288 °C and after 1500 hr at 316 °C. After these extended aging times the layer thicknesses were about the same, as shown in both figures. There were significant differences in the numbers and sizes of voids that were present within the surface layers. More and larger voids occurred in the polymer treated at 316 °C than in the sample aged at 288 °C. The voids were more numerous near the surface than near the interface of the surface layer and the core. Also, the outer voids were ellipsoidal in shape while those further within the specimen had a circular cross section. The weight losses for the two different specimens were 10 and 3.3 percent, respectively.

4.4 Compositional Changes

The aged specimens were analyzed by x-ray diffraction (XD), x-ray photoelectron spectroscopy (XPS), infrared scanning microprobe (IRSM), x-ray energy dispersion spectroscopy (XEDS), and SEM backscatter electron emission. Figure 11 shows three XD scans of neat resin samples. Unaged PMR-15 neat resin (Fig. 11(a)) had a small peak at a scattering angle of about 16°, indicating that there is some crystallinity or order in an unaged neat resin sample. After the sample had been aged in air for over 500 hr the peak diminished in amplitude and width (Fig. 11(b)). Evidently, the ordering within the polymer had diminished. After the surface layer was removed by polishing, the original peak was again observed. The scan shown in Figure 11(c) is of the surface of a piece of the specimen shown in Figure 11(b) that had been sanded with 400-grit emery paper to remove the surface layer material. The return of the peak at the 16° scattering angle indicates that the specimen core had not been altered by the aging process, although the surface layer did change some. The surface material may have masked the signal from the underlying material, thus decreasing its intensity.

XPS results can be seen in Table 1. The types of specimens that were examined were unaged, aged, aged with the surface layer removed by sanding, and unaged with the surface layer removed by sanding. The major differences in chemical composition between the sanded and unsanded specimens were in the oxygen, carbon, and nitrogen contents. The oxygen and carbon content differences were reflected in the higher oxygen-to-carbon ratios in the surface layers that were formed during aging. Notice that the aging process and the chemical changes actually began during the postcure. There were minor differences in the amounts of silicon, chlorine, sodium, calcium, and sulfur. The unaged sample contained more silicon, chlorine, sodium, and sulfur on the surface than did the aged sample or the samples that had been sanded.

XEDS analyses were run. Unlike the XPS results, no differences were observed in oxygen-to-carbon ratios between the surface and the core of the specimen. However, because of XEDS' relatively low sensitivity at the lower end of the atomic number scale, which includes oxygen and nitrogen, the significance of the results is questionable. A silicon impurity was found to be present in the surface layer of the aged polymer sample. It was probably due to the release agent transferring from the mold to the composite.

The results of the IRSM scans are shown in Figures 12 and 13. These scans indicate two major differences in the compositions of the two different regions of the aged specimens. The differences in the amplitudes at region 0 (wavenumber of 1517) in Figure 12 suggest a decrease in the number of benzene rings in the aromatic radicals. Possibly the rings disappeared as fragments that were released from the polymer backbone. The core of the specimen is located at the 0 point along the horizontal distance axis. The surface layer that formed and grew during aging starts at 150 to 200 μm along the same axis. The absorbance at region 1 (wavenumber of 1605) indicates an increase in the carboxylic acid radical in scanning from the core area to the surface layer area. The data presented in Figure 13 show scans at 20-μm intervals starting from the center of the aged specimen. The changes are shown as the probe entered the surface layer. The mounting material begins at the 17th scan. Backscatter electron emission data show significant differences in the compositions of the two specimen areas. Established interpretation procedures indicate that the data also show that the surface layer material consists of atoms with higher atomic numbers than those of the core material.

5. DISCUSSION OF RESULTS

Except for the initial phase of air aging, the length of which was relatively short and dependent on the aging temperature, the rate of oxidation, or the aging degradation, of PMR–15 neat resin depended on the surface area that was exposed to the oxidizing environment. Because of this, it was necessary to either test specimens with the same surface-to-volume ratio or to normalize the data on a surface-to-volume basis. Thus, we could validly compare TOS data from different material batches or laboratories.

Initially, as noted, a rapid weight loss was more dependent on the specimen volume than on the exposed surface area. This initial weight loss was probably due to the release of cyclopentadiene from the bulk of the polymer. The possibility of this weight loss being due to moisture loss was rejected because it occurred even after the material had been baked in an oven at 122 °C for 24 hr. Moisture absorption/desorption studies(5) show that this is a satisfactory length of time to allow the release of all moisture from the PMR–15. After this initial weight loss the polymer oxidation process appeared to entail the concurrent formation of a surface layer that was structurally different from the initial cured polymer material, the formation and growth of voids in the surface layer, and polymer oxidation at the specimen surfaces. The oxidation products were most probably gaseous. After aging for a period of time that depended on the aging temperature, the growth rate of this surface layer approached its rate of material loss by oxidation. In other words, the surface layer thickness approached a constant value after the polymer had been aged for the times shown in Figure 7. The time needed to establish a surface layer of constant thickness can be related to the initial portion of the weight loss curves in Figures 1 to 3, with the constant-weight-loss-rate sections being established after the surface layer thickness was stabilized. The data displayed in Figure 2 indicate that there may exist a simple model for the oxidative aging of PMR–15 after the surface layer has stabilized. However, crack formation can affect these results.

The oxidation of the PMR–15 polymer, as described, consisted of the concurrent development of a reaction layer, voids, and oxidation. In this study the activation energy calculated by using the Arrhenius equation was 22.7 kcal/g-mole. This value is significantly smaller than the value calculated in an earlier study.(3) Although no definite reason for the difference can be deduced from the data, it may be that the formation of voids is not reproducible. This could be the reason that cracking was not always observed in specimens aged below 343 °C. The concentration of voids, which could act as stress risers, may not always be sufficient to generate cracks. In contrast to the 22.7-kcal/g-mole activation energy for oxidation, the formation of the degraded surface layers had an activation energy of 5.5 kcal/g-mole. At this time it is uncertain whether the void formation influenced the rate of surface layer growth. The oxidation reaction rate should remain constant, but the void formation activation energy could change depending on the availability and type of nucleation sites in the specimen. This change also could be a significant factor in the observed differences in the TOS of resins and their composites. It may be that different reinforcements and processing procedures produce different concentrations or types of nucleation sites for voids. Work is now in progress at this laboratory to study void formation in composites and its relation to fiber reinforcement.

Surface layer formation also probably resulted in crack formation at the surfaces of the neat resin specimens. The aging process has been shown to produce shrinkage in the aging specimen. This shrinkage appeared to coincide with the magnitude of the weight losses that accompany aging. The absolute decreases in the thickness and width dimensions appeared to be equal. On the other hand, changes along the specimen length were much larger than would be expected solely from the formation of surface layers. If surface layer growth were causing the dimensional change, the length change would be equal to the thickness and width changes. However, the measured decreases in length were about 10 times greater than the changes in the other two dimensions. Therefore, compressive strain or shrinkage may have occurred in the specimen core. The core material can be compressed by tensile stresses that may be generated by shrinkage in the surface layers. These tensile stresses can interact with the voids that are exposed to the atmosphere as the surface layers recede into the specimen and that then act as stress risers. Initially, the cracks were spaced at constant intervals along the specimen surfaces. This could indicate that a specific magnitude of stress had been developed within the surface layers that exceeded the failure stress of the layer material. The stress could then be relieved through the initiation of surface cracks. The length of the spacing between the surface cracks could indicate the magnitude of the stresses that were developed during aging. The higher the stress (or the greater the shrinkage in the surface layer), the shorter the distance between cracks.

These observed dimensional changes in the neat resin suggest that the mismatch between the fibers and the matrix material in composites, which is attributed to cure shrinkage and differences in coefficients of thermal expansion, continues to increase as a PMR–15 matrix composite ages at elevated temperatures. Surface cracking should be expected and, if subsurface voids are generated as they are in the neat resin, accelerated oxidation could occur in the surface layers because of the larger polymer and fiber reinforcement surface area that is exposed to oxidation. Figure 14 shows the end view (fiber ends) of a unidirectional composite that has been aged at an elevated temperature. The fiber is Celion 6000 (BASF) and the matrix is PMR–15. Notice the voids along both surfaces. The measured depth is 0.0079 in. This being the same thickness as was measured in the PMR–15 neat resin specimens suggests some possible similarity between the composite degradation and the neat resin degradation. Work is currently being conducted to obtain more details about composite damage mechanisms.

Changes are apparent from the chemical, physical texture, and atomic structural differences between the surface layer and the core materials. The oxygen-to-carbon ratios for the matrix and the fiber were 0.304 and 0.284 in the surface layer and 0.205 and 0.173 in the core. Also the nitrogen content of the polymer in the oxidizing layer decreased significantly as the layer was formed. The nominal measurement error was 10 percent. The cores of the polymer specimens did not appear to undergo any significant chemical changes during aging. The x-ray diffraction data and the XPS results indicate that the cores of the neat resin specimens did not undergo an observable change during aging at elevated temperatures. This suggests that the bulk of the dimensional and gravimetric changes occur in the surface layers of polymer specimens. This is in agreement with the observed dependence of polymer weight loss on surface area. Backscatter electron emission data showed a significant difference in composition between the core and surface layer materials. As reported, the surface layer material appears to contain atoms of higher atomic number than the core material. This could be due to the higher oxygen-to-carbon ratio in the surface layer. The results drawn from the backscatter electron emission data are in agreement with the general conclusions drawn from the other chemical characterization tests.

From the micrographs and the chemical characterization results, it appears that the weight loss in the neat resin polymer took place in a layer that was only 0.17 mm thick. This is about the thickness of one ply of cured prepreg. If this layer can be prevented from moving inward, the TOS should be improved. The information that was obtained about the surface layer formation and its limited growth, along with the lack of significant chemical change in the core of the polymer specimen, indicates that it may be feasible to protect against or retard the thermo-oxidative degradation of this material by applying a coating with a better TOS than the PMR–15. Another method for retarding this degradation may be to physically change the surface of the material in order to eliminate or retard void formation, cracking, and/or surface layer penetration into the bulk of the material. Some possible solutions might be to use on the surface either an oxygen scavenger, a nonoxidative mat material to prevent cracking, or a resin-rich coating. The resin coating could possibly be renewed periodically as the degradation progresses.

6. CONCLUSIONS

The following conclusions have been made drawn from this work:

1. Polymer degradation occurs within a thin surface layer that develops and grows during thermal aging.

2. The core of the polymer specimen is protected from degradation by the surface layer and is relatively unchanged by the high-temperature aging environment.

3. Surface cracking that is observed in PMR–15 resins is due to an interaction between voids that form in the surface degradation layer and the tensile stresses produced by a density change in this layer.

4. The weight loss of PMR–15 during aging at elevated temperatures may possibly be represented by a simple model for long-time life prediction.

7. REFERENCES

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TABLE 1.—XPS DATA FOR PMR-15 POLYMER[a]

Element	Content, at.%
Unaged specimen	
O	21
C	69
Si	2.5
S	1.3
Cl	------
Ca	1.1
N	3.9
Aged specimen	
O	19
C	67
Si	4.5
N	7.9
S	1.3
Aged specimen with surface layer removed by sanding	
O	16
C	78
Si	------
N	6.2
Unaged specimen with surface layer removed by sanding	
O	14
C	81
Si	------
N	5.3

[a] Nominally 10-percent error.

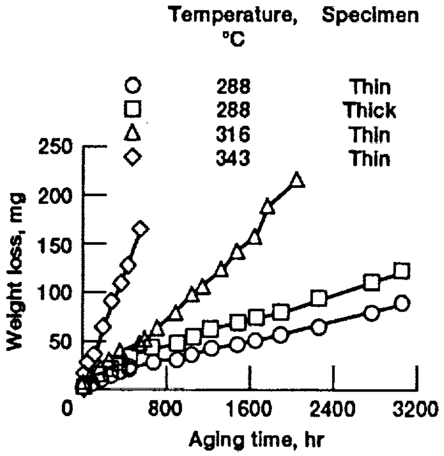


Figure 1.—PMR-15 weight loss in air at different temperatures.

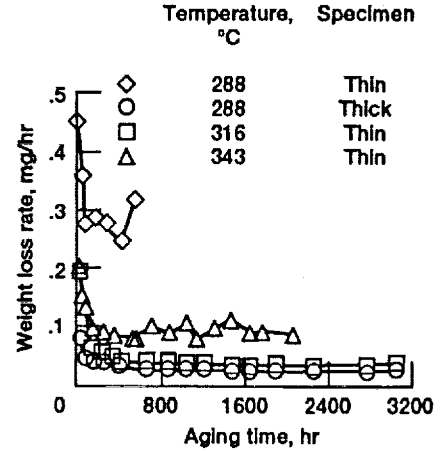


Figure 2.—PMR-15 weight loss rate in air at different temperatures.

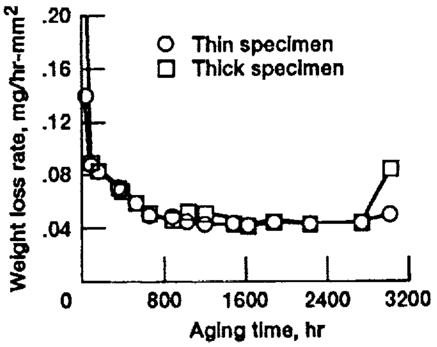
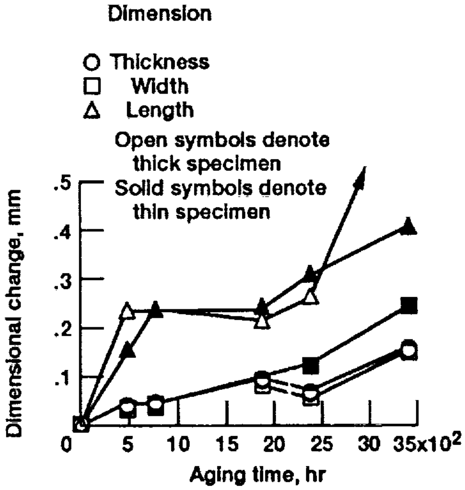
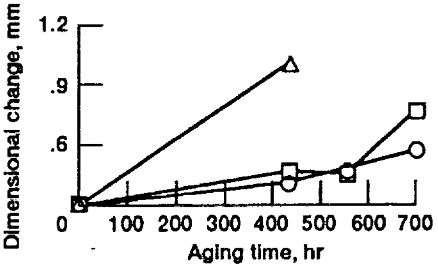


Figure 3.—PMR-15 weight loss rate in air at 288 °C.



(a) Temperature, 288 °C.

(b) Temperature, 316 °C.



(c) Temperature, 343 °C.

Figure 4.—Dimensional changes in PMR-15 in air at different temperatures. (Specimens measure 7.5 cm long by 0.64 cm wide by 0.25 cm (thin) or 0.64 cm (thick) wide.)

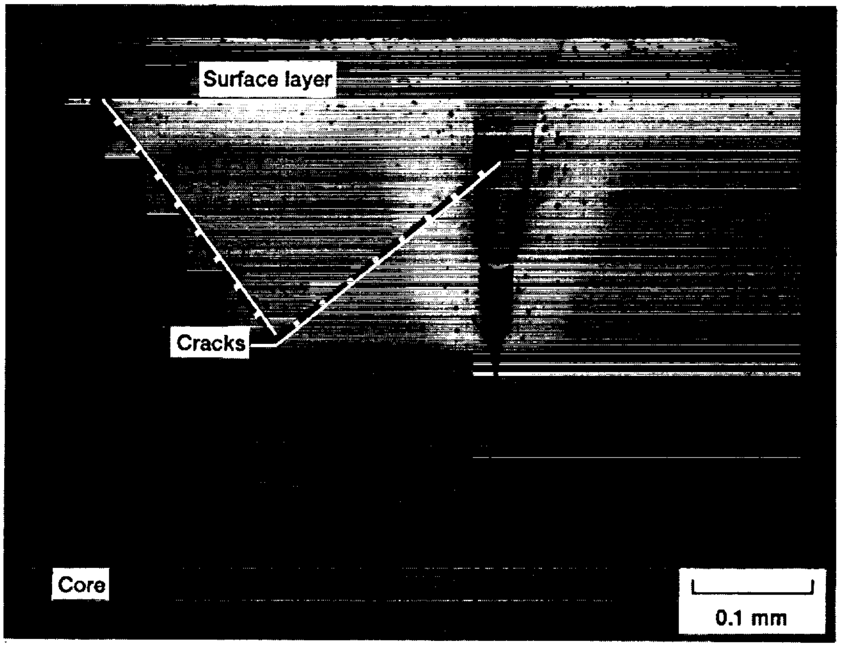


Figure 5.—PMR-15 resin surface degradation after aging in air at 316 °C for 362 hr.

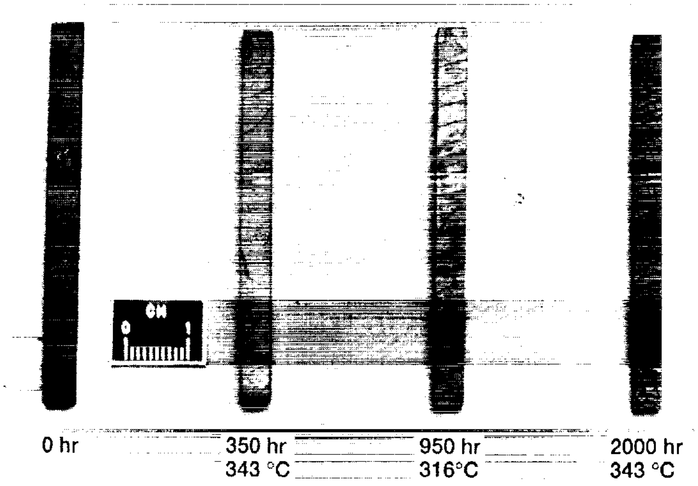


Figure 6.—Development of surface cracks in PMR-15 while aging in air.

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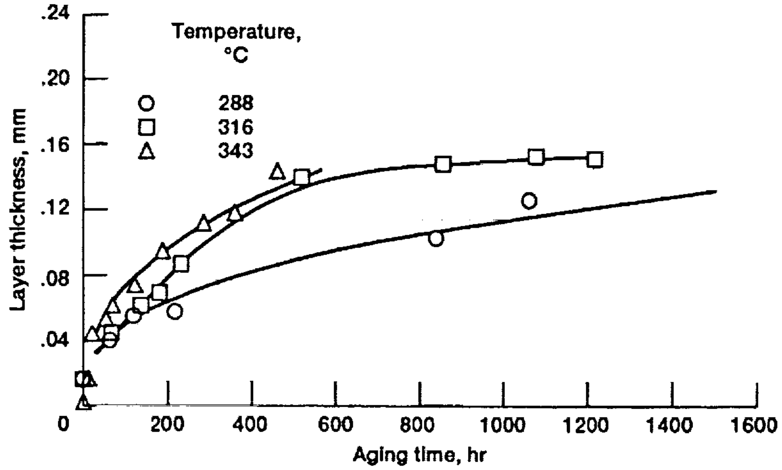


Figure 7.—Initial growth of PMR-15 surface layer thickness in air at different temperatures.

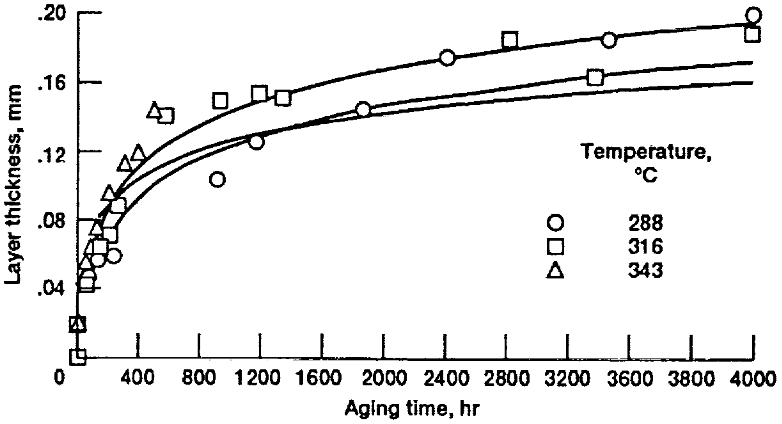


Figure 8.—PMR-15 surface layer thickness in air at different temperatures.

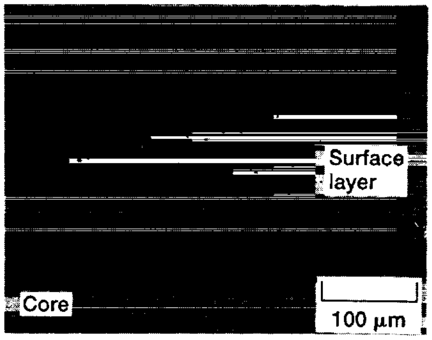


Figure 9.—PMR-15 surface layer after aging in air at 288 °C for 1000 hr.

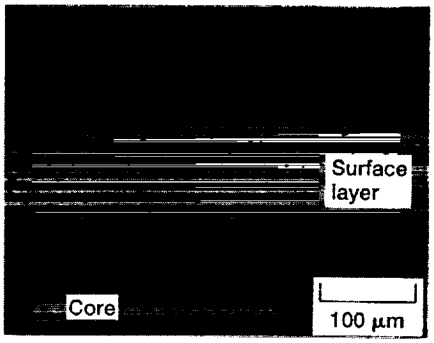
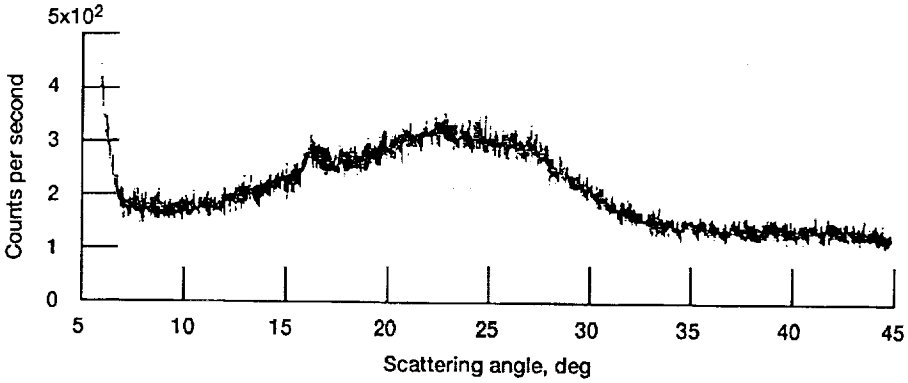


Figure 10.—PMR-15 surface layer after aging in air at 316 °C for 1500 hr.

(a) Unaged PMR-15.



(b) Aged PMR-15.

(c) Aged PMR-15 with surface removed by sanding.

Figure 11.—X-ray diffraction scans of PMR-15 under different conditons.

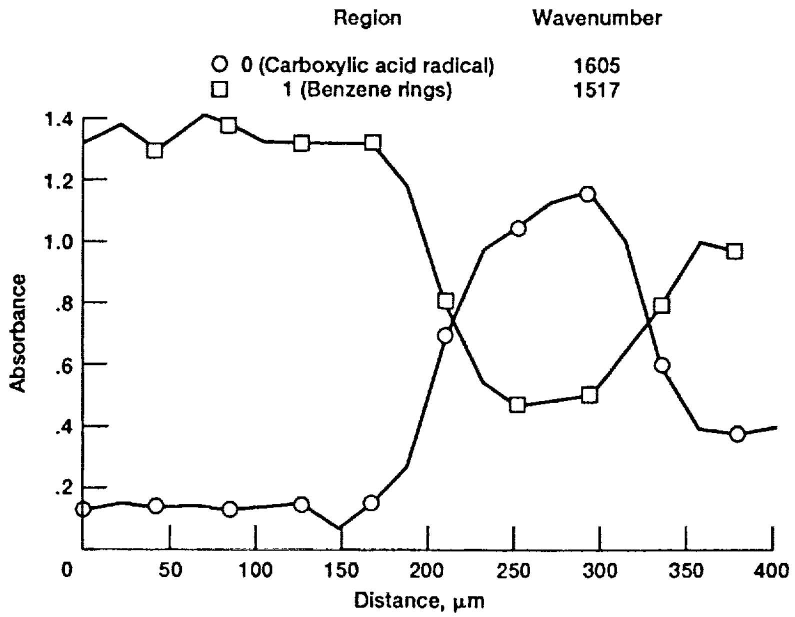


Figure 12.—Infrared scanning microprobe analysis of PMR-15 after aging in air at 316 °C.

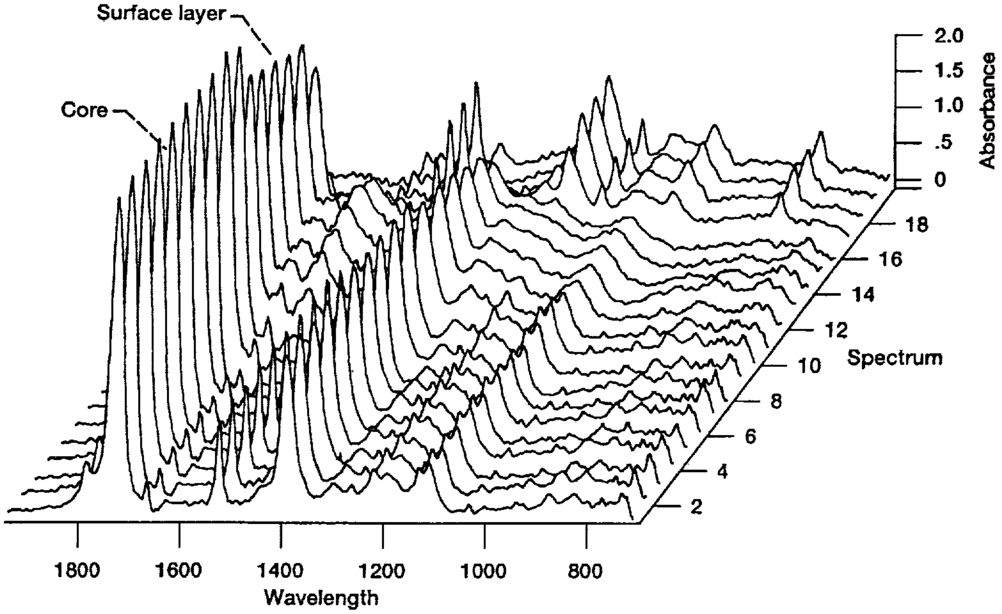


Figure 13.—Infrared scanning microscope scans of aged PMR-15. Scan interval, 20 μm.

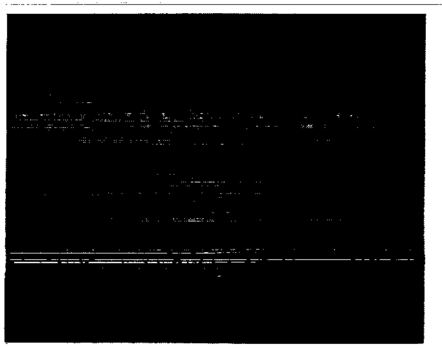


Figure 14.—Celion 6000/PMR-15 composite after aging in air at 316 °C.

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13. ABSTRACT ***(Maximum 200 words)***

Specimens of PMR-15 polyimide neat resin were aged in air at temperatures of 288, 316, and 343 °C. Weight losses and dimensional changes were monitored during the course of the exposure time. Physical changes were also observed by optical and electron microscopy. As a result of this study it was found that polyimide polymer degradation occurred within a thin surface layer that developed and grew during thermal aging. The cores of the polymer specimens were protected from oxidative degradation, and they were relatively unchanged by the thermal treatment. Surface cracking was observed at 343 °C and was probably due to an interaction between voids and stresses that developed in the surface layer.

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