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A Limited Comparison of the Thermal Durability of Polyimide Candidate Matrix Polymers With PMR–15

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This report contains preliminary findings, subject to revision as analysis proceeds.

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Summary

Studies were conducted with six different candidate high-temperature neat matrix resin specimens of varied geometric shapes to investigate the mechanisms involved in the thermal degradation of polyimides like PMR–15. The metrics for assessing the quality of these candidates were chosen to be glass transition temperature (T_g), thermo-oxidative stability, dynamic mechanical properties, microstructural changes, and dimensional stability. The processing and mechanical properties were not investigated in the study reported herein. The dimensional changes and surface layer growth were measured and recorded. The data were in agreement with earlier published data. An initial weight increase reaction was observed to be dominating at the lower temperatures. However, at the more elevated temperatures, the weight loss reactions were prevalent and probably masked the weight gain reaction. These data confirmed the findings of the existence of an initial weight gain reaction previously reported (refs. 1 to 10). Surface- and core-dependent weight losses were shown to control the polymer degradation at the higher temperatures.

Introduction

There is a concentrated effort to develop an equivalent or superior replacement for PMR–15, a suspected carcinogen, as a high-temperature composite matrix resin for aerospace structure applications. Reductions in weight and cost are also sought. To accomplish this, the upper operating temperature of this material must be rigorously evaluated and established. Recent publications have addressed the need for the development of a reliable, predictive-mechanistic model to describe the effects of elevated-temperature isothermal aging of polymer matrix composites on the mechanical and chemical durability of these materials (refs. 1 to 4 and 8 to 10). Data describing the thermal durability of these materials are necessary for the development of such a model. A coupled reaction-diffusion model was used to identify the degradation mechanism for PMR–15 neat resin. The mechanisms considered for modeling are based on either diffusion-controlled degradation or reaction-controlled oxygen effects (refs. 1 to 5). Two extreme conditions were considered in the cited studies. They were both based on oxygen consumption rates. At one extreme, the consumption rate in the polymer was small, and the reaction rate of the oxygen with the core of the material controlling. In the second scenario, the reactions in the composite or neat resin readily digested the oxygen as it diffused into the surface material so that the degradation was controlled by the availability of oxygen. Two points of interest in these studies are the role(s) of oxygen in the mechanisms of thermo-oxidative degradation of these composite materials and the dimensional changes that occur during their usable lifetime.

In evaluating the thermal durability of polymer matrix composites, it has been found (refs. 1 to 4 and 8 to 12) that the durability, as assessed by weight loss and mechanical property degradation, is influenced by the reinforcement, sizing, processing, and dimensional parameters. When different matrices are included in a study, the procedure for evaluation becomes more complicated. The fiber-induced and composite processing variables were eliminated by limiting the study to neat resins.

Studies were conducted with six candidate high-temperature neat matrix polyimides, BAX, DMBZ, PMR–15, BIM, BIP, and AMB–21, at 204, 260, 288, and 316 °C, in varied geometric shapes, to further investigate the mechanisms involved in the thermal degradation of polymers like PMR–15. The data obtained can support the development of models of the thermal degradation mechanisms of these polyimides. The properties examined for assessing the quality of these candidates were glass transition temperature T_g, thermo-oxidative stability (TOS), dynamic mechanical properties, microstructural changes, and dimensional stability. The processing and mechanical properties were not investigated in the study reported herein. The dimensional changes and surface layer growth were in agreement with data published in references 1 and 2. An initial weight increase reaction was dominant at the lower temperatures. However, at the more elevated temperatures, the weight loss reactions were prevalent and probably masked the weight gain reaction. These data confirmed the findings of the existence of an initial weight gain reaction published in reference 2. Both surface- and core-dependent weight losses controlled the polymer degradation at the higher temperatures.

Structures of the six polymers (including PMR–15) are presented in figure 1. Table I contains processing parameters for all of them. The dimensional changes and surface layer growth were measured and recorded. The data for PMR–15 were published previously in reference 5. Only BAX, DMBZ, and PMR–15 sustained aging at 316 °C for over 1000 h, and they suffered severe cracking after 1900 h of exposure. BIM, BIP, and AMB–21 severely deformed because the test temperature was above their T_g. Both DMBZ and PMR–15 lost weight at a slower rate than the other candidates at the lower temperatures. Weight losses of the PMR–15, DMBZ, and BAX neat resin specimens were concentrated in surface material burnoff at temperatures of 288 °C and above. At the lower temperatures, weight loss was divided between the surface material and the core material. The percentage of weight loss in the core increased as the aging temperature decreased.

Materials Studied

The materials studied were candidate high-temperature polyimides developed at the NASA Glenn Research Center. They are designated as DMBZ, BAX, BIM, BIP, and AMB–21. The materials were cured and postcured as shown in table I. All materials were postcured in air at the cure temperature for 16 h. Specimens of different dimensions were machined to size by a water-cooled micromachining diamond saw. The dimensions, surface areas, and volumes of the specimens are listed in table II. Some of the materials data for PMR–15 presented herein were obtained from references 1 to 6. The details of the processing for these materials are available in those publications. Materials were fabricated in matched metal die molds. The quality of these materials was confirmed by nondestructive evaluation procedures and by metallographic photography during aging. The structures of these polymers are presented in figure 1.

Testing

The specimens were aged in air-circulating ovens after drying at 125 °C for 24 h. This was a sufficient amount of time to reduce the moisture content to very low levels. A traveler specimen was included for destructive evaluation of the crystallographic changes due to aging. The oven airflow rates were maintained at 100 cm^3/min. The aging temperatures studied were 204, 260, 288, and 316 °C. Temperatures were measured by nine calibrated thermocouples as specified in ANSI/ASTM E145–68. The specimens were removed from the ovens at regular intervals and placed in desiccators where they cooled to room temperature. The specimens were not removed from the desiccators until they were to be weighed. The weights were recorded, and the dimensions were measured. Also, the traveler specimens were removed and samples were cut for microstructural examination of the surface layers. Specimens were then returned to the ovens. The maximum aging time was limited to about 4000 h.

Dimensional measurements were made by one person using a Nicon Measurescope 10 traveling microscope with an accuracy of ±0.00127 mm. Ten separate measurements were made of each specimen thickness at indexed points around the perimeter as shown in figure 2. Seven measurements of length and width were made at the same indexed locations. Three length and four width measurements were recorded. Average values of the dimensions were used in all calculations. In some instances there were uncertainties in the length measurements due to warping of the polymer specimens.

The T_g's for the neat polymer and composites were measured by dynamic mechanical analysis (DMA). The measurements were made with rectangular test pieces using a Rheometrics RMS–800 rheological spectrometer. The two components of the complex shear modulus were measured as a function of temperature. The test pieces were stressed in torsion across the specimen widths. The heating rate was 5 °C/min; the frequency, 6.28 rad/sec; and the strain, 0.2. All specimens were dried in an air-circulating oven at 125 °C for 24 h before they were tested. This was a sufficient amount of time to reduce the moisture content to very low levels. The T_g was determined by measuring the intersection of the two tangents to the linear portions of the stored shear modulus G' curve where the curve suddenly drops to a minimum (see fig. 3).

The densities of the neat resin specimens were measured by water immersion as specified in ASTM D792 before aging and after the maximum number of hours of aging at the four elevated temperatures. A traveler specimen was aged with the test specimens. Small slices were removed from the traveler when the test specimens were removed for weighing and dimensional measurements. The layer thickness measurements were made from photomicrographs that were taken using differential interference contrast to accentuate the changes in gray tones at the damage surface interface with the visibly undamaged core. The final polishing medium used in preparing the mounted specimen was a 0.05-μm colloidal silica emulsion.

Results and Discussion

Density Changes

The measured density values for the six polyimide neat resin specimens are presented in table III. The densities of the PMR–15 specimens increased by about 1.5 percent for the specimens aged for 4000 h at 204 and 260 °C and by almost 0.9 percent after aging for 3300 h at 316 °C. The data in figure 4, taken from reference 5, confirm the measured data in table III. They indicate that PMR–15 neat resin specimens do exhibit an increase in density during thermo-oxidative aging in air. In contrast to this observation, the specimen densities decreased during aging in nitrogen (fig. 4 in ref. 5). These data suggest that the central core is not completely isolated from the oxidative atmosphere since the measured density increases after aging in air and decreases when air is excluded. The data also suggest that the degradation occurs by a thermal mechanism, causing a decrease in volume and an initial rapid loss in weight by the specimens aged at higher temperatures (above 260 °C). In both cases this is probably due to the diffusion of gaseous cure reaction products from the bulk of the specimens and oxygen-induced crosslinking. Data for the other five polymers (table III) show little change in density during their prolonged aging periods.

Dynamic Mechanical Analysis

Table III shows the dynamic shear modulus properties data for all the neat resins examined. Unaged specimen data are also presented as a reference point. It is evident that some oxygen crosslinking continues during the duration of aging for all the specimens aged at 316 and 260 °C. This crosslinking probably contributes to the shrinkage in the volume of the polymer and possibly to the higher thermo-oxidative stability (TOS) since some of the oxygen diffusing into the central core was removed in the cross-linking reaction. The stored shear moduli for the PMR–15 specimens aged at 316 and 204 °C as well as for the DMBZ and BAX specimens aged at 316 °C are lower than that for the same specimens aged at 288 °C because these specimens experienced cracking at the surfaces during aging. The cracks on the surface of the PMR–15 specimens aged at 316 °C penetrated farther into the thickness than those aged at 204 °C.

Thermo-oxidative Stability

The only candidate polymers that qualified for complete TOS testing at 316 °C were PMR–15, BAX, and DMBZ. The others warped, and their thickness dimension increased because of their low T_g's. Weight loss curves for the three polymers are shown in figure 5. The ranking, based on increasing weight loss, is DMBZ, PMR–15, and BAX (15, 19, and 27 percent, respectively, at 2500 h).The data in this figure were measured from specimens nominally measuring 5.08 by 1.27 by 0.2 cm to assure that no geometric effects would bias the comparison of measured data. Surface cracks were observed at 2800, 2530, and 1960 h for PMR–15, DMBZ, and BAX, respectively. The BAX specimens showed signs of char formation at the corners, suggesting a more severe degradation than observed for the other two polymers. The last data point on the PMR–15 curve in figure 5 was measured after the cracking was first detected. The change in slope illustrates the accelerating effect the cracking has on the weight loss.

Weight loss data for specimens aged at 288 °C were measured for the PMR–15, BIM, BIP, and BAX polymers and are presented in figure 6. AMB–21 was not included because of its low T_g, which again caused an extreme amount of dimensional instability at this temperature. The ranking at 288 °C based on increasing weight loss per unit weight (weight loss fraction) is PMR–15, BAX, BIP, and BIM. The data separate into two distinct groups after aging for 1000 h, probably due to similarities in the chemistries between the members of each group (see fig. 6). Initial unaged areas and volumes were used for the calculations. This results in a slight spread in the data after extended aging times.

Figure 7 presents the data measured during aging at 260 °C. The ranking is similar to that of the data measured at 288 °C. The data again separate into two separate groups after aging for 2000 h. AMB–21 weight loss data are somewhat higher than the BIM and BIP data.

The fractional weight loss data at 204 °C shown in figure 8 show that the weight loss for each of the six polyimides quickly reaches a constant value during the 4000 h of aging. The BAX, BIM, and DMBZ appear to undergo a weight gain reaction during the early aging period. The BIM and BAX then equilibrate near the zero weight loss value as the aging time increases, which suggests increasing crosslinking and carbonyl formation (fig. 8, ref. 2).

Ultrasonic C-scans indicate, by a decrease in through-transmission, a degradation of the bulk polymer during aging. An initial weight gain observed (see fig. 8) for PMR–15 specimens aged at temperatures of 225 °C and below (ref. 2) was probably due to reactions such as carbonyl formation and thermo-oxidative crosslinking. No metallographic evidence of core degradation was observed. The observed initial weight gain is consistent with the more intensive (shorter time between measurements) lower temperature thermo-oxidative study results reported in reference 2. No mass changes were observed at 150 °C, but changes were observed at 175 °C and above. The duration of time that the weight gain persisted was 600+ h at 175 ° C and 50 h at 250 ° C.

Figure 9 shows the weight loss of PMR–15 polymer specimens as a function of aging time at all four temperatures investigated. Data for the other polymers were treated in the same way, and then Arrhenius curves for each polymer were plotted. The plots are presented in figure 10. The activation energies and frequency factor are listed in table IV.

Weight Loss Partitioning

The thermo-oxidative durability ranking can also be documented on a weight loss per unit area or volume basis. This is done by plotting weight loss data for polymer specimens of different dimensions on one graph of weight loss per unit volume or surface area against aging time. Table V presents the weight loss per unit surface area and weight loss per unit volume for each polymer. The final weight losses after aging as well as initial unaged areas and volumes were used to calculate the data in table V. The small changes in volume and areas during aging results in a slight spread in the data after extended aging times. The specimens were machined into four dimensional groups. Thus, when the weight loss per unit volume or surface area is close to the same value for each different-sized specimen of the same polymer and aging temperature, there is no dependence on that particular dimensional quantity.

It is apparent from table V that upon aging at 316 °C, the weight loss of the PMR–15 and DMBZ polymers are independent of both volume and surface area. BAX appears to be independent of volume, but does exhibit a dependence on surface area. DMBZ shows a smaller weight loss per unit area and unit volume than the other two polymers.

When the aging temperature is reduced to 288 °C, PMR–15 appears to retain the independence from surface area, while BAX weight loss exhibits surface area dependence. There is still a weight loss independence from specimen volume for PMR–15 and BAX at this temperature. Calculations indicate that the weight loss of BIM is independent of both volume and area. BIP weight losses appear to be dependent on both variables. At the lower temperatures, PMR–15 appears to be dependent on both variables. The weight loss per unit area is about 100 percent more for the BIM than for the PMR–15.

When the aging temperature of BIM is reduced to 204 °C, the weight loss data appear to be partially dependent on both the surface area and the volume. As shown in Figure 8, the larger BIM specimens experienced an initial weight gain. This is not so clear in the data of the smaller specimens. Thus, in order to accurately compare weight loss data for specimens aged at 204 °C on a percent basis, the specimen surface areas or volumes must be similar. It would further clarify the aging behavior if the aging times were increased significantly at the lower temperatures.

Another method for evaluating partitioning is comparing actual measured weight losses with weight losses calculated from changes in volumes. The weight losses are both surface and volume related with the surface weight loss being dominant at the higher aging temperatures. If the changes in measured specimen volumes are calculated after reaching the maximum aging times of the tests, they can be converted to weight loss changes by multiplying them by the polymer density:

$$\Delta W = \Delta V \times \rho \tag{1}$$

where ΔW is the change in weight, ΔV is the change in volume, and ρ is the polymer density, which is shown in table III to change only slightly during these tests. Also, the change in volume can be calculated from the relationship

$$\Delta V = \frac{\Delta W}{\rho} \tag{2}$$

The changes in dimensions, which are used to calculate the volume differentials, are assumed to be due to the loss of surface material and the shrinkage of the core material. Surface layer effects are considered to be negligible but to control the diffusion of oxygen to the layer-core interface. The weight change in the layer is unknown, but because of the small thickness, it is also neglected. The dimensions were monitored during the aging process, and the polymer densities were measured before and at the completion of the aging phase. Thus, both variables in equation (1) are known. The measured weight losses were compared with the weight losses calculated from the changes in specimen volumes. Three possible scenarios can be expected: (1) they could be equal (dominated by surface area weight loss), (2) the measured weight loss could be greater than the calculated weight loss (effects of both volume and surface area weight loss are significant), and (3) the value of the measured weight loss could be less than the calculated value (dominated by volume weight loss).

In table VI, the data for the first three—larger—volumes of PMR–15 neat resin specimens measured after aging at 316 °C show that the measured values of weight loss are larger than the calculated values. This result suggests that the measured weight loss includes the surface material loss (which causes the specimen to become thinner) and the loss of degradation fragments that diffuse out from the polymer core material. The interior weight loss may be due to the more rapid diffusion of oxygen into and out of the core of the specimen at 316 °C.

At temperatures of 260 °C and below, the measured weight loss for the polymers is equal to or less than the loss calculated from the specimen volume decrease, indicating that the volume weight loss is probably the dominant mechanism at this temperature and consists mostly of the changes in the polymeric core material. A considerable amount of the shrinkage appears to be due to thermally induced chemical changes of the core material. Surface oxidative reactions are much slower than thermally induced chemical changes (diffusion of oxygen) into the core material. This statement is in agreement with the data in table V, which shows a strong relationship between weight loss and volume. DMBZ, BIM, and BIP have calculated weight losses greater than measured weight losses.

The DMBZ data indicate that the differences between the measured and calculated weight and volume losses remain constant at all temperatures and for all specimen volumes. The observed shrinkage is somewhat more than the reduction that would be caused by the weight of lost polymer from the surface areas. In contrast, at 316 °C the PMR–15 specimens appear to lose most of the weight at the specimen surfaces, and not from the core material. The calculated volume fraction changes are negative at the lower temperatures for these two polymers.

The weight losses for the polymers except AMB–21 and BIP, calculated from the volume differences, are greater than the actual measured losses when the aging temperature is below 288 °C. This result suggests that most of the dimensional changes are due to core shrinkage and not from surface material loss, indicating a considerable amount of the shrinkage is due to thermally induced chemical changes of the core material. Surface oxidative reactions are much slower than the diffusion of oxygen into the core material.

Results are mixed at 260 and 204 °C for each polymer. BIM appears to undergo a weight change at 204 °C. No general conclusions can be drawn from the data to characterize low-temperature durability of these polymers. It is apparent that more aging time is needed to clarify the relationships.

Thermally Induced Surface Layer Growth

Figure 11 (ref. 7) shows a schematic of the development of an oxidized surface layer on a neat resin specimen. The layers in the neat resin are uniform in thickness throughout all outer surfaces. They are of very small thickness. The thickness approaches a maximum of about 0.25 mm during aging at 204 ° C. Surface layer growth data for neat resin specimens during aging at 204, 260, 288, and 316 °C can be found in figure 12. All of the data mass together below 0.30 mm thickness. The data from specimens aged at 316 °C are in agreement with those published in references 6, 13, and 14. (Although there are a number of misconceptions and misstatements in ref. 14, the data are acceptable.) There are differences in the initial portion of the curves. This portion represents the time to approach the maximum thickness. At 204 °C the maximum surface layer thickness is reached in about 750 h, whereas it takes longer at higher temperatures. This can be explained by the surface weight loss rates and the oxygen diffusion rates. Since the weight loss rate at 204 °C is much smaller than that at 316 °C, the surface of the specimen aged at the lower temperature loses less surface material weight than the specimens aged at the higher temperatures, and the specimen becomes thinner at a faster rate. The oxygen is not consumed at a significant rate in oxidative surface reactions until the maximum surface layer thickness has been established. The diffusion of the oxygen is hindered by its consumption in the oxidative reactions at the higher temperatures. In simple terms, the surface reaction and the interfacial (layer-core) reaction must come to equilibrium for the surface layer thickness to reach a maximum. The layer-core reaction is controlled by oxygen diffusion through the layer.

Thickness Shrinkage

Thickness measurements were chosen for evaluation because the largest number (10) of measurements was made of this dimension and also because this dimension showed fewer effects of any warping that may have occurred during aging. Table VII presents the average fraction of thickness shrinkage of the six polymers at the listed aging times at the four aging temperatures. At the higher temperatures, some of the materials are not listed because their T_g's are lower than the aging temperatures. Data for DMBZ at 288 °C are not included in the table. The data indicate no consistent significant differences in shrinkage between the six polymers over all four temperatures. Figure 13 presents shrinkage data for PMR–15 specimen lengths aged at the four temperatures. At the higher temperatures, the data show a linear relationship with weight loss.

Other Factors Affecting Ranking

PMR–15, BAX, and DMBZ have higher temperature capabilities than the other candidate polymers; however, no comparisons of process ability or fiber-matrix interfacial compatibility have been addressed in this study and are of extreme importance in selecting a suitable replacement for PMR–15. References 15 to 18 present results of previous work with PMR–15 and DMBZ composites. The DMBZ composite experiences extensive microcracking during exposure to temperatures around 316 °C and higher.

No mechanical properties data for BAX, BIP, BIM, or AMB–21 have been published in the open literature to date. The rate at which the mechanical properties degrade is dependent on the rate at which the surface is oxidized and the specimen becomes thinner (ref. 17). This dependence can be assumed to be true for neat polymer specimens, also. The mechanical properties are dependent on the specimen thickness and should not initially be severely degraded as the weight loss increases unless the specimen thickness is a small multiple of the layer thickness. When the weight loss is spread throughout the specimen and accompanying damage is distributed throughout the core, it would be expected that the mechanical properties would be susceptible to a more rapid decrease as a function of the amount of weight loss that is experienced by the core of the specimen than if only the surface material were involved. The core mechanical properties become more controlling as the thickness of the specimen increases. To keep the mechanical property degradation at a minimum with weight loss increases, it would be necessary to reduce the surface burnoff at the higher temperatures, which would reduce the infiltration of oxygen through the surface layers in both neat resins and composites (ref. 17). This may be one metric for evaluating candidate matrix performance rating.

Summary of Results

Based on T_g and isothermal weight loss, only PMR–15, BAX, and DMBZ polymers are capable of sustaining 316 °C exposure for short time durations. PMR–15 and DMBZ maintained longer crack-free surface times at this temperature. BAX experienced the greatest amount of weight loss, whereas DMBZ lost less weight than PMR–15 after 1000 h of aging at 316 °C. During aging at 288 °C, all polymers performed similarly for the first 1000 h. All aged polymers performed similarly for the first 2000 h at 260 °C. BIP and BIM lost weight at a faster rate than PMR–15 and BAX at 288 °C, whereas AMB–21 and BIP experienced a faster rate of weight loss than the other resins during aging at 260 °C. BIM exhibited a much lower weight loss rate than BIP or AMB–21 at this temperature. The results of aging tests at 204 °C are similar for all polymers except AMB–21. AMB–21 shows a slight weight gain for the first 2500 h. AMB–21 has a performance rating worse than the other polyimides in relation to the above criteria and cannot be considered a candidate for high-temperature structural composites. Short-term, elevated-temperature aging tests for a duration less than 2500 h may give misleading results.

The surface layer growth does not appear to be of any significant use in evaluating and rating candidate matrix polymer performance. The layer appears to approach a maximum thickness of between 0.20 to 0.30 mm for the group studied herein. Individually, the differences in maximum thickness are small. The changes in density are also not indicative of polymer durability and performance.

Even when the weight loss from the surface is significant, the core of the specimen also sustains thermal and/or oxidative damage. For a graphite-fabric-reinforced composite, this damage is dependent on the aging temperature because the diffusion of oxygen varies with temperature.

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TABLE I.—PROCESSING PARAMETERS OF CANDIDATE POLYIMIDES

Polymer	Cure		Postcure	
	Temperature, °C	Time, h	Temperature, °C	Time, h
PMR–15	316	2.0	316	16
BIM	324	2.0	232 260 316 324	2 2 4 4
BIP	324	2.0	232 260 316 324	2 2 4 4
BAX	324	2.0	232 260 316 324	2 2 4 4
AMB–21	324	2.0	232 260 288 316 324	2 2 2 4 4
DMBZ	177 260 316	0.5 1.5 2.0	274 316	1 16

TABLE II.—DIMENSIONS, VOLUMES, AND SURFACE AREAS OF CANDIDATE POLYIMIDES

Polymer	Aging temperature, °C	Length, cm	Width, cm	Thickness, cm	Volume, cm^3	Area, cm^2
BAX	316	9.89	2.40	0.24	5.62	53.20
		9.88	1.17	.22	2.54	27.99
		5.06	2.41	.25	3.06	28.14
		4.94	1.14	.24	1.38	7.07
	288	9.96	2.53	0.21	5.35	55.63
		9.96	1.28	.21	2.73	30.35
		4.99	2.54	.23	2.87	28.77
		4.91	1.17	.22	1.27	14.17
	260	9.87	1.17	0.22	2.50	27.89
		4.91	2.40	.27	3.21	27.52
		5.03	1.16	.25	1.41	14.72
	204	9.88	2.40	0.23	5.51	53.10
		10.04	1.13	.26	2.95	28.51
		4.94	2.40	.28	3.26	27.76
		4.97	1.17	.24	1.42	14.65
DMBZ	316	10.00	2.41	0.25	5.91	27.73
		10.00	1.14	.26	2.95	28.61
		4.97	2.41	.27	3.26	15.98
		4.99	1.19	.26	1.57	15.17
	260	10.00	2.41	0.24	5.80	54.17
		10.01	1.14	.25	2.88	28.50
		4.98	2.40	.25	3.04	27.69
		4.98	1.17	.27	1.54	14.80
	204	10.02	2.41	0.24	5.81	54.35
		10.01	1.17	.26	3.06	29.21
		4.96	2.44	.26	3.20	28.10
		4.97	1.13	.27	1.53	4.58
PMR–15	316	3.90	0.73	0.11	4.98	6.70
		3.90	.50	.10	3.27	4.79
		2.00	.50	.10	1.71	2.63
		2.00	.50	.11	1.72	2.52
	288	9.91	1.86	0.27	4.98	43.25
		9.92	1.27	.26	3.27	30.92
		5.08	1.28	.26	1.71	16.31
		5.07	1.27	.27	1.72	16.24
	260	10.18	2.54	0.28	7.16	58.67
		10.18	1.27	.26	3.36	31.77
		5.07	2.59	.28	3.73	30.66
		5.12	1.28	.28	1.86	16.69
	204	9.92	2.54	0.26	6.64	56.92
		9.91	2.53	.26	6.59	56.67
		5.07	2.54	.26	3.33	29.68
		5.08	1.27	.27	1.74	16.32
		5.08	1.27	.26	1.71	16.29
BIM	288	10.21	2.52	0.23	5.98	57.28
		10.25	1.15	.24	2.87	347.12
		5.08	1.47	.25	1.83	18.11
		5.18	1.00	.23	1.18	13.15
	260	10.06	2.40	0.21	4.99	51.23
		9.88	1.13	.22	2.43	24.58
		4.96	.94	.22	1.05	9.80
		4.88	1.18	.24	1.40	12.03
	204	10.07	2.40	0.20	4.93	53.34
		10.07	1.18	.19	2.30	28.05
		4.87	2.41	.24	2.81	26.92
		4.95	1.16	.23	1.31	14.23

TABLE II.—DIMENSIONS, VOLUMES, AND SURFACE AREAS OF CANDIDATE POLYIMIDES (Concluded)

Polymer	Aging temperature, °C	Length, cm	Width, cm	Thickness, cm	Volume, cm^3	Area, cm^2
BIP	288	7.51	3.52	0.19	4.95	57.10
		7.53	1.07	.19	1.50	19.34
		5.16	2.43	.19	2.37	27.89
		5.16	1.30	.21	1.40	16.14
		5.08	1.28	.17	1.11	15.19
	260	9.93	1.13	0.24	2.67	27.74
		4.93	2.54	.24	2.99	28.63
		4.92	1.30	.24	1.56	15.79
	204	9.92	2.43	0.22	5.19	53.53
		9.91	1.27	.23	3.89	30.25
		4.95	2.55	.25	3.13	28.90
		4.93	1.30	.25	1.61	15.92
AMB–21	260	9.98	2.38	0.21	5.03	52.71
		9.97	1.33	.25	3.25	31.99
		5.01	2.39	.26	3.16	27.84
		4.91	1.12	.27	1.47	14.24
	204	10.04	2.43	0.22	5.36	54.32
		10.04	1.15	.20	2.36	27.63
		5.03	2.42	.29	3.47	28.55
		4.95	1.13	.29	1.59	14.61
		5.04	1.47	.28	1.64	15.07

TABLE III.—DYNAMIC MECHANICAL ANALYSIS AND DENSITY MEASUREMENTS

Polymer	Aging temperature, °C	Aging time, h	Glass transition temperature, T_g, °C	Stored shear modulus, G', dyn/cm^2	Density, ρ, g/cm^3
PMR–15	No aging		339	2.68×10^{10}	1.32
	204	4400	344	8.54×10^{9}	1.34
	260	4312	341	1.05×10^{10}	1.34
	288	4072	352	8.02×10^{9}	1.33
	316	3324	368	5.09×10^{9}	-----
DMBZ	No aging		----	----------	1.28
	204	4200	388	5.74×10^{9}	1.30
	260	4000	380	----------	1.29
	316	2534	372	3.52×10^{9}	-----
BIP	No aging		316	----------	1.27
	204	4000	318	8.89×10^{9}	1.27
	260	4000	322	9.20×10^{9}	1.27
	288	4000	319	1.10×10^{10}	1.27
BIM	No aging		316.5	----------	1.27
	204	4100	276	1.04×10^{10}	-----
	260	4046	303	----------	1.28
	288	4000	312	7.83×10^{9}	1.28
BAX	No aging		337	----------	1.28
	204	4200	332	8.15×10^{9}	1.29
	260	4042	347	8.13×10^{9}	1.29
	288	4000	349	9.20×10^{9}	1.29
	316	1960	360	1.30×10^{9}	-----
AMB–21	No aging		----	----------	1.26
	204	4200	275	8.72×10^{9}	1.28
	260	4100	306	8.13×10^{9}	1.28

TABLE IV.—ARRHENIUS ACTIVATION ENERGY OF OXIDATION

Polymer	Activation energy, cal/g·mol	Frequency factor
PMR	–25 274.27	-7.91×10^{-5}
BAX	–27 920.34	-7.16×10^{-5}
DMBZ	–22 271.01	-8.98×10^{-5}
BIM	–27 918.92	-7.16×10^{-5}
BIP	–32 561.94	-6.14×10^{-5}

TABLE V.—WEIGHT LOSS PER UNIT SURFACE AREA AND VOLUME DURING AGING

Polymer	Aging temperature, °C	Volume, cm^3	Area, cm^2	Weight change, g	Weight change per unit area, g/cm^2	Weight change per unit volume, g/cm^3
BAX	316	5.62	53.20	1.74	0.03	0.31
		2.54	27.99	.80	.03	.31
		3.06	28.14	.79	.03	.26
		1.38	7.08	.39	.06	.31
	288	5.35	55.63	1.06	0.02	0.20
		2.73	30.35	.58	.02	.21
		2.87	28.77	.54	9.14×10^{-3}	.19
		1.27	14.17	.26	.04	.21
	260	2.50	27.89	0.13	4.55×10^{-3}	0.05
		3.21	27.52	.13	4.65×10^{-3}	.04
		1.46	14.72	.07	4.55×10^{-3}	.05
	204	5.51	53.10	–0.051	-9.60×10^{-4}	-5.65×10^{-4}
		2.95	28.51	–.044	-1.54×10^{-3}	-9.09×10^{-4}
		3.26	27.76	.00	1.08×10^{-4}	5.61×10^{-5}
		1.42	14.65	.00	$6.83'10^{-5}$	4.30×10^{-5}
DMBZ	316	5.91	27.73	1.29	0.05	0.22
		2.95	28.61	.63	.02	.21
		3.26	15.98	.77	.05	.24
		1.57	15.18	.36	.02	.23
	260	5.80	54.17	0.25	4.60×10^{-3}	0.04
		2.88	28.50	.13	4.67×10^{-3}	.05
		3.04	27.69	.13	4.73×10^{-3}	.04
		1.54	14.80	.07	4.86×10^{-3}	.05
	204	5.81	54.35	0.03	4.60×10^{-4}	4.30×10^{-3}
		3.06	29.21	.01	3.08×10^{-4}	2.94×10^{-3}
		3.20	28.10	.02	7.12×10^{-4}	6.26×10^{-3}
		1.53	14.58	.01	8.92×10^{-4}	8.49×10^{-3}
PMR–15	316	4.98	43.25	1.55	0.04	0.31
		3.27	30.92	1.11	.04	.34
		1.71	16.31	.74	.05	.43
		1.72	16.24	.58	.03	.34
	288	4.98	43.25	0.68	0.02	0.14
		3.27	30.92	.38	.01	.12
		1.71	16.31	.34	.02	.20
		1.72	16.24	.12	7.39×10^{-3}	.07
	260	7.17	58.68	0.28	4.69×10^{-3}	0.04
		3.36	31.77	.15	4.60×10^{-3}	.04
		3.73	30.66	.14	4.60×10^{-3}	.04
	204	6.64	56.92	0.05	8.08×10^{-4}	6.92×10^{-3}
		6.59	56.67	.03	5.12×10^{-4}	4.40×10^{-3}
		3.33	29.68	.03	9.10×10^{-4}	8.11×10^{-3}
		1.74	16.32	.02	9.80×10^{-4}	9.18×10^{-3}
		1.71	16.29	.02	1.04×10^{-3}	9.93×10^{-3}
BIM	288	5.98	57.28	0.77	0.01	0.13
		2.78	34.71	.39	1.12×10^{-3}	.14
		1.83	18.11	.24	.01	.13
	260	4.99	51.23	0.32	6.17×10^{-3}	0.06
		2.43	24.58	.16	6.31×10^{-3}	.06
		1.05	9.80	.16	.02	.15
		1.40	12.03	.08	6.48×10^{-3}	.06
	204	4.93	53.34	0.06	1.20×10^{-3}	0.01
		2.30	28.05	.03	9.98×10^{-4}	.01
		2.82	26.92	.02	8.17×10^{-4}	.01
		1.31	14.23	.01	7.73×10^{-4}	.01

TABLE V.—WEIGHT LOSS PER UNIT SURFACE AREA AND VOLUME DURING AGING (Concluded)

Polymer	Aging temperature, °C	Volume, cm^3	Area, cm^2	Weight change, g	Weight change per unit area, g/cm^2	Weight change per unit volume, g/cm^3
BIP	288	4.95	57.10	0.60	0.01	0.21
		1.50	19.34	.41	.02	.27
		2.37	27.89	.28	.01	.12
		1.40	16.15	.23	.01	.16
	260	2.67	27.74	0.20	7.28×10^{-3}	0.08
		2.99	28.63	.19	6.78×10^{-3}	.06
		1.56	15.79	.11	6.65×10^{-3}	.07
	204	5.19	53.53	0.01	1.87×10^{-4}	1.93×10^{-3}
		2.89	30.25	.02	6.61×10^{-4}	7.00×10^{-3}
		3.13	28.90	.02	7.27×10^{-4}	.01
		1.61	15.92	.01	7.54×10^{-4}	.01
AMB–21	260	5.03	52.71	0.36	6.79×10^{-3}	0.07
		3.25	31.99	.23	7.03×10^{-3}	.07
		3.16	27.84	.74	.03	.23
		1.47	14.24	.10	6.88×10^{-3}	.07
	204	5.36	54.32	0.03	5.89×10^{-4}	5.97×10^{-3}
		2.36	27.63	.03	1.16×10^{-3}	.01
		3.47	28.55	.03	9.11×10^{-4}	7.50×10^{-3}
		1.59	14.61	.02	1.10×10^{-3}	.01

TABLE VI.—DIFFERENCE BETWEEN MEASURED AND CALCULATED WEIGHT LOSSES DURING AGING

Polymer	Aging temperature, °C	Volume, cm^3	Volume change, cm^3	Weight change, g	Measured minus calculated weight change, g
BAX	316	5.62	1.30	1.74	0.08
		2.54	.60	0.80	.03
		3.06	.62	0.79	–.00
		1.38	.23	0.39	.10
	288	5.35	0.90	1.06	–0.10
		2.73	.53	0.58	–.10
		2.87	.46	0.26	–.32
		1.27	.26	0.54	.21
	260	2.50	0.12	0.13	–0.03
		3.21	.13	0.13	–.03
		1.46	.08	0.07	–.04
	204	5.51	0.07	–0.05	–0.14
		2.95	.08	–.04	–.15
		3.26	.04	.00	–.05
		1.42	.07	.00	–.09
DMBZ	316	5.91	1.19	1.29	–0.24
		2.95	.92	.63	–.55
		3.26	.54	.77	.07
		1.57	.37	.36	–.12
	260	5.80	0.25	0.25	–0.08
		2.88	.14	.13	–.04
		3.04	.14	.13	–.05
		1.54	.07	.07	–.02
	204	5.81	0.10	0.03	–0.10
		3.06	.06	.01	–.07
		3.20	.04	.02	–.04
		1.53	.03	.01	–.03
PMR–15	316	4.98	0.96	1.55	0.28
		3.27	.67	1.11	.23
		1.71	.37	.74	.25
		1.72	.47	.58	–.03
	288	4.98	0.66	0.68	–0.19
		3.27	.35	.38	–.07
		1.71	.34	.34	–.12
		1.72	.14	.12	–.07
	260	7.17	0.04	0.28	0.22
		3.36	.28	.15	–.22
		3.73	.14	.14	–.04
	204	6.64	0.09	0.05	–0.08
		6.59	.04	.03	–.02
		3.33	.06	.03	–.05
		1.74	.04	.02	–.04

TABLE VI.—DIFFERENCE BETWEEN MEASURED AND CALCULATED WEIGHT LOSSES DURING AGING (Concluded)

Polymer	Aging temperature, °C	Volume, cm^3	Volume change, cm^3	Weight change, g	Measured minus calculated weight change, g
BIM	288	5.98	0.75	0.77	–0.18
		2.78	.47	.39	–.20
		1.83	.23	.24	–.05
	260	4.99	0.38	0.32	–0.81
		2.43	.12	.16	–.31
		1.05	.09	.16	–.27
		1.40	.12	.08	–.23
	204	4.93	0.14	0.06	–0.12
		2.30	.09	.03	–.09
		2.82	.06	.02	–.05
		1.31	.07	.01	–.08
BIP	288	4.95	0.16	0.60	0.40
		1.50	.15	.41	.22
		2.37	.08	.28	.17
	260	2.67	0.16	0.20	0.00
		2.99	.15	.19	.00
		1.56	.08	.11	.00
	204	5.19	0.16	0.01	–0.19
		2.89	.13	.02	–.14
		3.13	.12	.02	–.13
		1.61	.05	.01	–.05
AMB–21	260	5.03	0.45	0.36	0.36
		3.25	.26	.23	.23
		3.16	.22	.74	.74
		1.47	.12	.10	.10
	204	5.36	0.01	0.03	0.03
		2.36	.01	.03	.03
		3.47	.01	.03	.03
		1.59	.01	.02	.02

TABLE VII.—DECREASE IN THICKNESS AFTER AGING

Polymer	Aging Temperature, °C	Aging time, h	Thickness decrease, cm
PMR–15	316	2800	0.016 .016 .016 .024
	288	4000	0.109 .110 .112 .112
	260	4312	0.004 .008 .004 .008
	204	4400	0.001 .001 .001 .001 .001 .011 .007 .003
	260	4046	0.005 .003 .004 .004
	204	4100	0.000 .001
BIM	288	4000	0.008 .011 .007 .003
	260	4046	0.005 .003 .004 .004
	204	4100	0.0003 .001 .002 .001
BIP	288	4000	0.009 .007 .010 .009
	260	4000	0.093 .094 .096
	204	4000	0.002 .002 .002 .002
DMBZ	316	2534	0.014 .013 –.001 .017
	260	4000	0.004 .004 .004
	204	4200	0.001 .001 .001 .002
BAX	316	1960	0.019 .016 .014 .009
	288	4000	0.012 .008 .012 .014
	260	4024	0.004 .003 .003
	204	4200	0.001 .015 .001 .002
AMB–21	260	4100	0.064 .056 .047 .050
	204	3500	0.002 .002 .003

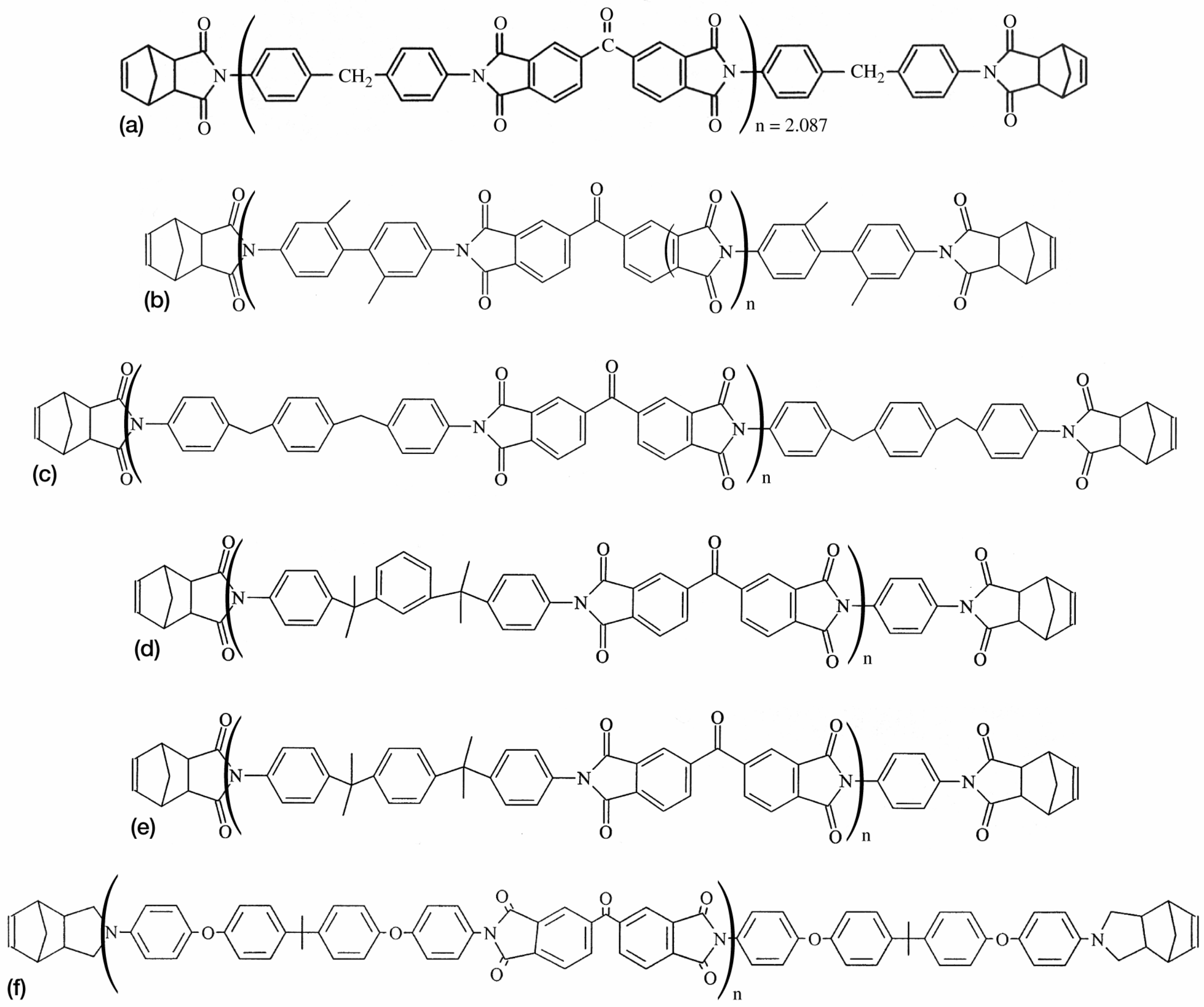


Figure 1.—Molecular structure of candidate polyimides. (a) PMR–15. (b) DMBZ. (c) BAX. (d) BIM. (e) BIP. (f) AMB–21.

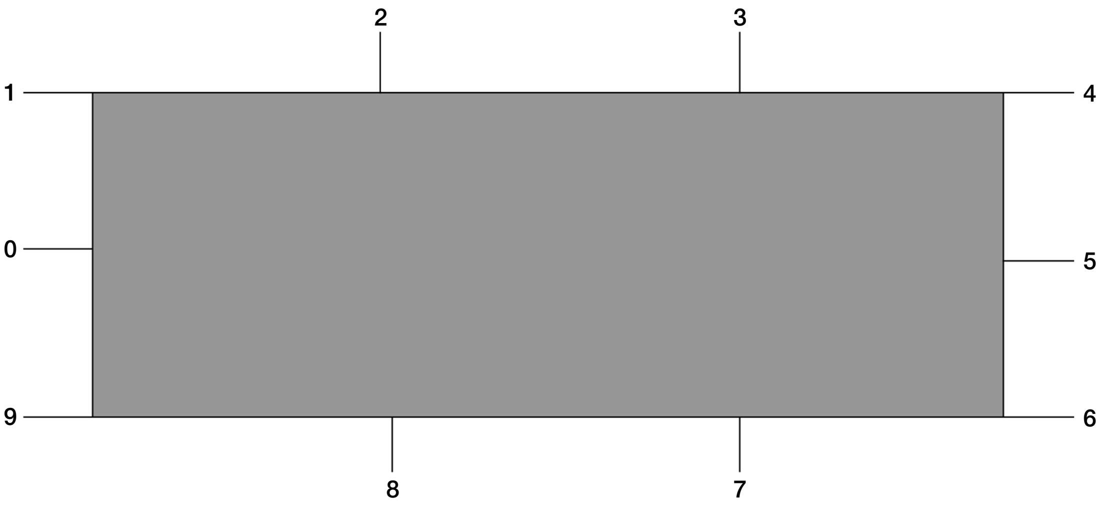


Figure 2.—Marked index positions for dimensional measurements of polyimides. Total measurements made: 10 thicknesses, 4 widths, and 3 lengths.

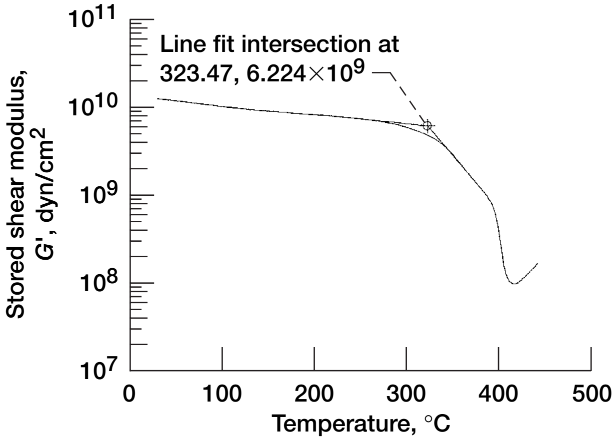


Figure 3.—Dynamic mechanical analysis data showing determination of glass transition temperature, T_g.

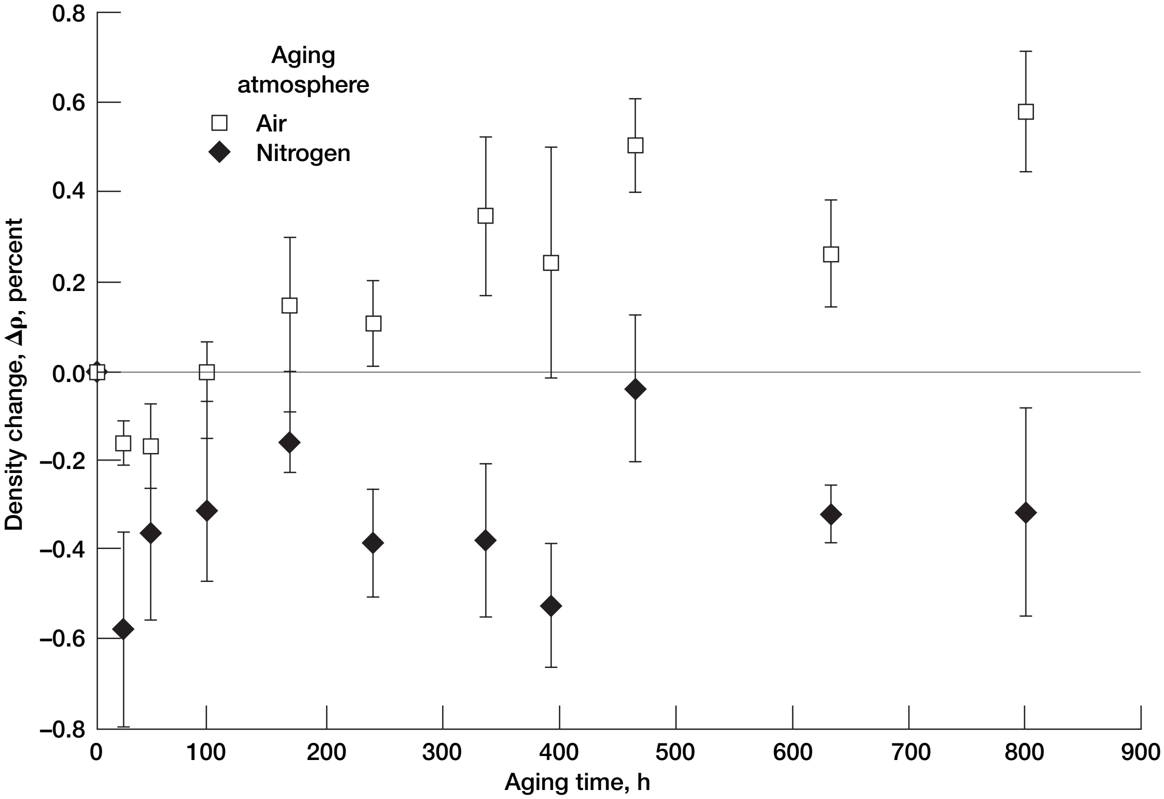


Figure 4.—Density changes of PMR–15 neat resin during aging in air and nitrogen at 316 °C (ref. 5).

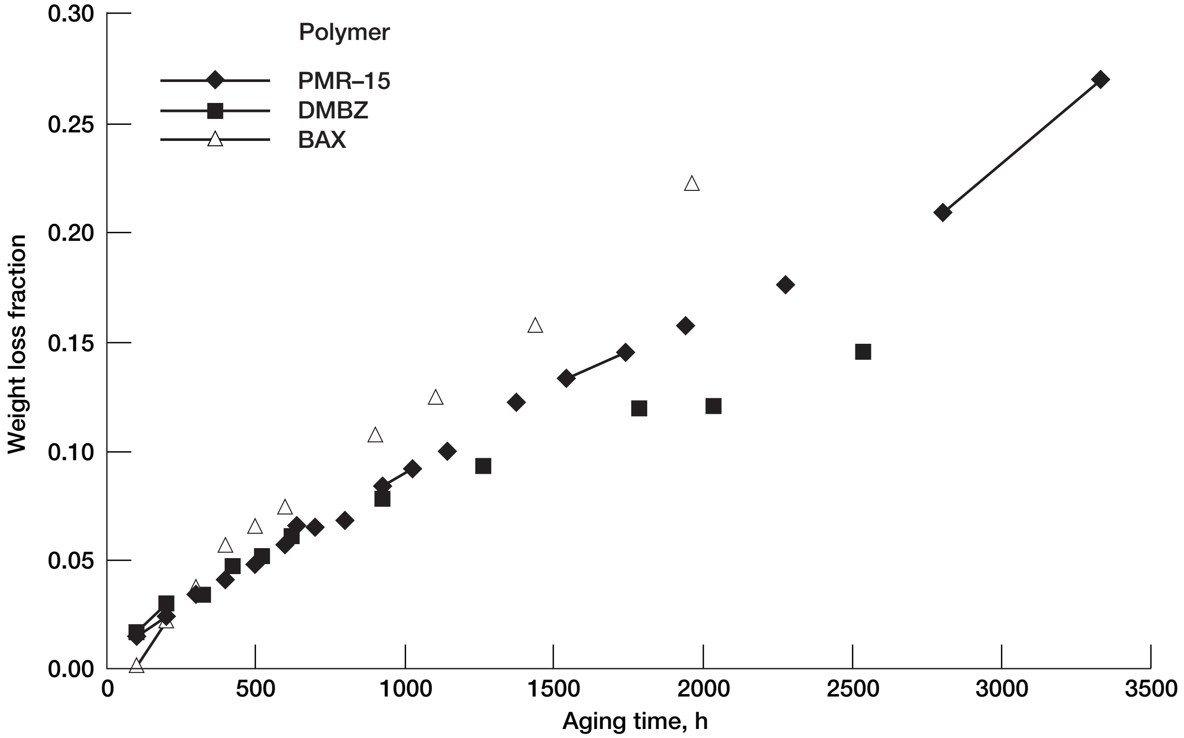


Figure 5.—Weight loss at 316 °C of candidate high-temperature polyimides with comparable dimensions.

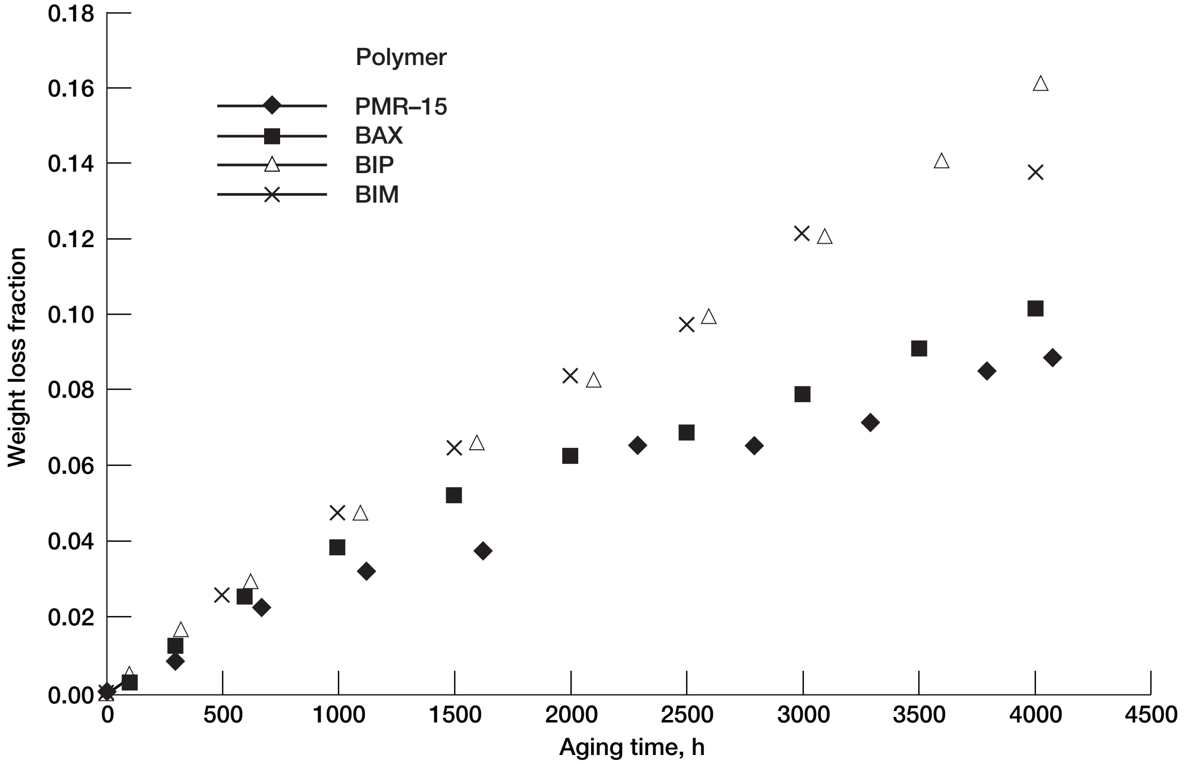


Figure 6.—Weight loss of polyimides during aging at 288 °C.

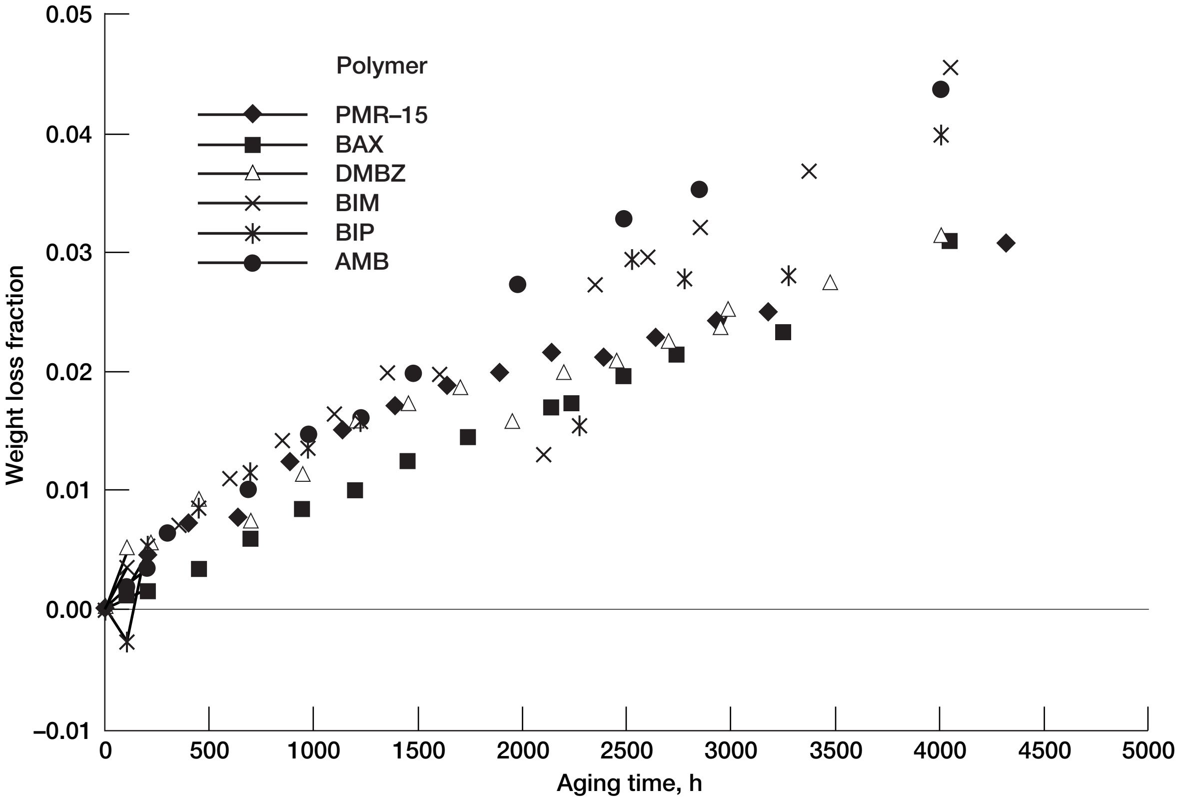


Figure 7.—Weight loss of polyimides during aging at 260 °C.

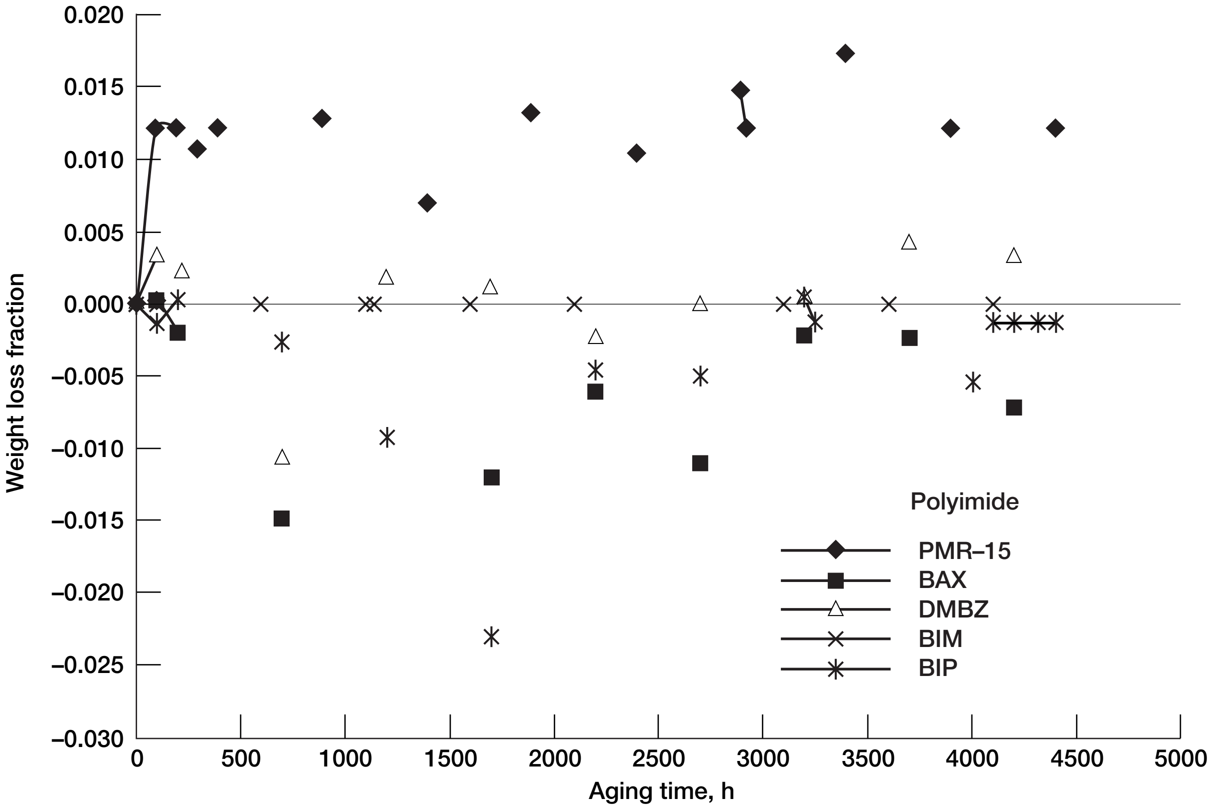


Figure 8.—Weight loss of polyimides during aging at 204 °C.

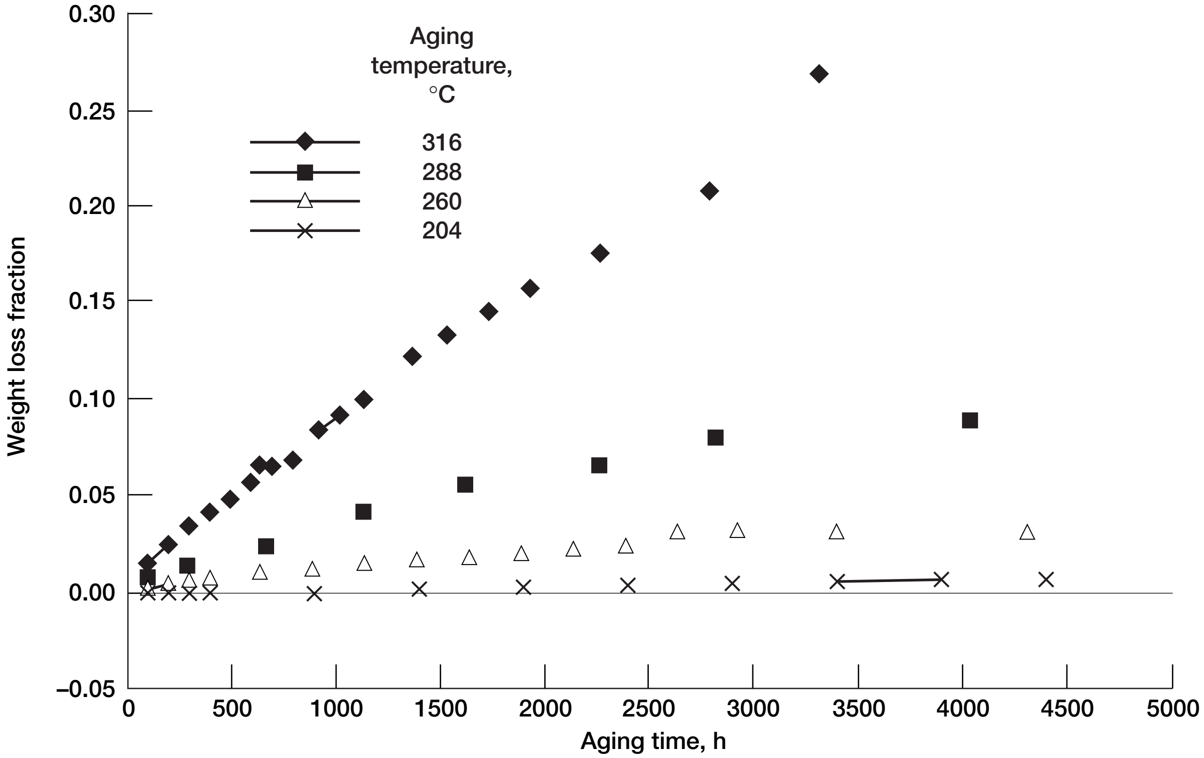


Figure 9.—Weight loss of neat resin PMR–15 during aging at various temperatures.

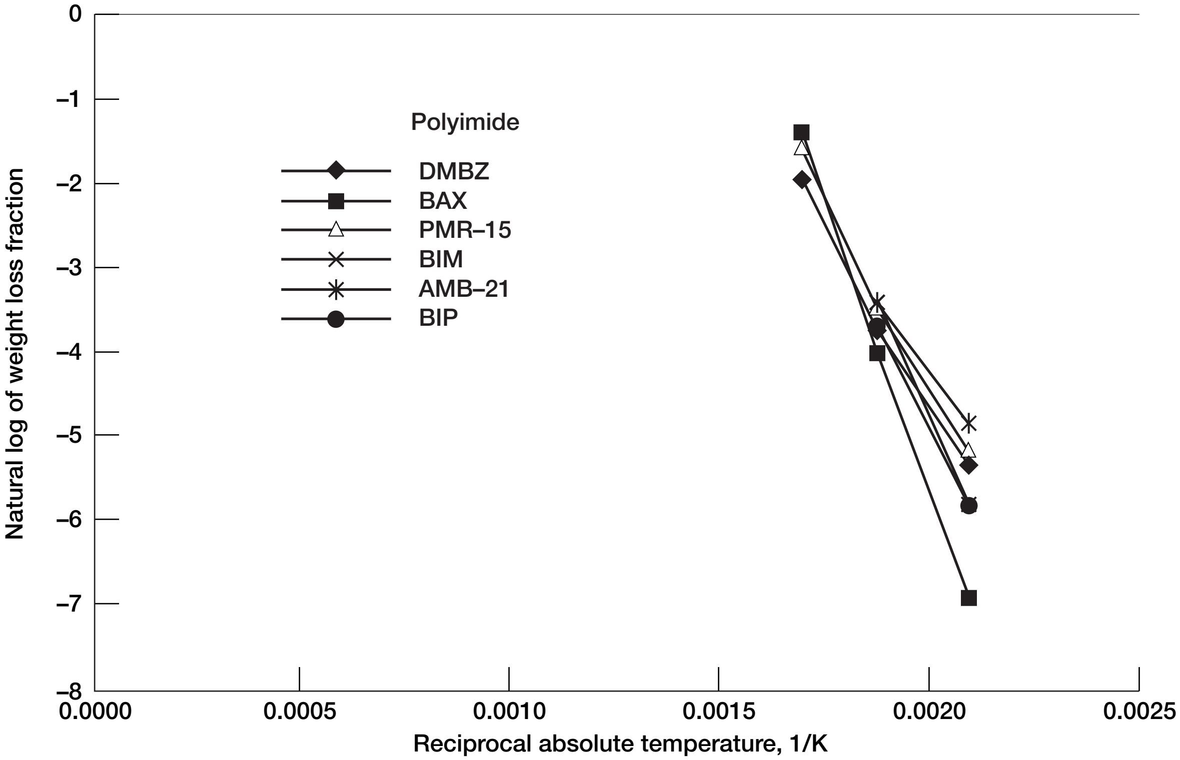
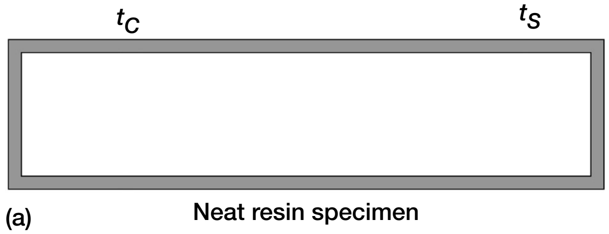


Figure 10.—Arrhenius plot of weight loss of polyimides during aging up to 2500 h.



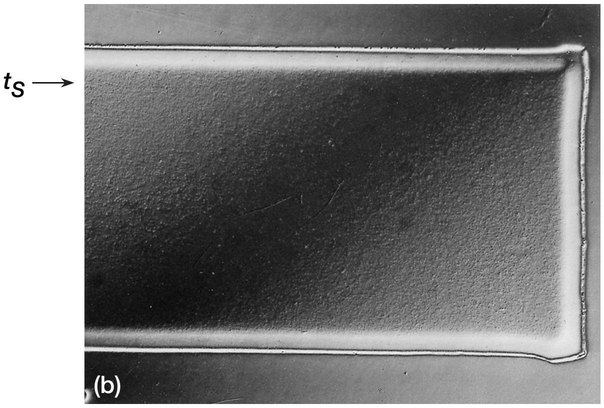
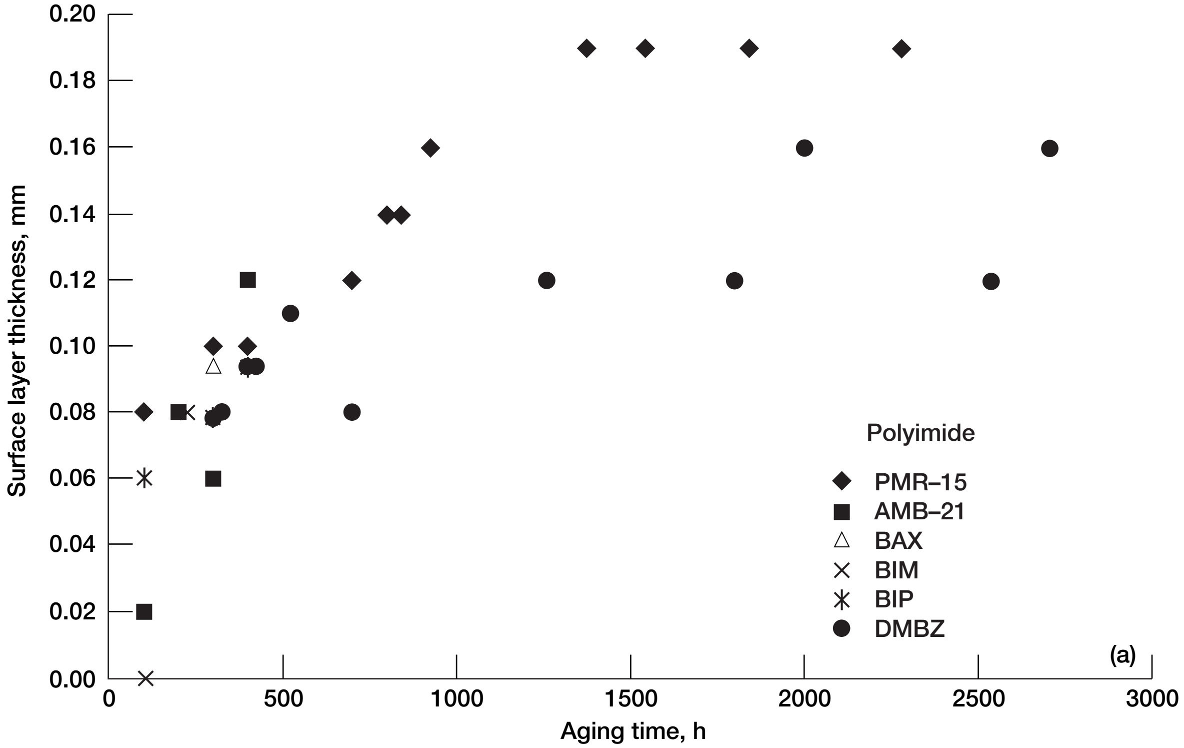


Figure 11.—Polymer after aging at elevated temperature. (a) Schematic. (b) Microphotograph.



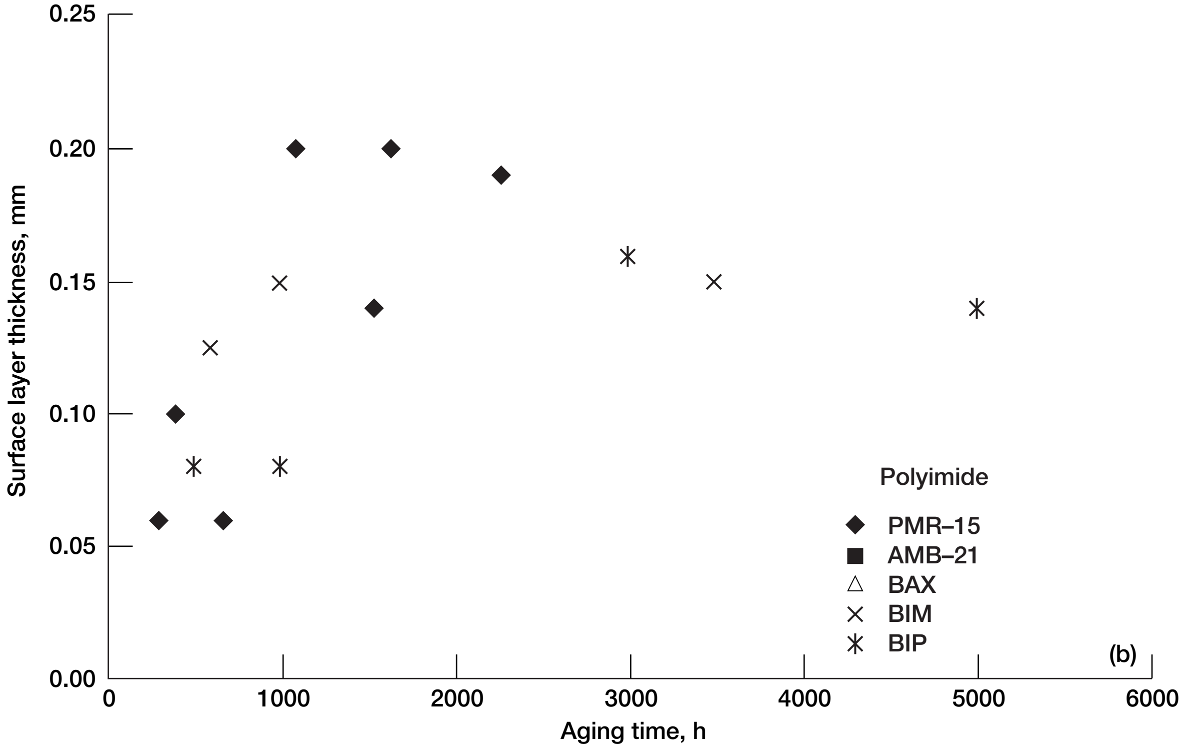
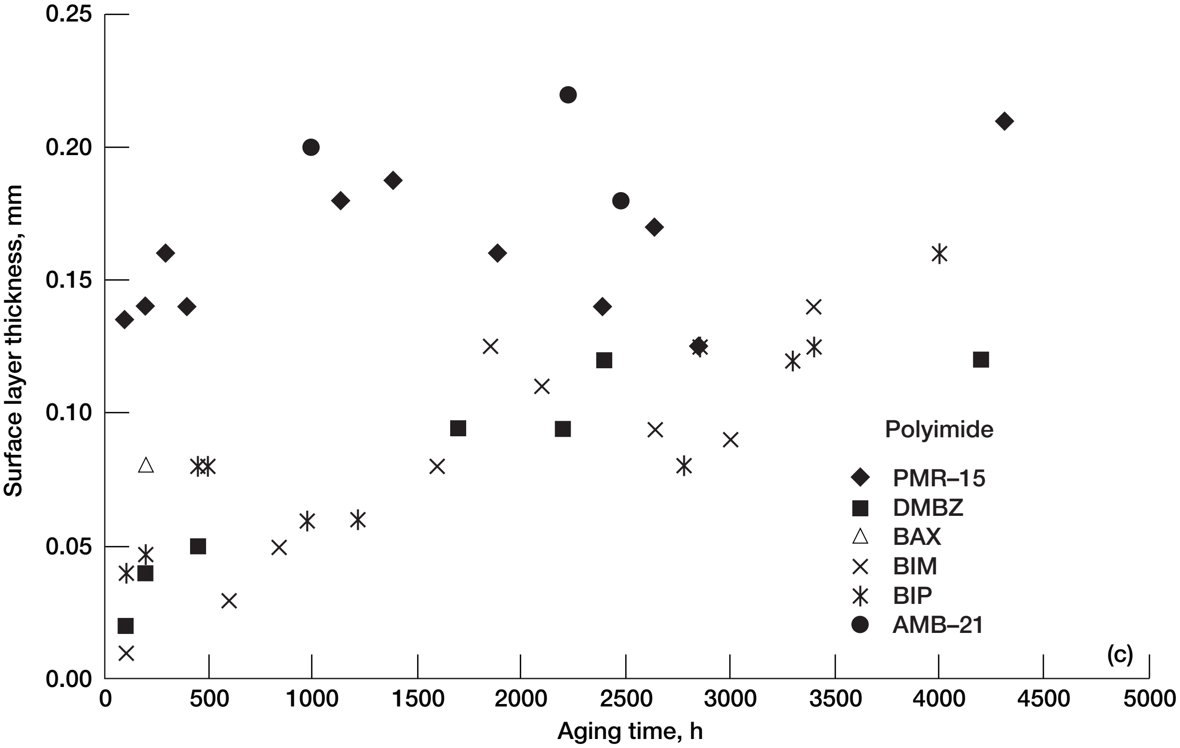


Figure 12.—Oxidized surface layer growth of polyimides during aging. (a) Aging at 316 °C. (b) Aging at 288 °C. (c) Aging at 260 °C. (d) Aging at 204 °C.



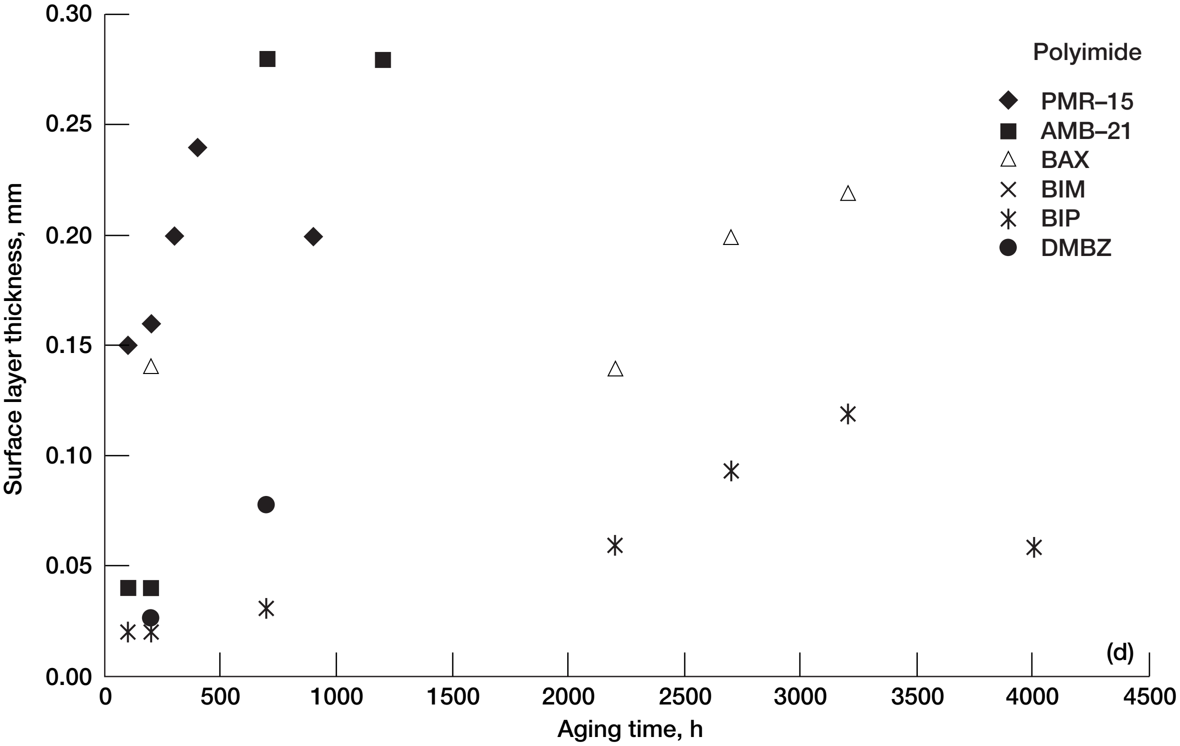


Figure 12.—Concluded.

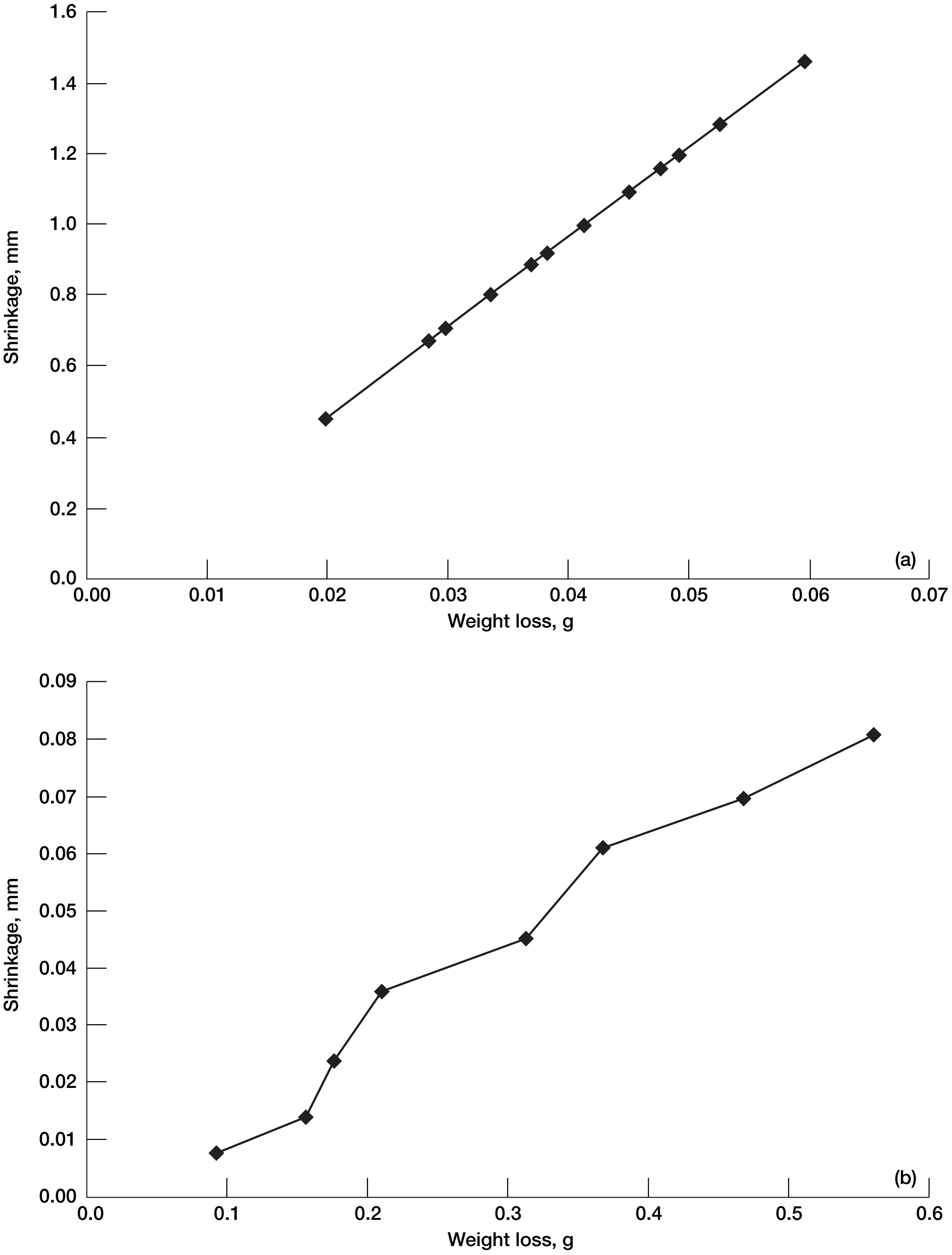
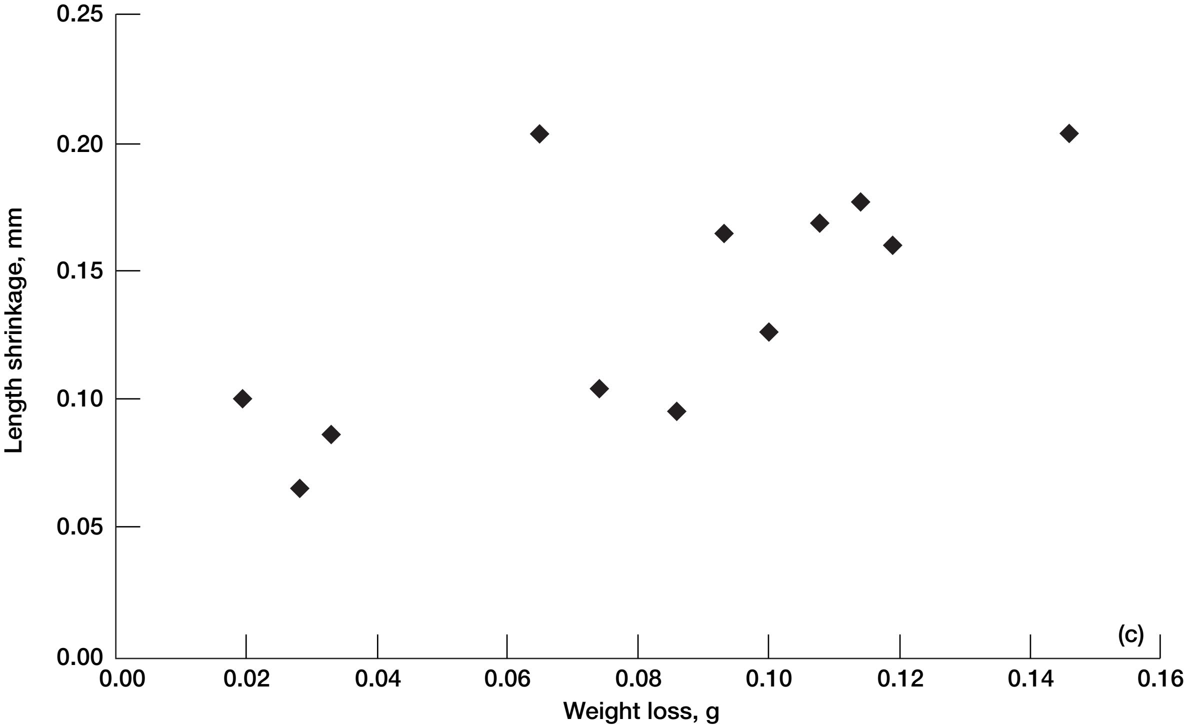


Figure 13.—Shrinkage of PMR–15 specimen length during aging as function of weight loss. (a) Aging at 316 °C. (b) Aging at 288 °C. (c) Aging at 260 °C. (d) Aging at 204 °C.



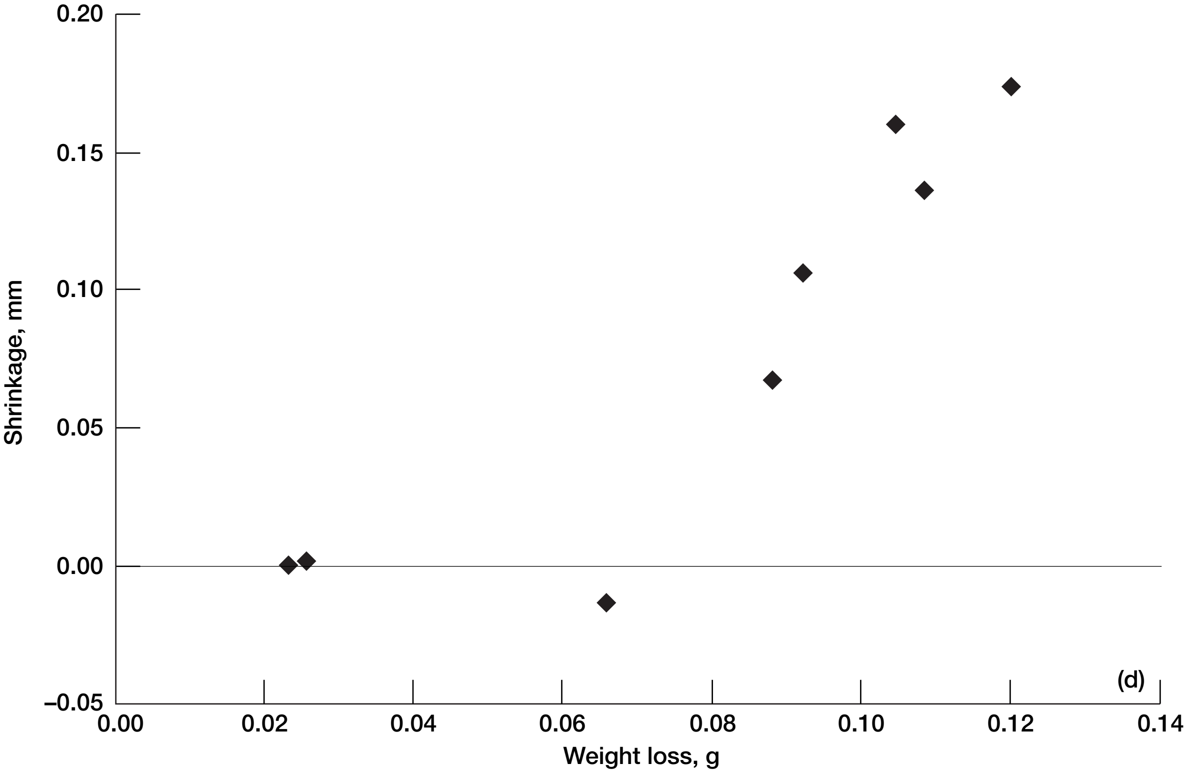


Figure 13.—Concluded.

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

Studies were conducted with six different candidate high-temperature neat matrix resin specimens of varied geometric shapes to investigate the mechanisms involved in the thermal degradation of polyimides like PMR–15. The metrics for assessing the quality of these candidates were chosen to be glass transition temperature (T_g), thermo-oxidative stability, dynamic mechanical properties, microstructural changes, and dimensional stability. The processing and mechanical properties were not investigated in the study reported herein. The dimensional changes and surface layer growth were measured and recorded. The data were in agreement with earlier published data. An initial weight increase reaction was observed to be dominating at the lower temperatures. However, at the more elevated temperatures, the weight loss reactions were prevalent and probably masked the weight gain reaction. These data confirmed the findings of the existence of an initial weight gain reaction previously reported. Surface- and core-dependant weight losses were shown to control the polymer degradation at the higher temperatures.

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