

# Effects of Humidity and Elevated Temperature on the Density and Thermal Conductivity of a Rigid Polyisocyanurate Foam

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## ABSTRACT

Measurements of apparent thermal conductivity are presented for specimens of rigid polyisocyanurate (PIR) foam cut from a commercial insulation product and aged in air at 60°C and different humidities. Eight specimens, nominally 600 by 600 mm, were prepared from two boards (1.2 by 2.4 by 0.05 m) of rigid PIR foam blown with trichlorofluoromethane (CCl<sub>3</sub>F) and having permeable organic-inorganic facers. Facers and excess foam were removed by sanding the specimens to a thickness of 27.9 ± 0.1 mm. Four specimens were placed in ambient conditions of 22°C and 40% relative humidity (RH). The remaining four specimens were each placed in one of the following environments: (1) 60°C and <10% RH; (2) 60°C and 40% RH; (3) 60°C and 60% RH; and, (4) 60°C and 75% RH. Measurements of apparent thermal conductivity were conducted at 24°C and a temperature difference of 22°C using a heat-flow-meter apparatus conforming to ASTM Test Method C 518. Measurements were conducted for a period of 357 days at approximately 50-day intervals. Aging curves of specimen mass, volume, density, and thermal conductivity for rigid PIR foam are presented and implications of changes in these properties are discussed in the paper. Supplemental measurements using Fourier transform infrared spectroscopy and scanning electron microscopy are also described in the paper.

## INTRODUCTION

Polyisocyanurate (PIR) and polyurethane (PUR) foams are cellular plastics that entrap gaseous trichlorofluoromethane (CCl<sub>3</sub>F) or dichlorodifluoromethane<sup>1</sup> (CCl<sub>2</sub>F<sub>2</sub>) within microscopic cells of a polymer matrix. For rigid boards of PIR and PUR foams, the blowing agent is

primarily R-11. The foam is primarily closed-cell, and because of the low thermal conductivity of the entrapped gas it is an effective insulator. Unfortunately, however, the cell walls of PIR and PUR foams are permeable, allowing ambient gases, such as N<sub>2</sub>, O<sub>2</sub>, and water vapor to diffuse through the cell walls and permeate the foam. Conversely, gaseous refrigerant diffuses from the foam, but at a slower rate [1]. For some products, manufacturers have laminated barriers, such as metallic facers, to retard the effects of diffusion. Over time, however, the net result is a decrease in the insulating capability of the foam. The extent of the decrease is subject to debate and the effect is commonly described as the thermal aging of the insulation.

Previous work [2,3] at the National Institute of Standards and Technology (NIST) has indicated that liquid moisture has a significant effect on the thermal aging of rigid PIR foam. Consequently, in 1991, NIST conducted an investigation of the thermal aging of rigid PIR foam conditioned in air at a temperature of 60°C and relative humidities of 10, 40, 60, and 75%. The investigation was a combined effort of the Building Environment and Building Materials Divisions in the Building and Fire Research Laboratory. The objectives were:

1. To quantify the effect of elevated temperature and humidity on the aging of PIR foam
2. To attempt to correlate material degradation with measurements of apparent thermal conductivity<sup>2</sup>

In this paper, we have focused primarily on the first objective. The paper describes the preparation of specimens, conditioning environments, and measurements of specimen mass, volume, density, and thermal conductivity. Also described in the paper are supplemental measurements of chemical and material properties using Fourier transform infrared spectroscopy and scanning electron microscopy. The microstructure and chemical properties of a similar rigid PIR foam have been discussed in detail previously [3].

<sup>1</sup>Also known as Refrigerant-11 and Refrigerant-12, respectively. For the remaining text, all numeric references to refrigerants will be described by standard designations of refrigerants in accordance with ANSI/ASHRAE Standard 34-78. Specifically, the prefix "R" will be used to denote a refrigerant (i.e., R-11 for Refrigerant-11 and R-12 for Refrigerant-12).

<sup>2</sup>For brevity, the term "thermal conductivity" shall be used in the remaining text.

## DESCRIPTION OF SPECIMENS

Eight specimens were prepared from two boards of rigid PIR foam. Figure 1 illustrates the sampling pattern of a single board. Specimens were selected from the center of the board parallel to the direction of production (Figure 1). The foam was a polyurethane-modified polyisocyanurate made by mixing a polymeric diphenyl methane diisocyanate (PMDI) with a mixture of polyol, catalyst, and surfactant. Trichlorofluoromethane ( $\text{CCl}_3\text{F}$ ) was used as the blowing agent. The facers were cellulosic material with reinforcing glass-fibers.

Seven boards were selected from the same production lot manufactured during the last quarter of 1990 and delivered to NIST on January 22, 1991. After delivery, the boards were stored in an environment of  $22 \pm 2^\circ\text{C}$ ,  $40 \pm 10\%$  RH for three months. For preparation of specimens, two of the boards were cut into four equal-size sections (600 by 1220 mm) and then passed several times through a belt-driven sander to remove the facers and excess foam. Care was taken to remove equal portions of foam from both sides of the specimens. All specimens were sanded on the same day (April 25, 1991) to a final thickness of  $27.9 \pm 0.1$  mm.

## DESCRIPTION OF CONDITIONING ENVIRONMENTS

The conditioning environments are detailed in Table 1. Laboratory ambient of  $22^\circ\text{C}$  and 40% RH was selected as a basis for comparison. Four specimens from one board

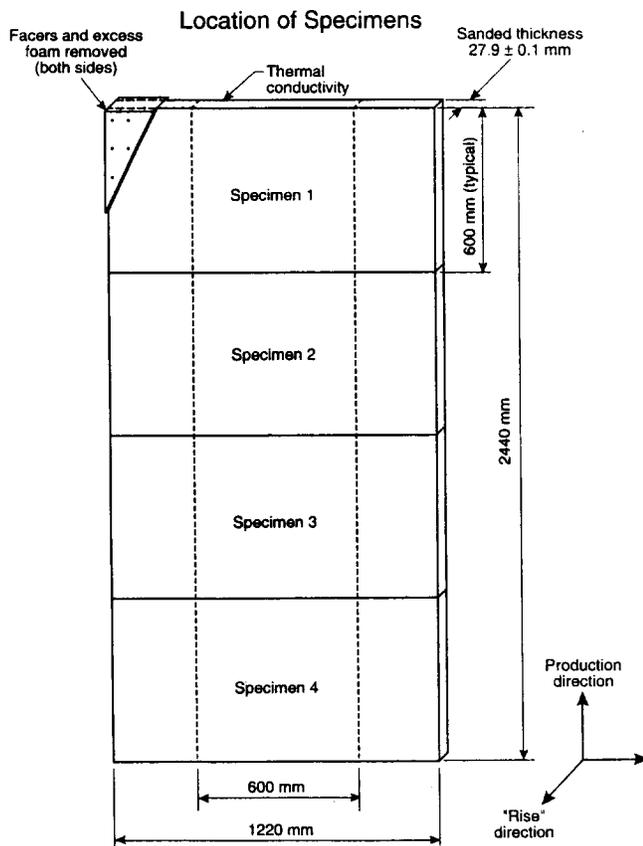


Figure 1. Preparation of specimens of rigid PIR foam (Lot #2, 1991).

Table 1. Conditioning environments.

Environment	Specimen	Board	Temperature ( $^\circ\text{C}$ )	Humidity (% RH)
1	1,2,3,4	1	$22 \pm 1$	$40 \pm 1$
2	5	2	$60 \pm 1$	$< 10^*$
3	6	2	$60 \pm 1$	$40 \pm 1$
4	7	2	$60 \pm 1$	$60 \pm 1$
5	8	2	$60 \pm 1$	$75 \pm 1$

\*Humidity uncontrolled.

were wrapped in a black polyethylene bag and placed in this environment. The second set of four boards was placed in one of the following environments: (1)  $60^\circ\text{C}$ ,  $< 10\%$  RH (humidity uncontrolled); (2)  $60^\circ\text{C}$ , 40% RH; (3)  $60^\circ\text{C}$ , 60% RH; and (4)  $60^\circ\text{C}$ , 75% RH. A temperature of  $60^\circ\text{C}$  was selected because of its historical popularity in several aging studies [4-7].

## EXPERIMENTAL

Initial measurements of specimen mass ( $m$ ), volume ( $V$ ), density ( $\rho$ ) and thermal conductivity ( $\lambda$ ) were determined within eight days after the specimens were sanded. Immediately after the initial measurements, the specimens were placed in their respective conditioning environments described in Table 1. Subsequent measurements of  $m$ ,  $V$ ,  $\rho$ , and  $\lambda$  were conducted at approximately 50-day intervals for a period of 357 days. Specimens conditioned at  $60^\circ\text{C}$  and at 40%, 60%, and 75% RH were placed in an environment of  $60^\circ\text{C}$ , 10% RH (dry heat) for 24 hours prior to measurement.

### Material Properties—Mass ( $m$ ), Volume ( $V$ ), and Density ( $\rho$ )

Material properties— $m$ ,  $V$ , and  $\rho$ —of each specimen were determined prior to measurements of thermal conductivity. The mass ( $m$ ) was measured with a precision digital scale having a resolution of 0.1 g and corrected for the buoyant force of air at ambient conditions ( $\rho_{\text{air}} = 1.2 \text{ kg/m}^3$  [8]). Linear dimensions ( $l, d$ ) were measured at the positions illustrated in Figure 2, averaged, and used to compute  $V$ . The specimen density ( $\rho$ ) was determined from the relation  $\rho = m/V$ . The uncertainty in  $\rho$  was estimated to be  $\pm 0.6\%$ . For specimens conditioned at  $60^\circ\text{C}$  and high humidity, the uncertainty in  $\rho$  increased to about  $\pm 1.3\%$  due to specimen warping.

### Thermal Conductivity Measurements

Measurements of thermal conductivity were conducted using a commercial heat-flow-meter (HFM) apparatus conforming to ASTM Test Method C 518. As illustrated in Figure 3, the HFM apparatus utilized a single heat-flux-transducer embedded at the center of the electrically heated bottom plate. Measurements of thermal conductivity were conducted at a mean specimen temperature ( $T_M$ ) of  $24^\circ\text{C}$  and a temperature difference ( $\Delta T$ ) of  $22^\circ\text{C}$  across the thickness of the specimen. Heat flow was in the upward direction.

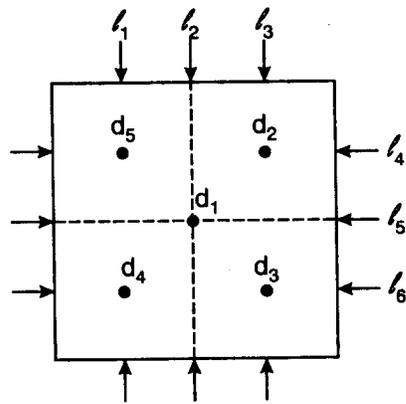


Figure 2. Location of dimension measurements.

Prior to each set of measurements of PIR specimens, the HFM apparatus was calibrated using a Transfer Standard selected from an internal lot (Lot 1970) of Standard Reference Material of high-density fibrous-glass boards [9]. Calibration measurements were conducted at a  $T_m$  of 24°C and  $\Delta T$  of 22°C across the thickness of the specimen. The thickness and bulk density of the Transfer Standard were 26.2 mm and 139 kg/m<sup>3</sup>, respectively. Estimates of uncertainty in the apparatus have been presented previously [10,11]. Repeatability of the apparatus was better than 1%; overall uncertainty,  $\pm 3.5\%$  [11].

## RESULTS AND DISCUSSION

The changes in mass ( $m$ ), volume ( $V$ ), density ( $\rho$ ), and thermal conductivity ( $\lambda$ ) of the rigid PIR foam are illustrated in Figures 4 through 7. Values of  $m$ ,  $V$ , and  $\rho$  were determined at 22°C;  $\lambda$  at 24°C. As mentioned above, the specimens conditioned at 60°C, 40%, 60%, and 75% RH were placed in an environment of 60°C, 10% RH for 24 hours prior to measurement in order to minimize the effect of water on the thermal conductivity measurements. The initial time ( $t_0$ ) was taken to be when the specimens were sanded.

Data for the specimens conditioned in laboratory ambient (22°C, 40% RH) are represented by open points; data at 60°C and different humidities, by solid points. In general, the results indicated that the changes in  $m$ ,  $V$ ,  $\rho$ , and  $\lambda$  were more substantial for exposure at 60°C than for laboratory conditions. Furthermore, the results indicated that at 60°C, the changes were greater at higher humidities. These results suggest that elevated temperature and

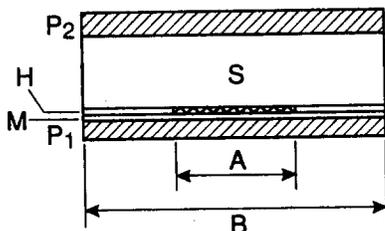


Figure 3. Heat-flow-meter apparatus (ASTM Test Method C 518): A = 254 mm; B = 610 mm; H = heat-flux-transducer; M = acrylic plastic substrate; P = heating or cooling plate; S = specimen.

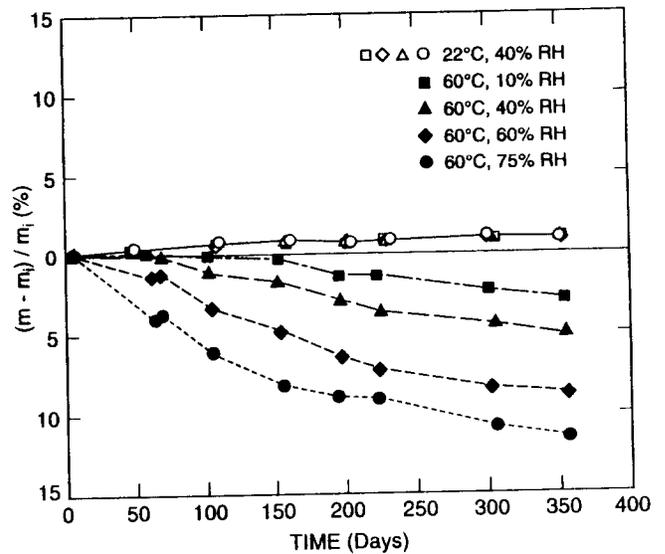


Figure 4. Percentage change of specimen mass ( $m$ ) at 22°C for a rigid PIR foam aged at 22°C, 40% RH and 60°C at humidities of 10, 40, 60, and 75% RH.

humidity may interact to produce greater changes in rigid PIR foam than either parameter alone.

### Change in Mass with Time

At laboratory ambient (22°C, 40% RH), mass increased about 1% after 110 days and remained nearly constant thereafter (Figure 4). However, at 60°C, the specimens lost mass and the rate was accelerated by the level of humidity. Humidities of 10, 40, 60, and 75% RH at 60°C decreased the mass by 3.0, 5.1, 8.8, and 11%, respectively, after 357 days.

The net change in mass of a rigid PIR foam is a complex phenomenon that results from several simultaneous pro-

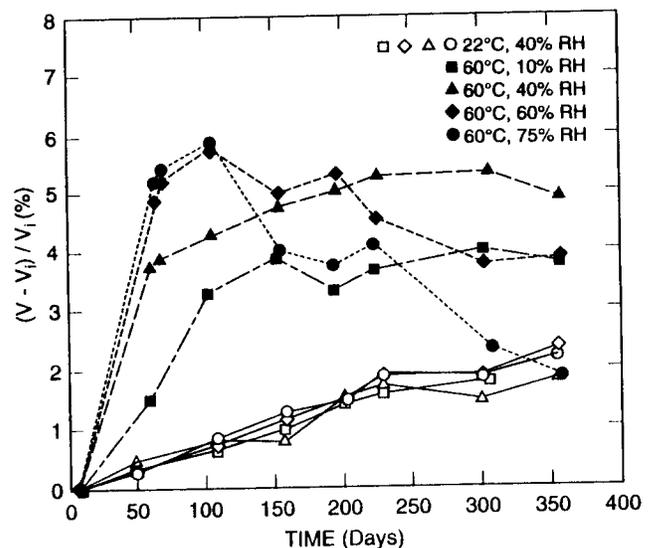


Figure 5. Percentage increase of specimen volume ( $V$ ) at 22°C for a rigid PIR foam aged at 22°C, 40% RH and 60°C at humidities of 10, 40, 60, and 75% RH.

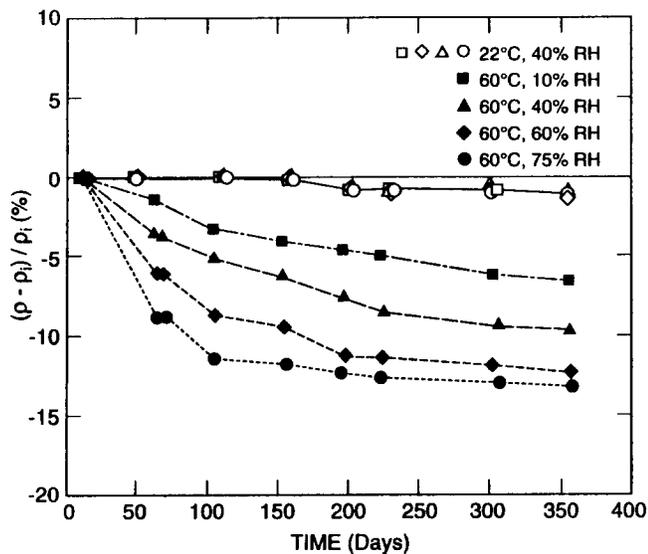


Figure 6. Percentage decrease of specimen density ( $\rho$ ) at 22°C for a rigid PIR foam aged at 22°C, 40% RH and 60°C at humidities of 10, 40, 60 and 75% RH.

cesses. We have postulated three processes that contribute to a gain in mass and three that contribute to a loss. The processes contributing to a gain were (1) formation of reaction products from unreacted isocyanate with water during exposure; (2) diffusion of air and water vapor into the cell cavities; and, (3) adsorption of water in the cell-wall polymer (membranes and struts). The processes contributing to a loss were (1) loss due to unreacted materials evaporating from the polymer; (2) erosion of foam material; and, (3) loss of R-11, either by diffusion or cell rupture.

The net change in mass is the algebraic sum of the gains and losses of each individual process. Determining the prevailing process during exposure to different environments would provide a better understanding of changes in the

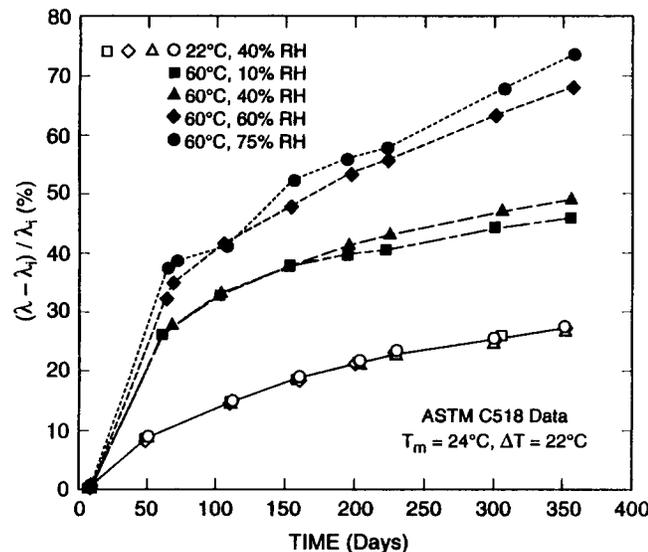


Figure 7. Percentage increase of specimen thermal conductivity ( $\lambda$ ) at 24°C for a rigid PIR foam aged at 22°C, 40% RH and 60°C at humidities of 10, 40, 60, and 75% RH.

physical properties and thermal conductivity of the foam. Unfortunately, a complete analysis of the above processes was beyond the scope of this study. However, we acquired insight into the dominant process responsible for the net change by reviewing the literature and conducting additional measurements using Fourier transform infrared spectroscopy (FTIR).

The increase in mass due to the reactions of unreacted isocyanate (NCO) with water was believed small for two reasons. The residual amount of NCO group in the foam was small as shown by the FTIR measurement [3] and the gain was offset by the loss of gaseous products ( $\text{CO}_2$ ) resulting from the reactions [12]. Therefore, the increase of mass was due primarily to the diffusion of air and water vapor into the foam, and the adsorption of water in the polymer. The relative effects of these two processes in contributing to a net gain in mass are not known. We speculate that both processes contributed to the small net gain in mass ( $\approx 1\%$ ) for the specimens conditioned at 22°C and 40% RH.

As indicated above, three processes were postulated for the loss of mass: loss of unreacted material, erosion of foam material and escape of R-11 from the foam. The loss due to unreacted materials evaporating from the polymer was dismissed because of their small residual amount [3] and high temperature of evaporation ( $\geq 60^\circ\text{C}$ ). The process of foam erosion must be accompanied by a reduction in volume and should have little effect on the density. In actuality, the specimens exposed at 60°C and different humidities increased in size (Figure 5) and the density decreased (Figure 6), suggesting that little erosion occurred. Therefore, for these specimens, we hypothesized that the loss of mass (Figure 4) was due to the escape of R-11 from the foam. The loss of R-11 was subsequently confirmed by FTIR-transmission measurements of small, thin specimens of the same rigid PIR foam. This loss was substantial because the initial mass of R-11 was calculated to be about 20% of the mass of the foam, based on the following values:  $\rho_{\text{polymer}} = 1200 \text{ kg/m}^3$ ,  $\rho_{\text{R-11}} = 5.8 \text{ kg/m}^3$  at 101.3 kPa and 25°C [13], and initial foam density  $\rho_0 = 26.9 \text{ kg/m}^3$ .

A brief overview of the FTIR technique is presented here. Details have been described previously [3]. Four disks, about 12 mm diameter by 3 mm thick, were cut from the same rigid PIR foam in March, 1992. The disks were cut normal to the rise of the foam using a sharp razor blade. Based on previous cell measurements on a similar lot of foam [3], the dimension of each cell parallel to the rise direction was estimated to be about 0.3 mm. Therefore, the 3 mm thick disk contained approximately ten rows of cells. One disk was placed in each of the following environments: (1) 22°C, 40% RH; (2) 60°C, <10% RH; (3) 60°C, 60% RH; and, (4) 60°C, 75% RH. FTIR-transmission measurements were determined prior to exposure and then periodically over a 33-day interval.

Figure 8(a) presents the FTIR spectra of rigid PIR foam before and after exposure for 16 days at 60°C, 75% RH. The results indicated that the intensity of the bands at 1084 and 844  $\text{cm}^{-1}$  decreased substantially during exposure. Subsequent FTIR analysis of gaseous R-11 revealed two prominent bands at 1084 and 844  $\text{cm}^{-1}$  as illustrated in Figure 8(b). For reference, the JANAF Thermochemical Tables [14] give the vibrational frequencies of gaseous  $\text{CCl}_2\text{F}$ , among others, as 1085 and 847  $\text{cm}^{-1}$ . These results confirm that the two bands at 1084 and 844  $\text{cm}^{-1}$  observed in Figure 8(a) were from the gaseous R-11 in the foam.

Using the initial intensity ( $I_0$ ) of the band at 844  $\text{cm}^{-1}$  as a reference, the relative change in intensity ( $I/I_0$ , where  $I$  is the intensity during exposure) as a function of time is il-

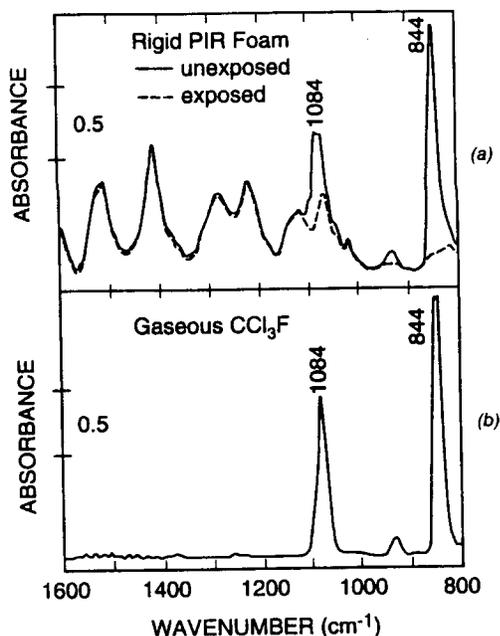


Figure 8. (a) FTIR spectra of rigid PIR foam before and after 16-day exposure to 60°C and 75% RH; (b) FTIR spectrum of gaseous  $\text{CCl}_3\text{F}$ .

illustrated in Figure 9. The results indicated that the band intensity, which is proportional to the amount of R-11, declined for all specimens. After 33 days at 22°C and 40% RH (square symbol), nearly 40% of the initial amount of R-11 was still present in the foam. At 60°C and different humidities (solid symbols), less than 15% was present after 33 days. The results indicated that at 60°C, high humidity accelerated the loss of R-11.

Of considerable interest was whether cells in the foam ruptured during exposure to 60°C and different humidities. We investigated this question by examining the microstructure of eight specimens (10 by 10 by 3 mm) using a scanning electron microscope (SEM). The specimens were cut, in April 1992, from the center and 1 mm below the surface of four specimens of foam aged for six months at 60°C and 10, 40, 60, and 75% RH. For comparison, two

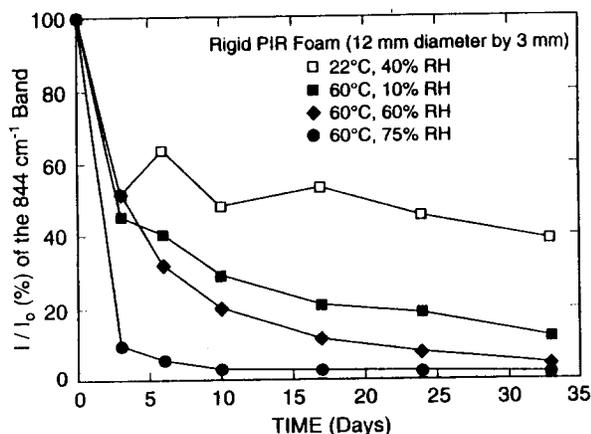
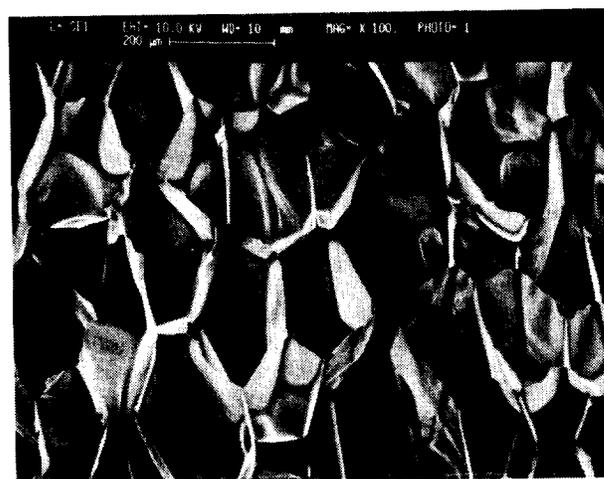


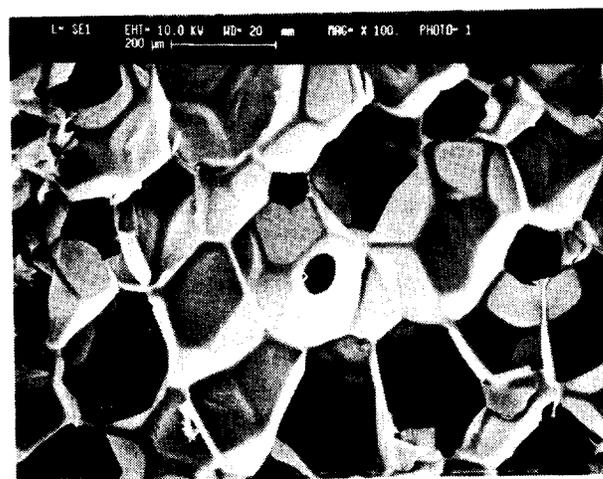
Figure 9. Relative change of the FTIR intensity band at  $844\text{ cm}^{-1}$  (R-11) of rigid PIR foam. (Change in the intensity is expressed as the ratio of the intensity ( $I$ ) at a particular exposure and the initial intensity ( $I_0$ ) for the same specimen.)

“unexposed” specimens were cut from another board of the same rigid PIR foam. The specimens were cut normal to the rise direction with a razor blade, bonded to the SEM mounting stubs with epoxy, and sputter-coated with a nominal 100-nm gold-film to prevent surface charging.

Figures 10(a) and 10(b) are the SEM micrographs of foam “unexposed” and exposed to 60°C, 75% RH for six months, respectively. Examination of the eight specimens indicated that the majority (>95%) of cell walls was still intact. A few holes in the cell membranes were discovered in specimens exposed to 60°C and 40, 60, and 75% RH [Figure 10(b)]. There were no holes found in the specimens of foam “unexposed” or exposed to 60°C and 10% RH. This suggests that their origin was due to exposure to humidity at elevated temperature. Also, the smooth, rounded-nature of the holes was not indicative of a rupture, but perhaps of chemical dissolution.



(a)



(b)

Figure 10. SEM micrographs of specimens of rigid PIR foam: (a) 1-mm below the surface, “unexposed;” (b) 1-mm below the surface, exposed for six months at 60°C, 75% RH (arrow indicates hole in cell membrane).

The effect of temperature on the loss of R-11 from the foam was examined by the relation between diffusivity and temperature for a gas through a polymer [15]. The relation is expressed as  $D = D_0 \exp(E_a/RT)$ , where  $D$  is the diffusion coefficient;  $D_0$  and  $E_a$  are the pre-exponential factor and activation energy, respectively;  $R$  is the gas constant; and,  $T$  is the absolute temperature. The relation indicates that diffusion follows an activated process, that is, diffusion increases with temperature. Diffusion in a polymer is generally described by a jumping from an equilibrium position to a vacancy (free volume) adjacent to it [16]. As a first approximation, the relation implies that the probability of a diffusive motion occurring is proportional to the probability that a vacancy of sufficient size is adjacent to the molecule. Thus, the rate of diffusion depends on the size and distribution of the pre-existing vacancy, and the ease of vacancy formation. Both of these depend on the ease and degree of chain packing which relate to the free volume and to the density. The higher the temperature, the greater the free volume in the polymer, which facilitates the diffusion or permeation of gases through the polymers. Usually, the less permeable membranes are more sensitive to temperature [17].

The effect of water probably accelerated the loss of R-11 by affecting the chain mobility and/or plasticizing the foam polymers. The presence of water molecules between the polar chains of the polyurethane-polyisocyanurate polymers increased their free volume. This enhanced the gas permeability of the polymer and also its capability to adsorb solvents. The effects of water vapor on chain mobility in polymers with affinity for water have been documented. For example, Kettle [18] exposed several specimens of semi-crystalline nylon 6 in relative humidities of 12 to 97% RH for six months (temperature not specified). The glass transition temperature,  $T_g$  (i.e., the temperature at which a polymer changes from a glassy to a rubbery state, corresponding to an abrupt increase in volume), decreased from 71 to  $-6^\circ\text{C}$  for 12 to 97% RH, respectively [18].

### Change in Volume with Time

The linear dimensions of each specimen were measured at ambient conditions prior to determining thermal conductivity. At  $22^\circ\text{C}$  and 40% RH, volume increased nearly 2% over 357 days (Figure 5). The rate and amount of increase were affected by temperature and humidity as illustrated in Figure 5. At  $60^\circ\text{C}$  and 60 to 75% RH, volume increased to a maximum of almost 6% after 105 days, followed by a subsequent reversal in volume. At  $60^\circ\text{C}$  and 40% RH, the volume obtained a maximum (5%) between 225 and 306 days, while at  $60^\circ\text{C}$  and 10% RH, volume obtained relative maximums of 4% at 152 and 301 days.

As was the case with specimen mass, the change in volume of rigid PIR foam was the result of many factors, including thermal expansion of the polymer, cell-gas pressure, cell structure (e.g., cell rupture), or sorption of R-11 and water in the polymer. In our study, the dimensional changes due to thermal expansion and cell-gas pressure were small (0.25%) as determined experimentally and abated after five to ten minutes at ambient conditions. Hilado [19] reported that "in extreme cases" (temperature not specified), exposure caused cell rupture of rigid PUR foam. However, we saw little evidence of cell rupture in the SEM micrographs (Figure 10). Therefore, we contend that

swelling observed in Figure 5 was primarily a result of R-11 being adsorbed by the polymer with the presence of water vapor being a secondary factor. The solubility of R-11 in the solid phase of rigid PUR foam has been previously measured by Steinle [20] using gas chromatography analysis. His results indicated that 50 to 60% by weight of the R-11 content was soluble in the solid phase of the foam. Using a similar analysis, Brandreth and Ingersoll [21] found the percent of R-11 in the polymer ranged from 8 to 63% for eleven different types of rigid PUR foam.

In theory, swelling occurs in a polymer when the solvent (the adsorbate) has sufficient affinity for the polymer (the adsorbent) to form intimate "solid solutions" (e.g., adsorbate molecules held between the adsorbent side chains) with the polymer. Swelling is maximized when the adsorbate and the adsorbent have similar solubility characteristics (or parameters). When an adsorbate is held only on pre-existing surfaces of a powder or rigid pores of a solid, very little swelling accompanies adsorption. Thus, swelling in a rigid PIR foam occurs only when the polyurethane-polyisocyanurate polymers adsorb solvent, in this case R-11. The subsequent contraction of volume (Figure 5) was probably due to desorption of R-11 from the polymer.

Figure 5 shows that even in the presence of very little moisture (at  $60^\circ\text{C}$  and  $<10\%$  RH), the foam swelled substantially during exposure. Since the only adsorbate in the foam was R-11 and there was also a gradual loss in mass as a function of time (Figure 4), the swelling at  $60^\circ\text{C}$  and  $<10\%$  RH was interpreted as due to the formation of solid solution in the cell walls (cell membranes and struts) of the PIR foam by R-11 solvent. Because the solubility parameters of R-11 and a polyurethane polymer are closer to each other than water and a polyurethane polymer, it is expected that polyurethane polymers adsorb more R-11 than water.

Trichlorofluoromethane ( $\text{CCl}_3\text{F}$ ) enters the cell walls from the cell cavities by processes of adsorption and diffusion. Both processes are temperature dependent, which explains the difference in swelling at  $60^\circ\text{C}$  and  $22^\circ\text{C}$ , 40% RH (Figure 5). An increase in temperature will increase both the pressure in the cell cavities (an increase of about 13% from  $22^\circ\text{C}$  to  $60^\circ\text{C}$ ) and the solvation of the polymers by the R-11 solvent (Figure 5). Increasing the pressure in the cell cavities increases the pressure gradient between the interior and exterior of the foam. Since the rate of permeation is directly proportional to the pressure difference across the membrane, this pressure gradient should accelerate the rate of permeation of R-11 into the cell walls. An increase in temperature also increases the polymer free volume, which subsequently increases the adsorption of the R-11 solvent by the polymer.

Humidity also affects the swelling of PIR foam as observed in Figure 5. The difference in the swelling at different humidities was attributed to the effect of sorbed water. As noted above, sorbed water would tend to plasticize the cell walls. An increase in relative humidity would increase the water content in the cell walls and accelerate the adsorption and diffusion of R-11 in the cell walls, as discussed above. The reduction in the rate of swelling observed at  $60^\circ\text{C}$  (Figure 5) was probably due to the adsorption of R-11 in the foam polymers reaching an equilibrium condition. Reversal of swelling may in fact be due to the rate of desorption of R-11 surpassing the rate of adsorption into the cell walls. Conversely, the rate of adsorption of R-11 should be the greatest in the initial stage of exposure. Note in Figure 5, the sharp initial increase at  $60^\circ\text{C}$  for the first 60 days of exposure.

### Change in Density with Time

Specimen density ( $\rho$ ) is dependent on specimen mass ( $m$ ) and volume ( $V$ ), as defined by the relation  $\rho = m/V$ . The change in  $\rho$  (Figure 6) was similar to the change in specimen mass (Figure 4), except for specimens aged at laboratory ambient (22°C, 40% RH). For these specimens,  $\rho$  decreased about 1% due to swelling of about 2% (Figure 5) and a mass gain of 1% (Figure 4). Elevated temperature and different humidities produced the greatest decrease in density; 6.5, 9.6, 12, and 13% for humidities of 60°C, 10, 40, 60, and 75% RH, respectively.

### Change in Thermal Conductivity with Time

At 22°C and 40% RH, the thermal conductivity ( $\lambda$ ) at 24°C of rigid PIR foam increased 28% in 357 days (Figure 7). After exposure to 60°C and 10% RH,  $\lambda$  at 24°C increased 46% during the same time period. These results are in agreement with several experimental studies [4–7, 22–25] that have also indicated a temperature effect on the rate at which the thermal conductivity of rigid PIR/PUR foam changes. After exposure to 60°C and different humidities, the thermal conductivity at 24°C also revealed a significant humidity effect (Figure 7). For humidities of 40, 60, and 75% RH,  $\lambda$  at 24°C increased by 49, 68, and 74%, respectively.

The thermal conductivity ( $\lambda$ ) of foam can be expressed as the sum of three individual contributions:

$$\lambda = \lambda_g + \lambda_p + \lambda_r$$

where  $\lambda_g$  is the thermal conductivity of the gas mixture in the cells;  $\lambda_p$  is the thermal conductivity of the cell wall polymer (cell membranes and struts); and  $\lambda_r$  is the radiative component of thermal conductivity. Convective heat transfer is negligible for the small cells (generally less than 2 mm in diameter) of present production foams [26]. The contributions of  $\lambda_g$ ,  $\lambda_p$ , and  $\lambda_r$  have been estimated by Cunningham and Sparrow [27] to be 44, 23, and 33%, respectively, for a free-rise laminate of PUR foam (30 kg/m<sup>3</sup>).

The aging of a rigid PIR/PUR foam is primarily the result of diffusion processes changing the cell-gas mixture and increasing  $\lambda_g$ . With time, ambient gases (N<sub>2</sub>, O<sub>2</sub>) having a relatively high thermal conductivity and water vapor diffuse into the cells, while R-11 departs by both adsorption into the polymer and diffusion through the cell wall. The net effect is that the thermal conductivity of the cell-gas mixture ( $\lambda_g$ ) increases, thereby increasing  $\lambda$ . As will be discussed below, aging in humid environments also appeared to affect one or both of the other mechanisms of heat transfer ( $\lambda_p$ ,  $\lambda_r$ ), but to a lesser extent.

### Change in Thermal Conductivity with Mass and Density

Figure 11 illustrates the fractional change in thermal conductivity ( $\Delta\lambda$ ) at 24°C as a function of the fractional change in specimen mass ( $\Delta m$ ). The data from specimens aged in different environments delineated five distinct curves. After exposure at 22°C and 40% RH (open symbols),  $\Delta\lambda$  increased linearly as the specimens gained mass. As noted above, the net gain in mass was attributed to the effects of the diffusion of air and water vapor into the foam and water adsorption in the polymer.

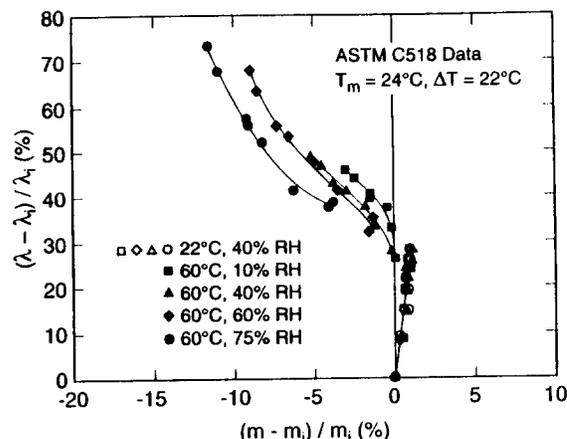


Figure 11. Change in thermal conductivity at 24°C as a function of change in mass for a rigid PIR foam.

After exposure at 60°C and different humidities (solid symbols),  $\Delta\lambda$  at 24°C increased as  $\Delta m$  decreased, with the effect being accelerated for higher humidities. Note that these curves were not coincidental, but parallel. For a given decrease in  $\Delta m$ , the corresponding increase in  $\Delta\lambda$  was 5 to 10% less for higher humidities. As noted above, the net loss of mass was due primarily to R-11 departing from the foam, which increased  $\lambda_g$ . However, the presence of R-11 solvent and/or water vapor in the cell walls may affect the rates of diffusion of the cell gases (R-11, N<sub>2</sub>, and O<sub>2</sub>) and so for given  $\Delta m$ , the cell-gas composition may not be the same for all exposures. The systematic differences may also be due to changes in one or both of the other components of thermal conductivity ( $\lambda_p$ ,  $\lambda_r$ ). In theory, R-11 solvent or water adsorption in the cell walls could change the thermal conductivity of the polymer, the radiative properties of the polymer, or both.

A more common practice is to plot  $\lambda$  as a function of  $\rho$ , as illustrated in Figure 12. The  $\lambda$ ,  $\rho$  data revealed a similar set of five curves, delineating three regimes of aging (Figure 12). At an initial density ( $\rho_0$ ) of 26.9 kg/m<sup>3</sup>,  $\lambda$  was independent of  $\rho$ , i.e., the plot of the thermal conductivity increased vertically. In this regime (1), air diffused into the foam, but the R-11 was for the most part captive (i.e., in-

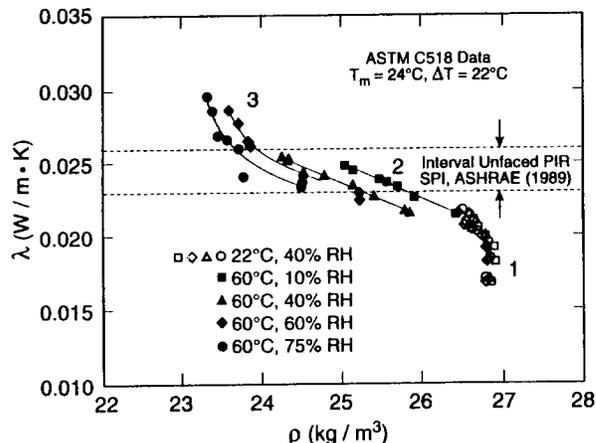


Figure 12. Thermal conductivity at 24°C as a function of density for a rigid PIR foam.

creasing  $\lambda$ , but constant  $\rho$ ). During this time-period, some of the R-11 left the cell-cavities by adsorption and diffusion into the polymer cell walls. This hypothesis is consistent with the swelling noted in these specimens (see the section, Change in Volume with Time). For  $24.5 < \rho < 26.9$  kg/m<sup>3</sup>, the data revealed a regime (2) where R-11 was leaving the foam (i.e., increasing  $\lambda$  with decreasing  $\rho$ ) and intrusion of air (and water vapor) continued. In regime 2, the presence of humidity at 60°C produced systematic trends in  $\lambda$  similar to those observed in Figure 11. At values of  $\rho < 24.5$  kg/m<sup>3</sup>,  $\lambda$  increased in a curvilinear fashion as  $\rho$  decreased, indicating a regime (3) where R-11 was depleted in the cells and only the intrusion of air (and water vapor) continued.

## SUMMARY AND CONCLUSIONS

This study examined the macroscopic thermal and material properties of rigid PIR foam ( $\rho_0 = 26.9$  kg/m<sup>3</sup>) cut from commercial product and aged in air for a period of 357 days. Specimens, nominally 600 by 600 mm, were aged in one of five environments: ambient conditions of 22°C and 40% RH; and 60°C at 10, 40, 60, or 75% RH. During this period, measurements of specimen mass ( $m$ ), volume ( $V$ ), density ( $\rho$ ), and thermal conductivity ( $\lambda$ ) were determined at intervals of about 50 days. Measurements of thermal conductivity were determined at 24°C using a heat-flow-meter apparatus (ASTM C 518).

The results indicated that the aging of rigid PIR foam affects not only the thermal conductivity ( $\lambda$ ), but also the specimen mass ( $m$ ), volume ( $V$ ), and consequently density ( $\rho$ ). Changes in these properties indicated that the combined factors of elevated temperature and humidity may interact to accelerate the aging of rigid PIR foam more than either parameter alone. These macroscopic changes were interpreted primarily as the result of air and water vapor penetrating into the foam and the refrigerant, R-11, adsorbing and diffusing through the polymer, and eventually departing from the foam. The presence of water vapor at 60°C was believed to "plasticize" the polymer in the cell walls. Further research is suggested in this area.

An interesting correlation was found by plotting thermal conductivity ( $\lambda$ ) at 24°C as a function of its corresponding specimen density ( $\rho$ ) (Figure 12). The correlation revealed three regimes of aging. In regime 1,  $\rho$  was constant and  $\lambda$  increased; in regime 2,  $\lambda$  increased linearly as  $\rho$  decreased; and, in regime 3,  $\lambda$  increased in a curvilinear fashion as  $\rho$  decreased. We interpreted these changes as, in regime 1, R-11 captive but dissolving in the polymer, air intrusion in the foam; in regime 2, R-11 departing from the foam, air intrusion continues; and, in regime 3, depletion of R-11, air intrusion. It is believed that accelerated aging with similar environments and plotting the corresponding  $\lambda$ ,  $\rho$  data may provide a statistical technique in characterizing a production lot of foam over its lifetime. Measurements of a second production lot of rigid PIR foam are in process to verify this method.

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