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Publisher's version / Version de l'éditeur:

Journal of Thermal Insulation, 14, Jan, pp. 241-267, 1991-01

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NRCC-35471

A version of this document is published in : Journal of Thermal Insulation, 14, (Jan), pp. 241-267, January-91

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Effect of Time and Temperature on R-Value of Rigid Polyurethane Foam Insulation Manufactured with Alternative Blowing Agents

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ABSTRACT: A non-destructive technique, involving specimen encapsulation and determination of the dependence of thermal resistance on temperature, to measure the blowing agent pressure in cellular plastic insulation was recently presented. This technique was applied to a polyurethane foam manufactured with different blowing agents and the results were compared with those obtained from model calculations. The results indicate that the long-term solubility of the gas in the polymer matrix may differ from that determined from short-term experiments. The paper presents results for HCFC-123 and HCFC-141b as well as CFC-11 and discusses their implication for long-term thermal resistance of polyurethane foams.

This paper was presented at The Society of the Plastics Industry, Inc., (SPI) 33rd Annual Polyurethane Technical/Marketing Conference, Orlando, Florida, September 30–October 3, 1989.

JOURNAL OF THERMAL INSULATION Volume 14—January 1991

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0148-8287/91/03 0241-27 \$06.00/0
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INTRODUCTION

IT IS WELL known that the thermal resistance of gas-filled foam (cellular plastic insulation) diminishes with time. This phenomenon is referred to as aging and illustrated with aging curves, i.e., thermal resistivity (inverse of thermal conductivity) shown as a function of time. These aging curves, though useful in representing the average change of material performance, do not shed much light on the details of the aging phenomena. While it is believed that the transport of nitrogen and oxygen from ambient air into the material and that of the blowing agent (BA) out of the material dominate amongst the aging processes, there may be other mechanisms which are yet not completely understood. For example, what is the part played by the polymer matrix as the foam ages? What is the effect of the environment in which the foamed insulation performs? In various environments the interaction between the polymer and the cell-gases may differ. Moreover, the ability of the polymer matrix to retain the blowing agent may change and hence alter the long-term performance of the insulation. These details can not be derived from the aging curves unless the investigation is complemented with other experimental techniques.

At a time when the industry is hard pressed to develop new blowing agents to replace CFCs, experimental techniques that can give detailed information on the changes in the blowing agent pressure during foam aging are invaluable. One such experimental technique was recently developed and reported by the authors [1]. In this technique, the exchange of gases between specimen and its environment is prevented by means of specimen encapsulation. The encapsulation allows the measurement of the dependence of the thermal resistance of the encapsulated specimen on temperature without further aging. This paper reports the application of this experimental technique to sprayed polyurethane foam and the interpretation of the experimental results by comparing with those obtained from calculations based on an aging model [2].

Experimental Procedure

Three foams with the same chemical composition were manufactured under controlled conditions [3], however, with different blowing agents: CFC-11 in foam 1 (called Base 88 [3]), HCFC-123 in foam 2 and HCFC-141b in foam 3.

Four, 10 mm thick, 300 mm $\times$ 300 mm squares were cut from each material and allowed to age in the laboratory environment (temperature $22 \pm 1^\circ\text{C}$ and relative humidity $50 \pm 10\%$). Since these materials had aging curves previously determined [3] encapsulation of specimens was performed at preselected stages of aging. Most of the encapsulation took place

during the first four weeks (short-term aging, e.g., 10, 15, 20, and 25 days). For comparison, however, one specimen was also encapsulated in the middle term, after 62 days, when the fraction of air in the cell-gas was much higher but the process of air ingress was still incomplete, and one specimen after long-term exposure (365 days), when the air ingress process was essentially completed [3]. Then, after approximately one more week of storage, to allow some cell gas equalization, the temperature dependence of the thermal resistance of these encapsulated specimens was measured. The specimens were again left in the laboratory environment for a period of up to one year, after which temperature dependence of their thermal resistances was remeasured.

Research Approach

The above experiments were designed to observe the changes undergone by the encapsulated specimens while left in the laboratory. One or more of the following changes may possibly happen:

1. Redistribution of the gases in the enclosed space
2. Change in the physical properties of the polymer
3. Adsorption or desorption of the blowing agent from the cell-gas (affecting its partial pressure)
4. Adsorption or desorption of the air components from the cell-gas

The above changes 1–4 will affect thermal resistivity–temperature curves. While using the curves to study the above effects, one must remember that the experimentally determined thermal resistivity–temperature curves will differ from one test specimen to another. The experimental variability may be caused by three reasons. First, the specimens were encapsulated at different stages of aging so that the above discussed changes might have been advanced to different extent. Next, each of the specimens might have started aging at different initial pressures of blowing agent (established during foaming). Third, the rate of gas diffusion may differ between various specimens, so that different degrees of aging are attained during the same time. This makes the interpretation of the experimental data a rather challenging task. Even if the experiments would include different specimens as well as the same specimen retested after different periods of storage, the experimental data alone may not be sufficient to establish the cause–effect relations. On the other hand, if an appropriate model is used to establish the cause–effect relations and to simulate one or more of the above changes, their cumulative effect on thermal resistance can be calculated.

First, to examine the effect of experimental conditions on thermal resistivity–temperature curves, $r = r(T)$, the model calculations were performed

on a homogeneous layer of the ideal material (the blowing agent does not dissolve in the polymer matrix). These calculations examined such effects as the change in specimen thickness, applied thermal gradient or the period of storage after encapsulation.

Then, the model calculations were used to provide a basis for the understanding of such effects as redistribution of pressure in the encapsulated specimen, absorption of air components or absorption of the blowing agent by the polymer matrix. Some of these processes will result in a vertical, while others in lateral shifts of the thermal resistivity-temperature curves.

The next step in the research was to apply the experimental procedure and collect information on $r = r(T)$ curves for foams manufactured with different blowing agents: CFC-11, HCFC-123 and HCFC-141b. To understand the actual processes occurring in the foam, some of the experimental data were compared with the model calculations. The use of model calculations is, however, limited by the difficulty in developing the input data, particularly the full description of aging conditions since the specimen manufacture. Only the Base 88 was, therefore, analyzed with help of the model.

These findings were further verified with a technique [1] based on the Clausius-Clapeyron equation, called the beginning of condensation (BC) method. All the experimental results gave evidence to the fact that during the prolonged storage period a significant reduction in the blowing agent pressure took place within the encapsulated specimens. Some of the non-encapsulated specimens were also tested after long-term laboratory storage and found to have a similar reduction in the blowing agent pressure.

The repeated testing highlighted also another issue, namely the material variability. To address the cumulative effects of material variability, short and long-term blowing agent solubility, environmental factors, etc., the authors postulate a new methodology making a division between time-dependent and time-independent variables and propose a new agenda for the research on performance of alternative blowing agents in foams.

MODEL CALCULATIONS

A finite difference model [2], was used for the calculation of thermal resistivity. This model accommodates the effect of condensation and evaporation of the blowing agent under conditions applied during the measurements of thermal resistivities. The different parameters needed for calculations as well as typical values for the parameters for an idealized material [homogeneous polyurethane foam with no capability to absorb or dissolve the blowing agent (CFC-11) by its polymer matrix] are listed in Table 1.

To begin with, the effect of thermal gradients applied during laboratory

Table 1. Material characteristics used for an idealized material as input to the model of aging.

Material Characteristics	Value Used
Blowing agent (CFC-11) characterization:	
initial pressure [5]	0.66 atm
solubility*	0
Foam structure characterization:	
(1) effective diffusion coefficient for	
oxygen [8,9,10]	$0.1 \times 10^{-6} \text{ cm}^2/\text{s}$
nitrogen	$0.1 \times 10^{-7} \text{ cm}^2/\text{s}$
CFC-11	$0.2 \times 10^{-9} \text{ cm}^2/\text{s}$
(2) mass extinction coefficient [2,11]	55 m ² /kg
(3) fraction of struts	0.85
Solid polymer characterization [8,11]:	
polymer thermal conductivity	0.27 m. K/W
polymer density	1220 kg/m ³
polymer specific heat	900 J/(kg.K)

* Solubility is zero by definition.

measurements on the idealized material was considered. Theoretically, to get the true thermal resistivity, measurements should be carried out with thermal gradients that approach zero. To generate this theoretical data, a temperature difference of 0.2°C was applied across a 25 mm thick material, aged for two weeks in the laboratory, and thermal resistivity was calculated for the range of temperatures between 40°C and -20°C. The results are denoted in Figure 1, as "theory." The above calculations were repeated for two other situations. First, measurements according to ASTM standard test methods C177 or C518 were simulated by assuming a thermal gradient of 26°C across a specimen of thickness 25 mm. Next, the test conditions used in previous research [1] were simulated (10°C difference across a specimen of thickness 10 mm). The results from these two calculations are denoted in Figure 1, as "ASTM" and "NRC test" respectively.

The theoretical curve shows that when the specimen is cooled from 40°C, its thermal resistivity increases linearly until a point where the blowing agent starts to condense. This point, called the beginning of condensation (BC) point may be observed at about 16.5°C on the theoretical curve. Any further reduction in temperature successively decreases the amount of the blowing agent in the cell gas mixture until the whole blowing agent has been liquified out of the cell gas mixture [1].

Because of a large temperature difference applied in the second curve in Figure 1 (corresponding to the typical conditions in an ASTM test), the blowing agent may condense at the cold surface while the rest of the speci-

FIGURE 1. Effect of thermal gradient on the average thermal resistivity of a test specimen as shown by model calculations.

men does not participate in the condensation process. Further reduction in specimen temperature will increase the region of condensation until at a certain stage the blowing agent condensation occurs in all parts of the specimen. In two regions: (1) when there is no condensation at all and (2) when all parts participate in the condensation process, the "ASTM" curve coincides with the theoretical curve. But in between these regions, the experimental curve determined according to ASTM standards C177 or C518 deviates from the theoretical curve.

The third curve, (NRC test) shows a deviation in the region of partial condensation, but smaller than that observed in the ASTM test. Since the agreement between the NRC test and the theoretical curve appears sufficient, all subsequent simulations are done on 10 mm thick specimens with 10°C thermal gradient.

The "NRC test," i.e., the experimental curve in Figure 1 is denoted "(1) initial" in Figure 2 since the thermal resistivity measurements were done immediately after the encapsulation. What could happen if the measurements are done after some time? How will the curve be affected if one or more of the changes listed earlier occur? To answer these questions the initial test

curve (1) in Figure 2 is compared to four other curves simulating the following conditions:

- Curve (2) uniform air pressure: the oxygen and nitrogen that entered the specimen prior to the encapsulation had been redistributed, (e.g., during six months storage), and have uniform pressure throughout the specimen.
- Curve (3) air absorption: uniform pressure but 10% of air components (each nitrogen and oxygen) were absorbed by the polymer matrix.
- Curve (4) blowing agent absorption: uniform pressure but 10% of the blowing agent alone was absorbed by the polymer matrix.
- Curve (5) cell-gas absorption: uniform pressure but 10% of each cell-gas (nitrogen, oxygen and blowing agent) was absorbed by the polymer matrix.

Figure 2 indicates that the redistribution of nitrogen and oxygen consistently reduces the thermal resistance through the entire range of temperature and hence there is a vertical shift between curves (1) and (2). When 10% each of nitrogen and oxygen is absorbed by the polymer matrix, thermal resis-

FIGURE 2. Effect of redistribution and absorption of gas components as shown by model calculations.

tivities consistently increase through the temperature range producing again a vertical shift between curves (2) and (3).

Curves (4) and (5) address the effect of the blowing agent absorption. Curve (4) introduces 10 percent blowing agent absorption to the equalized cell-gas pressures that were obtained after six months of redistribution [curve (2)]. Curve (5) deals with uniform cell-gas pressure but air pressure is 10% lower than in case (4)—in other words both air and blowing agent had their partial pressures reduced by 10%. Comparing curve (4) to curve (2) and curve (5) to curve (3) (both analyzing the effect of 10% blowing agent absorption) one may notice a lateral shift. The magnitude of this lateral shift differs depending on cell-gas composition. The lateral shift between curves (3) and (5) is larger than that shown between curves (4) and (2). The same blowing agent absorption changes the cell-gas composition to a larger extent for the curve (5) than for the curve (4). This difference may be associated with the change in the air pressure that altered the cell-gas composition since in the latter case the air pressure is 10 percent higher.

Thus, the model calculations performed on the ideal foam showed that while vertical shift of the $r = r(T)$ curves may be associated with a number of phenomena, such as redistribution or absorption of the air components within the encapsulated specimen, there is only one reason for the lateral shift of these curves, namely a change in the blowing agent pressure. The fact that the lateral shift in the beginning of condensation (BC) point is uniquely correlated to the change in the blowing agent pressure will be utilized later in this paper.

EXPERIMENTAL RESULTS

Foam Blown with CFC-11

Figures 3(a) through 3(d) show the thermal resistivities as a function of temperature measured on four specimens encapsulated during short-term aging in the laboratory. These specimens were tested after 7 to 14 days of laboratory storage, again stored for 6 to 12 months and retested. An exception is shown in Figure 3(a) where the retesting was additionally performed after 1 and 4 months. One may observe the gradual shift in thermal resistivity-temperature curves that occurs with prolonged storage. Such a shift between curves established initially and after an extended laboratory storage may be also seen in all four specimens shown in Figures 3(a) through 3(d). Figures 3(b) through 3(d) show a number of repeated measurements, primarily to illustrate that these measurements were made with the precision high enough to observe the gradual shift in the $r = r(T)$ curves performed after different periods of storage.

FIGURE 3. Experimental data on Base 88 (CFC-11) specimens, encapsulated at different stages of aging: (a) after 9 days, (b) after 15 days, (c) after 20 days, and (d) after 25 days.

FIGURE 3 (continued). Experimental data on Base 88 (CFC-11) specimens, encapsulated at different stages of aging: (a) after 9 days, (b) after 15 days, (c) after 20 days, and (d) after 25 days.

FIGURE 4. Experimental data on foam 2 (HCFC-123) specimens, encapsulated at different stages of aging.

Foam Blown with HCFC-123

Figure 4 shows initial measurements of thermal resistivity on three specimens encapsulated after short-term and one specimen encapsulated after medium-term aging. The latter specimen (encapsulated after 62 days), displayed a thermal resistivity-temperature curve lower and laterally shifted from the curves obtained for three specimens.

Figures 5(a) through 5(c) show thermal resistivity-temperature curves for the same specimens when retested after long laboratory storage (8 to 9 months) compared with the initial measurements. Similar to the tests on specimens from CFC-11 blown material, retesting after long storage was associated with shifts in the thermal resistivity-temperature curves.

Foam Blown with HCFC-141b

Figure 6 shows initial measurements of thermal resistivity, i.e., 7-14 days after encapsulating the specimens. The specimens were encapsulated after 12, 16, 21, 27 and 360 days of aging. The latter specimen (encapsulated after 360 days), displayed a thermal resistivity-temperature curve much lower and laterally shifted from the curves obtained for the other four specimens. These four specimens that were encapsulated after short term aging, were

FIGURE 5. Effect of storage period on the thermal resistivity-temperature curves for foam 2 (HCFC-123) specimens encapsulated at different stages of aging: (a) after 10 days, (b) after 15 days, and (c) after 25 days.

FIGURE 5 (continued). Effect of storage period on the thermal resistivity-temperature curves for foam 2 (HCFC-123) specimens encapsulated at different stages of aging: (a) after 10 days, (b) after 15 days, and (c) after 25 days.

FIGURE 6. Experimental data on foam 3 (HCFC-141b) specimens encapsulated at different stages of aging.

retested after 10–11 months of the laboratory storage. The results are shown in Figures 7(a) through 7(d). Again, all specimens retested after an extended storage time displayed significant shift in the thermal resistivity–temperature curves.

DISCUSSION

All encapsulated test specimens prepared from the three materials included in this work, when retested after long storage, exhibited shifts in their thermal resistivity–temperature curves. These shifts, however, varied depending both on the duration of aging before encapsulation and the period of time before testing.

Application of the Aging Model

As indicated earlier, to interpret these experimental findings, supporting model calculations were performed. To do so, the input data must comprise the following elements:

1. Material characteristics, i.e., quantities characterizing the structure of the foam and properties of solid polymer
2. Blowing agent characterization, i.e., distribution of the blowing agent partial pressure and solubility of the blowing agent in the polymer matrix at the stage of aging for which the calculation is performed
3. Other initial conditions, such as distribution of the oxygen and nitrogen partial pressures and their solubility in the polymer matrix
4. Boundary conditions, i.e., temperature and gas pressures at the specimen surfaces for the whole period of aging starting from the moment of manufacturing and ending at the moment of calculations

A list of material characteristics used in the calculations on actual materials, derived [2] from representative experimental data on attenuation of infrared radiation, initial thermal resistivities and aging curves, can be found in Table 2. In addition to these material characteristics, initial conditions (initial pressure distributions of oxygen, nitrogen and blowing agent) and boundary conditions are needed as the input to the model. While the actual cold and hot plate temperatures in the Heat Flow Meter apparatus were used as the boundary conditions, the determination of the pressure distributions of each cell–gas component at the actual stage of the aging process was much more difficult.

The pressure distributions of oxygen and nitrogen were calculated as a function of time for each type of subsequent exposure since the material manufacturing (e.g., transport and storage of a 60 mm thick board for 45 days, cutting 25 mm specimens and their storage in the laboratory, cutting

FIGURE 7. Effect of storage period on the thermal resistivity-temperature curves for foam 3 (HCFC-141b) specimens encapsulated at different stages of aging: (a) after 12 days, (b) after 16 days, (c) after 21 days, and (d) after 27 days.

FIGURE 9 (continued). Comparison of experimental thermal resistivity-temperature curves determined on two batches of foam 2 (HCFC-123) specimens encapsulated at different stages of aging: (a) after 10/11 days, (b) after 20 days, and (c) after 25 days.

Table 2. Material characteristics used as the input data to the model of aging.

Material Characteristic		Foam 1 (Base 88, CFC-11)	Foam 2 (HCFC-123)	Foam 3 (HCFC-141b)
Property	Material			
Effective diffusion coefficient, cm ² /s	Oxygen	1.7×10^{-7}	—	—
	Nitrogen	0.8×10^{-8}	2.3×10^{-8}	2.0×10^{-8}
	Blowing agent	2.5×10^{-9}	4.5×10^{-9}	6.0×10^{-9}
Mass extinction coefficient, m ² /kg		55	45	43
Polymer matrix characterization		Identical to that in Table 1		

10 mm thick specimen, further aging for 9 days prior to the encapsulation and finally 14 days storage after encapsulation). Then, the calculated pressure distributions of oxygen and nitrogen were used as the input (initial conditions) to the model simulations of the $r = r(T)$ curves. The initial partial pressure of the blowing agent was determined to be 0.52 atmosphere by means of applying Clausius-Clapeyron equation [1].

Using these input data, the model generated thermal resistivity-temperature curves, which are shown in Figure 8. The encapsulation was simulated in the model calculations by adding a very high flow resistance at the specimen surface and the calculation was continued for the actual storage period. Similarly to the results shown in Figure 2 on the ideal foam, the cell-gas pressure equalization occurring as the effect of encapsulation introduced only a vertical shift into $r = r(T)$ curves. To reproduce the lateral shift shown by the experimental curve determined after 9 months of laboratory storage [see Figure 3(a)] the blowing agent pressure had to be changed. Furthermore, it became clear from repeated model calculations, that to match the actual shift in $r = r(T)$ curves of the encapsulated specimen, the process of nitrogen and oxygen redistribution had to be complemented by their absorption. The best fit, shown in Figure 8, was obtained with blowing agent pressure equal to 0.46 atmosphere, i.e., reduction of 0.06 atm and with the average oxygen and nitrogen pressures reduced to 94 percent of those at the moment of encapsulation.

Lateral Shift in Thermal Resistivity-Temperature Curves

Since the goal of our work was to examine the long-term changes in cell-gas concentration, the encapsulated specimens were stored, for a period of minimum 6 months, to complete the redistribution of nitrogen and oxygen within the specimen. Uniform distribution of pressure across the specimen allows application of the BC method [1] to find if any change in the blowing agent pressure occurred during the storage period.

Figure 8 compared model calculations with the experimental results shown in Figure 3(a) [typical of the results presented in Figures 3(a) through 3(d)]. They all show shifts in the thermal resistivity-temperature curves that can be attributed to two effects:

1. Cell-gas pressure equalization
2. Absorption of cell-gas components

Figures 3(a) through 3(d) show that the effect of redistribution of oxygen and nitrogen on $r = r(T)$ curves, the vertical shift, is gradually decreasing with increasing the aging period before encapsulation. (Similar conclusion had been drawn from the ideal foam results shown in Figure 2.) A few weeks increase in the aging period, however, did not affect the lateral shift [shift of

FIGURE 8. Comparison of measured and experimental thermal resistivity-temperature curves for Base 88 (CFC-11) specimens encapsulated after 9 days of aging.

the beginning of condensation (BC) point]. The shifts in BC point of 4.0 and 4.3°C determined for the specimens encapsulated after 20 and 26 days of aging are not significantly different from the values of 5.0 and 4.8°C shown by the specimens encapsulated after 9 and 15 days of aging.

The effect common to all four encapsulated test specimens of Base 88 appears to be a significant decrease in the blowing agent pressure during the extended storage. Model calculations performed to reproduce the experimental data shown in Figures 3(a) through 3(d) indicated that after extended storage of the encapsulated specimens blowing agent partial pressure ranged between 0.42 and 0.46 atmosphere. These figures are comparable to the estimates derived from BC method (0.43–0.44 atm) (Table 3). These values are, however, much lower than the range of 0.60 to 0.65 established on the fresh foam by means of indirect test methods [4,5].

Measurements performed on foams manufactured with HCFC-123 and HCFC-141b showed even larger apparent* shifts in the BC point. As shown in Tables 4 and 5 the apparent shift in the BC point varies in the range between 8.5 and 6.0°C for foam manufactured with HCFC-123 [Figures 5(a),

*The word apparent underlines the fact that the non-uniform distribution of oxygen and nitrogen through the specimen may affect the character of the $r = r(T)$ curve.

Table 3. Changes in thermal resistivity-temperature curves observed over 7 to 9 months period in the spray polyurethane foam manufactured with CFC-11.

Figure Number	Encapsulated after Days	Apparent Shift in BC Point °C	Long Term Values for	
			BC Point °C	BA Pressure atm
3(a)	9	5.0	2.4	0.43
3(b)	15	4.8	3.0	0.44
3(c)	20	4.0	2.7	0.43
3(d)	26	4.3	3.2	0.44

Table 4. Changes in thermal resistivity-temperature curves observed over 8 to 9 months period in the spray polyurethane foam manufactured with HCFC-123.

Figure Number	Encapsulated after Days	Apparent Shift in BC Point °C	Long Term Values for	
			BC Point °C	BA Pressure atm
4(a)	11	8.5	2.8	0.35
4(b)	15	6.0	2.8	0.35
4(c)	25	6.5	3.0	0.35

Table 5. Changes in thermal resistivity-temperature curves observed over 10 to 11 months period in the spray polyurethane foam manufactured with HCFC-141b.

Figure Number	Encapsulated after Days	Apparent Shift in BC Point °C	Long Term Values for	
			BC Point °C	BA Pressure atm
7(a)	11	11.5	5.0	0.33
7(b)	16	14.0	4.5	0.33
7(c)	21	12.5	4.8	0.33
7(d)	27	10.0	6.0	0.35

(b), (c)] and between 10 and 14°C for HCFC-141b [Figures 7(a), (b), (c), and (d)]. Such a large shift in the BC point indicates an increased solubility of the HCFC in the polymer matrix.

Larger solubility of the HCFC may also be inferred from the lateral shift in BC point observed during the initial testing. Figure 4 shows initial testing of the foam with HCFC-123 blowing agent for specimens encapsulated after 11, 20, 25, and 62 days. The curve for the last specimen shows also a lateral shift in BC point relative to the other three curves. Figure 6 shows initial testing of foam manufactured with HCFC-141b for specimens encapsulated after 12, 16, 21, 27, and 360 days. In the last case, the BC point is approximately 5.0°C giving partial pressure of HCFC-141b equal to 0.33 atm, i.e., identical to the results determined on specimens encapsulated after 10 to 30 days and tested after 8 to 12 months of storage. It is important to realize, comparing these encapsulated specimens and those exposed to laboratory air, that even though their overall thermal resistivity differed approximately 10%, the same BC point was determined after one year time. The fact that the results obtained on encapsulated and non-encapsulated specimens were similar indicates that the blowing agent pressure reduction cannot be fully attributed to the outward diffusion of blowing agent but that the total solubility of the blowing agent (either blowing agent absorption on the surface or blowing agent dissolution in a polymer matrix) must also be taken into consideration.

Material Variability

Another issue examined in this work, was that of differences between experimental results. There are four reasons to expect differences between thermal resistivity-temperature curves, namely:

1. Different initial pressure of blowing agent (differences up to 30% were shown previously [3])
2. Variation in the rate of gas diffusion (for Base 88 the effective diffusion coefficient for nitrogen varied between 0.8 and 1.8 cm²/s)
3. Variation in the cell structure (the mass extinction coefficient varied between 45 and 55 m²/kg [3])
4. Variation in the blowing agent solubility in the polymeric material

Thus, to examine variability in the thermal resistivity-temperature curves another batch of foam 2 (HCFC-123) was produced and an identical test program was performed.

Results obtained on the specimens representing the same product but manufactured at different occasions are reported in Figures 9(a) through 9(c). These figures compare thermal resistivity-temperature curves established on specimens from two batches but subjected to identical aging conditions.

While results shown in Figures 9(a) through 9(c) display the same character of the $r = r(T)$ curves, they also illustrate that direct comparisons between curves generated on different batches are difficult. Therefore, as previously postulated [3,6], one should perform two different types of measurements:

1. To establish variability in thermal performance of the product (e.g. variation in the initial thermal performance)
2. To establish time-dependent effects. The latter requires that a non-destructive testing is performed on the same specimen over extended period of time.

CONCLUDING REMARKS

To optimize thermal performance of the foams one must consider a number of different physical and chemical phenomena, some of which are better understood than others. The importance of ingress of the air components into the foam has been known for many years. In a parallel fashion all reduction in the blowing agent pressure has been associated with the outward diffusion of the blowing agent. This paper shows that such an assumption may be incorrect and that the solubility of the blowing agent cannot be neglected.

Long-Term Solubility of the Blowing Agent

This paper focused attention on the long-term changes in the cell-gas composition which are affected by the polymer matrix. To eliminate the change in the composition of cell-gas caused by the diffusion processes the experiments were performed on encapsulated specimens.

Significant shifts in thermal resistivity-temperature curves were measured on the encapsulated specimens. The shifts between $r = r(T)$ curves established initially and after an extended laboratory storage were shown to exist in all tested specimens. Using the model of aging and comparing various calculated curves with those experimentally obtained, two reasons for these shifts were established:

1. Redistribution of the gases in the enclosed space, (pressure equalization)
2. Sorption of various components of the cell-gas mixture which in turn affect the composition of the cell-gas (reduction of pressure of the cell-gas components)

It is not known whether the latter process is caused by a surface phenomenon associated with a change in the interaction between the polymer and the cell gas, or by a penetration of the cell-gas into the polymer matrix. One may even assume that a change in the physical properties of the polymer may

FIGURE 9. Comparison of experimental thermal resistivity-temperature curves determined on two batches of foam 2 (HCFC-123) specimens encapsulated at different stages of aging: (a) after 10/11 days, (b) after 20 days, and (c) after 25 days.

FIGURE 9 (continued). Comparison of experimental thermal resistivity-temperature curves determined on two batches of foam 2 (HCFC-123) specimens encapsulated at different stages of aging: (a) after 10/11 days, (b) after 20 days, and (c) after 25 days.

further affect the interaction of cell-gas and the polymer and affect the cell-gas composition. While we may not understand these mechanisms in a detailed manner, we should recognize their influence on long-term thermal performance of the foam.

For an idealized spray polyurethane foam (polymer with no capability of absorbing or dissolving blowing agent), immediately after the foaming the blowing agent partial pressure ranges between 0.65 and 0.70 atm [4,5]. The specific polymeric composition used for Base 88 material resulted in a drop in the short-term CFC-11 partial pressure to approximately 0.53 atmosphere [1], a level close to that previously reported for polyurethane boards [7].

The CFC-11 pressure determined on the encapsulated specimens of the same material aged for one year were found to be much lower. While small differences between four tested specimens and two methods of evaluation were observed, the blowing agent partial pressure, ranging from 0.42 to 0.46 atmosphere, was much lower than expected. It appears that the long-term solubility of the blowing agent may differ from that obtained under short-term experiments on the same foamed cellular plastic.

The main finding of this work is the fact that after one year of service of

the studied foam, HCFC contribution to its thermal resistance is only one half of the theoretically possible maximum contribution. This finding justifies a revision of the many assumptions currently used both in the academic and the industrial research on blowing agents to replace the CFCs.

Research Recommendations

One should observe a significant contribution of solubility to the effective diffusion coefficient of the blowing agent. The measurements of HCFC diffusion which do not take into consideration changes in the blowing agent solubility may result in significant errors. Moreover, since the blowing agent solubility is such an important factor in the thermal performance of the foam, one must also examine how the blowing agent solubility is affected by the environment in which the foamed insulation performs—for instance the interaction between polymer and cell-gas may differ in various environments. Furthermore, the ability of the polymer matrix to retain the blowing agent may change and hence alter the gas diffusion characteristics.

The fact that for the studied material only a half of the HCFC initially helping to achieve high thermal performance continues to contribute to this end after one year period, indicates an urgency in the development of experimental techniques for predicting long-term field performance of the foams. First of all, one must be able to measure long-term performance of the foam under laboratory as well as various environmental and service conditions. Secondly, one must develop some predictive techniques which shorten the time necessary to evaluate a given polymeric foam. Then, one may consider means to reduce the actual solubility of the blowing agent in the polymer matrix. In effect, such methodology would create a significant potential for improving thermal performance of the foams.

Such a methodology is being attempted in the collaborative research project between the Institute for Research in Construction of the National Research Council of Canada and DuPont Canada Inc. While this project is still in progress (e.g., environmental effects will first be addressed in the next stage), one may already see how the methodology of non-destructive testing on the material exposed to various conditions may be useful to evaluate performance of commercial polymers which may lead to significant improvements in long-term performance of foams produced with alternative blowing agents.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support from DuPont Canada Inc. for this work. They are indebted to Mrs. Nicole Normandin for carrying out the measurements reported in this work.

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