Microstructure and blowing agent concentration analysis in accelerated aged polyurethane & polyisocyanurate insulation

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Abstract. Some closed cell foam insulation products show an increase in thermal conductivity at low temperatures. This reduction in thermal performance has been attributed to the diffusion of air and blowing agent through the foam and to the condensation of the blowing agent. Aging processes and polymer degradation further increase the thermal conductivity of foams. The initial cell structure plays a role in dictating the thermal performance and changes with foam aging which is rarely investigated. To understand the loss of thermal performance in closed cell foams, a microstructure and chemical characterization of pristine and aged samples was performed in this study. The aging behaviour was analyzed by SEM imaging and by measuring the blowing agent concentration in the foam. Changes in the polymer physical attributes were identified. This study also used gas chromatography and quantified changes in pentane concentration in aged polyisocyanurate foams. Results show that aged foams undergo change in their polymer appearance and cellular elongation. Gas chromatography quantified a decrease in blowing agent in the range of 11-85% for polyisocyanurate foams after aging.

1. Introduction

Energy conservation is a critical element in high performance buildings. Energy conservation is achieved by minimizing heat losses that occur through the exterior envelope, critical joints and pipes. These components of a building are designed with thermal insulation to minimize energy losses. The ability of a material to transfer heat is expressed by its thermal conductivity. This property is often linearly proportional to the temperature, as it assumes higher values at higher temperatures. However, with closed cell foam insulation products, this is not always the case. Foam insulation products used for exterior walls, roofs, seals and pipes, typically exhibit a non-linear relationship to temperature and at some temperature ranges, the thermal conductivity increases as temperature decreases. This phenomenon has been demonstrated in various foam insulations (polyurethane and polyisocyanurate) which contained a variety of blowing agents (i.e. CFC, HCFC, pentane) [1]. The reduction in thermal performance due to increased thermal conductivity has been attributed to the diffusion of air into the polymer, effusion of blowing agent out of the polymer, and polymer degradation. Moreover, the listed effects that degrade foam insulation product thermal performance increase as the material undergoes aging [2]. The morphology of the polymer used in as foam insulation plays a pivotal role in dictating the thermal performance [3]. Insight into the aging behaviour of foam insulations can be evaluated based off of foam, cell wall thickness, elongation, percentage of open cells, and density. During the aging process, changes in the polymer physical attributes could occur and cause additional loss in the thermal performance of foams [2,4,5].

This research aims to combine microstructure and blowing agent chemical analysis to the study of spray polyurethane foams and polyisocyanurate foam aging. Specifically, the microstructure was characterized and changes in blowing agent concentration were measured. An understanding of polyisocyanurate is evident in current literature, but there is a gap in the cell gas analysis of rigid
polyisocyanurate boards for building applications, a gap in building foam insulation, a gap in connecting microstructure and blowing agent concentration.

2. Literature Review

2.1. Polyurethane and polyisocyanurate insulations

Polyurethane and polyisocyanurate foam insulations are produced by combining MDI, polyols, blowing agent, fire retardant, surfactant, resin, water, and catalysts [6]. Polyurethane foams are typically spray applied while polyisocyanurate foams are laminated. Polyurethane foams could either be open cell or closed cell, while polyisocyanurate foams are typically closed cell. Closed cell foams consist of fully encapsulated cells surrounded by polymeric cell walls and are not interconnected with surrounding cells. Open cells are not encapsulated and are interconnected with surrounding cells [7]. With closed cell foams, the blowing agent remains trapped in the material, causing a lower thermal conductivity. While, the blowing agent for open cell foams is carbon dioxide which is a by-product of the exothermic reaction between water and isocyanate [6]. The carbon dioxide diffuses out and is replaced with air leading to a higher thermal conductivity that closed cell foams.

2.2. Mechanisms detrimental to thermal performance

At low temperatures (below approx. 5°C), it has been observed that closed cell foams increase in thermal conductivity. This is most notable with polyisocyanurate boards [8]. The temperature dependency of thermal conductivity can be described in three regions. Above the boiling point of the blowing agent, thermal conductivity increases with temperature as per kinetic gas theory. Below the boiling point, the blowing agent condenses to liquid phase and the thermal conductivity increases. As the blowing agent condenses to liquid, air diffuses into the foam. Once all the blowing agent is condensed, the dominant gas in the cell is air, which has a higher thermal conductivity [9]. In addition to the effects of temperature, as closed cell foams age over time, further increase in their thermal conductivity occurs [8]. Within the first few years, air diffuses into the foam which both increases the pressure within the cell and dilutes the blowing agent. After a longer period of time, the blowing agent becomes absorbed by the polymeric cell walls due to the increased pressure. The change in the composition of gases in the cell is what causes the increase in thermal conductivity [9].

2.3. Cell microstructure

The understanding of foam cellular microstructure is important to the thermal performance of foam insulation products. The determination of cell geometry and cell parameters have been used to study heat transfer and gas permeability through analytical models [5]. To understand the effective diffusion of gasses in aged polyurethane foams, experimental studies and analytical models were done by Ostrogorsky et al. [5]. This study defined aging as the degradation of thermal conductivity due to diffusion of air into the foam. Models using microstructure measurements were used to determine cell wall permeability and cell geometry. A foam with the lowest density, thinnest cell walls, and largest cell size had the highest permeability which highlights the relationship between polymer density to the permeation of gasses through the foam cell wall [5].

2.4. GC-FID for foam insulation

The application of gas chromatography (GC) to analyse the gas phase of polyurethane foams was done by Macchi-Tejeda et al. [10] and Svanstrom et al. [11]. The objective of Svanstrom’s work was to quantify cell gas composition using GC while Macchi-Tejeda analysed cell gas composition of aged foams. The polyurethane foams studied were from an insulating panel product consisting of HCFC141b blowing agent. It was found that the concentration of air in freshly made foam is very low relative to carbon dioxide. The cell gas composition was different throughout the depths of the foam, showing the heterogeneous nature of closed cell foams. The two foams studied had densities of 40 kg/m³ and 45 kg/m³ respectively. The change in cell gas composition after aging was smaller in the foam with the higher density compared to the lower density foam. A higher foam density would result in thicker cell walls which would impede the diffusion of gas showing the interrelation between cell microstructure and diffusion mechanisms.
3. Materials

In this study, boards of three polyurethanes and two faced polyisocyanurates were obtained from local manufacturers. The select samples studied are summarized in Table 1. The polyisocyanurate boards possessed adhered facers: the PIA series possessed a foil facer while the PIB series foams possess a felt facer.

| Material Name | Cell    | Thermal conductivity [W/mK] | Density [kg/m3] | Blowing agent                  | Boiling Point [°C] |
|---------------|---------|-----------------------------|------------------|--------------------------------|--------------------|
| PIA           | Closed cell | 0.0173          | 32.0             | 75:25 n-pentane/isopentane    | 36.06              |
| PIB           | Closed cell | 0.0248          | 32.0             | 75:25 n-pentane/isopentane    | 36.06              |
| PUX           | Closed cell | 0.0240          | 30.0             | HFO-1233zd(E)                 | -18.5              |
| PUC           | Open cell  | 0.0378          | 6.83             | Water, CO₂                    | 100, -78.5         |
| PUD           | Open cell  | 0.0333          | 17.2             | Water, CO₂                    | 100, -78.5         |

4. Experimental

4.1. Accelerated Aging

The aging treatments performed were oven heating and freeze thaw cycling. One set of foam samples were aged in an oven set at 60°C for four months. This accelerated aging over 6 years. A second set of samples underwent freeze-thaw cycling between 40°C and -30°C every 24 hours. The duration of freeze-thaw cycling was 150 days. Samples were labelled with suffixes to represent treatment: not aged = NA, oven aged = O, and freeze-thawed = FT. The accelerated aging method was based on the work of Berardi et al. [12].

4.2. Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to analyse the structure of the foam insulation cells. Foam samples were prepared by removing any facers then cutting cubes of 1cm³. One of each sample type (Table 1, column 1) and treatment was used. The SEM images were taken using a JEOL-6380LV model microscope. The magnifications used were 30X and 130X at 10kV in a low vacuum, 25 Pa. The structural elements of interest were: appearance, cell wall thickness, cell aspect ratio, cell size, and strut thickness. The thicknesses of the cell walls were measured at the centre of wall. Measurements of the structural elements were taken from the images using ImageJ microscopy image processing software.

4.3. Gas Chromatography-Flame Ionization Detection

GC-FID (gas-chromatography-flame ionization detection) was used to quantify the amount of blowing agent in the oven aged and not aged polyisocyanurate samples PIA and PIB. To quantify the concentration of blowing agent, foam samples in the solid polymer matrix were placed in a solution of hexane at a temperature below the boiling point of the blowing agent. A cylinder of foam that weighed approximately 0.5g was cut from both the edge and the core of the material in the shape of a 1cm³ cube(s). The cylinder of foam was placed in a 40mL weighing bottle and 15mL of hexane was pipetted. The bottle was sealed with a glass stopper and wrapped with aluminium foil to ensure no solvent evaporated. After sealing, the prepared sample was stored for 72 hours at room temperature, after which, approximately 5mL was passed through the solid phase extractor (BondElut SPE). The eluted liquid was then collected in a glass vial. The sample was then injected in the GC-FID. For the GC, a SUPELCO100 column was used. The initial column temperature was 170°C with a heating rate of 10°C/min for 14 minutes. This allowed for the complete resolution of pentane and hexane peaks. To quantify the amount of blowing agent detected by GC-FID, the area normalization method was used. The concentration of pentane was determined as a percentage relatively to the hexane solvent.
5. Results

5.1. SEM

The SEM images were taken of the closed cell polyisocyanurate (PIA, PIB), closed cell polyurethane (PUX) and open cell polyurethane (PUD and PUC) foam samples (not all shown). The PIA series samples are shown in Figure 1. At the 130X scale, differences in cellular structure between the PIA samples are more prominent, especially where the material was cut. When cut, the PIAFT sample exhibits more abrupt breakage at the cell walls compared to PIANA and PIAO. The cell walls appeared to become more brittle (Figure 1 a), b), and c)). A similar observation was made for PIB samples.

![Figure 1. a) Not aged PIA (PIANA) at 130x b) Freeze-thawed PIA (PIAFT) at 130x c) Oven aged PIA (PIAO) at 130x (where not aged = NA, oven aged = O, and freeze-thawed = FT)](image)

5.2. Cell microstructure measurements

The cell aspect ratios are summarized in Figure 2. The aspect ratios of aged open cell foams PUCO and PUDO exhibited the smallest aspect ratios indicating they possessed the most elongated cells of all foams studied. The PIAO and PUXO foams possessed smaller aspect ratios compared to their not aged and freeze-thaw cycled samples. The PIB series foams did not display cellular elongation when aged as the average cell aspect ratio of PIBNA is smaller than that of PIBO and PIBFT.

The cell cross section areas measured are summarized in Figure 2. Of all foam samples, the open cell foams possessed the largest cell areas. On average, the cell area increased in aged samples of PUD, PIA, and PIB when compared to not aged samples. The PUXO foam possessed the smallest cell area. There is no clear correlation between cell area changes between samples that are not aged, aged and freeze-thaw cycles. Conversely, the average cell area of PUXO was smaller than the PUXNA and PUXFT samples. Between not aged, oven aged and freezer thawed samples, there appears to be no indication that cell wall thickness changes amongst the foam samples. Similar observations were made from the measurements of cell strut thickness.

![Figure 2. Cell aspect ratios (left) and cell areas (right) of polyurethane and polyisocyanurate foams that underwent aging and freeze-thaw cycling (where not aged = NA, oven aged = O, and freeze-thawed = FT)](image)

5.3. GC-FID pentane quantitation

The reduction in pentane concentration was calculated by subtracting the oven aged pentane concentration from the not aged pentane concentration that was measured. Comparing aged samples to
not aged samples taken from the edge, there was a measured decrease in the concentration of pentane (Figure 3). All cuts from the edge resulted in higher concentrations of pentane blowing agent compared to cuts from the core (Figure 3). The difference in pentane concentration between not aged and oven aged PIA was -19.76%±2.73% while with PIB the difference was -84.77%±1.68%. For cuts taken from the core, PIA resulted in a -1.34%±3.22% difference in pentane concentration while PIB resulted in a -12.48%±7.20% difference in pentane concentration. For cuts taken from the edge, differences in pentane concentration for samples PIA and PIB were -11.84%±4.28% and -12.48%±7.20% respectively.

![Figure 3. Comparing not aged to oven aged samples (left) and comparison of pentane blowing agent concentration at the core and edge of samples (right).](image)

The results also showed differences in pentane concentration at the edge and core of the samples. For the not aged foams, the difference in pentane concentration at the edge and core was smaller compared to the aged foams. At the core, not aged PIA had 942.88±3.39% more pentane while PIB had 143.28±2.57% higher pentane. For aged PIA and PIB, the difference in concentration between the core and edge was 1182.17%±2.51% and 1298.41%±7.09% respectively.

6. Discussion

6.1. Cell microstructure

The cause of the brittle edges in foams that have been oven aged or freeze thaw cycled could be due to loss in plasticity in the solid polymer. The observation of open cell foams and oven aged foams (PIAO and PUXO) having the smallest aspect ratios mean that the cells of these products are more susceptible to elongation and deformation as they age. The causes of the elongation could be because of the effect of heat to the cell wall. The reason that other oven aged foams did not exhibit a smaller aspect ratio (PIBO) is likely due to fewer measurements. For these samples, there was a lack of whole cells visible in the image. Open cell foams were observed to have the largest cell areas which is to be expected due to the lower density of the foam polymer. The smallest cell areas were measured in the PUX series of foam which was the densest foam (Table 1). There was indication that foams which have been freeze thawed have smaller cell sizes than foams that have been oven aged. However, the cell area measurements performed resulted in the largest magnitudes of error compared to all other measurements. The reason for the inconsistency in cell area is due to the two-dimensional nature of SEM images. In 3D, the cells are polyhedron in shape where their cross-sectional area would vary from the position of the slice during sample preparation. The SEM images provide a 2D representation of the cells, however, determining the cell cross section area through the center of the cell or determining the cell volume would require 3D imaging techniques like computer tomography (CT). Cell wall thickness and cell strut thickness did not present a consistent difference between not aged, oven aged and cell strut thickness thus, those results have been omitted from this paper.

6.2. GC-FID pentane quantitation

It was expected that overall the oven aged samples would result in less pentane quantified than not aged samples. Overall, measurements of pentane concentrations from all aged samples were lower than not aged samples. This is consistent with literature that states that diffusion of air occurs in polyisocyanurate
foam which dilutes the blowing agent. Because the foam samples were not ground, it was assumed that the quantities that were measured represent the amount of blowing agent in the polymer. Consistently, a higher concentration of pentane was measured at the core than at the edge. This is because the core of the sample had two faced surfaces through which air diffused in while the edge had an exposed foam surface. The PIA samples overall resulted in lower concentrations of pentane compared to PIB sample. This finding was contrary to what would be expected based off the permeability of the facers. The PIA samples are faced with an impermeable sheet of foil, while, the PIB samples are faced with more permeable felt. This could have been due to differences in how the products were prepared.

7. Conclusions
The SEM images provided insight into how the polyurethane and polyisocyanurate foam microstructure changes after oven aging and freeze thaw cycling. Future SEM imaging should take into consideration the foam rise direction when blown. This would assure that elongation is not observed due to foam rise during production. The GC-FID method presented quantified the pentane blowing agent in PIA and PIB. A decrease in pentane was observed for all oven aged samples. A significant increase in pentane concentration was observed between samples cut from the core and the edge of a foam sample, which supports that diffusion through faced insulation occurs at the exposed edges. The foil faced PIA experienced a smaller difference in pentane concentration compared to the felt faced PIB due to the lower permeability of foil. Future work should consider 3D imaging techniques and also, aim to quantify the blowing agent of polyurethane foams containing newer HFO blowing agents.

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