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# Chemical gradients in PIR foams as probed by ATR-FTIR analysis and consequences on fire resistance

Joël Reignier<sup>a</sup> (joel.reignier@polymtl.ca), Françoise Méchin<sup>a</sup>, Alexandru Sarbu<sup>b</sup> <sup>a</sup> Univ Lyon, INSA Lyon, CNRS, IMP UMR 5223, F-69621, Villeurbanne, France <sup>b</sup> SOPREMA, 89330, Saint-Julien-du-Sault, France \*Corresponding author.

### Abstract

Taking into account numerous results from the literature, an in-depth exploratory study on the chemical gradients in the rise (or depth) direction was performed on polyisocyanurate rigid (PIR) foam insulation panels using ATR-FTIR spectroscopy. In particular, it was found that the isocyanurate/phenyl ratio is a quick and effective technique for providing an indication of the level of trimer conversion within each sample. More importantly, a detailed analysis of the C–N stretching vibration of the isocyanurate ring as a function of depth revealed a linear decrease in the frequency peak maximum with the increase in the isocyanurate ratio for all investigated PIR foams. This result suggests for the first time that the position (frequency) of peak maximum (C–N stretching of isocyanurate ring) may be used to quantify the extent of isocyanurate formation without the issues linked to the use of absorbances. It is proposed that this reduction in the frequency of the C–N stretching vibration of isocyanurate ring reflects the decrease in hydrogen bonding between N–H of urethane group and C=O within the isocyanurate ring when the isocyanurate content increases (lower mobility associated with higher level of cross-linking). The heterogeneity of the isocyanurate content was physically confirmed by investigating the flammability of the foam samples taken at different positions in the rise direction (z-axis).

### Keywords

Polyurethane; Polyisocyanurate; Foam; Infrared spectroscopy; Flame resistance; Chemical gradients; Frequency shift; Hydrogen bond

### Introduction

Polyurethane rigid (PUR) foams are widely used for the thermal insulation in construction, transportation and industrial applications. Since mid-1970's, a great effort was made to improve heat and flame resistance of polyurethane foams in response to increasingly demanding standards for the foam used in construction. In the first approach, foams with good fire retardancy were obtained by incorporating halogen and/or phosphorous fire-retardant compounds into the foam system. Unfortunately, the main drawback of this method was that combustion of polyurethane foams released toxic gaseous products. In another approach, the high thermal stability of isocyanurates discovered more than a century ago [1] encouraged industrial chemists to prepare polyisocyanurate rigid (PIR) foams made from multifunctional isocyanates, but they were found to be too friable and brittle for practical use because of their high cross-link density [2]. Therefore, considerable efforts were put forth to modify polyisocyanurate foams in order to improve thermal stability while maintaining the beneficial properties of PUR foams. Among the various segments that have been incorporated prior to or during the crosslinking step of cyclotrimerization (for example, epoxy-functional modifiers generating oxazolidone groups, or amines leading to urea bonds), the most popular has been the urethane bonding [3,4]. In addition, the type of used polyol was also found to affect the flame-resistance of PIR foams. Aromatic polyester polyols were found to reduce-flammability and smoke with respect to polyether polyols [5]. Higher flammability PIR foams were obtained with polyols containing secondary hydroxyl groups (vs primary OH) and/or with high polyol OH equivalent weight (=molar mass/functionality) [6]. In addition, knowing the isocyanate index was not an indication of the potential fire resistance of the foam unless the polyol equivalent weight was also known [7]. In a general manner, it is now well accepted that the main factor controlling flammability is the isocyanurate content (wt.%).

Conceptually, urethane-modified polyisocyanurate foams are copolymers of polyurethane and polyisocyanurate units. Polyurethane is formed by the reaction of polyol hydroxyl groups with isocyanates while isocyanurate groups are formed from the cyclotrimerization of three isocyanate functions, as shown in Fig. 1. In addition, secondary reactions also occur. These include urea formation from amines, obtained from the reaction between isocyanate and water, as well as side reactions leading further on to allophanates and biurets, as schematically represented in Fig. 1. The question that arises is how much trimer is needed to obtain a good fire resistance without imparting too much friability. An important parameter of such polymer matrix is the so-called isocyanate index, as defined by the excess isocyanate over the theoretical amount for a stoichiometric reaction with all "active" hydrogen-bearing groups capable of interacting with isocyanates (such as –OH and –NH) and expressed in percentage terms (i.e. 1:1 = 100). Thus,

Isocyanate index = 100 x (Actual amount of NCO used) / (Theoretical amount of NCO required) (1)



Fig. 1. Schematic of competing reactions in the synthesis of poly(urethane-isocyanurate) foams.

Some authors made the distinction between PIR material and PIR-modified PUR when the index is higher and lower than 400, respectively [8]. For others, polyisocyanurate insulation foams are typically reacted at an index of approximately 250, which means that there are on average and theoretically 2.5 isocyanate groups present for every OH or NH group, whereas the excess isocyanate is converted into isocyanurate trimers [9]. Nowadays, the PIR term is used to describe foams which exhibit good fire resistance (at least a B-2 class fire rate, in accordance with DIN 4102) rather than a specific index. But everything is not so simple and internal works (not published) clearly indicate that the level of halogen and/or phosphorous flame retarding components can still upset the rankings. As a result, the use of fire tests to classify PUR and PIR foams is not a guarantee of the nature of the polymer network (isocyanurate content). In order to avoid overcomplicated phrasing, the term PIR will be further used to identify both PIR and PIR-modified PUR foams.

Even if the presence of thermal gradients in PIR foams and its influence on isocyanurate content have been discussed a few times in the literature, a detailed analysis of the chemical gradients existing in the thickness direction (rise direction) of PIR foams using ATR-FTIR is still lacking. For that purpose, PIR foam panels taken from the European market were analyzed and compared. Correlations between the ATR-FTIR spectroscopy results and the flammability characteristics will be also addressed for some of them.

## **Experimental details** Materials

Nineteen PIR and four PUR foam insulation panels produced by ten European manufacturers (Bauder, Iko, Kingspan, Knauf, Puren, Recticel, Soprema, Stiferite, Swissport, Unilin) with thickness ranging from 40 to

180 mm were analyzed. Samples were identified by a code number in the form of FML-XXX-YY where FML represent the formulation (PUR or PIR), XXX the panel thickness (expressed in mm) and YY the panel number. Basically, they were obtained from a reactive foaming process with polymeric methylene bis (phenyl isocyanate) (pMDI) and polyester or polyether polyol using a physical blowing agent (isopentane, cyclopentane, *n*-pentane or various mixtures of two of the aforementioned hydrocarbons). The boards were manufactured by a continuous "double-belt lamination" process in which the formulation mixture is applied between two lamination facings. The density of the closed-cell foam specimens ranged from 30 to 35 kg/m<sup>3</sup>.

#### Foam characterization ATR-FTIR spectroscopy

The chemical structure of the various foams was characterized by Fourier Transform Infrared Spectroscopy (FTIR) in attenuated total reflectance mode (ATR) using a Thermo Scientific Nicolet iS10 spectrometer. The samples were analyzed by absorbance, in the range of 4000–600 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> using 32 scans, which gave a data spacing (i.e. the minimum peak interval that can be distinguished) of approximately  $0.48 \text{ cm}^{-1}$ . An atmospheric background was collected before sample analysis, all measurements were done at room temperature ( $25 \pm 2^{\circ}$ C). A square base foam column (around 2 cm × 2 cm) with the long axis parallel to the foam rise direction (z-axis) was first cut in the center of the foam panel and was subsequently sliced in approximately 5 mm-thick layers using a razor blade in preparation of the test. Each layer was pressed against the IR-transmitting ATR crystal (Diamond), with a constant clamping force (pressure) to ensure tight contact between the sample and the prism in the ATR. This pressure was strong enough to collapse the foam sample, leading to an almost "bulk" film with a thickness of around 0.5 mm. All spectra were analyzed with OMNIC Spectra software. ATR correction was applied (the sample spectrum was multiplied by a wavelength-dependent factor) in order to compensate the higher penetration depth of longer wavelengths (lower frequencies).

#### **Burning tests**

The single-flame source test (EN ISO 11925-2) used to qualify the fire reaction of PU insulation panels (multilayer products greater than 10 mm thick, as described by the reference standard) is usually conducted by exposing a small flame to the mid-point on the bottom edge of the test specimen, either on the external surface including the facing or with the specimen turned at 90° round its vertical axis, which allows to test the foam material only. Unfortunately, both these methods do not allow the observation of any potential fire reaction gradients as a function of depth (z-axis). To circumvent that issue, a set of samples were cut in each panel as shown in Fig. 2 for a 160 mm thick panel. Two neighboring blocks (named A and B) were collected in the center of a given panel and were subsequently sliced in 20 mm thick layers after having removed the thin external layer including the facing. Please note that the thickness of the first slice of each block (which is not used in the test) is different (2 mm in the block A and 12 mm in the block B). Shifting the layers of

blocks A and B by about 10 mm thus allowed to determine the ignitability of foam layers as a function of depth, with a 10 mm step, by alternating samples from A and B blocks (A<sub>1</sub>, B<sub>1</sub>, A<sub>2</sub>, B<sub>2</sub>...). The fire reaction of PIR foams was evaluated by exposing each parallelepipedal foam sample (280 mm  $\times$  90 mm x 20 mm) hung vertically to a small flame (around 20 mm in height), along its central line and at a distance of 3 cm from the bottom edge, as shown in Fig. 3. The flame was applied for about 15 s and the height of the resultant propagation was measured, thanks to the lines drawn on each sample at a 10 mm spacing. The repeatability of the ignitability measurements can be reasonably estimated to about ±1 cm. Unlike EN ISO 11925 that recommends testing six representative specimens for a given product, only one sample was tested for each 20 mm thick layer in our case, which nevertheless ensured consistent results. It is worth mentioning that all PIR foam samples tested self-extinguished after an initial flame propagation lasting just a few seconds and during which the maximum flame height was estimated.



Fig. 2. Details of the sample preparation for the fire resistance tests in the case of 160 mm thick foam panels. Each of the 13 specimens possesses a thickness equal to about 20 mm. The black arrow indicates the lamination production direction. Please note the difference in the thickness of the first layer (scrap) in order to offset the foam layers of each block.



Fig. 3. Schematics of the burning test. The test sample (280 mm  $\times$  90 mm x 20 mm) is mounted vertically and is subjected to surface exposure from a small gas flame (2 cm long) along its central line and at a distance of 3 cm from the bottom edge. During the test, the maximum flame height is registered. The graduations directly drawn on the sample make it easier to measure the flame height.

## **Results and discussion**

#### Spectroscopic characterizations

This part is dedicated to the ATR-FTIR analysis of the different layers (from the surface to a depth of 50 mm) corresponding to the panel referenced PIR-160-01. The complete spectra depicted in Fig. 4 at selected depths confirmed the presence of chemical groups characteristic for the rigid polyisocyanurate foams among other moieties. Assignments of the main absorption bands are detailed in the following sections.



*Fig. 4. ATR-FTIR spectra of the evolution of the PIR-160-01 foam samples as a function of depth (mm) in the range 600-4000 cm<sup>-1</sup>. "0 mm" represents the surface of the foam panel just underneath the facing.* 

#### C-N stretching vibration (1350-1450 cm<sup>-1</sup>) of isocyanurate ring

The isocyanurate ring, product of the isocyanate trimerization, can usually be identified using the C–N stretching band in the 1410 cm<sup>-1</sup> region [9–12] as shown in Fig. 5, but care must be taken not to confuse it with uretidinedione which also possesses a similar band. The final distinction between these two functional groups can be done using the carbonyl bands in the 1700-1800 cm<sup>-1</sup> region [13]. In our case, the carbonyl bands in the 1755-1780 cm<sup>-1</sup> region are very weak in the spectrum (see Fig. 8) and this clearly indicates that it is not uretidinedione but rather isocyanurate (see the infrared spectra of diphenyl-2,4-uretidinedione in SI1). It is worth noting that the C–N stretching band in the 1410 cm<sup>-1</sup> area does not include the C–N stretching

vibration of urethanes, which is rather found around 1530-1540 cm<sup>-1</sup>, in combination with N–H bending vibration [10,14]. This feature is particularly useful, as it provides a way to compare solely the proportion of isocyanurate. It was previously demonstrated that the absorbance at 1409 cm<sup>-1</sup> increases as the isocyanate index of PIR foams increases from 200 to 500 [15]. In our case, the intensity of the C–N stretching of the isocyanurate peak (1410 cm<sup>-1</sup>) slightly increases as one moves from the surface to the core of the PIR-160-01 foam panel, which suggests that the isocyanurate content of this PIR foam increases with the depth. A more fascinating observation, however, is that the peak maximum wavenumber (often called "peak position") progressively decreases from 1410 cm<sup>-1</sup> to about 1407 cm<sup>-1</sup> as the depth increases from 0 to 30 mm and remains constant thereafter for the PIR-160-01 foam sample, as shown in Fig. 6. To the best of our knowledge, this subtle frequency shift of the C–N stretching vibration of the isocyanurate peak has never been reported in the literature and this raises the question of its origin. The latter point will be discussed in part 3.2 of this work. For comparison purposes, the corresponding peak maximum of the PUR-160-01 foam sample is centered around 1412 cm<sup>-1</sup> (i.e. close to the value obtained for PIR-160-01 at the surface under the facing) and does not seem to depend on the depth (Fig. 6).



Fig. 5. ATR-FTIR spectra of the evolution of the PIR-160-01 foam samples as a function of depth (mm) in the range  $1340-1570 \text{ cm}^{-1}$  corresponding to the C–N stretching vibration of isocyanurate ring and the N–H in-plane bending vibration of the urethane groups (amide II band). "0 mm" represents the surface of the foam panel just underneath the facing.



*Fig. 6. Effect of depth on the maximum intensity position (wavenumber) of the C–N stretching vibration of isocyanurate (peak maximum) for the PIR-160-01 and PUR-160-01 foam panels.* 

#### N-H bending vibration (1500-1560 cm<sup>-1</sup>)

The infrared spectra of the PIR-160-01 sample reported in Fig. 5 also show a band around 1508 cm<sup>-1</sup> (amide II band) which is mainly due to the N–H in-plane bending vibration of urethane groups [16] as well as the C–N stretching vibration of urethane groups [10], but to a lesser extent. This amide II band is sensitive to both chain conformation and intermolecular hydrogen bonding, which renders its interpretation very difficult. It has been demonstrated [17] for a linear aromatic polyurethane in the 1500 to 1560 cm<sup>-1</sup> region that the best fitting-curve was obtained by using three bands. The first one at 1535 cm<sup>-1</sup> was attributed to the H-bonded N–H bending vibration between N–H and C=O groups, whereas the band at 1517 cm<sup>-1</sup> was ascribed to the "free" N–H bending vibration. A very weak absorption band at 1526 cm<sup>-1</sup> was assigned to the H-bonded N–H bending vibration between the N–H and the  $\pi$  orbitals of the aromatic rings, suggesting that this latter type of H-bonding is weaker than H-bonding between N–H and C=O groups. In the case of the PIR-160-01 foam sample, the whole band (including the shoulder near 1530 cm<sup>-1</sup>) gains in intensity as one moves from the core to the surface (facings), which may suggest an increase in the proportion of urethane linkage near the surface. In addition, the maximum intensity position seems to slightly increase within the first 20 mm, as shown in Fig. 7.



*Fig. 7. Effect of depth on the maximum intensity position (wavenumber) of the N–H bending vibration (peak maximum) for the PIR-160-01 foam panel.* 

#### C=O stretching vibration (1630-1760 cm<sup>-1</sup>)

The strong and broad absorption envelope around 1710 cm<sup>-1</sup> shown in Fig. 8 corresponds to the stretching vibration of carbonyl (C=O) and is also called the amide I band. This large band (typically, between 1620 and 1760 cm<sup>-1</sup>) is very complicated and difficult to interpret because it encompasses several individual absorption bands. First, this band is mainly composed of the carbonyl vibration of urethane linkage and it is influenced by H-bonds [18–20]. The carbonyl bands of "free" urethanes, loosely associated urethanes and Hbonded urethanes were associated with the frequency of 1730, 1715 and 1700  $\text{cm}^{-1}$ , respectively [11]. The amide I region is also characteristic of the carbonyl stretching vibration of urea in all its forms ("free", loosely associated or hydrogen bonded urea) [11]. Even if the proportion of water cannot be neglected in our case, (as a rule of thumb, industrial formulations contain about 3 to 7 times more OH groups coming from the polyol with respect to  $H_2O$ ) the influence of urea on the overall band of C=O stretching should however be constant within each PIR foam panel taken individually. More importantly, the C=O stretching vibration of isocyanurate ring also contributes to the amide I region with values of 1708 cm<sup>-1</sup> [11] or 1712 cm<sup>-1</sup> [21] reported in the case of PIR foams. Apart from the case of PIR foams, several authors studied the trimerization of phenyl isocyanate using various catalysts and reported values of C=O stretching vibration at 1709  $cm^{-1}$ [22,23], 1705 cm<sup>-1</sup> [24] and 1710 cm<sup>-1</sup> [25]. In addition, the C=O stretching vibration of uretoneimine, often present when liquid 4,4'-methylene bis(phenylisocyanate) (MDI) is used, can be found at 1726 cm<sup>-1</sup> [26,27]. Eventually, allophanates, obtained from the reaction(s) between urethane and isocyanate may also be present [28,29] with C=O stretching vibration absorption bands at 1710 cm<sup>-1</sup> [30] or at 1724 and 1689 cm<sup>-1</sup> [31].



Fig. 8. ATR-FTIR spectra of the evolution of the PIR-160-01 foam sample as a function of depth (mm) in the range 1560–1780 cm<sup>-1</sup> corresponding to the carbonyl stretching and aromatic C=C in-plane vibrations. "0 mm" represents the surface of the foam panel just underneath the facing.



Fig. 9. Effect of depth on the maximum intensity position (wavenumber) of the C=O stretching vibration (peak maximum) for the PIR-160-01 foam panel.

As shown in Fig. 9, the C=O peak maximum (wavenumber) of the PIR-160-01 foam progressively decreases from around 1711 cm<sup>-1</sup> to around 1705 cm<sup>-1</sup> as the depth increases from 0 to 20 mm, showing that there is a chemical gradient of the different species containing carbonyl functional groups. A possible explanation for this decrease may be the increase in the proportion of C=O belonging to isocyanurate rings with respect to other types of carbonyl as one moves towards the core of the foam panel but care must be taken in interpreting data given the high number of superimposed peaks in this C=O stretching region.

#### Aromatic C=C in-plane stretching vibration (1570-1630 cm<sup>-1</sup>)

Fig. 8 also shows an absorption band at about 1595 cm<sup>-1</sup> representative of the C=C (in-plane) stretching vibrations of the aromatic rings coming from the diisocyanate units. According to a study dedicated to the effect of hydrogen bonding in an amorphous linear aromatic polyurethane at different temperatures, this envelope was characterized by a principal band at 1598 cm<sup>-1</sup> and a shoulder at 1614 cm<sup>-1</sup> [17]. More importantly, it was found that both bands were systematically shifted to lower wavenumbers with increasing temperatures from 25 to 165°C and this phenomenon was attributed to the presence of hydrogen-bonds between the N–H groups of urethane and the  $\pi$  orbitals of the aromatic rings of the diisocyanate units which almost disappeared at high temperatures. In other words, the more H-bonds between N–H groups and the  $\pi$  orbital of the aromatic rings, the more the aromatic C=C in-plane vibration shifts to higher wavenumbers. Referring to this paper, the increase in the peak position (maximum) from about 1594 cm<sup>-1</sup> to around 1596 cm<sup>-1</sup> as the depth increases from 0 to 25 mm shown in Fig. 10 may suggest that there are hydrogen bonds between the  $\pi$  orbitals of the aromatic ring and the N–H groups of polyurethane and that they increase as the depth increases.



Fig. 10. Effect of depth on the maximum intensity position (wavenumber) of the C=C in-plane stretching vibration (peak maximum) of the aromatic rings (phenyl) for the PIR-160-01 foam panel.

#### Unreacted isocyanate (R-N=C=O) stretching vibration (2273 cm<sup>-1</sup>)

The band at 2273 cm<sup>-1</sup> reported in Fig. 11 for the PIR-160-01 foam panel is due to the asymmetric stretching vibration of unreacted isocyanate (-N=C=O function). Finding residual unreacted -NCO functions was not unexpected. It has been estimated that about 30% of the isocyanate groups remained unreacted after 100 min for PIR foams blown with 100% CFC (index 450) or with a mix 50/50 wt% of CFC/water (index 350), while the maximum temperature was reached within 5 min [11]. Other authors have demonstrated for PIR foams of various index values that the isocyanurate yield (as defined by the proportion of NCO groups theoretically available at the end of the reactions with hydroxyl and amine groups, and which has effectively reacted to form isocyanurate) is never 100% [32]. In the best case, these authors obtained a yield of about 90% (index 200) with potassium 2-ethylhexanoate as trimerization catalyst. Even if the isocyanurate content increases when the NCO index increases [33], it was found that the final degree of isocyanate conversion into isocyanurate decreases with increasing isocyanate index. The "apparent" proportion of unreacted isocyanate reached after equilibrium (as estimated from the ratio  $I_t/I_0$  where  $I_t$  is the absorbance of isocyanate peak at time t, and  $I_0$  is the absorbance of isocyanate peak at time = 0) was found to increase from about 5 to 34% as the isocyanate index increases from 200 to 500 [34]. This phenomenon is related to the restricted mobility of -NCO groups as the cross-linking density increases [8,32,35]. In our case, each tested panel is supposed to exhibit a constant index throughout its entire volume and the lower intensity of the isocyanate peak in the core of the PIR foam may suggest that the isocyanurate content is higher in the core.



Fig. 11. ATR-FTIR spectra of the evolution of the PIR-160-01 foam sample as a function of depth (mm) in the range 2020–2400 cm<sup>-1</sup> corresponding to the unreacted isocyanate (R-N=C=O) and carbodiimide (R-N=C=N-R') stretching vibrations. "0 mm" represents the surface of the foam panel just underneath the facing.

#### Carbodiimide (R-N=C=N-R') stretching vibration (2100-2150 cm<sup>-1</sup>)

One other aspect of the spectral series that deserves comment in Fig. 11 is the emergence of carbodiimide functional groups identified by the two peaks at 2138 and 2111 cm<sup>-1</sup> (stretching vibrations) as one penetrates deeply into the core of the PIR-160-01 foam sample. According to the literature, the presence of carbodiimide may be generated through different mechanisms. The first one would be that carbodiimide can be produced by the thermal degradation of the uretoneimine structure above 40°C, and this reaction was found to increase as a function of processing temperature [11,36]. The relevant question is whether uretoneimine is present in our case. Commercial pMDI (the crude version of liquid 4,4'-methylenediphenyl diisocyanate) used for the preparation of PIR foam insulation panels is often a mix of pure MDI and uretoneimine because the latter makes it more stable and slightly viscous at ambient temperature [26,36]. The spectrum reported in SI2 seems to support this since it reveals the presence of uretoneimine at 1738 cm<sup>-1</sup> (C=O stretching vibration). Returning to Fig. 5, it is interesting to notice the presence of a small shoulder around 1377 cm<sup>-1</sup> only visible for the layers close to the surface which may correspond to the C-N stretching vibration of uretoneimine four-membered ring [36]. However, it tends to disappear with the increase in depth, but it is difficult to conclude whether it is embedded inside the larger C–N stretching peak of the isocyanurate ring or if it no longer exists. Carbodiimides can also be produced by the condensation of isocyanates with themselves, provided that the right catalyst (phosphorus compounds, carbonyl metal groups or metallic derivatives) is used [37-39]. In the case of PIR foam formulations currently used on the European insulation market, trimerization catalysts are often carboxylic acid salts such as potassium 2-ethylhexanoate which may be good candidates for this latter reaction. In both cases, the increase in the intensity of these two peaks towards the core may indicate that the maximum temperature of the foam was higher in the core (see SI3 for more detail about the temperature gradients).

#### **Isocyanurate gradients in PIR foam panels**

In this part of the study, the authors are particularly interested in the quantitative analysis of the bands associated with isocyanurate and their evolution as a function of depth (z-axis). Assuming a perfect contact between sample and crystal, the intensity of each peak (absorbance), *I*, is dependent on the absorptivity coefficient ( $\varepsilon$ ), the light penetration depth or path length (*I*), and the concentration (*c*) in terms of the Beer-Lambert law ( $I = \varepsilon x l x c$ ). Both the absorptivity coefficient and the penetration depth are rather constant for a given peak. To this must be added the contact area which may slightly vary, even at a constant clamping force. The contact area depends on the hardness of the sample which is not necessarily constant in our case because the cellular morphology and foam density may slightly vary along the z-axis (i.e. perpendicular to the in-plane direction) [40]. However, differences in contact area can be largely corrected using the peak intensity of a component which may not vary. To best quantify the variation of isocyanurate content, it was chosen in our study to normalize all spectra with respect to the absorbance of the C=C stretching (phenyl) at 1595 cm<sup>-1</sup>

because the absorption of the phenyl peak should not depend on the extent of the various reactions for a given polyol/isocyanate formulation [41]. Before that, the height of each peak of interest was estimated with regard to the position of a baseline connecting the lower points on either side of the peak where there is no significant underlying absorbance. The anchor points were at 1350 cm<sup>-1</sup> and 1470 cm<sup>-1</sup> for the C–N stretching of isocyanurate, and at 1565 cm<sup>-1</sup> and 1630 cm<sup>-1</sup> for the C=C stretching vibration of the aromatic ring (phenyl), respectively. Despite providing comparative results within the same foam panel, this standardization method obviously does not necessarily work when comparing foam samples made with different formulations.

Fig. 12 provides the evolution of the  $h_{1410}/h_{1595}$  ratio as a function of depth for part of the investigated foam panels. The data volume was intentionally limited so as not to overload the chart while at the same time giving the widest possible range of panel thickness. It can be clearly seen that the isocyanurate/phenyl ratio of all PIR foams dramatically increases from the surface toward the core of the foam with a chemical gradient typically spreading over a distance of 20–30 mm. However, the maximum level of isocyanurate seems relatively constant between each gradient, except for samples PIR-100-06 and PIR-140-16. Somewhat surprising, these scattered patterns may be due to a bad mixing between the polyol premix and the pMDI, leading to chemical discontinuity. Eventually, it is interesting to note that each profile of isocyanurate appears symmetrical, which implies that the level of isocyanurate is the same on both faces. For comparison purpose, the isocyanurate/phenyl peak height ratio of PUR foams is also reported in Fig. 12 and appears unaffected by depth with values close to unity. This low isocyanurate content can be explained by the fact that PUR formulations contain a NCO/OH ratio slightly above stoichiometric values for urethane obtention. Note however that the ( $h_{1410}/h_{1595}$ ) ratio does not directly correspond to the real composition ratio (mainly because of differences in absorption coefficients).



Fig. 12. Evolution of the isocyanurate/phenyl ratio (as probed by the peak height ratio  $h_{1410}/h_{1595}$ ) as a function of depth for part of the various PIR and PUR foam panels investigated.

To better characterize the chemical gradients, the evolution of the  $(h_{1410}/h_{1595})_{max}/(h_{1410}/h_{1595})_{min}$  ratio for each investigated PIR foam panel is reported in Fig. 13 as a function of panel thickness. This max/min ratio should give a rough estimate of the difference in isocyanurate content between the core and the surface for each foam panel, unless the absorptivity coefficient of each group may vary a lot between the maximum and minimum value. It appears that the isocyanurate content is about 2.7 times lower at the surface than in the core (average value:  $2.69 \pm 0.42$ ). On the contrary, the variation of isocyanurate content between the surface and the surface for each surface to unity (average value:  $1.18 \pm 0.15$ ).



Fig. 13. Plot of the ratio  $(h_{1410}/h_{1595})_{max}/(h_{1410}/h_{1595})_{min}$  for the various PIR and PUR foam insulation panels. The lines correspond to linear regressions for each formulation.

This phenomenon seems typical of PIR foams and is generally attributed to the occurrence of heat loss at the surface of the foam, leading to a temperature difference during manufacturing between the core and the surface of the foam [8,32]. In our case, the variation of trimer conversion was estimated in the thickness direction for a foam sample taken in the central line of the foam board width, but a similar effect was reported along the width (cross machine direction) of PIR foam panels (index around 250) near the lateral edges [9]. Laminated foam boards are particularly prone to heat losses because of the small amount of material that is metered to produce a panel of given thickness, which justifies the use of external heat sources such as oven or heated platens to maintain the trimerization reaction as homogenous as possible [2]. That is why the manufacturer specifications recommend to operate the double-belt of the production line above 60°C in the case of PIR foams (at least 15°C higher than for PUR foam boards). As a result, the isocyanurate gradients reported in Fig. 12 are mainly attributed to curing temperature gradients. Comparisons of the temperature profiles at three positions within the PIR foams (as a function of time) for mold temperatures of 25°C and

55°C led to the conclusion that the temperature near the foam center was unaffected by the mold temperatures for sufficiently thick samples because of the low thermal conductivity and low thermal diffusivity of the foam (the thermal diffusivity is defined by  $k/\rho C_p$ , where k is the thermal conductivity,  $\rho$  is the density and  $C_p$  is the heat capacity) [42]. For the sake of completeness, attempts were made to estimate the variation of foaming temperature as a function of depth inside a realistic PIR foam panel. The data reported in SI3 corroborate these expectations.

The comparison of Figs. 6 and 12 suggests that there is a direct relationship between the C–N frequency of isocyanurate ring and the  $h_{1410}/h_{1595}$  peak height ratio for the PIR-160-01 foam sample. The data plotted in Fig. 14 clearly indicate that the peak maximum (frequency) of isocyanurate rings of the PIR-160-01 foam samples decreases linearly from 1410 to 1407 cm<sup>-1</sup> with the increase in  $h_{1410}/h_{1595}$  ratio from 1.8 to 4.4. Moreover, the linear correlation between the peak position of isocyanurate ring and the isocyanurate/phenyl ratio ( $h_{1410}/h_{1595}$ ) is not limited to the PIR-160-01 samples but also seems to encompass the data obtained for the PUR-160-01 samples (bundled into almost one data point around 1412 cm<sup>-1</sup>), given the appealing correlation coefficient of more than 0.99.



Fig. 14. Evolution of the maximum intensity position of the C–N stretching vibration of isocyanurate ring as a function of isocyanurate/phenyl ( $h_{1410}/h_{1595}$ ) ratio for the PIR-160-01 and PUR-160-01 foam panels. The number in parenthesis represents the depth (in mm) of the probed surface for each data point.

To confirm the previous observation, the vibration frequency (peak position) of isocyanurate peaks was systematically measured in the first 50 mm (or up to half the thickness of each sample for a sample thickness lower than 100 mm, at least) for the twenty-three foam panels (4 PUR and 19 PIR formulations). Despite a few large discrepancies, the vast majority of the PIR foam data points reported in Fig. 15 seems to follow the

same master curve with a linear decrease in peak position as the isocyanurate/phenyl height ratio increases. The C–N (stretching vibration) frequency of isocyanurate ring varies from 1411 cm<sup>-1</sup> (surface) to 1406 cm<sup>-1</sup> (core) which gives a frequency variation of around 5 cm<sup>-1</sup> for the PIR formulations. On the other hand, all data points corresponding to PUR foam panels are gathered in the higher left part with values centered around 1412 cm<sup>-1</sup> and showing no frequency vibration below 1411 cm<sup>-1</sup>. A linear regression of the whole data set (PIR and PUR formulations) gives a correlation coefficient of about 0.86, which is actually acceptable given the many different sources of the foam panels.



Fig. 15. Evolution of C–N frequency of isocyanurate ring (peak maximum) as a function of isocyanurate/phenyl ( $h_{1410}/h_{1595}$ ) height ratio for all investigated PIR and PUR foam panels. Only the first 50 mm (or half the thickness if the sample thickness is lower than 100 mm) were analyzed, by increments of 5 mm.

The above results may therefore lead to the conclusion that the vibration frequency of isocyanurate (C–N stretching) is inversely proportional to the amount of isocyanurate. Accepting this statement, the question remaining is what causes the shift toward lower frequencies. On one side, many studies have shown that the formation of hydrogen bonds between the N–H proton-donor groups and the different proton-accepting groups (namely the carbonyl group of the urethane, the carbonyl of an ester group and the oxygen atom of an ether group) led to the reduction of their vibration frequencies [17,18,43–46]. But as a general rule, the frequency shift is usually narrower for bending than that for stretching vibrations [47]. In the case of

amorphous linear aromatic polyurethanes, differences of about 100 cm<sup>-1</sup> between "free" N–H stretching frequency (3447 cm<sup>-1</sup>) and H-bonded N–H with C=O (3347 cm<sup>-1</sup>) were reported but this frequency shift is reduced to  $\Delta v \sim 18$  cm<sup>-1</sup> for "free" N–H bending frequency (1535 cm<sup>-1</sup>) and N–H groups H-bonded with C=O (1517 cm<sup>-1</sup>) [17]. Thinking now specifically from the viewpoint of the proton-accepting groups, the frequency of the stretching vibration is also reduced but to a lesser degree than for the proton-donor group. Carbonyl absorption at 1733 cm<sup>-1</sup>(free) and 1703 cm<sup>-1</sup> (H-bonded) were reported for a polyether urethane composed of alternating blocks of soft (poly(tetramethylene oxide)) and hard (urethane) segments [48]. In the case of composite propellants, functionally substituted isocyanurates are used as universal bonding agents because they can form bonds with the surface of the crystalline oxidizers and with the binder of the propellant. It has been demonstrated that the frequency of the C=O stretching vibrations of isocyanurate shifted downward from 1698 cm<sup>-1</sup> to 1688 cm<sup>-1</sup> ( $\Delta v = 10$  cm<sup>-1</sup>) upon formation of hydrogen bonds between ammonium perchlorate and tris(2-hydroxyethyl) isocyanurate [49].

On the other side, it is well known that the frequency of bond vibration should decrease as bonds decrease in strength (or increase in length) because the frequency is directly related to the square root of the force constant [47]. In that respect, hydrogen bond formation leads to the weakening of the  $\sigma$  bonds of each acceptor and donor group. In our case, the decrease in the vibration frequency of isocyanurate ring (C–N stretching) with the increasing amount of isocyanurate is an indication that the strength of that C–N bond decreases. However, the C-N bond of the isocyanurate ring should not directly participate in the hydrogen bond with the N-H proton donor group of the urethane linkage, so why this change in vibration frequency? In a study dedicated to the thermodynamic stability of isocyanurate rings as a function of substituents (aliphatic and/or aromatic) attached to the trimer, it is written that "any lengthening of the carbonyl bond of an amide group leads to shortening of the C–N bond and thus to its strengthening" [50]. If this reasoning is transposed in our case, it could be postulated that the presence of hydrogen bonding between the N-H groups of urethane and the C=O attached to the isocyanurate ring should weaken the C=O double bond (leading to longer C=O interatomic distance). This phenomenon should in turn strengthen the C–N bond of the isocyanurate cycle, i.e. shorten this bond, as schematically illustrated in Fig. 16, and leading to an increase of its frequency vibration. Conversely, the increase in strength of the carbonyl group only loosely involved in hydrogen bonds with the N-H groups may result in the decrease of the strength, therefore in the lengthening, of the C-N bond within the isocyanurate ring and as a result would shift of  $v_{C-N}$  to lower frequency. In this context, it is conceivable that the increase in isocyanurate content with the increase of depth observed in our case for all the investigated PIR foam panels implies a higher level of cross-linking, which should inevitably bring about a reduction of chain mobility and hence a possible reduction of the number of hydrogen bonds in the core of the foam. If the previous mechanism is correct, there should also be near the surface a higher proportion of urethane (the N–H suppliers) with respect to isocyanurate. A number of authors used the intensity of the peak at  $1710 \text{ cm}^{-1}$ to estimate the proportion of urethane, alone or in combination with other characteristic bands [33,35,51]. However, one needs to be aware that the C=O stretching vibration of the isocyanurate ring may also contribute to the intense band near 1710 cm<sup>-1</sup>, leading to possible overestimation of the proportion of urethane. This should be particularly true since the difference between the absorptivity coefficients of the various carbonyls is significant even if it is dwarfed in the case of the N–H stretching mode [11]. In our case, it was decided to use exclusively the intensity of the peak at 1220 cm<sup>-1</sup> (C–O bond stretching) to estimate the proportion of urethane (with anchor points between 1160 cm<sup>-1</sup> and 1345 cm<sup>-1</sup>) [9]. It is revealed from Fig. 17 that the  $h_{1220}/h_{1410}$  (urethane/isocyanurate) ratio decreases with the increase in depth and tends to level off beyond about 20 mm. Obviously, this reflects the peak height inversion reported in Fig. 5: the peak intensity (absorbance) associated with the C–N stretching of isocyanurate is higher than the peak intensity associated with the N–H bending of urethane in the core while the opposite applies at the surface. The higher relative proportion of urethane near the surface (under the facing) should favour the formation of hydrogen bonds between the N–H group of urethane and the C=O involved in the isocyanurate ring.



Fig. 16. Schematic showing the possible effect of hydrogen bond formation (dashed line), between the N–H groups of urethane and the C=O of the isocyanurate ring, on the inter-atomic distances of the C–N and C=O groups. The blue arrows indicate the change in inter-atomic distances. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 17. Evolution of the urethane/isocyanurate ratio (as probed by the peak height ratio  $h_{1220}/h_{1410}$ ) as a function of depth for PIR-160-01 foam panel.

In order to confirm this hypothesis, it can also be helpful to look closely to the spectral region of N–H stretching reported in Fig. 18. When moving from the core to the surface, a shoulder is emerging on the low frequency side of this peak and from a depth of about 30 mm. It becomes more and more noticeable as one gets closer to the surface of the foam panel and then turns into a distinct peak (3295 cm<sup>-1</sup>) at the surface. This frequency is assigned to H-bonded N–H groups, which seems to indicate that hydrogen bonds are favoured near the surface (under the facing) with respect to the core of the foam. On the contrary, the main peak located at a frequency of about 3360 cm<sup>-1</sup> attributed to "free" (non-associated) N–H groups is diminishing with respect to the absorbance at 3295 cm<sup>-1</sup> as one gets closer to the surface. It should be noted that this effect is not consistent with the spectrum of the surface layer (z = 0 mm) which is in contact with the facer and thus might have a particular behavior. In the same vein, it has been demonstrated for PUR foams (index 110) with various molar masses per branching unit (300  $\leq M_C \leq 1150$ ) that the proportion of hydrogen bonds between the urethane groups (estimated from FTIR spectroscopy data and the ratio NH<sub>bonded</sub>/NH<sub>free</sub>) increased with M<sub>c</sub> [52]. Transposing this conclusion in our case, this would indicate that a loose network (lower isocyanurate content) should promote the formation of hydrogen bonds.



*Fig. 18.* ATR-FTIR spectra of the PIR-160-01 foam sample as a function of depth (mm) in the range 3150–3500 cm<sup>-1</sup>corresponding to the N–H stretching vibrations. "0 mm" represents the surface of the foam panel just underneath the facing.

#### **Impact on fire behavior**

The above spectroscopic analysis unambiguously demonstrates that the isocyanurate content of the PIR foam panels is higher in the core than near the surface (under the facing). It is however questionable whether these differences are large enough to induce variation in fire behavior within the same panel. Accordingly, the variation of flame height obtained by following our specific protocol is shown as a function of the depth (z-axis) in Fig. 19 for samples PIR-160-01, PIR-140-02 and PIR-80-03. Obviously, the flame height is significantly higher near the surface of the foam panel with a difference greater than 6 cm for the PIR-160-01 foam panel. Regardless of the panel thickness, the gradient of flame height spreads from the surface to a depth of about 30–40 mm on each side, similarly to the isocyanurate/phenyl gradient reported in Fig. 12. As a result, the thicker PIR foam panels (PIR-160-01 and PIR-140-02) are characterized by a constant flame height between the gradients of the two edges, which gives a U-shaped curve with a long horizontal plateau. In contrast, the thinnest panel (PIR-80-03) is marked by a V-shaped curve with no horizontal plateau.



Fig. 19. Evolution with depth of flame height reached before self-extinguishing for a few PIR foam panels of different thicknesses ranging from 80 to 160 mm.

Fig. 20 shows the relationship between flame height and h<sub>isocyanurate</sub>/h<sub>phenyl</sub> ratio for the three different PIR foam panels. Despite a significant spread in the data, it is obvious that the flame height decreases with increasing isocyanurate/phenyl ratio within each panel, as shown by the linear regression including the whole set of data. It is worth noting that, generally, the z-depth of each data point increases from the top-left corner to the bottom-right corner of the plot. Making the hypothesis that the concentration of flame retardant is homogeneous within each panel, this result indicates that the isocyanurate concentration is the determining factor for controlling the fire resistance. Similar tendencies were reported on different pentane-blown PIR foams with index values ranging from 150 to 300 [32]. The flame height was lowest and the length of the charred part of the sample was shortest when the concentration of isocyanurate was highest. In the same way, the foam flammability properties were shown to be improved (for a given polyol) as the isocyanate index increased from 150 to 500 [7]. However, this reduction in foam burn pattern length tended to level off for isocyanate index values above 300, presumably because of sufficient crosslinking provided by the isocyanurate trimer. Likewise, the effect of index reduction from 400 to 225 on flame spread was found less significant when the polyol used (a highly pure aromatic difunctional polyester polyol) was specifically designed to optimize trimer conversion [53].



Fig. 20. Evolution of the flame height as a function of isocyanurate/phenyl ratio (as probed by the  $h_{1410}/h_{1595}$  peak height ratio) for three PIR foam panels of different thickness ranging from 80 to 160 mm. The dotted line represents a linear regression englobing the whole set of data.

### Conclusions

Much of our present research effort has been directed towards characterizing chemical gradients in PIR foams. For that purpose, nineteen PIR insulation foam panels taken from the European market were analyzed in detail using ATR-FTIR spectroscopy. Profiles of isocyanurate content (as probed by the  $h_{1410}/h_{1595}$  peak height ratio) were established as a function of depth (z-axis) and indicated that strong chemical gradients exist within each investigated PIR foam panel to a depth of around 20–30 mm, regardless of the panel thickness and manufacturer. Obviously, the maximum and minimum isocyanurate contents were found in the core and at the surface (under the facing) of the PIR foam panels, respectively. These chemical gradients are directly related to the thermal gradient occurring during panel manufacturing because heat loss is strongly minimized in the core of the panel thanks to the intrinsic thermal insulation properties of the foam.

For the first time, it is revealed for PIR foams that the maximum intensity position of the isocyanurate peak (C–N stretching around 1410 cm<sup>-1</sup>) shifts to lower frequencies ( $\Delta v_{max} \sim 6 \text{ cm}^{-1}$ ) as the depth increases (from the surface to the core). In addition, it is demonstrated that the peak maximum decreases linearly with the isocyanurate content as probed by the h<sub>1410</sub>/h<sub>1595</sub> peak height ratio. In our opinion, this shift to lower frequencies would be associated with the decrease in the concentration of H-bonding between N–H and C=O as the depth increases, due to the reduced chain mobility associated with higher content of isocyanurate trimer. It is worth noting that the use of frequency shift to compare isocyanurate levels seems advantageous over the use of peak height ratio because it is invariable to absorptivity coefficients, contact area, or even the ATR instrument used. On the contrary, this phenomenon is very limited in the case of PUR foams ( $\Delta v_{max} \sim 1 \text{ cm}^{-1}$ ), due to the lower content of isocyanurate but surprisingly, the corresponding data ( $v_{max} vs h_{1410}/h_{1595}$ ) were found to align with the data obtained for PIR foams.

Fire behavior tests confirmed that isocyanurate gradients are high enough to translate into a decrease of flammability (estimated through flame height) as one progresses from the surface toward the core of the PIR foam panels.

## Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

## **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A Supplementary data

Supplementary data to this article can be found online at <u>https://doi.org/10.1016/j.polymertesting.2020.106972</u>.

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