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Polymer 43 (2002) 6471–6479

polymer

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Thermal degradation behavior of rigid polyurethane foams prepared with different fire retardant concentrations and blowing agents

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Received 3 May 2002; received in revised form 20 August 2002; accepted 22 August 2002

Abstract

In order to understand the effect of flame retardant (FR) and blowing agents on the thermal stability of rigid polyurethane foams and their resultant chars, two series of polyurethane foams produced with different blowing agents (HCFC-141b and pentane) and various concentrations of a FR (0–50 wt%) were investigated using standard flammability test (ASTM, D-3014), solid-state ^{13}C NMR, TGA and Py–GC/MS. The unique combination of these analytical techniques has proved to be a valuable method for understanding the thermal degradation of rigid polyurethane foams. The standard flammability tests indicate an optimum FR concentration of about 15 wt% for foams using HCFC-141b as the blowing agent, while no optimum condition was determined with pentane. The percent mass retained (PMR) values or char yields have a linear relationship with combustion flame temperature in both series of blowing agents. The solid-state ^{13}C NMR studies clearly show that pentane is chemisorbed during the polymerization and is retained within the foam matrix. The chars have lower concentrations of methylene and oxygenated aliphatic carbons, but a subsequent increase in aromatics is observed. The FR investigated preserves the chemical structure of the polyurethane foam, and, therefore, results in a higher PMR or char yield. The TGA experimental data showed that the maximum combustion reactivities of the chars have a linear relationship with the FR concentration in the parent foams. Py–GC/MS results indicate that the aliphatic oxygenated functional groups are the first to evolve during the pyrolysis and combustion of the polymeric structure. Finally, this study has shown that the addition of FR to the foam formulation results in lower concentrations of small molecules being volatilized, and therefore, preserving the original chemical structure of the parent foam. However, the FR investigated does not seem to be as effective for the pentane series, and gives higher char aromaticities and PMR values than those reported for the HCFC-141b series. © 2002 Published by Elsevier Science Ltd.

Keywords: Rigid polyurethane foams; Thermal degradation; Flame retardant

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1. Introduction

Polyurethanes are copolymers containing blocks of low-molecular-weight polyesters or polyethers covalently bonded by a urethane group (–NHCO–O–) [1]. The most important commercial polyurethane products are foams that are commonly classified as either flexible or rigid depending on their mechanical performance and cross-link densities. Rigid polyurethane foams are widely used in building insulation and domestic appliances, due to their superior mechanical properties and low density [2]. However, the polyurethane industry is facing environmental challenges due to the type of auxiliary blowing agents used during the polymerization process. Chlorofluorocarbons (CFCs) have traditionally been the predominant blowing agents for rigid polyurethane foams [2]. Unfortunately, CFCs are one of the major causes for the destruction of the ozone layer due to their high ozone depletion potential (ODP), and therefore, are being phased out as blowing agents in the polyurethane foam industry. The polyurethane industry is searching for alternative blowing agents with low to zero ODPs, and has identified hydrochlorofluorocarbons (HCFCs) such as HCFC-141b (1,1-dichloro-1-fluoroethane), hydrocarbons like pentane and hydrofluorocarbons (HFCs) such as HFC-245fa (1,1,1,3,3-pentafluoropropane) and HFC-356mffm (1,1,1,4,4,4-hexafluorobutane) as possible substitutes

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0032-3861/02/$ - see front matter
PII: S0032-3861(02)00602-X

Table 1
Identification of the parent foam samples investigated

FR (wt%)	0	5	10	15	20	30	40	50
HCFC-141b series	18131-1	18131-2	18131-3	18131-4	18131-5	18131-12	18131-13	18131-14
Pentane series	18131-7	18131-8	18131-9	18131-10	18131-11			

[3–10]. Although rigid polyurethane foams blown with HCFCs have shown good thermal characteristics [3,4], and significantly smaller ozone depletion factors compared to CFCs, HCFCs will also be phased out worldwide under the Montreal Protocol from 2004 to 2010 [10]. Pentane and HFCs do not present any ozone environmental related problem due to their zero ODP. However, uncertainty about the cost and availability of HFCs has led the polyurethane foam industry to focus on pentane as the primary blowing agent, especially in construction [3]. Unfortunately, the inherent high flammability of pentane has resulted in polyurethane foams that fail to meet the required regulatory fire tests. Therefore, the polyurethane industry has to respond to these challenges by designing additive packages (catalysts, surfactants, cross-linkers and flame retardants) that can overcome these flammability shortcomings, while providing physical and mechanical properties comparable to those of rigid polyurethane foams blown with CFCs and HCFCs.

Previous work has investigated the structure, thermal conductivity and stability of polyurethane foams using different analytical techniques. M. Ishida et al. [13], H. Ishida et al. [14], Delides et al. [15], and Moreland et al. [16] used solid-state ^{13}C NMR to analyze the structure of polyurethane foams and elastomers. Alfani et al. [17], Guo et al. [18], Font et al. [19] and Dick et al. [20] studied the thermal properties of different polyurethane foams using thermogravimetric analysis (TGA) and pyrolysis or pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) in the temperature range from 200 to 800 °C. However, these previous studies focused on the parent polyurethane foams, and did not correlate the changes in the structural and thermal properties of the foams with their resultant chars. This paper presents an investigation of the thermal degradation behavior of rigid polyurethane foams and their chars produced using the Butler chimney standard test method (ASTM, D-3014). The parent foams as well as their counterpart chars were extensively characterized using various analytical techniques, including solid-state ^{13}C NMR, Py–GC/MS, and TGA analysis. Furthermore, to investigate the effect of the flame retardant (FR) concentration and blowing agents on the thermal stability of polyurethane foams and the structure of the chars, two blowing agents (HCFC-141b and pentane) at different levels of FR (0–50 wt% for HCFC-141b blown series and 0–20 wt% for pentane blown series) were used in the rigid foam preparation.

2. Experimental

2.1. Materials

Air Products and Chemicals, Inc. (APCI) supplied two series of rigid polyurethane foams prepared with HCFC-141b (1,1-dichloro-1-fluoroethane) and a 70% cyclo–30% iso pentane blend as the blowing agents. The 141b series consisted of eight samples containing different FR concentrations ranging from 0 to 50 wt%, while the pentane series consisted of five samples with FR levels 0–20 wt%. The size of each sample foam was $300 \times 30 \times 30$ mm^3, and Table 1 shows the sample nomenclature used in this work. The formula used was typical for construction systems and consisted of polyester polyols, catalysts, water, surfactant, fire retardants, and physical blowing agents. The foams were produced with MDI at an isocyanate index of 300.

2.2. Butler chimney test

A Butler chimney apparatus was fabricated following the ASTM D-3014 standard [11] and used for the flammability tests. The tests were conducted on six cut specimens from material of uniform density in the center part of the foam. Each foam specimen size was $254 \times 19 \times 19$ mm^3. The cut foams were mounted on the vertical Butler chimney and ignited with a Bunsen burner for 10 s. The temperature of the Bunsen burner was monitored with a thermocouple and set to be 960 ± 5 °C. The extinguishing time of the flame, after the burner was removed from the bottom of the foams, was recorded and reported as the burning time. The PMR (percent mass retained) or char yield was determined after each test run, and the char was collected for further analysis.

2.3. Solid-state ^{13}C NMR

The ^{13}C NMR measurements were carried out using a 5 mm o.d. tube on a Chemagnetics M-100 spectrometer with a field of 2.4 T at a spinning speed of 3.5 kHz, as previously described elsewhere [12]. The spectra were accumulated using the cross-polarization technique. Each analysis consists of 10,240 scans using contact times of 4 ms and recycle delays of 2 s. The areas of the peaks were measured using electronic integration. Since the most effective FR concentration for pentane is 20 wt% (see Section 3.1) and also in order to compare the difference of HCFC-141b and pentane, four foams (18131-1, 18131-5, 18131-7 and 18131-11) and their related chars were chosen

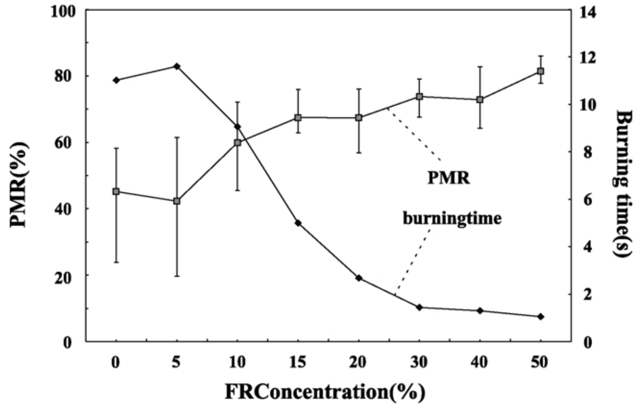

Fig. 1. Relationship of PMR and burn time with FR concentration for the HCFC-141b blown series.

for NMR analysis to show the effect of FR concentration on the structure of the chars.

2.4. Thermogravimetric analysis

All foams and their related chars were characterized using a PE-7A TGA instrument. A 5–10 mg foam or char sample was placed in a platinum holder and introduced into a micro-furnace. The heating rate was 10 °C/min under a flow of 100 ml/min air. The end temperature was 700 °C. The mass loss was continuously recorded as a function of time and temperature.

2.5. Pyrolysis–GC/MS

The Py–GC/MS studies using about 0.20 mg were conducted using a combination of a platinum pyroprobe (Pyroprobe 1000, CDS Instruments) and a HP 5890 Gas Chromatograph combined with a HP 5971A Mass Selective Detector. The pyrolysis temperature was 700 °C at a heating rate 10 °C/ms. The GC oven temperature was initially held at 35 °C for 5 min, and then was programmed to 310 °C at 4 °C/min. The temperature of the GC/MS interface was set at 300 °C. Four foams (18131-1, 18131-5, 18131-7 and 18131-11) and their related flammability chars were used in these analyses to better understand the effect of the FR on the char structure, as described in the NMR analyses.

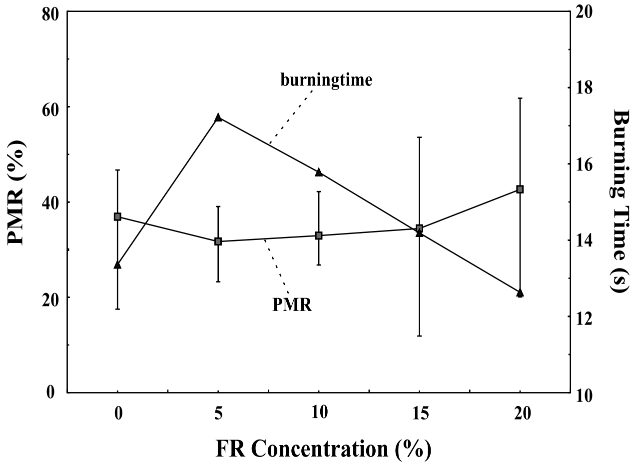

Fig. 2. Relationship of PMR and burn time with FR concentration for the pentane blown series.

3. Results and discussion

3.1. Flammability tests

3.1.1. PMR and burn times for the HCFC-141b and pentane blown foams

The variations of the burn time and PMR as a function of FR concentration are shown in Figs. 1 and 2 for the HCFC-141b and pentane series, respectively. Fig. 1 shows the variation in burn time and PMR for the rigid polyurethane foam series blown with HCFC-141b. As expected with an increasing FR concentration, the burn time decreases from 11 to 1 s, while the PMR or char yield increases from 45 to 67%. However, when the FR concentration increases over 15 wt%, no further improvement in the PMR or char yield is observed, which is consistent with an optimum FR concentration around 15 wt% for the HCFC-141b series. Similarly, the burn time decreases significantly for FR concentrations below 15 wt% going from 11 s for the foam without FR, down to 5 s for the foam with 15 wt% FR. A 1–2 s burn time is observed for FR concentrations in the range 30–50 wt%.

In contrast to the HCFC-141b series, Fig. 2 shows that with pentane blown foams, increasing the FR concentration does not result in higher PMR values until the FR level reaches a value of 20 wt%. Only when the FR concentration was over 20 wt%, did the burn time decrease to lower values than those of the foam without FR. A special phenomenon was observed for the pentane series during the flammability tests. The foam specimens melted during the combustion process and the drippings fell out of the Butler chimney holder for samples with low FR concentration (<20 wt%) or without FR. In contrast, no melting or dripping was observed for the samples with the highest FR concentration (20 wt%). This phenomena was not observed during the flammability tests of the HCFC-141b series, due to the low inherent flammability of HCFC-141b, which results in lower flame temperature during combustion (see Section 3.1.2).

Figs. 1 and 2 also show that the PMR values decrease and the burn times increase for foams with the lowest FR concentrations (5 wt% for HCFC-141b series, and 5–15 wt% in the pentane series). It appears that for low FR concentrations, the FR does not prevent the thermal degradation of the foams, and the PMR values do not increase as expected. Although the explanation for this trend is not clear, it could be attributed to direct weight loss of the FR. Further investigations will be conducted to ascertain the

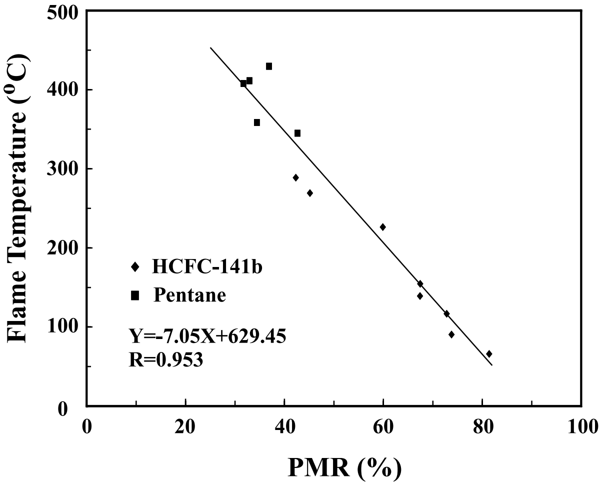

Fig. 3. Relationship of flame temperature with PMR (both HCFC-141b and pentane samples).

effect of low FR concentrations on the thermal degradation of the polyurethane foams.

For the HCFC-141b series, the FR appears to be very effective, doubling the PMR values with a significant 85% decrease in the burn times. However, the same FR does not seem to be effective for the pentane blown series, due to the inherent higher flammability of pentane compared to that of HCFC-141b [3]. Further investigations are being conducted to ascertain the different behavior of this FR in the two series and determine a suitable FR for the pentane blown polyurethane foams.

3.1.2. Flame temperatures for the HCFC-141b and pentane blown foams

Fig. 3 shows the variation of flame temperature during the flammability tests for both s foam series along with the associated PMRs. An extremely good inverse linear relationship between the flame temperature and PMR is observed, in which higher PMR correlates to lower flame temperature, regardless of the blowing agent. The results suggest that if the flame temperature can be reduced during combustion, the PMR would be increased. The flame temperature reduction can be attributed to the role of the FR in preventing volatile formation that will fuel the flame, and therefore, increase the flame temperature. Fig. 3 also shows that the flame temperature decreases with increasing FR concentration. This flame temperature reduction could be responsible for the elimination of melting and dripping in the pentane foams with higher FR concentration, even though not enough to increase the PMR values.

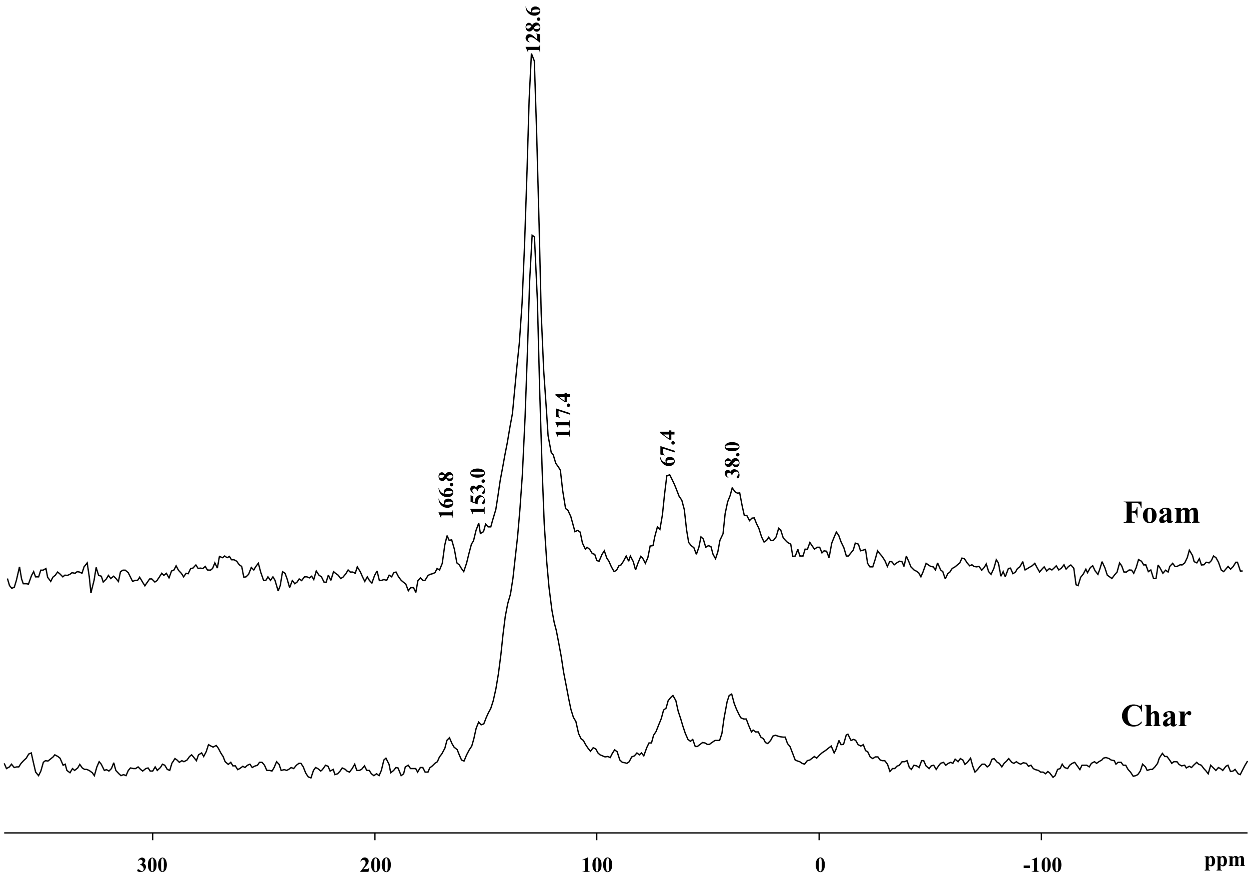

Fig. 4. ^{13}C NMR spectra of the parent 18131-5 foam (top) and char (bottom) blown using HCFC-141b with FR (20 wt%).

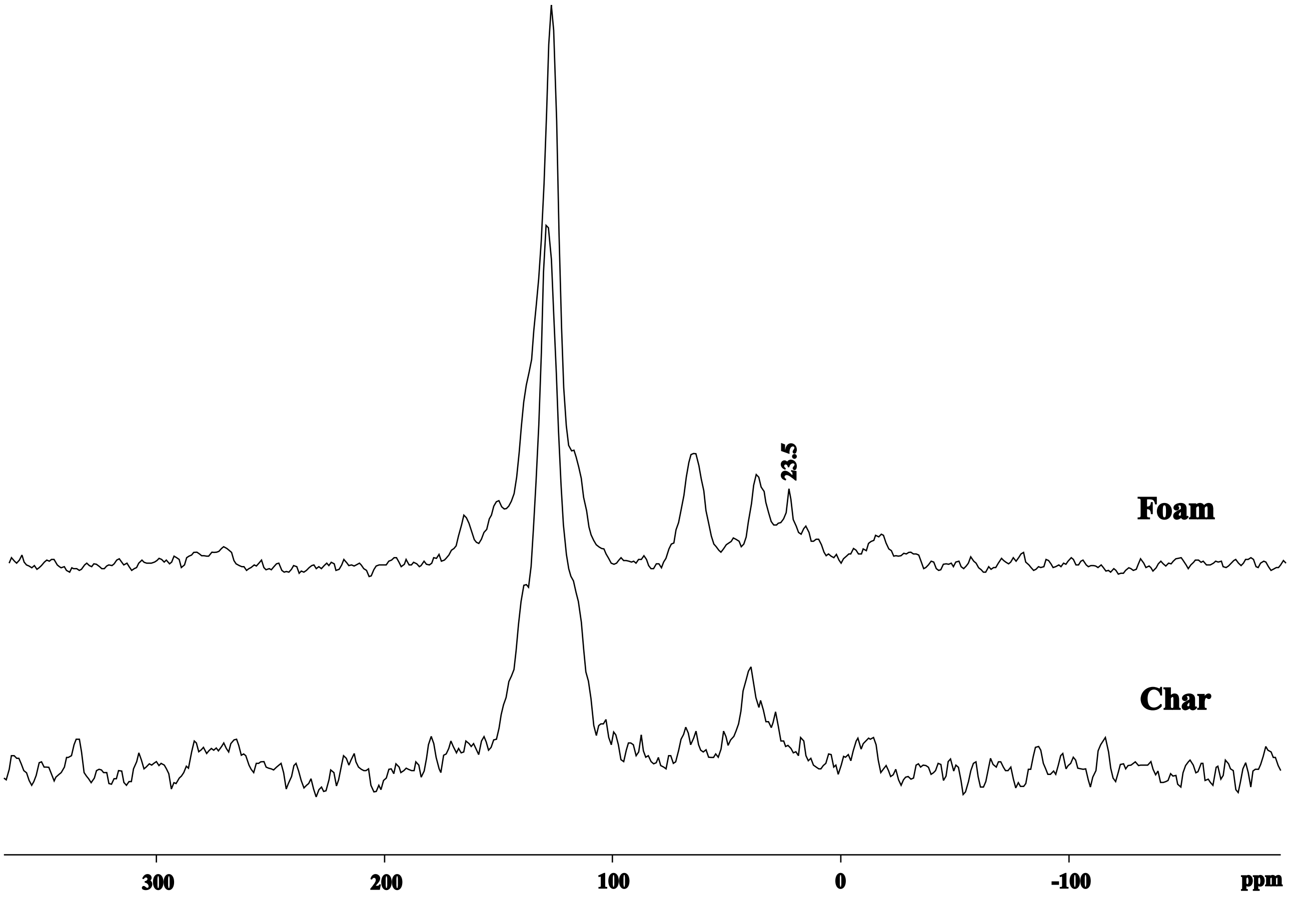

Fig. 5. ^{13}C NMR spectra of the parent 18131-11 foam (top) and char (bottom) blown using pentane with FR (20 wt%).

3.2. Solid-state ^{13}C NMR

3.2.1. ^{13}C NMR characterization of the parent foams

Figs. 4 and 5 show the ^{13}C NMR spectra of the parent polyurethane foams blown with 141b and pentane using 20 wt% FR and the resulting chars. The peaks observed at 38.5 ppm correspond to methylene aliphatic carbons, while the 66 ppm peak derives from methylene aliphatic carbons bound to oxygen. The 122 ppm peak is characteristic of aromatic carbon, and the shoulder observed at 152 ppm is the urethane carbonyl carbon (–NH–*COO–) [13–16,20]. Finally, the peak at 167 ppm is derived from carbonyl carbons from the polyester polyol.

The only difference between the spectra of the HCFC-141b and pentane foams is the presence of an additional peak at 23.5 ppm for the pentane blown sample that corresponds to the middle carbon within a methylene aliphatic chain [14]. The carbon signal derived from the HCFC-141b retained in the parent foam would be observed both in the aliphatic and the aromatic carbon regions and, compared to the pentane blown series, results in a higher total aromatic carbon content, as described below. The results indicate that some of the blowing agent is chemisorbed to the chemical structure of the polyurethane foams. Previous studies by M. Ishida et al. [13] and H. Ishida et al. [14] also observed the 23 ppm peak, but their study samples were polyurethane elastomers consisting of both soft and hard segments, and therefore, the 23 ppm peak in their results corresponded to the middle carbon within the long methylene chain structure. In this work, rigid

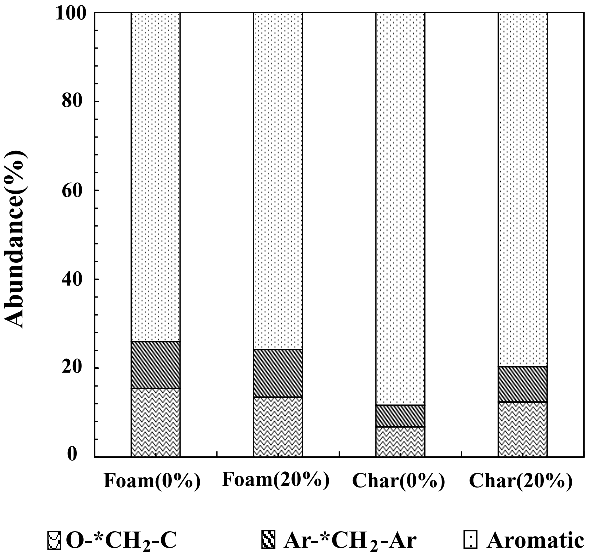

Fig. 6. Variation of the main carbon functional groups for the HCFC-141b foams with 0 and 20 wt% FR and their char counterparts.

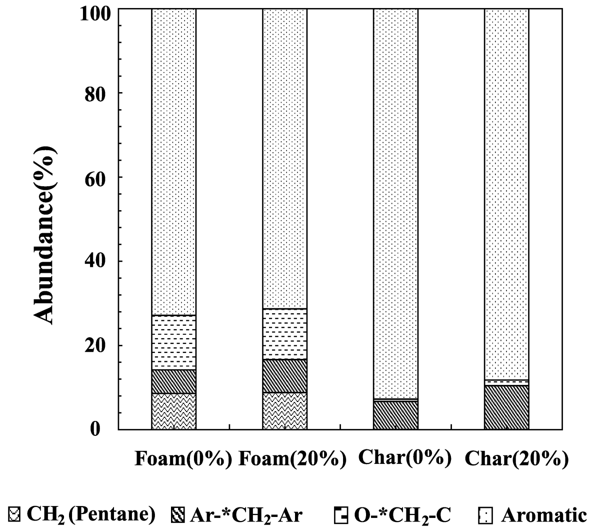

Fig. 7. Variation of the main carbon functional groups for the pentane foams with 0 and 20 wt% FR and their char counterparts.

polyurethane foams derived from poly(alkylene oxide) (phthalate esters) polyols were used, and therefore the 23 ppm peak cannot be attributed to the elastomer structure, but rather to residual pentane absorbed by the foam.

3.2.2. Comparison of the ^{13}C NMR spectra for the parent foams and the chars

Solid-state ^{13}C NMR was also used to investigate the structure of the chars generated by the flammability tests. The spectra of Figs. 4 and 5 showed mainly the same carbon functional groups for the chars and their parent counterparts, but the intensity or concentration of each carbon group varied significantly. Fig. 6 shows the variation of the main carbon functional groups for the HCFC-141b foams with 0 and 20 wt% FR and their char counterparts. As expected, there was no significant difference in the chemical moieties present in the parent foams with FR addition, indicating that the FR does not modify the parent foam chemical structure and acts only as an additive. The chars showed a lower concentration of methylene carbon and aliphatic carbon alpha to oxygen carbon with a subsequent increase in aromatic carbons. However, the char with 20% FR showed smaller changes in the abundance of the carbon functional groups than the char without FR, indicating that the FR preserves the chemical structure of the parent polyurethane foam, and therefore, also causes a higher PMR or char yield.

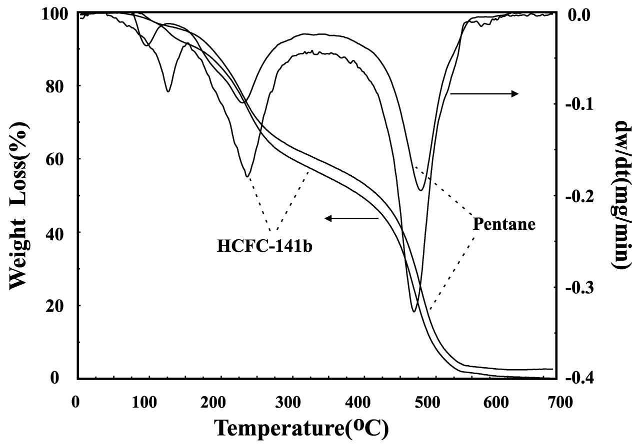

Fig. 8. TGA/DTG profiles of polyurethane foams without FR.

Fig. 7 shows the variation of the main carbon functional groups for the pentane blown foams with 0 and 20 wt% FR and their char counterparts. As previously described, the parent pentane foams have a lower aromatic content than the HCFC-141b foams, and present an additional methylene peak at 23.5 ppm. The FR is ineffective for the pentane blown series, as reflected in the higher aromatic content of the chars as previously reported by the flammability studies. The methylene aliphatic carbon that derives from pentane disappears completely even with the addition of FR, indicating the high inherent flammability of residual pentane absorbed to the polymeric network.

3.3. Thermogravimetric analysis

Fig. 8 shows the TGA/DTG profiles for both HCFC-141b and pentane foams without FR in air. It can be seen that the HCFC-141b and pentane foams have similar behavior under an air atmosphere, where three characteristic temperature regions were observed: (1) at 120–140 °C, (2) at 270–280 °C and (3) at ~510 °C. Dick et al. [20] reported similar thermal profiles under air for two regions around 300 and 550 °C. The first region (120–140 °C) can be assigned to moisture absorption by the foam, while the second (270–280 °C) is due to the thermal pyrolysis of the polymer, and the third region (~510 °C) is from the combustion of the foam. The three weight loss steps observed in the TGA/DTG profiles are consistent with previous TGA studies conducted in our laboratories under N_2 environment (unpublished work) and also reported by Font et al. [19]. The TGA profiles under N_2 have two characteristic regions at ~110 and ~280 °C, while as expected, the combustion region at 530 °C does not appear under a N_2 atmosphere.

Fig. 9 shows the TGA/DTG profiles under air for the chars obtained from the flammability tests of the foams prepared without FR. For the char samples, the TGA/DTG profiles only show one characteristic temperature region around 500 °C, which corresponds to the char combustion. The other two weight loss regions observed at lower temperatures (120–140 and 270–280 °C) for the parent foams are not observed for the chars. This is probably because during the flammability tests, the foams have lost the moisture and the polymer network has pyrolyzed, and therefore, the two lower temperature regions are not observed in the TGA/DTG profiles of the chars. Furthermore, for the char produced from the pentane sample, the DTG also shows a high temperature weight loss peak at around 600 °C. This peak is probably due to the higher temperature that the pentane foam sample experienced during the charring process, as reported from the flammability tests

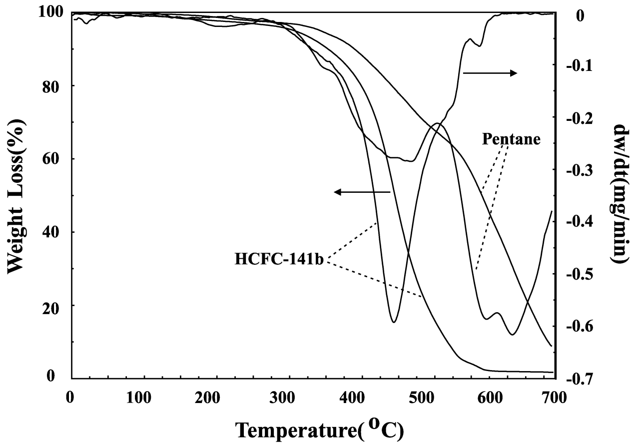

Fig. 9. TGA/DTG profiles of the chars without FR.

(Fig. 3). This high temperature charring results in condensed aromatic structures, which react with oxygen at higher temperatures. This is also consistent with the NMR data that showed that the chars from the pentane blown series have higher aromatic content than the 141b chars (Figs. 6 and 7).

Figs. 10 and 11 show the TGA/DTG profiles under air for the chars from the flammability tests of HCFC-141b and pentane foams with FR. These chars have different profiles compared to the foams without FR described above. The TGA profile of the char from the HCFC-141b foam containing 5 wt% FR is very similar to that described for the char of the foam without FR (Fig. 9), where only the combustion region is observed. In contrast, the TGA/DTG profile of the char of the HCFC-141b sample containing 20 wt% FR concentration in the parent foam also presents a peak observed in the temperature region of about 270–280 °C, that represents the polymer pyrolysis, as reported for the TGA profiles of the parent foams in Fig. 8. The Butler chimney flammability tests show that the FR was effective when its concentration is over 10 wt% (Fig. 1). Accordingly, the polyurethane foams with high FR concentration do not decompose completely during the combustion process in the flammability test, and some original polymer structure still remains in the char giving rise to the peak at 270–280 °C in the TGA/DTG profiles.

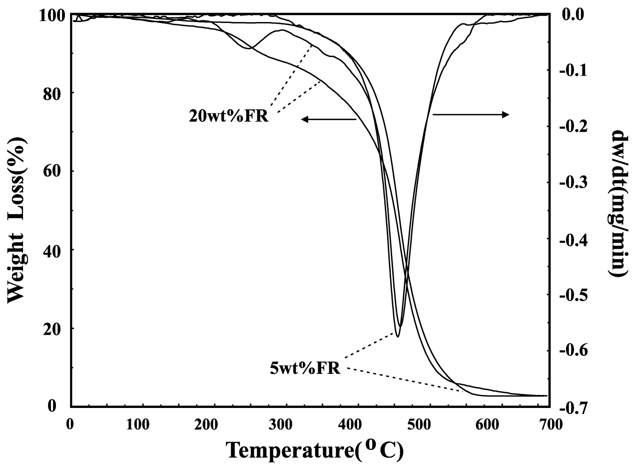

Fig. 10. TGA/DTG curves of HCFC-141b series chars with FR.

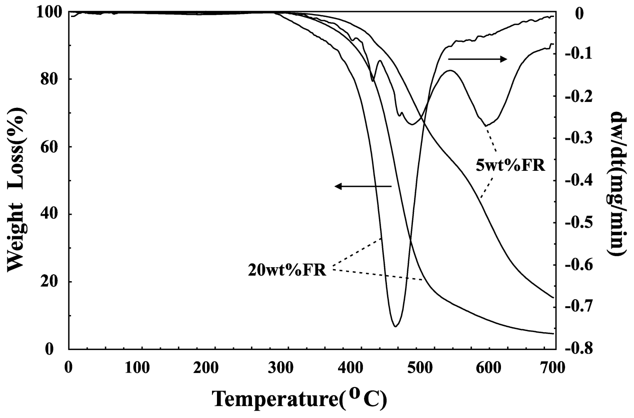

Fig. 11. TGA/DTG curves of pentane chars with FR.

On the other hand, the TGA/DTG profiles of the pentane chars (Fig. 11) do not show the pyrolysis region (270–280 °C), since these chars have reacted more extensively during the flammability tests (Fig. 7). Furthermore, there were two peaks for the pentane chars containing low FR concentration in their foams at temperatures around 500 and 600 °C, respectively. However, when the FR concentration gets to 20 wt%, the peak at 600 °C disappears. This DTG peak at 600 °C was previously observed for the char produced from the pentane sample without FR (Fig. 9), and was attributed to the higher temperature that the pentane foam samples experienced during the charring process (Fig. 3). This will result in more condensed aromatic structures, as reported by the NMR studies (Fig. 7), which will react at higher temperatures. Furthermore, the 600 °C peak is more predominant for the char without FR (Fig. 9) than for the char with 20 wt% FR (Fig. 11). This is consistent with the higher temperature experienced by the char without FR (430 vs. 408 °C) and its higher carbon aromaticity (86 vs. 79).

The maximum reactivity at maximum weight loss

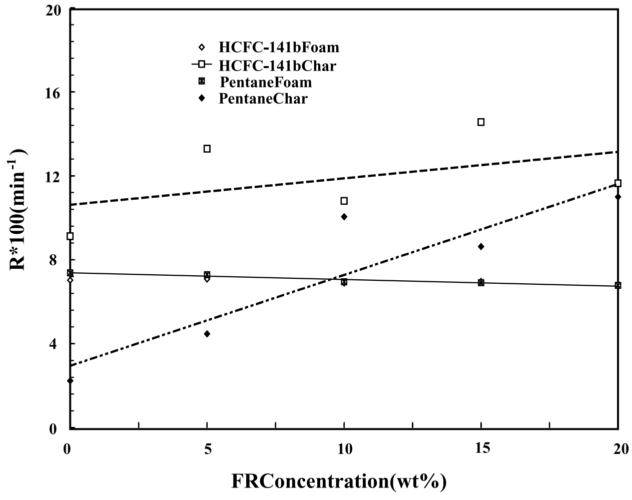

Fig. 12. Relationship of $R_{\mathrm{max,temp}}$ with FR concentration.

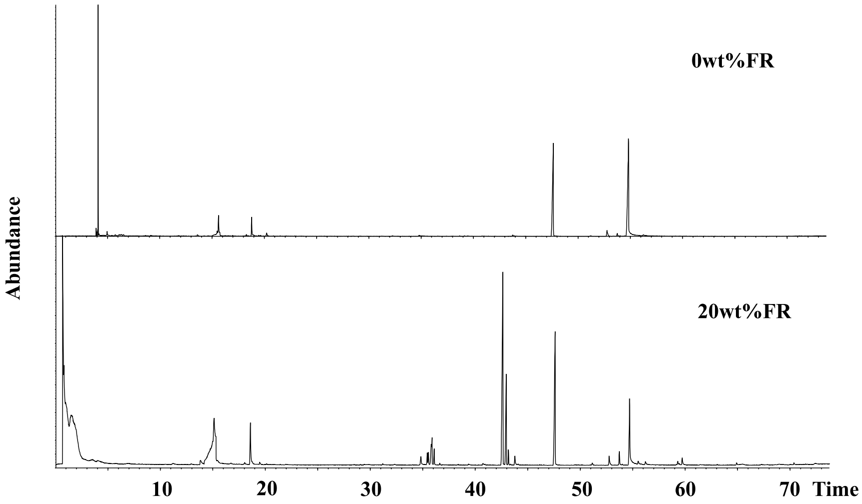

Fig. 13. Chromatograms of the Py–GC/MS products of the parent polyurethane foam blown using HCFC-141b with 0 wt% (top) and 20 wt% (bottom) FR.

temperature can be defined as follows

$$R_{\max,\text{temp}} = -\frac{1}{w_0}\frac{\mathrm{d}w_{\max}}{\mathrm{d}t}$$

where w_0 is the initial weight of the sample, and the DTG peak selected to calculate the maximum reactivity is the one observed at 500 °C.

Fig. 12 shows that the values of $R_{\max,\text{temp}}$ are very similar for all the HCFC-141b and pentane foams, while there is a slight variation for the values determined for the chars. It appears that the $R_{\max,\text{temp}}$ of the char increases with increasing FR concentration, indicating that the FR affects the structure of the char resulting from the combustion process. With higher FR concentration in the foam, the char has a more open structure and shows higher reactivity. In contrast, the chars with low or no FR concentration in the foam, have less open structures and are more difficult to react with air. The solid-state ^{13}C NMR studies show that the higher the FR concentration in the foam, the lower fraction of aromatic carbon in the char, and therefore, support these findings. However, the differences in reactivity observed by the TGA analysis are smaller than those observed from the flammability tests (Figs. 1 and 2). This could be due to the slow heating used in the TGA analysis, while the flammability tests use a high temperature flame environment, where the FR can more clearly show its retardancy during the combustion process.

3.4. Pyrolysis–GC/MS

Figs. 13 and 14 show the Py–GC/MS chromatograms of the parent polyurethane foams blown with HCFC-141b and pentane using 0 and 20 wt% FR, respectively. Both rigid foams have flash pyrolysis products at retention times 13–17, 17.5–20, 46–49 and 54–56 min in the GC, while their correspondent MS traces are 93/103, 106, 193 and 198*m/z*, respectively. The major difference between the two foams is observed in the products at retention times 35–37 and 41–44 min, which do not appear in the foam without the FR additive. The MS traces indicated that these products are

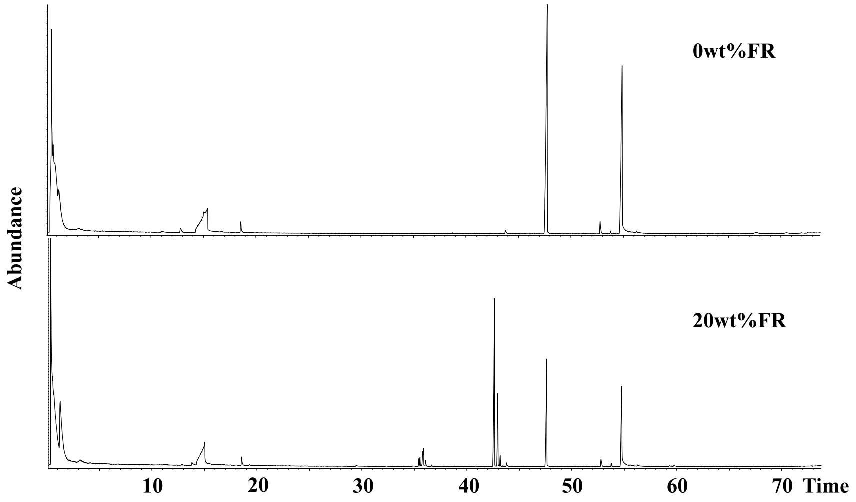

Fig. 14. Chromatograms of the Py–GC/MS products of the parent polyurethane foam blown using pentane with 0 wt% (top) and 20 wt% (bottom) FR.

fragments of the FR additive. In addition, the lower abundance of the pyrolysis products in the range of 48–55 min in the foam with 20 wt% FR indicates that the aromatic units are retained in the char and only the smaller units are being volatilized, due to the preserving effect of the FR. The major difference in the Py–GC/MS chromatograms for the HCFC-141b and the pentane foams is for the pyrolysis products observed at 55 min. The concentration of pyrolysis products for the pentane series is much larger than that for HCFC-141b series, and therefore, resulting in a higher weight loss for pentane foams during pyrolysis and combustion than for the HCFC-141b foams. This is in agreement with the flammability test results, where the pentane series presented much lower PMR values than those reported for the HCFC-141b series.

4. Conclusions

In order to understand the effect of FR and blowing agents on the thermal stability of the rigid polyurethane foams and the structure of their chars, two series of foams produced with different blowing agents (HCFC-141b and pentane) and various concentrations of a FR (0–50 wt% for HCFC-141b series and 0–20 wt% for pentane series) were investigated using standard flammability tests, solid-state ^{13}C NMR, TGA and Py–GC/MS.

The flammability tests indicate that there seems to be an optimum FR concentration of ~15 wt% for the polyurethane foam blown with HCFC-141b for this formulation. In contrast, for the pentane series an increase in the FR concentration did not result in higher PMR values until the FR concentration reached values of 20 wt%. The PMR results show an excellent linear relationship with flame temperature, where lower the flame temperature higher the PMR, regardless of the blowing agent used. Therefore, if the flame temperature can be reduced during combustion, the PMR would be increased. The flame temperature reduction can be attributed to the role of the FR that prevents volatile formation that will fuel the flame, and therefore, increase the flame temperature.

The solid-state ^{13}C NMR studies show that some of the blowing agent (pentane) is chemisorbed to the chemical structure of the polyurethane foams. The chars with FR have smaller changes in the abundance of the carbon functional groups than the chars without FR. The TGA results show that the maximum combustion reactivity of the char increases with increasing FR concentration in the foams. The results indicate that the FR can preserve the chemical structure of the polyurethane foam, and therefore, produce higher PMR or char yield. The Py–GC/MS studies indicated that the FR additive could be readily volatilized. In addition, the lower abundance of the pyrolysis products in the range of 48–55 min in the foam with 20 wt% FR indicate that the aromatic units are retained in the char and smaller units (aliphatic oxygenated functional groups) are being volatilized.

In summary, it can be concluded that the above analytical protocol, that includes a standard flammability test, solid-state ^{13}C NMR, TGA and Py–GC/MS has shown conclusively that the addition of FR to the foam formulation preserves the original chemical structure of the parent foam blown with HCFC-141b by limiting the volatilization of small molecules. The FR investigated here was not effective for the pentane blown series, as reflected in the lower PMR values reported and higher aromatic content of the flammability chars.

Acknowledgements

The authors of this paper would like to thank SAMCOM, Air Products and Chemicals Inc., for financial support of this research.

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