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ABSTRACT

With the ongoing phase-out of ozone depleting substances in accordance with the Montreal Protocol and with the increasing concern over global climate change, there is a continuing need to develop and understand more environmentally acceptable blowing agents, such as for the production of extruded polystyrene (XPS) foam used for thermal insulation. HFC-134a has been identified as a potential non-ozone depleting replacement for HCFC-142b in the production of thermal insulating XPS foam boards. However it is known to suffer from deficiencies due to its relatively low solubility in polystyrene resin, resulting in higher operating pressures and higher density foams with unacceptably small cell size. This work presents results examining the use of HFC-32 (difluoromethane) as a coblowing agent with HFC-134a in the production of XPS foams. HFC-32 was found to be a particularly effective blowing agent for polystyrene on its own and can be used to improve foams blown with HFC-134a while maintaining its attractive properties: good insulative value, low flammability, and high blowing power.

MATERIALS AND EQUIPMENT

The blowing agents used in this study were 1-chloro-1,1-difluoroethane (HCFC-142b), 1,1,1,2-tetrafluoroethane (HFC-134a) and difluoromethane (HFC-32). They were supplied by Arkema and provided under the trade names Forane® 142b, Forane® 134a, and Forane® 32, respectively. Table 1 compares selected physical properties of the pure component blowing agents. HFC-134a and HFC-32 are both non-ozone depleting with lower global warming potentials (GWP) than HCFC-142b. HFC-32 has a relatively low flammability, with its LFL, autoignition temperature, and heat of combustion between that of HCFC-142b and HFC-134a. The three blowing agents are of low toxicity, with TLV/TWA (threshold limit value / time weighted average) of 1000 ppm.

Three grades of general-purpose polystyrene were used in this study. Two grades were obtained from Total Petrochemicals: PS 535 and PS 523. PS 535 is a high heat, crystal polystyrene designed for injection molding, extrusion, and blow molding with a melt flow index (MFI) of 4.0 g/10min. PS 523 is a high flow, high heat strength foam grade polystyrene resin with a MFI of 11.0 g/10min. The third grade, PS-3, was another foam grade polystyrene resin with a reported MFI of 11.0 g/10min. Talc was used a nucleating agent at loadings from 0% - 0.5wt% in resin as indicated.

Foam extrusion runs were conducted using two extruder systems, a 50mm and a 27mm Leistritz counter-rotating twin-screw extruders setup for foam processing. Figure 1 shows the screw configuration and schematics of the overall setup used for the 50mm extruder. The first 4 zones of the extruder were used to heat and soften the base material. Molten PS was then pushed through a reversed flight kneading block and a series of four shear discs that generate the melt seal prior to the injection of the blowing agents. The remaining barrel sections, from the injection zones to the end of the extruder, were set at the selected measurement temperatures. A gear pump located at the end of the system was used to control the melt pressure in the system. The 50mm extruder was also equipped with an on-line process control rheometer (PRC) and an in-line ultrasonic sensor between the extruder outlet and the die. Detailed results on the rheological behavior of the PS mixed with the various blowing agents, as well as solubility results at processing temperatures, will be reported in a separate paper [3].

Table 1: Physical Properties of Pure Components

	HFC-134a	HFC-32	HCFC-142b
Formula	CF_3-CH_2F	CH_2F_2	CH_3-$CClF_2$
Molecular Weight (g/mole)	102	52	100
Boiling Point at 1 atm (°C)	-26.1	-51.7	-9.2
Vapor Pressure at 25°C (bar)	0.666	1.69	0.338
Lower Flammability Limit (%v/v)	None	14.4	8.0
Heat of combustion[1] (kJ/kg @25°C)	1193	3518	6169
Autoignition Temperature (°C)	743	648	632
TLV / TWA (ppm)	1000	1000	1000
Ozone Depletion Potential (ODP)	0	0	0.066
Global Warming Potential (100yr)[2] IPCC 2007 (SAR 1995)	1430 (1300)	675 (650)	2310 (1800)

Dies with openings ranging from 2 to 4 mm and standard die land length of 1 mm were used in extruding the foamed rod specimens. Die openings were selected in order to generate enough backpressure to inhibit premature cell nucleation.

Using the 50mm extruder, blowing agents were injected separately into the extruder with the feed rates adjusted to provide the desired blend composition and overall blowing agent loading. They were fed to the extruder using liquid chromatography pumps. Both HFCs were stored in autoclaves pressurized at 5.5 MPa (800 psi) using a blanket of dry nitrogen that maintains the HFCs in liquid state through the whole delivery system, thus ensuring a constant and proper operation of the liquid chromatography pumps. Loss in weight was constantly monitored to ensure accuracy in blowing agent concentrations.

The system was operated at a nominal resin feed rate of 20 kg/hr (44 lb/hr) of the Total Petrochemicals PS 535. Some formulations were modified by adding 0.5 wt% talc in order to promote cell nucleation. These formulations were typically those with less than 4 wt% HFC-134a.

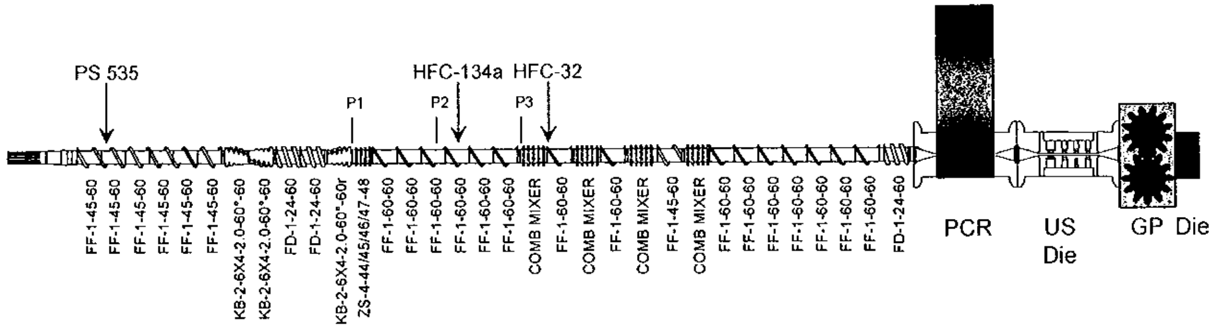

Figure 1: Schematic of the 50mm extrusion setup

The general setup and screw configuration of the 27mm extruder was similar to that of the 50mm extruder. Extrusion experiments using the 27mm extruder were conducted at a nominal feed rate of 4.54 kg/hr (10 lb/hr). The first zones of the extruder were used to heat and soften the base material and to generate a melt seal. Blowing agents were injected past the melt seal. The remaining barrel sections, from past the injection zone to the end of the extruder, were set to cool the melt to the desired temperature, T_{melt}. A gear pump located at the end of the extruder barrel was used to control melt pressure in the extruder. The extruder was equipped with either a 2mm strand die with a 1mm land length or an adjustable-lip slot die, gap width of 6.35mm, which permitted control of the die back pressure. Of the foam samples shown, only the one in Figure 6 was produced using the adjustable-lip slot die. The 27mm extruder was not equipped with either an on-line rheometer or an ultrasonic sensor.

With the 27mm extruder, blowing agents were pumped using high-pressure syringe pumps to a single injector port in the extruder barrel. Backpressure in the feed lines was maintained at around 12.4 MPa (1800psi) using a backpressure regulator. Loss in weight was monitored to ensure constant feed rates for the blowing agents. For blends of blowing agents, either multiple pumps were used, with the feed rates adjusted to achieve the desired composition, or the blends were prepared in advance and delivered using a single pump.

The density, ρ, open cell content (OCC), and cell size, d, were measured for foam specimens collected during each run. For samples collected from the 50mm extruder system, foam density measurements were made by carefully weighing foam specimens followed by their volume evaluation by water displacement. Reproducibility was found sufficiently good to limit measurements to three replicates. For foam samples collected from the 27mm extruder system, density was measured according to ASTM D792. For all samples, open cell content was estimated by gas pycnometry following ASTM D6266 standard. SEM micrographs were taken from freeze-fractured surfaces of foamed specimens.

FOAMING WITH PURE COMPONENT BLOWING AGENTS

Using the 27mm extruder, polystyrene foams were produced using HFCFC-142b, HFC-134a, and HFC-32 as pure component physical blowing agents.

HCFC-142b

To benchmark the extrusion system, XPS foams were produced using HCFC-142b as the physical blowing agent. Using any of the three grades of polystyrene resin, it was relatively easy to produce closed-cell, low density foams, as low as 32 kg/m^3 (2 pcf), with cell size of around 0.2 – 0.3mm using a formulation with 10 – 11wt% 142b. Figure 2 shows an SEM micrograph of a typical 142b-blown XPS foam for this extrusion system. A nucleating agent (e.g. talc) is required to achieve efficient foaming and was normally used at a loading of around 0.5wt% in the resin.

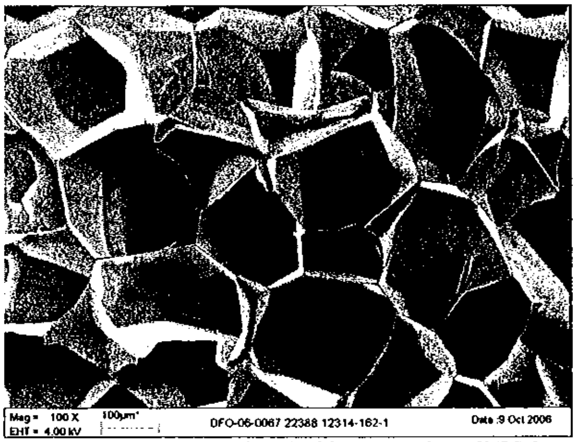

Figure 2. SEM micrograph (100x) of fracture surface of XPS foam blown with 11wt% HCFC-142b. $\rho = 32.6$ kg/m^3, OCC < 5%, d ~ 0.2 – 0.3mm. Resin: PS 535, 0.5% talc. $T_{melt} = 112$°C

HFC-134a

When using HFC-134a as the physical blowing agent, the low solubility of 134a in polystyrene may lead to processing difficulties. This includes requiring higher operating pressures to prevent premature degassing of the blowing agent. Additionally, using 134a also tends to result in higher density foams of smaller cell size while being more prone to defects such as blow holes and macrovoids. In foam extrusion trials the practical solubility limit of 134a was found to be between 6 and 7wt%, which is similar to results from other studies [4]. Increasing the loading above this level tended to increase the occurrence of open cells, macrovoids, blowholes, skin defects, and foam collapse. At 6.8wt% 134a, closed-cell foam of fine cell structure can be extruded as shown in Figure 3, which had a density of 65.1kg/m^3 (4.1pcf). Increasing the 134a content to 8wt%, however, resulted in an even finer cell structure with high open cell content, macrovoids and defects without much reduction in density as seen by foam sample shown in Figure 4. No nucleating agent was used in the production of the foams shown in Figures 3 and 4 as HFC-134a has a high enough nucleation potential to initiate foaming.

The fine cell structure commonly seen in HFC-134a-blown foams is useful for some applications, such as for the production of microcellular foams. However, for XPS insulating foam, a larger cell size, such as seen in Figure 2, is normally preferred in order to provide acceptable mechanical strength while limiting the overall thermal conductivity. In contrast, low density foams with very small cell size may be soft and easily compressed.

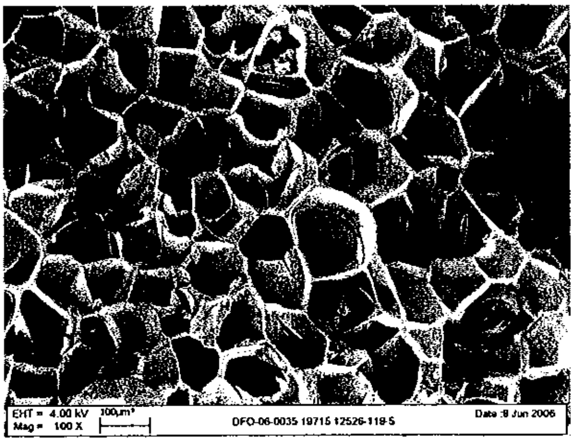

Figure 3. SEM micrograph (100x) of fracture surface of XPS foam blown with 6.8wt% HFC-134a. $\rho = 65.1$ kg/m^3, OCC < 10%, d < 0.15mm. Resin: PS-3, 0% talc. $T_{melt} = 128°C$

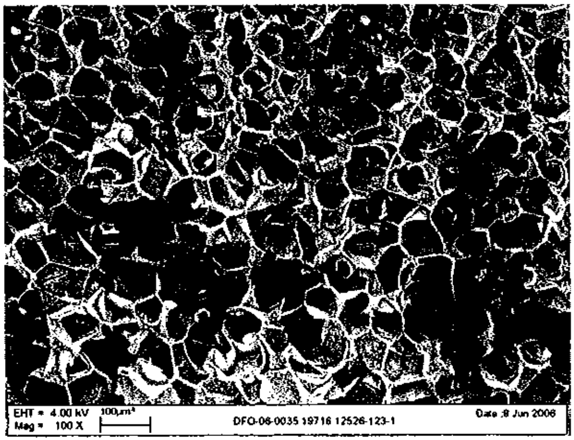

Figure 4. SEM micrograph (100x) of fracture surface of XPS foam blown with 8wt% HFC-134a. $\rho = 58.9$ kg/m^3, OCC > 15%, d < 0.13mm. Resin: PS-3, 0% talc. $T_{melt} = 131°C$

HFC-32

HFC-32, with its relatively low molecular weight of just over half that of HFC-134a, can be used at a lower loading than HFC-134a or HCFC-142b to achieve the same reduction in density. Density reduction is driven by the gaseous volume of the blowing agent, which in turn is dependent upon the moles of blowing agent used. As such, though foaming formulations are often expressed on a weight basis it is often useful to compare them on a molar basis. When considering a foaming formulation we define the 134a-equivalent composition as the wt% of HFC-134a required to provide the same molar quantity of total blowing agent as the formulation we are considering.

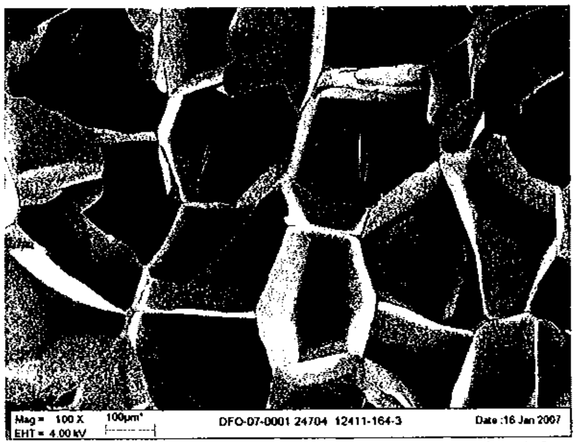

Figure 5. SEM micrograph (100x) of fracture surface of XPS foam blown with 4.0wt% HFC-32. $\rho = 44.4$ kg/m^3, OCC < 5%, d ~ 0.2 – 0.4mm. Resin: PS-3, 0.25%talc. $T_{melt} = 125°C$

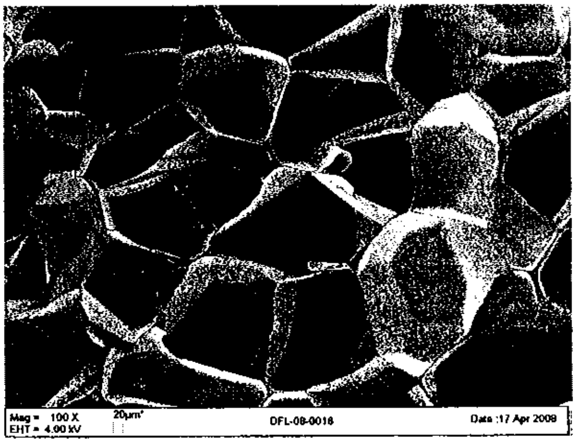

Figure 6. SEM micrograph (100x) of fracture surface of XPS foam blown with 4.9wt% HFC-32. $\rho = 39.8$ kg/m^3, OCC < 10%, d < 0.13mm. Resin: PS 523, 0.5%talc. $T_{melt} = 123°C$

Using 4.0wt% HFC-32 in the formulation, equivalent to 7.8wt% 134a on a molar basis, permitted production of low density, closed-cell foam as shown in Figure 5. Increasing the HFC-32 content to 4.9wt% in the formulation, which is equivalent to 9.6wt% 134a on a molar basis, results in a further reduction in density, down to about 40 kg/m^3 (2.5pcf), but with a slight increase in defects and open cells. HFC-32 was found to have a much lower nucleation density than 134a, likely due to a combination of increased solubility in polystyrene, lower use level, and greater diffusivity through the resin. A minimal quantity of talc in the resin formulation was required to yield efficient foaming without over-nucleation; 0.25wt% talc in the polystyrene resin was found to be sufficient. Average cell sizes of 0.2 – 0.3 mm were achievable when using HFC-32 as the physical blowing agent.

HFC-32 was found to be a very effective blowing agent for extruded polystyrene foaming, permitting production of low density and closed-cell foams of enlarged cell size at a reduced blowing agent loading. HFC-32 is an emissive blowing agent and therefore will not likely contribute to the long-term R-value of thermal insulating foams. However, HFC-32 is very useful in the production of non-insulating extruded thermoplastic foams such as those used for packaging, thin sheets, graphic art board, floral craft, etc.

Combining HFC-134a with HFC-32 in blowing agent compositions will take advantage of the positive traits of both pure components: the thermal insulating contribution of 134a with the blowing efficiency and cell size enlargement of 32.

FOAMING WITH BLOWING AGENT BLENDS OF HFC-134a / HFC-32

27mm Leistritz extrusion system: In this work, the use HFC-134a and HFC-32 as coblowing agents for XPS foaming was first studied using the 27mm Leistritz extrusion system previously described. Two blends were tested, an 80/20 and a 63/37 wt/wt blend of 134a/32. Blowing agent blends were pre-prepared to the desired component ratios with the formulated blend pumped to the extruder during the foaming experiments.

Using the 80/20 blend of 134a/32, the resulting foam properties were similar to those using pure 134a as the blowing agent. At 6.6wt% loading of the 80/20 blend, equivalent on a molar basis to 7.3wt% 134a, the resulting XPS foam, shown in Figure 7, had a fine cell structure and low open cell content. This is similar to what was observed using ~ 7wt% pure 134a and can be inferred by comparing Figure 7 to Figures 3 and 4.

Increasing the ratio of HFC-32 in the blend was found to have a beneficial impact on the resulting foam properties. As shown in Figure 8, using a 63/37 blend of 134a/32 permitted production of lower density, closed-cell foam with larger cell size than with pure 134a. At about 6.1wt% of the 63/37 blend, the resulting foam had a density of only 51.9 kg/m^3 (3.2pcf) while maintaining a large cell size, with an average cell diameter of approximately 0.2 mm.

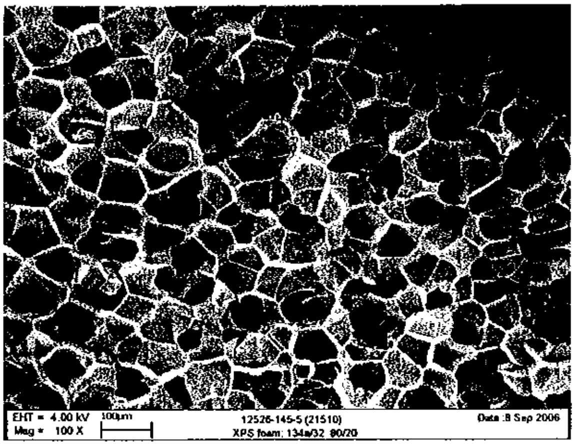

Figure 7. SEM micrograph (100x) of fracture surface of XPS foam blown with 6.6wt% 134a/32 (80/20). $\rho = 56.9$ kg/m^3, OCC < 10%, d = 0.07 – 0.13 mm. Resin: PS-3, 0%talc. $T_{melt} = 121°C$

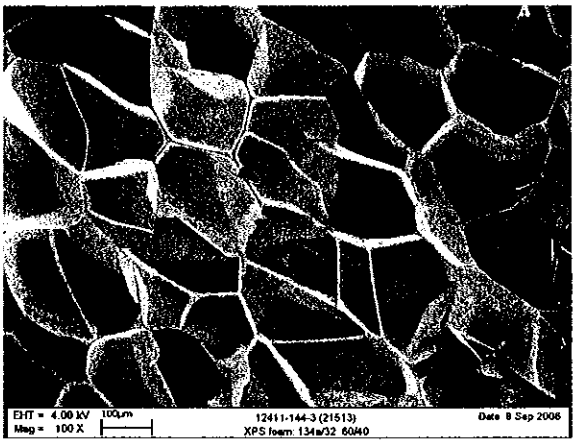

Figure 8. SEM micrograph (100x) of fracture surface of XPS foam blown with 6.1wt% 134a/32 (63/37). $\rho = 51.9$ kg/m^3, OCC < 5%, d ~ 0.2mm. Resin: PS-3, 0%talc. $T_{melt} = 126°C$

The 6.1wt% loading of the 63/37 blend would be equivalent to 8.5wt% 134a on molar basis. Though one might expect a resulting foam density of around 52 kg/m^3 or lower using 8.5wt% 134a, it would require very high operating pressures and likely generate foams with significant defects, very fine cell structure, and increased open cell content.

50mm Leistritz extrusion system: Following the initial foam extrusion experiments on the 27mm Leistritz extrusion system, a more detailed analysis of blowing agent blends of HFC-134a and HFC-32 was conducted using the 50mm Leistritz extrusion system described earlier

Emphasis was placed on blowing agent compositions containing a majority of HFC-134a in order to maintain the thermal insulating benefits brought by HFC-134a in the final foamed product. Four different blowing agent blend compositions were investigated, nominally containing 0%, 20%, 30%, and 40wt% HFC-32. In terms of the blowing agent content in the overall formulation, the HFC-32 content ranged from 0 – 5.5wt% and the HFC-134a content ranged from 3.5 – 8.1wt%.

Figure 9 shows the foam density plotted versus the total physical foaming agent (PFA) content in terms of the wt% equivalents of HFC-134a on a molar basis. As already mentioned, density is mostly driven by the overall molar content of blowing agent, and as such the various sets of data for different ratios of 134a/32 nearly collapse onto a single master curve.

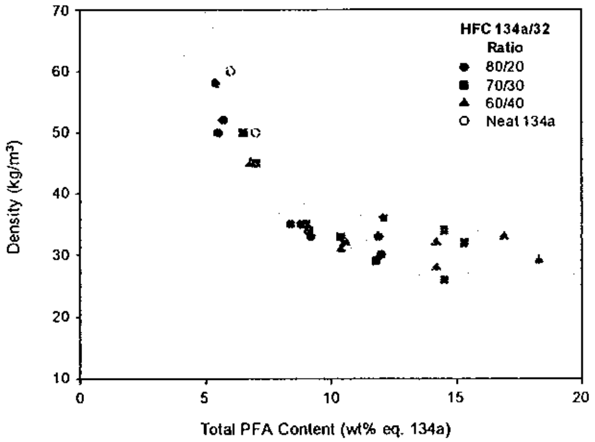

Figure 9. Density of XPS foams blown with various 134a/32 mixtures. Melt temperature ranged from 120°C to 140°C.

The results can be separated into two regions: In the low blowing agent content region, as the blowing agent loading increases there is a steady decrease in resulting foam density up to approximately 7.5 to 8wt%-equiv. of 134a. Further increases in the blowing agent loading, into the high content region, do not provide for much additional density reduction. Even though HFC-32 required lower pressures to be maintained in solution compared to an equivalent molar quantity of HFC-134a [3], these high blowing agent loading formulations may require very high operating pressures while also being more prone to defects, open cell formation, etc.

This critical concentration that lies in the 7.5-8wt% range of 134a, and above which no further density reduction can be achieved, can be compared to a similar observation by Gendron and co-workers [5] who noted a plateau in the plasticization curve for polystyrene at around 7.5wt% 134a, which is believed to correspond to the practical solubility limit of HFC-134a in polystyrene extrusion foaming. The present results tend to indicate that blends of HFCs still obey to that same practical limit.

The same data can also be represented as a function of the individual blowing agent contents. Figures 10 and 11 show the density and cell size of the 134a/32 blown foam samples as a function of the wt% HFC-32, for various specific 134a contents.

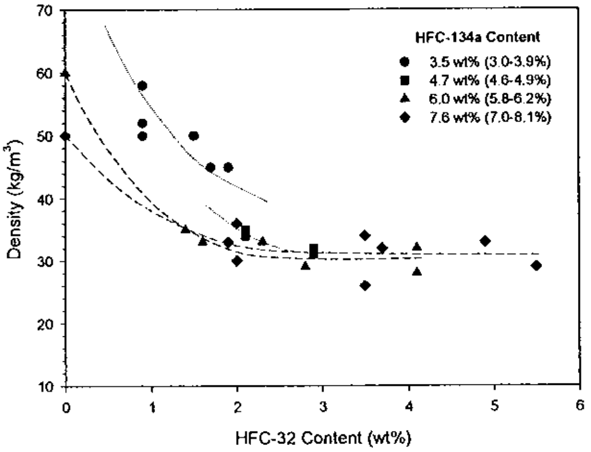

Figure 10: Density of XPS foams blown with various 134a/32 mixtures. Melt temperature ranged from 120°C to 140°C.

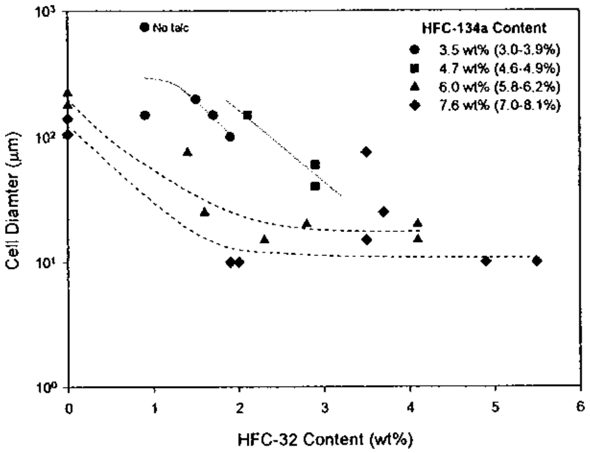

Figure 11: Average cell diameter in XPS foams blown with 134a/32 mixtures. Melt temperature ranged from 120°C to 140°C. Foams blown with 3-4 wt% 134a were nucleated with 0.5 wt% talc, the only exception being the data point identified on the graph

Of particular interest are the data shown as squares for 4.7% (4.6 – 4.9%) 134a that displayed a good balance between cell size and density. Though not shown in this paper, most of the foam specimens shown in Figures 10 and 11 unfortunately had high open cell content or signs of significant over expansion, unlike the samples produced in the first stage of the study using the smaller 27mm Leistritz extruder. This is partly due to the very fine cell structure exhibited by foam samples produced at higher blowing agent content, but other possible causes for this include inadequate die design or inappropriate resin grade selection, or both. In some cases, the foamable resin could not be cooled and extruded at the optimal foaming temperature due to problems with extrudate melt fracture, high torque loads, or excessive die backpressure. Optimizing the die geometry and resin selection should improve this as evidenced by tests conducted on the smaller extrusion system.

CONCLUSIONS

Extruded polystyrene foaming trials showed that HFC-32 is a particularly effective blowing agent for polystyrene, permitting production of low density, closed-cell foam with large cell size while using a limited content of blowing agent in foamable formulations. HFC-32 should therefore be a useful blowing agent for the production thermoplastic foams used for packaging, floral craft, thin sheet, graphic art board, and the like.

To identify blowing agent formulations useful in the production of XPS insulating boards, blowing agent combinations of HFC-134a and HFC-32 were investigated to take advantage of HFC-134a's contribution to long term R-value and of HFC-32's blowing efficiency. The results indicate that limiting the overall blowing agent loading will help reduce the occurrence of defects and allow for less challenging processing conditions.

The best results were seen when using blowing agent compositions containing at least 30% HFC-32 to produce foams with a good balance between density and cell size. The results suggest that using formulations containing between 4 and 5wt% HFC-134a and between 1 and 2wt% HFC-32 should be useful in producing low density foams that may have application for thermal insulation.

This study also examined the processing characteristics for extrusion foaming with 134a/32 blends, including on-line rheology and in-line degassing pressure behavior. Results from that part of the project will be published at a later time [3].

ACKNOWLEDGEMENTS

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