

PROCESSING AND PROPERTIES OF POLYSTYRENE FOAMED USING HYDROFLUOROOLEFINS

*Richard Gendron and Michel F. Champagne, National Research Council of Canada, Boucherville
James M. Bowman, Honeywell, Buffalo, NY*

Abstract

The environmental pressure on extruded polystyrene (XPS) insulation foam manufacturers has continued since the early days of ozone-depleting substances regulation. Further, insulation performance and standards for construction applications continue to increase globally, as energy costs increase. The challenges of producing high performance products from a constantly evolving family of blowing agents forced industry to massively invest in R&D. This paper examines the properties and processing behavior of XPS foams blown from the latest generation of blowing agent: hydrofluoroolefin (HFO). The focus of the paper will be on the solubility of the HFO in polystyrene, its impact on the gas-laden melt rheology and on the structure/properties of the resulting foams. Honeywell is commercializing this HFO platform as Solstice™ Blowing Agents.

Background: Solstice™ Blowing Agents

Honeywell has developed two such fourth-generation products: trans-1,3,3,3-tetrafluoropropene, (1234ze(E)), trade named Honeywell Solstice™ Gas Blowing Agent (GBA), a gaseous blowing agent; and a liquid blowing agent: trans-1-chloro-3,3,3-trifluoropropene (1233zd(E)) trade named Honeywell Solstice™ Liquid Blowing Agent (LBA). Both products successfully incorporate required environmental properties, while maintaining the no flammability, non-VOC, and high performance characteristics that have differentiated fluorocarbon blowing agents as the best choice for high performance foam insulation applications. These two fourth-generation blowing agents are also ideal for those applications where a flammable blowing agent is unsafe, too costly to use, or fails to provide the desired foam performance. These new high performance materials, while they contain fluorine, also contain an olefin structure, and are therefore referred to as haloalkenes. Because of the presence of a double bond in the molecule backbone, these haloalkenes are a separate and distinct class of materials from their predecessor HFC materials, resulting in a much shorter atmospheric lifetime than their precursor fluorocarbons, thereby resulting in a much lower global warming potential, or GWP.

In the EU, Solstice LBA is in the REACH Registration process, and has been approved for use in

Japan under the Japan Chemical Substances Control Law. In the U.S., Honeywell has completed Solstice LBA SNAP and PMN filings and the U.S. EPA is currently reviewing these filings. Solstice LBA development is significantly underway, with major successful customer trials completed or underway in all major applications. Recently, Honeywell announced plans to build a commercial Solstice GBA (1234ze(E)) commercial manufacturing plant at Baton Rouge, Louisiana, USA – the plant is expected to be in operation in 2013.

Introduction

This work examines the use of Solstice GBA, hereafter referred to as 1234ze(E) (trans 1,3,3,3-tetrafluoropropene) as the main blowing agent and Solstice LBA, hereafter referred to as 1233zd(E) (trans 1-chloro-3,3,3-trifluoropropene) as a co-blowing agent in the production of XPS foams. Other combinations based on carbon dioxide, ethanol or water were also investigated as co-agents. 1234ze(E) and 1233zd(E) are particularly interesting due to their low environmental impact as well as their contribution to long term R-value. The extrusion foaming processing characteristics of 1234ze(E)-based formulations will be reported, with an emphasis on on-line rheology, in-line degassing pressure behavior and potential interactions between the physical foaming agent (PFA) components. The properties of the resulting low-density foams will also be presented

Experimental

The primary blowing agents used in this study were 1234ze(E) and 1233zd(E). They were provided by Honeywell and are commercialized under the trade name *Solstice*™. Table 1 reports selected physical properties of these blowing agents, along with three other co-agents tested, namely carbon dioxide, ethanol and water. 1234ze(E) and 1233zd(E) are both non-ozone depleting substances with very low global warming potential (GWP). Both substances are non-flammable. A general-purpose polystyrene grade - PS 1900, kindly provided by Ineos Nova - was used in this study. This polymer has a reported melt flow index (MFI) of 23.0 g/10min. The formulations tested for rheology and degassing conditions contained no talc. The foams extruded for physical characterization purpose were nucleated using 0.5wt% of talc.

Table 1: Selected Physical Properties of Pure Components

	1234ze(E)	1233zd(E)	Ethanol	Carbon Dioxide	Water
Formula	CFH=CHCF ₃	CClH=CHCF ₃	CH ₃ CH ₂ OH	CO ₂	H ₂ O
MW (g/mol)	114.04	130.5	46.07	44.01	18.02
BP at 1 atm (°C)	-19	19	78.4	-78.4	100
P _{vapor} at 20°C (kPa)	498	106	5.8	5700	2.3
Critical P (MPa)	3.63	3.77	6.3	7.38	22.06
Critical T (°C)	109	156.6	241	31.05	373.9
GWP – 100yrs	< 6 [2]	< 7 [2]	< 25	1	-

Foam extrusion runs were performed on a 50mm Leistritz counter-rotating twin-screw extruder set up for foam processing. It was operated at a nominal resin feed rate of 20 kg/hr. The screw speed was set to 60 rpm. The blowing agents were injected separately into the extruder using liquid chromatography pumps, with their feed rates adjusted to provide the desired blend composition. Foaming agent concentrations were chosen to produce foams of low density, typically less than 75 kg/m³, optimally close to 40 kg/m³. Loss in weight data were constantly monitored to ensure that nominal and experimental feed rates were as expected. Orifice strand dies having diameters of 2 and 3mm (die land of 1 mm) were used to produce foams with cylindrical shape.

Depending on the level of plasticization achieved for the given PFA content, temperature along the barrel and at die were lowered toward the 130-140°C range, known to be adequate for low-density close-cell PS foam extrusion.

Figure 1 shows the screw configuration and schematics of the overall setup used for the 50mm extruder, indicating the location of the on-line process control rheometer (PCR-620, formerly from Rheometric Scientific, now available from Thermo Scientific) and an in-line ultrasonic sensor. A gear pump located at the end of the line was used to control the melt pressure in the system.

Viscosity measurements and degassing pressure determination were conducted for 13 different formulations based on 1234ze(E) as the main foaming

agent and various concentrations of the other co-agents. Depending on level of plasticization reached, measurements were taken at 120, 140, 160 and/or 180°C. The PCR used for the on-line viscosity measurement enabled stress sweeps to be performed according to the volumetric flow rate limitation of the instrument and the sensitivity of the pressure transducers. This yields a shear stress range of 10 to 60 kPa, corresponding to apparent shear rates ranging between 0.1 and 100s⁻¹. Measurements were obtained typically at nine different stress levels. Pressure was set in the slit to a minimum of 5.0 MPa in order to maintain the PFAs dissolved and avoid a premature phase separation in the rheometer. Corrections were further applied to the viscosity results to account for temperature variation [1]. Extent of plasticization was further deduced from these measurements and was further translated into a decrease of the glass transition temperature of polystyrene.

A set of ultrasonic sensors was used to detect the occurrence of bubbles when a phase separation was purposely induced. An instrumented slit die (5 mm thick by 4 cm wide and 20 cm long) was mounted between the end of the extruder and the gear pump entrance. This die was equipped with two identical ultrasonic probes installed at mid-stream and perpendicular to the slit, so that the ultrasonic beam was normal to the flow channel. Three pressure transducers were also mounted to measure the pressure profile across the die, enabling the extrapolation of the pressure at the ultrasound detector location. Gradually increasing the gear pump speed reduces the pressure inside the slit die down to the said degassing pressure (taken here as an estimator of the

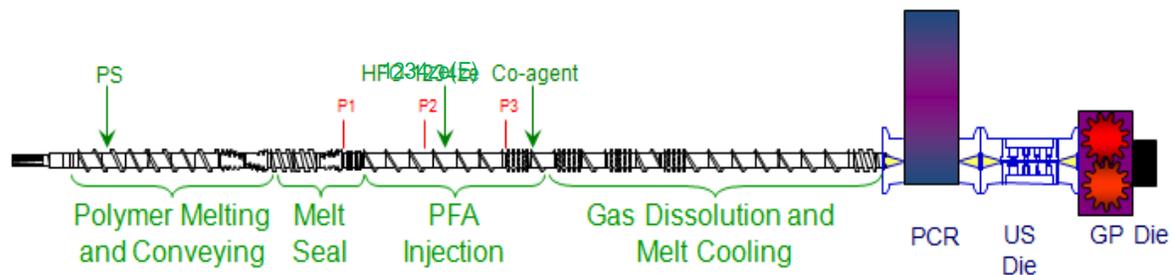


Figure 1: Schematic of the 50mm extrusion setup, showing location of the on-line rheometer (PCR) and the ultrasonic sensors (US Die), upstream the gear pump (GP)

equilibrium solubility pressure), where a sharp increase of the ultrasonic signal attenuation is taken as an indication of phase separation [3].

Results and Discussion

On-line Characterization

Plasticization As it can be seen from Figure 2, where the shear stress is plotted as a function of the apparent shear rate, the viscosity curves of every composition/temperature conditions tested showed the same shape and curvature observed for the neat PS system. The curves are essentially shifted along the shear rate axis. Such shift corresponds to the amount of plasticization induced by the presence of the dissolved foaming agents. This curve shifting is similar to a temperature effect, as displayed in the same figure. A decrease in viscosity, obtained through a temperature increase or blowing agent addition, translates into a lowering of the shear rate for a constant shear stress value.

Calculation of the Depressed Glass Transition Temperature (T_g) The quantitative comparison of the viscosity shift induced by the blowing agent dissolution was evaluated by arbitrary selecting a shear stress (39.5kPa in the present cases) and finding the corresponding shear rate on each of the “shear stress vs shear rate” curves measured. The corresponding rates were then reported as a function of the temperature. Figure 3 shows the data obtained from the viscosity measurements generated using neat 1234ze(E). Temperature dependency for each curve, corresponding to a given 1234ze(E) content, remains the same and is a function of the glass transition temperature.

The well-known Williams-Landel-Ferry (WLF) equation, Eq. (1), relates the variation of the viscosity to the temperature, in reference to the glass transition temperature of the polymeric system:

$$\log (\eta/\eta_g) = -\frac{c_1(T-T_g)}{c_2+T-T_g} \quad (1)$$

with c_1 and c_2 set to 13.7 and 50.0 respectively, which are standard values for polystyrene. Equation 1 is also valid for a mixture of a polymer with a solvent. Constants c_1 and c_2 are reported to be practically independent of the solvent fraction for concentrated solutions [4]. T_g is the single parameter reflecting the composition of the mixture: the glass transition temperature of a polymer is lowered when a liquid or a gas of low molecular weight is dissolved into the polymer, as shown in Figure 4.

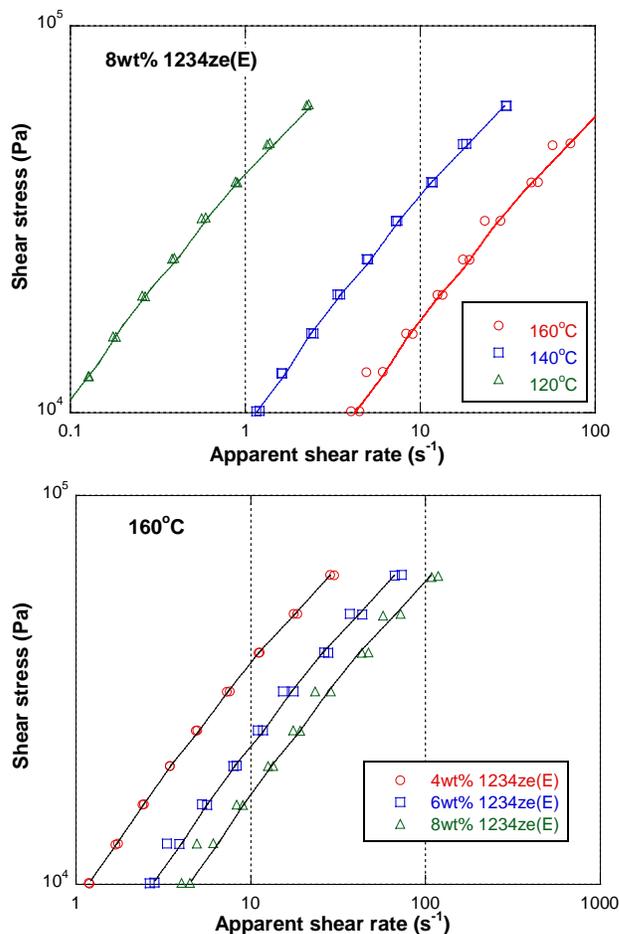


Figure 2: Viscosity results for (top) a formulation containing 8wt% 1234ze(E) measured at three temperatures and (bottom) three formulations containing increasing amounts of 1234ze(E) measured at 160°C.

The same figure also incorporates the prediction obtained from a theoretical relation developed by Chow [5] and based on the molecular weights of the solvent, in the present case the 1234ze(E) foaming agent. The coordination number in the Chow’s equation was set equal to 2, a value found appropriate for mixtures of polystyrene with diluents of molecular weights in the order of 75-250 g/mol.

For 1234ze(E) content up to 4wt%, the resulting prediction, shown in Figure 4 by the red line, is in good agreement with the values experimentally measured from viscosity data. Above this concentration, the experimental results exhibit the same trend, the glass transition temperature drops linearly by roughly -5°C per wt% of dissolved 1234ze(E), while the calculated decrease of the T_g using Chow’s equation is less steep.

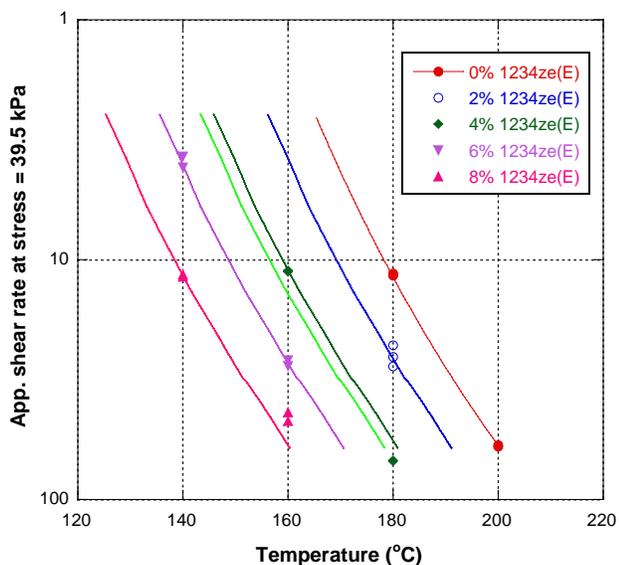


Figure 3: Plasticization induced by 1234ze(E) for various content of blowing agent (Note: For the green curves: 4.25wt% 1234ze(E) at 180°C, 3.85wt% 1234ze(E) at 160°C).

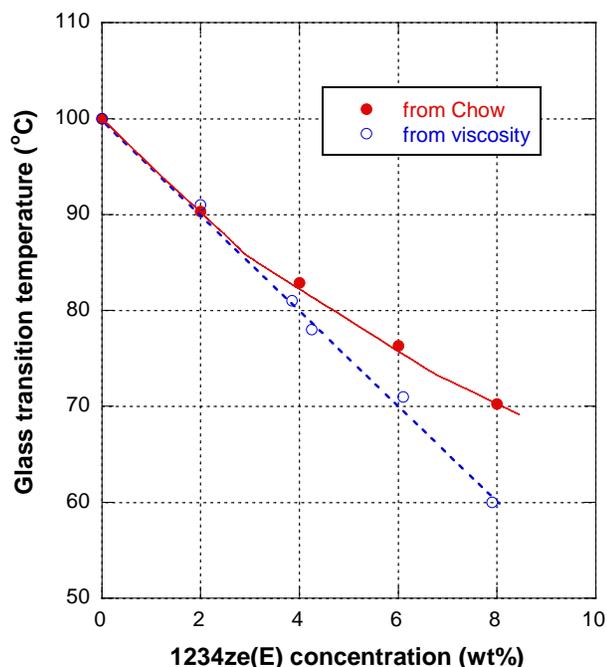


Figure 4: Variation of the glass transition temperature as a function of the blowing agent content, as determined from viscosity results and compared to data calculated using a model proposed by Chow [5].

Degassing of PFA blends Figure 5 reports the typical behavior observed for melt pressure and ultrasonic wave attenuation during the gear pump speed increase. The onset of degassing is estimated from the abrupt increase of the attenuation, associated with scattering from the newly formed bubbles.

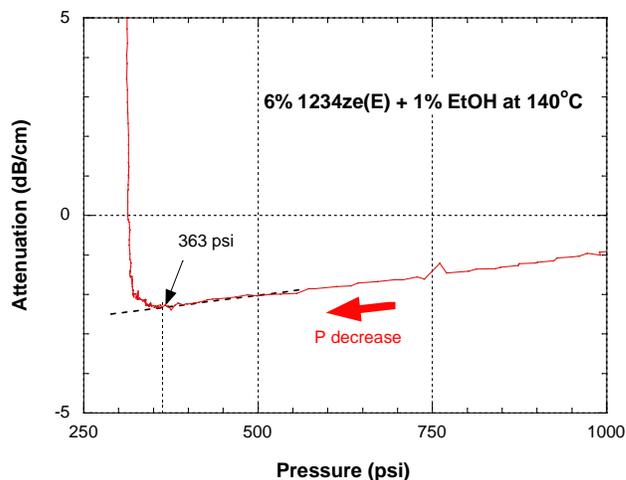


Figure 5: Typical degassing curves showing the abrupt ultrasound attenuation increase during phase separation. These results were gathered from a blend of 6wt% 1234ze(E) with 1wt% ethanol at 140°C.

The degassing pressure, associated to a solubility measurement made in “dynamic mode”, was gathered from neat 1234ze(E) and its blends at four different temperatures, ranging from 120°C to 180°C. At low concentration of 1234ze(E), plasticization was limited so investigated temperatures remained in the high value range. At 160°C, the data points corresponding to the three concentrations investigated follow a linear relationship typical of Henry's law (see Figure 6). However, as the temperature was lowered, several discrepancies occurred. At temperatures lower than 160°C, data points deviate significantly upward the expected linear behavior, and much higher pressure results were obtained. One would expect that solubility increases as the temperature is lowered, which means that a lower pressure would be needed for a given concentration. The results obtained for systems with 6 and 8wt% of 1234ze(E) follow the opposite trend, i.e. as the temperature is reduced (toward the critical temperature, 109°C), phase separation occurred at higher pressures. As previously observed for other HFCs (HFC-134a, HFC-245fa and HFC-152a), such departure from a linear trend occurs for pressures higher than the critical pressure [6]. In the present case, the critical pressure of 1234ze(E) is 3.632 MPa (526.76 psi), which is much higher than the actual onset of deviation that we estimate to be roughly 300 psi. In any case, the solubility of 1234ze(E) in PS advantageously compares to data reported for HFC-based systems currently in commercial use.

Co-agents were added to 1234ze(E) in various concentrations and degassing pressures were measured at 140 and 160°C. Results at 160°C are displayed in Figure 6. It is usually expected that degassing pressures of a mixture of gas correspond to the sum of the respective pressure of each foaming agent. For instance, as displayed

in Figure 6, degassing pressure increases tremendously when adding carbon dioxide, since this later is not very soluble in polystyrene. Same comment also applies to water.

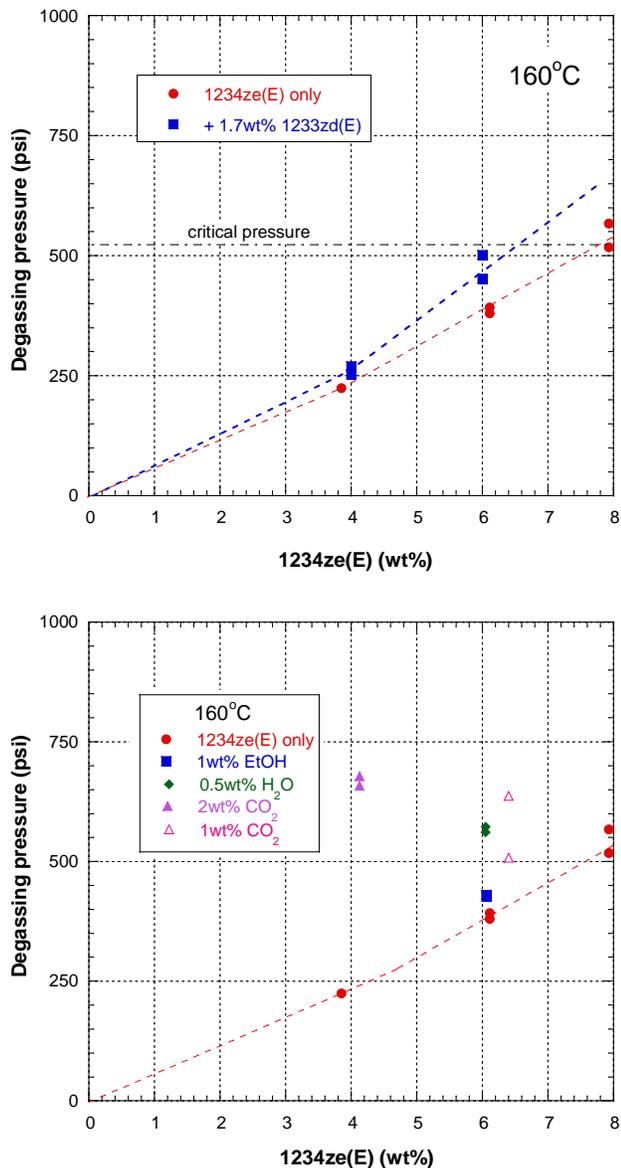


Figure 6: Solubility of various 1234ze(E)-based mixtures in PS 160°C. Top figure focused on 1233zd(E) as co-agent, while the bottom figure groups data from the other investigated co-agents (ethanol, carbon dioxide and water).

Interestingly, this simple additivity rule does not apply to 1233zd(E) and ethanol. Some beneficial interaction should prevail since the measured degassing pressures are sometime lower than the value obtained from the neat 1234ze(E) formulation. For example, adding 1wt% ethanol to a 6wt% 1234ze(E) foam formulation at 140°C actually decreases the degassing pressure of the

system by *ca.* 100 psi. A similar behavior is observed when 1233zd(E) is added to high levels of 1234ze(E). It is then anticipated that using either 1233zd(E) or ethanol would help the extrusion foaming process to be more stable when using high content of 1234ze(E) as the main blowing agent, a prerequisite for reaching the low density foam range.

Foam Properties

A summary of the extruded 1234ze(E) blown foam characteristics is given in Table 2. Experimental work was focused on mixtures of 1234ze(E) and 1233zd(E), but mixtures with either carbon dioxide or ethanol were also investigated for comparison purpose. Foaming agent compositions were chosen such as the plasticization level obtained allows extrusion in the 120-135°C temperature window while bringing down the foam density in the 40 kg/m³ range.

Foam Density A limited number of formulations allowed density reduction below the 40 kg/m³ range. Some of the formulations based on the mixture of 1234ze(E) and 1233zd(E) have successfully met this objective. Addition of ethanol was also highly beneficial to low-density foaming. Blending 2 to 3wt% ethanol efficiently reduce the density of systems foamed with 6 to 8wt% 1234ze(E).

Cell Morphology Extrusion of PS foams at 1234ze(E) content larger than 8wt% generated an unstable processing zone that led to specimens with unacceptable surface defects (blisters, blow holes, etc...) and cell size smaller than 100 μm. Fortunately, the addition of a well-chosen co-blowing agents critically improves the process stability and foam structure.

The most stable foam obtained throughout these trials was the one based on 6wt% 1234ze(E) and 2wt% ethanol. Average cell size was approximately 200 μm (with 0.5wt% talc) for a foam density of 40 kg/m³. Small modifications to this formulation, by either increasing 1234ze(E) or ethanol content, slightly deteriorate the process stability and the resulting foam structure, with only a minor impact on density reduction. Increasing both ethanol and 1234ze(E) had severe negative effects: serious process fluctuations appear, foam density increases and microcellular cell sizes are generated. As ethanol and 1234ze(E) are both very efficient plasticizers of PS melts, small concentration changes are expected to significantly modify the optimum foam processing temperature. Samples extruded at the larger blowing agents contents might then not have been processed in optimal conditions.

Table 2. Selected properties of extruded PS foams blown from 1234ze(E)-based blends.

1234ze(E) (wt%)	1233zd(E) (wt%)	EtOH (wt%)	CO ₂ (wt%)	Talc (wt%)	T _{melt} (°C)	Cell Size (µm)	Density (kg/m ³)	OCC (%)	k (mW/m·K)	Comment
6				0.5	140	100-150	61	<5	20.9	Blow holes
6				-	140	300-600	77			Fewer blow holes
6			1.25	0.5	135	80-150	55	<5	21.8	Blow holes
6			1.25	-	135	200-400	63			Blow holes
6			2.5	0.5	135	50-80	49	<5	22.5	Blow holes
6		2		0.5	130	200	40	<5	21.6	Very nice foam
6		2		-	130	1000	48			Very nice foam
8		2		0.5	120	80	39		14.8	Nice, some surface defects
6		3		0.5	120	100-150	38		20.0	Nice, limited surface defects
8		3		0.5	115	30-60	42			Unstable process
4	4			0.5	130	100-150	48		27.6	Few blow holes
4	6			0.5	130	80-100	47	<5	22.3	Nice foam
4	6			-	130	200	45			Nice foam
4	8			0.5	125	80-100	40	<10	18.1	Nice, minor surface defects
4	8			0.5	120	60-100	41	<25	19.8	Nice, minor surface defects
4	10			0.5	120	60-100	38	<10	17.5	Surface defects
6	2			0.5	130	100	65	<5	25.5	Few blow holes
6	4			0.5	130	60-100	46	<10	19.1	Surface defects
6	4			-	130	100-200	50			Very nice foam
6	4	2		0.5	120	60	37	<10	20.3	Surface defects

Interestingly, nice foams were also obtained while extruding formulations combining moderate 1234ze(E) content (4wt%) with fairly large 1233zd(E) concentrations (6-8wt%). The processing conditions were reasonably stable, but the cell size tends to be below the 100 µm threshold. Such small cell size is most likely generated by the large overall blowing agent content (leading to high cell density), rather than the hypersensitive nucleation conditions usually associated to foaming agents in their supercritical state. In the current case, it should be easy to control size through the concentration of talc added in the systems, as evidenced by the much larger cell size exhibited by the control specimens extruded with no nucleating agent (talc). It should be noted that no specific efforts has been made at this stage of the work to develop the nucleating agent package of the extruded foams. The structure and performance of these foams could certainly be improved.

Thermal Conductivity Measurements were made using a simple transient method described elsewhere [7]. The technique is useful for characterizing specimen too small for the conventional methods and has a reported 4% accuracy. However, it should be noted that bias induced by the very small size of the sample tested in this work might be observed. For this reason, the data reported here should be mostly used for comparing the relative difference in thermal conductivity of the various specimens extruded.

Using the formulation blown with 6wt% neat 1234ze(E) as a reference, it is clear that adding either carbon dioxide or ethanol did not bring any detrimental effects on the thermal insulation performance of the 1234ze(E) blown foam. The differences observed are most likely within the experimental error of the method. Since ethanol addition as a co-blowing agent is providing many beneficial processing and foam structural improvements, this latter result is particularly interesting.

In fact, of all the results gathered, the lowest value of k was obtained with a mixture of 8wt% of 1234ze(E) and 2wt% of ethanol. While the alcohol addition did not show any significant impact on k at lower content of 1234ze(E) (6wt%), it must be concluded that the low conductivity was a result of the high content of 1234ze(E). The process stability issues observed with neat 1234ze(E) at such a high content were almost completely resolved by the addition of ethanol.

Addition of 1233zd(E) was also beneficial to the 1234ze(E)-based foam process and properties. Providing that enough 1233zd(E) and 1234ze(E) are added in the blowing agent mixture, low k value foams are manufactured. The lowest conductivities obtained with this blend are observed when the combined 1234ze(E)/1233zd(E) content is larger than 10wt%.

Conclusions

1234ze(E) has demonstrated a clear potential as a blowing agent for extruded polystyrene foam insulation manufacturing. It has a good solubility in PS and it is efficiently plasticizing the polymeric matrix, thus allowing the low melt temperature required by the foaming process. Reaching PS foam density in the 40 kg/m³ range using only neat 1234ze(E) alone is challenging. These difficulties were easily overcome by using an adequate co-blowing agent. Low density foams with appropriate processability, structure and properties can then be extruded, provided that 6-8wt% 1234ze(E) is combined with either 2-3wt% ethanol or 6-8% 1233zd(E). Future work on this topic should focus on the optimization of the processing conditions, including the nucleating agent concentration and the processing temperature.

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