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Foaming Polystyrene with a Mixture of CO₂ and Ethanol*

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ABSTRACT: Use of mixtures of blowing agents in thermoplastic foam extrusion has been an industrial practice for a long time. However, it has gained renewed interest in the past few years due to the introduction of difficult-to-process alternative gases, targeted as potential replacement for the banned ozone-depleting blowing agents. Reasons for blending physical foaming agents (PFA) are numerous. The incentives may be economical, environmental, or technical. With respect to that latter factor, blending suitable PFAs is often regarded as providing a better control of processing conditions. For example, a specific PFA could be selected for its inflation performance and blended with other co-blowing agents chosen for their stabilizing role. Although a considerable amount of work has been done in that area, very little information has been disclosed in open literature.

Carbon dioxide (CO_2) has been reported as an interesting candidate for low-density polystyrene (PS) foaming, although the required concentrations

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Figures 1-6 appear in color online: http://cel.sagepub.com

are associated with high processing pressures due to the low solubility of the gas. Thus, stable processing conditions are difficult to achieve. This work studies the effect of blending CO_2 with ethanol (EtOH) as a co-blowing agent for PS foaming. Extrusion foaming performance of this mixture is discussed, with respect to its solubility (i.e., degassing conditions) and rheological behavior. The function of each blowing agent during the process is analyzed with respect to the plasticization, nucleation, expansion, and stabilization phases. Attention is also paid to the interaction involving the two PFA components.

KEY WORDS: foam extrusion, carbon dioxide, ethanol, plasticization, degassing.

INTRODUCTION

Due to environmental and safety concerns, carbon dioxide has been identified as one of the most promising foaming agents. However, processing polystyrene (PS) with carbon dioxide (CO_2) with the objective of producing low-density foam still remains challenging, due to its low solubility and high diffusivity, which can cause open cells and surface defects such as corrugation.

Combining CO_2 with an alcohol or a ketone has already been proposed in a patent literature to circumvent the aforementioned problems. For instance, in a patent assigned to BASF in 1993 [1], ethanol (EtOH) or acetone have been identified as potential candidates to assist CO_2 in the extrusion foaming of PS down to densities as low as 25 kg/m^3 . On a weight basis, ratio of CO_2 with respect to the other component is comprised between 3:7 and 1:1. Other patents have extended this formulation through the inclusion of additional components such as water [2] or hydrofluorocarbons [3].

While scientific information is usually scarce in the patent literature, it was essential to develop a more thorough understanding of the role of each physical foaming agent (PFA) component during the foaming process, from the plasticization stage to the growth and stabilization of the extruded foam. Rheological behavior, conditions leading to phase separation and resulting foam characteristics were investigated for mixtures of PS, CO_2 and EtOH [4].

EXPERIMENTAL

A commercial polystyrene, PS Scott C-35 from Scott Polymer Ltd. (melt flow index MFI = 3.5 dg/min) was combined with mixtures of CO_2 (supplied by Praxair Canada Inc.) and EtOH (from Aldrich Chemical Co.) as the blowing agents to produce extruded foam.

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	Carbon dioxide	Ethanol
Formula	CO ₂	C ₂ H ₅ OH
Molecular weight (g/mol)	44.01	46.069
Boiling point (°C)	-78.45	78.35
Critical temperature (°C)	31.05	243.05
Critical pressure (MPa)	7.38	6.38
Dipole moment (debyes)	0.0	1.7

Table 1. Physical properties of foaming agents.

The physical properties of these foaming agents are listed in Table 1. The EtOH had been denatured with 5% methanol and 5% isopropanol. Neither nucleating agent nor flame retardant has been used in this study.

Samples were produced on 34 mm (co-rotating) and 50 mm (counterrotating) Leistritz twin-screw extruders, with the screws specially designed to accommodate foam extrusion based on the use of physical foaming agents. A gear pump was installed after the extruder and before the die. The strand die used was 2.0 mm in diameter with a 1.0 mm die land. The throughput was maintained constant at 10 kg/h. A highprecision gravimetric feeder was used to feed the PS. The blowing agents were independently injected in the extruder and their flow rates continuously monitored through loss-in-weight. Ethanol was injected via a HPLC pump, while the CO_2 , pressurized in a 10L capacity autoclave, was delivered through a controlled valve. The respective concentrations of CO_2 and EtOH explored were kept below 6 wt%. The temperatures of the extruder and the die were adjusted for each experiment to maintain a pressure drop at the die level in the neighborhood of 17.2 MPa (2500 psi). The plasticization induced by an increasing amount of blowing agent enabled the extrusion to be conducted at temperatures close to 100° C.

The in-line characterization was performed specifically on the Leistritz 50 mm twin-screw extruder. A commercial on-line rheometer (melt flow monitor (MFM), from Rheometric Scientific), located before the gear pump, was used to characterize the rheological behavior of the PS/foaming agent mixture under different PFA concentrations and temperatures. The use of such on-line apparatus is particularly attractive, since at all times the mixture is maintained above a given pressure level which prevents the phase separation of the components. Details on these types of measurements, as well as data treatment, can be found elsewhere [5]. For the determination of the conditions under

which phase separation occurs, a slit channel equipped with in-line ultrasonic sensors was installed before the gear pump. Increasing the gear pump speed induces a reduction of the pressure prevailing within the slit channel until the phase separation (nucleation) conditions are met. Since the ultrasonic waves are scattered in the presence of bubbles, this technique enables the detection of the early cell formation. This technique was described in detail in [6].

RESULTS AND DISCUSSION

Rheology

Examples of raw viscosity results are displayed in Figure 1. These results correspond to a fixed concentration of EtOH (4wt%), with an increasing content of CO₂, from 0 to 4.8 wt%, with the temperature maintained constant at 150°C. Increasing the total amount of foaming agents obviously decreases the viscosity, which is translated onto this figure by a shift of the stress-rate curves to higher rate values. In order to simplify the data treatment, computation of the corresponding glass transition temperature from the viscosity measurements, as described



Figure 1. Viscosity reduction for PS mixed with various compositions of CO_2 and EtOH, at $150^{\circ}C$.

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Figure 2. Glass transition temperature (T_g) of different mixtures of PS with EtOH and CO_2 used as the foaming agents.

in [5], was done at a constant stress value, $\sigma_{12} = 39.9$ kPa. Analysis was conducted for three separate systems: considering only one type of blowing agent at a time, either CO₂ or EtOH alone, or combination of the two PFAs.

The calculated variation of the glass transition temperature as a function of the total blowing agent content $(CO_2 + EtOH)$ is displayed in Figure 2, for different sets of results, as indicated on the graph. From the curves for the individual foaming agents, it is fair to conclude that EtOH and CO_2 share the same degree of plasticization (approximately $-8^{\circ}C/wt\%$ of blowing agent). This could have been anticipated using a theoretical relation developed by Chow that predicts the glass temperature depression based on the respective molecular weight of the diluent and the polymer repeat unit [7]. Since these two PFAs have roughly similar molecular weights, 44.01 g/mol for CO₂ and 46.07 g/mol for EtOH, we conclude that the higher polarity of the EtOH due to its hydroxy group does not impact its interaction with PS. The curve for CO_2 is particularly interesting, since it indicates that, when this gas concentration lies above a certain threshold value of approximately 4 wt%, its contribution to the plasticization of the polymer becomes limited. This observation, associated with some limit of solubility, has also been previously reported for the PS/HFC-134a mixture [5].

However, this behavior tends to diminish as EtOH is added to CO₂: this translates into a straight line even in the concentration range above 4 wt% for CO₂, which was found critical previously. The slope for the decrease of the glass transition temperature (T_g) with PFA content is maintained approximately constant for any combination of foaming agent, which suggests a simple additivity rule for their respective plasticization effect.

Phase Separation: Ultrasounds

The degassing pressures, i.e., the pressure at which phase separation is said to occur according to the ultrasonic signals variations, are plotted in Figure 3(a) for different combinations of CO_2 and ethanol, as a function of the melt temperature. All curves show a characteristic parabola shape. For the right side of the curve (i.e., at high temperatures), degassing pressures correspond fairly to solubility data associated to the content of CO_2 in the PFA mixtures. This is illustrated in Figure 3(b) that reports some degassing results experienced at $180^{\circ}C$ as a function of the CO_2 concentration. A single trend is observed irrespective of the EtOH content, and this linear dependency is in fair agreement with solubility results obtained using a magnetic suspension microbalance [8].

However, still from Figure 3(a), the degassing results observed at lower melt temperatures follow an upward turn that would be associated to increasing elasticity of the melt submitted to tensile deformation as it enters the converging channel [9]. The minimum of the parabola is shifted to the left, i.e., in the low temperature direction as the total amount of foaming agent is increased, which is associated to the plasticization effect. However, the magnitude of plasticization required for the curve shifting would indicate a lower plasticization effect for the ethanol component compared to that induced by the CO_2 , which is in disagreement with the previous findings from shear viscosity measurements. However, the plasticization prevailing during the degassing mechanism could be more associated with the elastic component that may be differently affected by the different plasticizing PFAs.

Figure 3(a) also displays that pure ethanol resulted in very low degassing pressures, i.e., less than 1 MPa, compared to CO_2 . The dominance of CO_2 is still reflected in the curves obtained with mixtures of the two PFAs, with the absolute level of the curve being proportional to the concentration of CO_2 as shown in Figure 3(b).



Figure 3. (a) Degassing pressures obtained from ultrasonic monitoring as a function of the melt temperature, for various PFA compositions and (b) degassing pressures compared to solubility data (excerpted from [8]), as a function of CO_2 content, at 180°C. Content (wt%) in EtOH is specified for the degassing experiments.

Extrudate Expansion

Radial expansion of the foam extrudates was measured by hand using a pair of calipers. Figure 4(a) reports the growth of the strand diameter with position after the die exit for different CO_2 concentrations at a set concentration of EtOH (approximately 2.1–2.5 wt%). As indicated earlier, temperatures were adjusted to maintain a fixed pressure drop at the die exit, thus lower temperatures are associated with increasing foaming agent contents. Profile expansion can be divided into subsequent phases: swell from elastic recovery, dilation, nucleation, growth, and stabilization. The onset of the growth stage is clearly shifted to shorter times (or distances) as the concentration of CO_2 is increased. However, the location of growth onset is less impacted for CO_2 concentrations above 2 wt%. At 3 wt% of CO_2 , the maximum expansion is observed.

Figure 4(b) compares two expansion profiles obtained with similar CO_2 concentration, but with different EtOH contents. While the onset of nucleation and initial growth is practically unchanged, being essentially controlled by the CO_2 , addition of EtOH yields an extended expansion that, as detailed in the following section, is associated with lower foam densities.

Foam Densities and Morphologies

A 3-D representation of the foam density as a function of PFA composition is shown in Figure 5. A similar plot for the mean cell diameter is also given in Figure 6. Although EtOH can be used as a single blowing agent, the density reduction is limited to approximately 125 kg/m^3 with very large cells, i.e., above 1 mm. These results were obtained with the EtOH content set at 3 wt%, and no further improvement was observed for a higher alcohol content. Significant improvement in density reduction with stand-alone CO₂ was also observed during the first 2 wt%. Increasing CO₂ content still impacts the reduction of cell size, although the morphology of the cell structure is deteriorating with cell wall rupture and increase in open cell content. Moreover, for a CO₂ concentration above 4 wt%, the presence of blow holes, as illustrated in Figure 6, denotes a lack of solubility under these processing conditions.

The best results in terms of combined foam density and adequate cell morphology were obviously obtained with the combination of the two PFAs. Densities in the range of 40 kg/m^3 or less were achieved with at least 2 wt% of CO₂ and a minimum of 2 wt% of EtOH, with the cell size



Figure 4. Profile expansion of foam extrudates: (a) for various contents of CO_2 while keeping the ethanol concentration constant in the 2.1–2.5 wt%-range and (b) influence of EtOH with CO_2 content set in the 4.3–4.9 wt%.

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Figure 5. Foam densities of PS extruded foams based on different $CO_2/EtOH$ compositions.



Figure 6. Mean cell diameter of PS extruded foams based on different $CO_2/EtOH$ compositions. Foam structures are illustrated for foam produced with high CO_2 content, with increasing concentration of EtOH from left to right.

in the 100 µm-range or less, with no sign of open cells or heterogeneities. The smallest cell diameters were observed for foams prepared with 4% CO_2 and 5.4% EtOH, which gave an average cell diameter of 22 µm. High nucleation density provided by the high CO_2 content, combined with the

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severe plasticization induced by the overall PFA content, may explain this result.

CONCLUSIONS

The level of plasticization observed for the two blowing agents, CO_2 and EtOH, is approximately the same, i.e., $-8^{\circ}C/wt\%$. While CO_2 exhibits a lack of plasticizing effect at high content, probably associated with some limiting solubility, the presence of ethanol seems highly beneficial to CO_2 processing; blow holes in foams associated with dissolution problems vanish and rupture of the cell walls leading to open cells no longer prevail. This enables the extrusion of foams in the density range of 25–30 kg/m³ with adequate cell morphology. The most promising results were obtained with equivalent contents of both PFA components, with the overall concentration superior to 4.5 wt%.

The degassing conditions were mainly associated with the CO_2 component, which corresponds to the most volatile component. However, ethanol was found to contribute significantly to the overall plasticization of the system, which could be beneficial in the low-temperature range by reducing the pressure at which cells would start to nucleate, thus making the mixture less 'explosive'.

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