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Simple gases to replace non-environmentally friendly polymer foaming agents. A thermodynamic investigation

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ABSTRACT

Foaming constitutes one of the most important industrial activities in polymer engineering to produce efficient thermal insulating materials. In particular, rigid insulating boards are produced worldwide on a large scale using blowing agents which eventually are released in the environment where they adversely impact the natural friendly stratospheric ozone layer. Concomitantly, the chemicals used as blowing agents contribute to the creation of the unfriendly tropospheric ozone layer generating the disastrous green house effect around our planet. The traditional foaming intermediates currently named freons, like chlorofluorocarbons (CFC's) currently used as blowing agents as well as the hydrochlorofluorocarbons (HCFCs) often considered as alternative blowing agents, must be banned from industrial processes and new (friendly) foaming agents have to be suggested and evaluated in terms of both easy engineering and environmental neutrality. Undoubtedly thermodynamics plays a major role in assessing the effective capability of those chemicals. Some CFC's still accepted and other possible simple gases like carbon dioxide and nitrogen have been considered. The in-depth thermodynamic investigation has been made possible thanks to new experimental developments to determine gas solubility in polymers and associated swelling as well as the thermodynamic properties of (gas + polymer) systems, including the thermophysical properties of polymers under gas sorption. Pertinent data have been generated for such properties over extended *T* and *p* ranges.

1. Introduction

For the production of various polymeric foams which is one of the most important sectors in modern polymer technology, physical blowing agents must be used. A major issue is thus the development of improved processing methods which combine efficient and economic techniques having the lowest environmental impact. The CFC's currently used as blowing agents as well as the HCFCs often considered as alternative blowing agents, are subject to international regulation since research has shown that these compounds adversely affect the environment. The goal is to provide manufacturers of polymers with recommended gas/polymer systems and process methodologies for keeping the industry ahead in a competitive industrial area in modern technology without affecting the environment. As a matter of fact, the "ozone case" is a twofold problem. Ozone in the stratosphere (*i.e.* the upper atmospheric layer), the stratospheric ozone, is the friendly one which protects our planet, whereas ozone in the troposphere (*i.e.* the lower atmospheric layer), the tropospheric ozone, is the unfriendly one, because harmful, which must be kept as low as possible. Among blowing agents some, like CFCs, have an Ozone Depleting Potential (ODP) of the stratospheric (friendly) ozone and they should be banned. In this context, HCFCs have been used for substitution. Another advantage of the HCFCs is their low Photochemical Ozone Creation Potential (POCP) to generate tropospheric ozone.

The treaty on substances that deplete the ozone layer known as the Montreal Protocol is a landmark international agreement designed to protect the stratospheric ozone layer. It was originally signed in 1987 and substantially amended in 1990 and 1992. The Montreal Protocol stipulates that the production and consumption of compounds that deplete ozone in the stratosphere – CFCs, halons, carbon tetrachloride, and methyl chloroform – were to be phased in during the early 2000s. Scientific theory and evidence suggest that, once emitted to the atmosphere, these compounds could significantly deplete the stratospheric ozone layer. The Montreal Protocol and its subsequent reviews have presented a great challenge for the XPS (extruded polystyrene) foam industry. Indeed, CFC-12 had long been the blowing agent of choice in that

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application due to its unique properties such as non-flammability, non-toxicity, low thermal conductivity and excellent ability for processing.

In developed countries, the quick phase-out of CFC-12 was made possible due to the availability of HCFCs. The HCFC-142b became the reference blowing agent for XPS insulating boards owing to its superior properties, *viz.* non-toxicity, lower gas phase thermal conductivity than other alternatives, wide window in its ability to be processed. The main physical properties of these blowing agents are listed in table 1.

However, HCFCs are also subject to new regulations because of their low remaining Ozone Depletion Potential (ODP) and a call was issued for their phase-out as blowing agents for XPS boards to be used in insulated applications. HCFCs have also been included and have an elimination schedule of 2020 (gradual reduction from 2004 to 2020) for the developed countries.

Within the above international agreement for a phase-out of blowing agents potentially harmful for the ozone layer, it was admitted that the two fluids, trichlorofluoromethane CFC-11 (or Freon 11) and dichlorodifluoromethane CFC-12 (or Freon 12) could be momentarily replaced by 1,1-dichloro-1-fluoroethane HCFC-141b (or Freon 141b) and 1-chloro-1,1-difluoroethane HCFC-142b (or Freon 142b) at least in the developed countries. This appeared as a successful step for the ozone layer to begin its recovery process, although such process may take decades. At the turn of the 20th century, the HCFCs, despite their (still) weak effect on the ozone layer, have proven to be good alternatives as immediate substitutes to CFCs.

Nevertheless HCFCs are only transitional blowing agents and they must also in turn be completely eliminated. However, if undoubtedly, these blowing agents are by far less active on the depletion of the ozone layer, they may still have an impact on the environment through two other aspects: global warming and creation of ozone in the troposphere. The tropospheric ozone remains yet a quite unattended problem. The creation of this ozone layer which is highly pollutant may greatly depend on the potentiality of a compound to generate tropospheric ozone through chemical reactions. Another aspect of chemical concentration in the troposphere is the green house effect and the correlative Global Warming Phenomenon and Total Warming Equivalent Impact (see the GWP-TEWI index table 1). Global warming results from two contributions, *viz.* the direct contribution arises from the release of the chemical in the atmosphere, the indirect contribution stems from the more or less high energy consumption resulting from more or less effective insulation since such energy consumption (mainly electricity production) induces higher burning of fossil fuels which yields larger amounts of carbon dioxide into the atmosphere. This means that the positive contribution to the green house effect of the new blowing agents may be offset by the negative impact of energy production. Large scale calculations showing the contribution of insulation materials in building construction towards favorable energy efficiency are not yet available but HCFCs are considered as an appropriate answer for reducing the harmful emissions.

Dealing with insulating materials, HCFCs have a good thermal insulation. For example HCFC-142b advantageously replaces CFC-12 in keeping similar insulation properties. But with the total phase out of HCFCs, a new generation of blowing agents has to be recommended. Two candidates show promising properties which are CO_2 and some hydrofluorocarbons HFCs, like 1,1,1,2-tetrafluoroethane HFC-134a (also named Genetron 134a). Regarding the environmental issues addressed above, CO_2 and HFC-134a have both similar low ODP factors, and their contribution to the green house effect as expressed by the GWP-TEWI index is also similarly low (table 1). With regard to thermal efficiency in foamed materials, HFC-134a presents better qualities than CO_2, essentially because CO_2 diffuses out of the foam more easily than HFC-134a. In any case, selecting and promoting new blowing agents is an open question subject to more research efforts.

The object of the research program [1] was to study interactions between gases and polymers at high pressures and temperatures with the final goal to provide manufacturers of polymers with recommended gas/polymer systems and process methodologies in different areas essential in modern technology. Three main industrial activities are concerned by a better understanding and knowledge of gas/polymers systems and the specific interactions of gases and polymeric structures, *viz. the insulating material industry*, *the petroleum industry* and the *chemical industry*. In each case, gases and polymers of different types and nature are intimately interacting under external conditions of temperature (T) and pressure (p). The gas/polymer systems are either selected for a targeted industrial purpose *i.e. foaming materials* and *materials processing*, or are polymeric materials in contact with gas/liquid systems, *i.e. pipes or tank in gas and petroleum industry*. The industry of foaming materials is a rapidly growing area where constant innovation and added value products are key factors for economic success where international competition is high. The mastering of polymer degradation (typically blistering) by high pressure dissolved gases is another key issue. In all industrial and technical cases considered above, the knowledge of the interactions between gases and polymers or the mutual behavior of gases and polymeric matrices submitted to high pressure and elevated temperature must be clearly known and anticipated, that is to say correlated and predicted.

Our contribution to the basic research program consisted in developing the most accurate experimental techniques for measuring a coefficient of major importance for gases in polymers under high p and T, namely the solubility. Concomitantly, the necessary accurate experimental techniques had to be developed to measure the thermophysical coefficients of polymers subjected to high p and T in glassy and viscous liquid states. This basic research was supposed to deal with two main types of polymers: *thermoplastics* and *amorphous*, gases being of three main types: *simple gases* (CO_2, N_2), *gaseous hydrocarbons*, (C_1 to C_4) and HCFC. Typical pressures to

TABLE 1
Physical properties for blowing agents. Pressure at saturation p_{sat}, Ozone Depletion Potential (ODP) and Global Warming Phenomenon-Total Warming Equivalent Impact (GWP-TEWI).[a]

	CFC-12	HCFC-142b	HCFC-22	HFC-134a	HFC-152a	CO_2
Formula	CF_2Cl_2	CH_3CF_2Cl	CHF_2Cl	CF_3CFH_2	CH_3CF_2H	CO_2
Molar mass/$(g \cdot mol^{-1})$	120.9	100.5	86.5	102.0	66.0	44.0
Boiling point/°C	−29.8	−9.6	−40.8	−26.1	−24.7	–
p_{sat}/MPa at 25 °C	0.65	0.34	1.04	0.66	0.61	6.43
Flame limits as volume %	None	9.0 to 14.8	None	None	3.7-18.0	None
ODP	0.9	0.066	0.05	0	0	0
GWP-TEWI	8500	2000	1700	1300	140	1

[a] Information extracted from Climate Change 1995. The Science of Climate. Working group I. First published Cambridge University Press 1996.