



Solubility and interfacial tension of thermoplastic polyurethane melt in supercritical carbon dioxide and nitrogen



A. Primel^{a,b}, J. Férec^a, G. Ausias^{a,*}, Y. Tirel^b, J.-M. Veillé^b, Y. Grohens^a

^a Univ. Bretagne Sud, FRE CNRS 3744, IRDL, F-56100 Lorient, France

^b Cooper Standard, 194 route de Lorient, 35000 Rennes, France

ARTICLE INFO

Article history:

Received 22 July 2016

Received in revised form

25 November 2016

Accepted 28 November 2016

Available online 30 November 2016

Keywords:

Thermoplastic polyurethane

Solubility

Swelling ratio

Interfacial tension

ABSTRACT

Various industries, such as automotive and leisure, show a great interest in foaming thermoplastic polyurethane (TPU) with physical blowing agents. Hence, this study aims to investigate the effects of absorption of carbon dioxide and nitrogen by melt TPU on solubility and interfacial tension. Using a pressure–volume–temperature apparatus for high pressure and temperature combined with a magnetic suspension balance, the solubility of carbon dioxide and nitrogen in thermoplastic polyurethane melt was measured at temperatures from 190 °C to 220 °C and at pressures to 25 MPa. The solubility of both supercritical fluids (SCF) in the TPU melt was then compared with semiempirical data and theoretical values calculated from the Sanchez–Lacombe equations of state (S-L EOS). The surface tension of the TPU/SCF interface was measured using the axisymmetric drop shape analysis profile. It was observed that the dependency of interfacial tension on temperature at high pressures decreases because of a reduction in SCF solubility at high temperatures. The relationship between the interfacial tension and the density difference of polymer-supercritical fluid was also examined using the generalized Macleod's equation.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In a polymer–gas mixture, solubility is the maximum amount of gas that can be dissolved in a polymer at a specific temperature and pressure. Hence, solubility data helps to determine processing conditions for applications which require a single phase solution such as blending [1], wetting [2], dispersion of particles or fibers in polymers [3] and microcellular foaming [4]. Since the 1950s, much effort has gone into the investigation of gas solubility in polymer melts. Research methods have included experimental measurements and theoretical thermodynamic calculations. Phase equilibria [5], spectrometric [6], pressure–decay [7] and gravimetric [8] methods have been widely used to measure the solubility of physical blowing agents in polymers; however, none of them could precisely determine solubility at high temperatures and pressures because of the polymer–gas mixture swelling phenomena. To accurately measure solubility, the swollen volume or density of the polymer–gas solution must be obtained either by an equation of state (EOS) prediction or through an experimental method.

Two steps are involved in polymer foaming using physical blowing agents: nucleation [4] and cell growth [9]. Both these

processes modify the foam morphology which directly impacts on its mechanical properties [10]. The interfacial tension (IFT) of polymers is a key thermodynamic parameter in order to improve the foaming behavior of microcellular foams. Based on classical nucleation theory [11], the nucleation rate is related to the exponential cubic power of surface tension. A decrease of surface tension lowers the energy barrier for cell nucleation and exponentially increases the number of cells and the cell density.

Many researchers have predicted the solubility of different chemical and physical blowing agents (carbon dioxide (CO₂), nitrogen (N₂), hydrofluorocarbons, hydrochlorofluorocarbon, *n*-butane, isobutane, etc.) in various polymers [8,12–17]. However, apart from a few rare studies [18–20], such as those of Hossieny et al. [19], have provided butane solubility data for thermoplastic polyurethane. To our knowledge, no literature are dealing with strong solubility data as a function of temperature and pressure for CO₂, N₂ and TPU material. Recently, the automotive [21] and leisure industries have shown a great interest in replacing reticulated polyurethanes foamed with a chemical blowing agent by TPU foamed with a physical blowing agent because of its attractive mechanical, energy-absorbing, thermal-insulation properties and cost. Among physical blowing agents, supercritical fluids (SCF) such as CO₂ and N₂ are both suitable candidates to substitute conventional chemical blowing agents like chlorofluorocarbons [22].

* Corresponding author.

E-mail address: gilles.ausias@univ-ubs.fr (G. Ausias).

Therefore, a need exists to characterize the swelling and solubility at high temperatures and pressures and to determine their effects on the interfacial tension of a TPU/SCF mixture. In this study, the scaling parameters of Sanchez–Lacombe's [23,24] equations of state (S-L EOS) were obtained by applying pressure–volume–temperature data of thermoplastic polyurethane, carbon dioxide and nitrogen. These parameters were essential to get the swollen volume due to the sorption of the supercritical fluid by the polymer. The correct solubilities of TPU/CO₂ and TPU/N₂ mixtures were determined for a wide range of temperature and pressure. The IFT of the TPU/SCF interface was measured using an axisymmetric drop shape analysis profile (ADSA-P) and the relationship between the interfacial tension and the density difference of the polymer-supercritical fluid were examined with the generalized MacLeod's equation.

2. Materials and methods

2.1. Materials

The TPU material investigated in this study is the Irogran[®] A87H4615 and was received in the form of pellets from the Huntsman corporation. The soft segments are made from polyesters diols. Molecular weight was characterized by size exclusion chromatography: mass average molar mass was $\bar{M}_w = 108.90 \text{ kg mol}^{-1}$ and the polydispersity index was found to be $\text{PDI} = 1.912$. This TPU has a melting temperature of 180 °C, a specific gravity of 1.20, and a hardness of 80 Shore A at 23 °C. Carbon dioxide (99.995% purity) and nitrogen (99.999% purity) were provided by Westfalen AG, Germany.

2.2. Size exclusion chromatography

The high performance liquid chromatography technique requires solubilizing the polymer using a solvent, in this case a tetrahydrofuran (THF). Knowing the refractive index of the formed solution, the molar mass was determined using a light detector. Firstly, the refractive index was obtained by a linear regression using standard solutions analyzed by a differential refractometer (Optilab rEX) with a pump (Shimadzu LC20AD) and a valve with a 1 mL injection loop (Rheodyne). Then, the molecular masses of the polymer were determined by a multi-angle light scattering detector (Treas) with a pump (Shimadzu LC20AD), an online degasser (Shimadzu DGU-20A), a viscosimetric detector (Viscostar-II) and an ultraviolet array diode detector (Shimadzu SPD M20A). Four chromatographic columns, measuring 30 cm in length and 7.5 mm in internal diameter, containing PLgel (particle size of 5 μm) were used in series. THF was degassed using a fluoroethylene membrane and was used as the mobile phase at a flow rate of 1 mLmin⁻¹. The samples were dissolved in THF and were filtered through 0.45 μm pore size polytetrafluoroethylene (PTFE) filters. Measurements were performed at 23 °C.

2.3. Specific volume measurement

The specific volume measurements of TPU were performed using a high-pressure capillary rheometer (Goettfert Rheograph RG20) with three temperature controlled zones in the barrel (diameter 15 mm). This instrument allows PVT measurements to be taken using a specific length/internal diameter ratio (25/2) and a 15 mm piston diameter with a PTFE seal. The principle of this experiment is to measure the volume of polymer V at a fixed temperature T and compressive pressure P . Pressure increases in 5 MPa increments from 5 MPa to 25 MPa and the temperature sweep was performed at 5 °C min⁻¹ from 190 °C to 230 °C. Thermodynamic data (T, P, ρ)

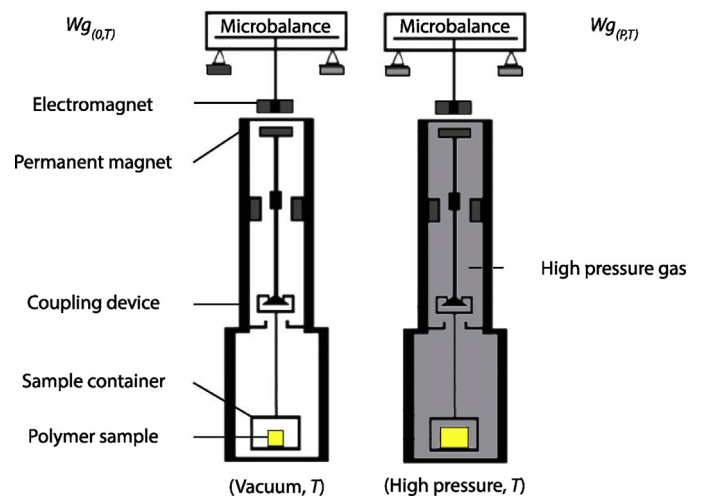


Fig. 1. A schematic of the magnetic suspension balance [13].

from the National Institute of Standards and Technology were used for carbon dioxide and nitrogen [25].

2.4. Solubility measurement

2.4.1. Apparatus for solubility measurement

Sorption isotherms of CO₂ and N₂ in TPU melts were determined gravimetrically using a magnetic suspension balance (MSB) from Rubotherm GmbH, as shown in Fig. 1.

At the initial stage, a polymer sample was placed in the container inside the sorption chamber. The chamber was sealed, evacuated, and preheated up. Initial weight $Wg_{(0,T)}$ was the balance data readout at vacuum ($P \approx 0 \text{ MPa}$) and temperature (T). The compressed fluid (CO₂ or N₂) was introduced and was maintained in the sorption chamber at the desired pressure value using a syringe pump. Temperature was controlled by a heating regulator during the whole sorption process. The weight of the sample kept increasing due to gas dissolution in the polymer sample until the equilibrium state was reached. When saturation remained stable, higher pressure gas was injected in 5 MPa increments up to a total of 25 MPa in such way that equilibrium could be obtained at each pressure stage. The weight of gas dissolved in the polymer Wg was calculated using the following relation:

$$Wg = Wg_{(p,T)} - Wg_{(0,T)} + \rho_1(V_H + V_2 + V_S) \quad (1)$$

where $Wg_{(p,T)}$ is the weight data readout at the equilibrium state at each condition (P, T), ρ_1 is the gas density, V_2 is the volume of the pure polymer sample at pressure P and temperature T ; V_H is the volume of the sample holder (including the sample container and the coupling device) and was measured using the buoyancy method at 200 °C and 20 MPa with Argon. Finally, V_S is the swollen volume of the polymer–gas mixture due to the gas dissolution. By neglecting the swollen volume term in Eq. (1), the measured weight gain was treated as the apparent weight gain (Wg_{app}) and was calculated using Eq. (2):

$$Wg_{app} = Wg_{(p,T)} - Wg_{(0,T)} + \rho_1(V_H + V_2) \quad (2)$$

Hence, the apparent solubility X_{app} can be evaluated:

$$X_{app} = \frac{Wg_{app}}{m_0} \quad (3)$$

where m_0 is the initial mass of the sample.

Download English Version:

<https://daneshyari.com/en/article/4909803>

Download Persian Version:

<https://daneshyari.com/article/4909803>

[Daneshyari.com](https://daneshyari.com)