

Rheology in Processing of Polymeric Foams

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ABSTRACT

Rheological properties of PCL and PLA were modified by means of reactive processing with chain extenders and/or peroxides and with the use of nanoclay. These materials were subsequently foamed in a batch process, by using mixtures of carbon dioxide and nitrogen at various foaming conditions.

INTRODUCTION

Foams can be defined as composite materials characterized by a solid or liquid continuous matrix which surrounds a gaseous phases. There are many examples of foams in nature, from wood to bone, and all of them are the evidence that in nature materials with different properties and, in particular gases, are employed to optimize the performance/weight of natural structures. The possibility of combining the properties of the continuous matrix and gas voids in a great variety of morphologies, is a powerful tool in the material industry to design and obtain objects having properties tailored for virtually any kind of application where performances and low weight are requested. For instance, foams can be rigid or flexible, low or high density, with closed or open cells and with different cell sizes and shapes.

The properties of these structures are therefore related both to the physical and mechanical properties of the matrix component and to the cellular morphology which develops under specific processing procedures and conditions. Several physical

and chemical phenomena, as well as process technology issues must be addressed to obtain foams with the desired performances. In particular, foam structure, morphology and properties are strictly related to the rheological and thermodynamic properties as well as to mass transport behaviour of the polymer/gas system, to the gas content, to processing conditions and to foaming dynamic¹.

The optimization of manufacturing processes of cellular polymers involves the control of rheological behaviour of macromolecular viscoelastic materials containing a dissolved gas at high concentration and at thermodynamic conditions able to promote the formation of gas bubbles in the melt. Nucleation and growth rates, which determine the final morphology of the foam, are, in turn, related to the physical and the rheological properties of the polymeric melt, i.e. surface tension, elongational viscosity of the polymer/gas system, solubility and diffusivity of the gas into the melt. Since most of these physical characteristics are not of simple experimental evaluation, due to the difficulties of measuring physical and mechanical properties of polymer/gas solutions, theoretical prediction of the effect of the operative conditions on the foaming process, possibly based on the available experimental data, becomes an important tool for an off-line optimization of the entire process. It requires the knowledge of reliable equation of state for polymer mixture, of models for mass transport

properties and surface tension as well as for rheological behaviour.

Suitable materials for industrial foaming applications must display adequate properties, and their manufacture process must be relatively simple and inexpensive. The main requirement is the foamability which, for thermoplastic polymers, is related to the rheological characteristics of the melt^{2,3}. In particular, the strain-induced hardening behavior is a fundamental characteristic for the foaming process, since it permits to withstand the stretching forces at the latter stage of the bubble growth. There are basically two possibilities to improve the elongational properties of the melt: i) optimize the molecular weight and molecular weight distribution of the polymer, ii) the branching of the macromolecules⁴.

In this work, the foaming process of biodegradable polyesters was investigated. In particular, poly(ϵ -caprolactone) (PCL) and poly(lactic acid) (PLA) were chemically modified by reactive processing. They were foamed under controlled conditions and the morphology was correlated to the modification of the rheological properties.

Another strategy for improving the foamability of thermoplastic biodegradable polymers is the use of nanoparticles^{5,6}. Nanometric filler, in effect, determine extensive modifications of properties such as gas sorption and diffusivity, local thermodynamic properties responsible for nucleation and growing phenomena, and rheological characteristics of the melt. In this study, nanocomposites based on PCL and PLA were prepared by melt mixing and subsequently foamed with a batch foaming process. The effects of the presence of nanoclay in PCL and PLA matrices on foaming were analyzed.

The present paper is also aimed to describe the prediction of shear viscosity of polymer/gas mixtures using a simple model in which the Simha-Somcynsky equation of state (SS-EOS) has been used to describe and predict both the volumetric and the free

volume properties of the polymer/diluent mixtures.

EXPERIMENTAL

Reactive processing/molecular architecture modification

Poly(ϵ -caprolactone) (PCL CAPA 6800, Solvay Interlox Ltd.) and poly(lactic acid) (PLA Nature Works® 3000D from Cargill-Dow, UK) were used through this study. PCL was chemically modified using dicumyl peroxide (DCP). Four concentration of DCP (0.25, 0.5, 1 and 2% wt) were used to modify PCL, according to procedure described elsewhere⁷. The reactive modification of PLA was carried with two chain extenders, 1,4-butanediol and 1,4-butane diisocyanate, as described in a previous paper⁸.

Nanocomposite preparation

Nanocomposites based on PCL and PLA and organically modified layered silicates were prepared by melt mixing. A commercial organoclay, named Cloisite 30B, was used for the preparation of nanocomposites. It was purchased from Southern Clay Products Inc., USA, and used as received. The processing conditions have been described elsewhere⁹⁻¹¹.

Rheological characterization

Dynamic rheological measurements were carried out using an ARES rheometer from TA Instruments, USA. The measurements were performed in an oscillatory shear mode using parallel plate under nitrogen atmosphere. Frequency sweeps between 0.01 and 10 rad/s were carried out at low strains (0.1-10%) which have been shown to be within the linear viscoelastic range of the measured samples. Experimental details can be found elsewhere^{8,10}.

Batch foaming

The materials were foamed in a batch

apparatus, a thermoregulated and pressurized cylinder that was suitably modified to allow a careful measurement and control of the main process parameters. Typical experiments were conducted using the following procedure: samples 2 mm thick, diameter 15 mm, were saturated with an 80/20% N₂/CO₂ mixture at fixed conditions of temperature and pressure. The vessel was then cooled to different foaming temperatures, and finally pressure-quenched to the ambient pressure, using a controlled pressure drop rate. A more detailed description of this system has been provided elsewhere¹².

The densities of the foamed samples were determined by weighing in water and in air, using a balance with a resolution of 10⁻⁴ g, according to ASTM D792. For microstructural analysis, the foamed samples were analyzed by a scanning electron microscope (LEICA mod. S440).

RESULTS AND DISCUSSION

Effect of molecular modification on rheological properties

Rheological properties are affected by the molecular architecture and, even at very low branching level, their measurement allows the analysis of the branching reaction extent¹³. The viscoelastic properties, measured in frequency sweep tests, show the extent of the rheological modification of the material. Figure 1 reports G' and G'' vs. frequency for neat PCL and selected PCL/DCP samples. The typical dynamic moduli distributions of incipient crosslinking systems are observed (see, for instance, Winter and Mours¹⁴), with G' and G'' proportional to each other at DCP composition intermediate between 0.5 and 1%.

Similar results were observed in chemically modified PLA. Neat PLA exhibits typical Newtonian behavior in the low frequency region and small shear

thinning starts from 10 rad/s that is a characteristic for linear polymers.

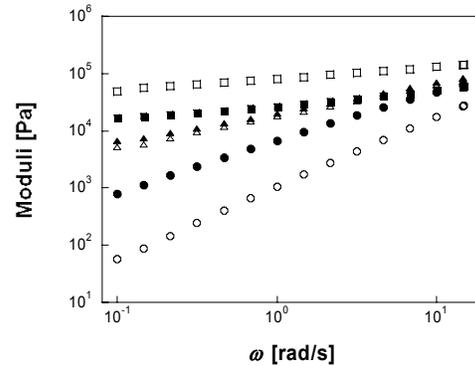


Figure 1: viscoelastic properties of neat and DCP modified PCL, 100°C. G' open symbols, G'' closed symbols. (●) neat PCL; (▲) 0.5 %; (■) 1%

Modified PLA showed a much higher complex viscosities than neat PLA with a marked non-Newtonian behavior even at low frequencies. Such modification has also caused a dramatic increase in storage modulus, G' , and loss modulus, G'' .

Effect of molecular modification on foam structures

The molecular architecture modifications affect the properties of the expanding matter and, hence, its foamability, as described in the introduction. The enhancement of the viscoelastic properties is expected to hinder cell growth and, also, reduce the cell wall rupture and the collapse of the cellular structure.

The chemical modified materials can be foamed at higher temperatures, since the enhanced viscoelastic properties prevent cell coalescence. In the case of DCP modified PCL, at a temperature as high as 55°C, neither coalescence, nor cell wall rupture were observed (see Figure 2b and 2c). Moreover, their morphologies are characterized by uniform cellular structure and fine cell dimensions. Neat PCL foams, conversely, at the same temperature have collapsed, as evidenced by the density increase and by the poor morphology, shown in Figure 2a.

Chemically modified PLA also showed improved foamability. In particular, the increase of melt elasticity of modified PLA led to lower density foams with a cellular morphology characterized by cells of smaller size.

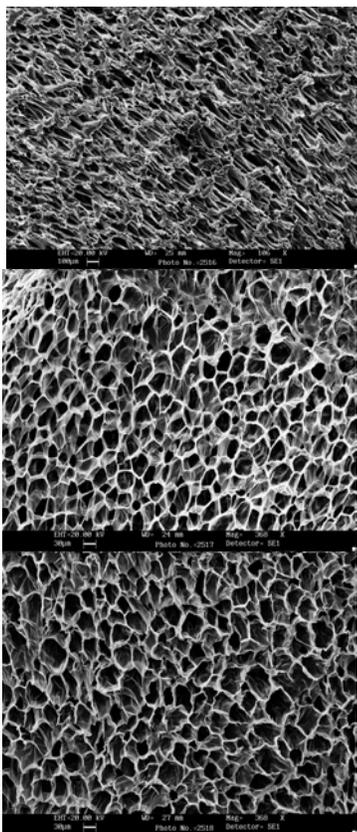


Figure 2: SEM micrographs of pure PCL (top, a) 100X; PCL/dicumyl peroxide (0.5%) (middle, b) 400X; PCL/dicumyl peroxide (1%) (down, c) 400X, foamed at 55°C

Effect of nanoclay on foam structures

The improved elastic and viscous properties of the nanocomposites melt have encouraged us to perform foam processing on them. Figure 3 reports the SEM images of neat PCL and of selected PCL based nanocomposites (neat PCL, 1% and 0.4%wt of Cloisite 30B, 3a, b and c, respectively, foamed at 40°C with a mixture of N₂ and CO₂). The nucleating effect of the clay particles is evident, showing a one-order of magnitude reduction in the mean cell diameter. The density of the 1%

nanocomposites foam is higher than that of the neat PCL (0.07g/cm³ instead of 0.04g/cm³ for the neat PCL). This was due to the increased viscoelasticity of the nanocomposites with respect to the neat PCL and to the increased crystallization rate of the nanocomposites with respect to the neat PCL^{9,15}. By comparing Figure 3c with 3a and 3b, an interesting effect can be noticed: at 0.4%wt of clay, an open-cell, very fine structure was achieved. This behaviour has been ascribed to the crystalline phase and bubble nucleating effect of the filler. In fact, at the very low clay concentration (0.4%wt) a maximum in the crystallization rate has been reported⁹. At the foaming temperature of 40°C, PCL containing 0.4% of clay crystallizes (as measured by the crystallization half time) in less than one minute, while neat PCL in approximately 6.5 min. Therefore, at this concentration of clay, polymer crystallization and cell expansion occur in the same time scale.

The competition between solidification and expansion led to the rupture of cell walls (with filamentary structure, and higher density, 0.12g/cm³)¹⁶.

In PLA/clay nanocomposites, the average cell size decreases greatly with 1 wt% of clay and then levels off at higher 30B concentration. The bulk foam densities were measured and found to be significantly affected by the clay content (neat PLA foam density was 0.12 g/cm³ compared to 0.21 g/cm³ for 1%wt clay nanocomposites). The cell densities increase with the organoclay content (from 0.008*10⁸ cell/cm³ for pure PLA to 5*10⁸ cell/cm³ for PLA/5 wt% 30B).

Rheology of polymer/gas solutions

The knowledge of rheology of polymer/gas solutions is important for several reasons. It gives important information for the optimization of the manufacturing processes based on extrusion (extrusion/foaming, injection molding) or for computer-assisted die design.

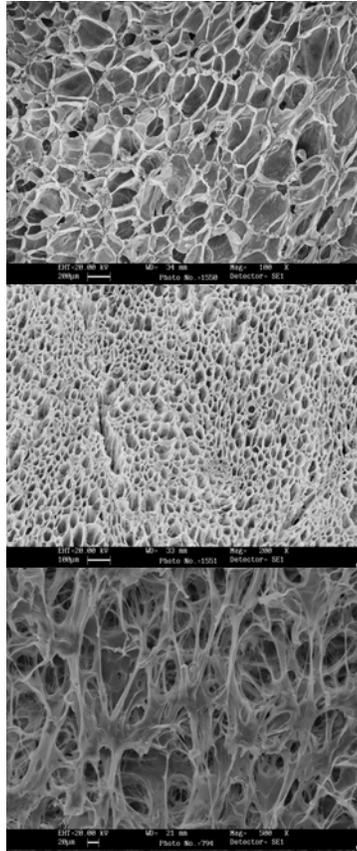


Figure 3: SEM micrographs of neat PCL (top, a) 100X; nanoclay PCL (1%) (middle, b) 200X; nanoclay PCL (0.4%) (down, c) 500X, all foamed at 40°C

The plasticization effect of the gas in the polymer melt results in lower viscosity whose extent depends upon the polymer/gas pair and the processability of new foam compound can be optimized by adjusting the composition and the processing parameters according to the rheological properties of the mixture. As already mentioned, rheology plays also a fundamental role in the development of the foam morphology. A low viscosity is generally desired for bubble nucleation and strain hardening elongational behaviour is necessary for the stabilization of the growing bubbles.

The measurement of the rheological properties of polymer/gas mixtures in shear is relatively simple. The principal accuracy is to avoid the formation of a biphasic flow

during the experiment. This can be obtained with several techniques, basically with *in-line* (directly in the process stream) or *on-line* (a sampling stream is taken from the process line and transferred to the measuring system) systems. For more details see the review by Gendron and Daigneault¹⁷. An *in-line* measurement can be performed by inserting a capillary die between the extruder at the exit die in such a way that the pressure inside the capillary is maintained above the critical pressure required for bubble nucleation.

The viscosity of the gas-containing melt is lower than the pure polymer. Experimental analysis on solution of polypropylene and polyethylene with foaming agents have shown that the ratio between the viscosity of the polymer/gas solution (η_s) and the viscosity of the pure polymer (η_p) is a function of the gas concentration and of the type of expanding gas^{18,19}.

If these two parameters are kept constant, this ratio is independent of the temperature, from the shear rate and the molecular weight of the polymer. This behaviour can be explained by considerations based on variations of the free volume fraction.

Following the approach proposed by Doolittle²⁰, the viscosity of a polymer above its T_g decreases as the free volume fraction increases, according the following equation:

$$a_c = \frac{\eta_{0,s}(C)}{\eta_{0,p}} = (1 - \omega_1)^n \left(\frac{V_p}{V_m} \right)^n \exp \left(\frac{1}{f_m} - \frac{1}{f_p} \right)$$

where $\eta_{0,s}$ and $\eta_{0,p}$ are zero shear rate viscosities, f_m and f_p are respectively the free volume fraction of the polymer/gas mixture and of the pure polymer, ω_1 is the weight fraction of the gas in the polymer melt, V_p and V_m are the specific volumes of the polymer and the polymer/gas mixture, n is the exponent for the dilution effect term. Based on the above equation, the ratio η_s/η_p

is a function of the variation of free volume fraction following the dissolution of the gas in the polymer melt. This variation is mainly dependent upon the polymer/gas system and its concentration and to the pressure. Most of the terms indicated in the above equation can be calculated if the equation of state of the polymer is known. In particular, V_p can be measured by performing PVT experiments, V_m can be predicted with EOS theories for polymer mixtures such as Sanchez-Lacombe^{21,22}, and Simha-Somcynsky^{23,24}, f_p and f_m can be computed from critical occupied volume²⁵ and free volume theories²⁶⁻²⁸, n is a phenomenological terms that can vary from 3 to 3.5²⁹⁻³⁰.

In Figure 4 are shown the rheological data of PCL and PCL/CO₂ measured by our group with the *in-line* technique. First of all, the viscosity measured with the *in-line* technique on neat PCL is in agreement with the viscosity data obtained with a capillary rheometer. Moreover, as expected, the rheological curve of the mixture containing 2.3% of CO₂ is only shifted to lower values maintaining a similar dependence on shear rate. The theoretical prediction obtained with the use of the above equation was in good agreement with experimental results (see Figure 4, dotted line). The model utilized for the prediction of parameters in equation was the Simha-Somcynsky EOS and the following parameters were used:

- For pure PCL: T=100°C, p=40bar; $V_p=0.9609\text{cm}^3/\text{g}$, $f_p=0.1049$
- For mixture with 2.3% of CO₂, T=100°C, p=80bar; $V_m=0.9585$; $f_m=0.1092$

CONCLUSIONS

Macromolecular modification and nanocomposite concepts were applied to the foaming of two biodegradable polyesters, PCL and PLA. Both approaches have been demonstrated extremely useful and effective in enhancing the foamability of the two materials. Both, in fact, allowed a finer control of the final foam properties such as

final density and cell topology (mean cell dimension, cell dimension distribution and eventual cell opening).

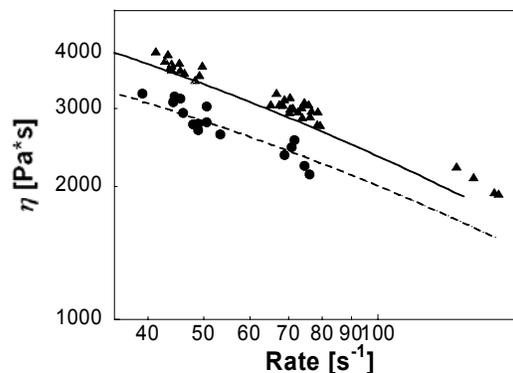


Figure 4: Shear viscosity of PCL and PCL/CO₂ mixture at 100°C: pure PCL, capillary rheometer (continuous line); (\blacktriangle) pure PCL, *in-line* measurements; (\bullet) PCL + 2.3%wt CO₂, *in-line* measurements

Peroxide-modification on PCL allowed an extension of the foaming window (in particular, towards higher foaming temperatures), while diisocyanate-modification on PLA resulted in foams with lower density and finer morphology with respect to the neat PLA. Nanocomposites, mainly, increased cell nucleation, resulting in foams with a finer morphology for both PCL and PLA, while the final density increases due to the increased viscosity of the nanocomposites and to the faster crystallization. Finally, open-celled PCL foams were obtained by a careful selection of the nanoclay concentration and processing conditions.

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