

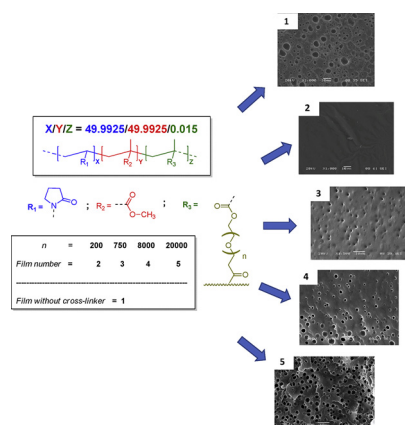
Microcellular polymer films based on cross-linked 1-vinyl-2-pyrrolidone and methyl methacrylate

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GRAPHICAL ABSTRACT



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ABSTRACT

A series of cross-linked copolymer films based on 1-vinyl-2-pyrrolidone and methyl methacrylate were produced using different poly(ethylene glycol) dimethacrylates as cross-linking agents. The average molecular mass of the cross-linking agent was varied, then allowing the foaming process using supercritical CO₂ (ScCO₂), obtaining microcellular films with different cellular structures as a function of the molecular mass of the cross-linking agent. The chemical structure, swelling behavior, CO₂ uptake and cellular morphology of the materials were studied. Finally, the influence of the different cross-linking agents in the mechanical properties was also evaluated by measuring the tensile properties of the microcellular films.

1. Introduction

In the last two decades, supercritical carbon dioxide (ScCO₂) has been used as foaming agent to obtain microcellular polymer foams. CO₂ presents numerous advantages, such as: non-toxicity, inertness, non-

expensive and it can be easily employed in supercritical state in several processing applications due to the accessible critical conditions (31 °C and 73 bar).

Concerning polymer foaming, CO₂ presents a good solubility in amorphous polymers, and it is employed in dissolution gas foaming

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processes to obtain micro and nanocellular polymers [1]. The foaming process begins with the saturation of the polymer with CO₂ in the supercritical regime, during a fixed time. After saturation of the sample, approaching or being in a rubbery state, system is depressurized to atmospheric pressure, taking advantage of the swelling and plasticization of the polymer, reducing the glass transition temperature, allowing the gas expansion. The cellular microstructure may be controlled by changing the saturation temperature and the depressurization rates. In the last years, the improvement of the processing techniques have led to the obtention of nanoporous polymeric materials, in which new properties have emerged due to the reduction of the cell size (i.e., below 200 nm) [2]. One of the most promising and analyzed properties is the thermal conductivity, which decreases drastically when reducing the cell size, due to the apparition of the knudsen effect [3], thus obtaining low-density polymers with super-isolating properties [4]. In this investigation line, our group has recently published a research work focused on the thermal properties of microcellular polymer foams based on 1-vinyl-2-pyrrolidone and butyl acrylate [5]. The physical properties of nanocellular polymers has been reviewed by Notario et al. [6].

In parallel, there is an increasing interest in the development of porous polymer thin films, due to the important number of applications based on these materials. The classical techniques include the use of organic solvent in several steps reactions. However, the use of ScCO₂ to generate nanoporous polymer films has attracted great attention only in the last years [7]. In this sense, different research works have been published reporting the fabrication of different micro or nano cellular polymeric films using ScCO₂ as foaming agent [8,9], but there are still several difficulties to overcome, mainly related to the rapid diffusion of the CO₂ out of the polymer during the depressurization process. The research works presented by Siripurapu et al. analyze the use of different processing parameters and inorganic charges to produce microcellular polymeric films based on PMMA [10,11], but only a few promising results have been reported up to date.

The confinement of the CO₂ during the depressurization process is one of the key problems to obtain homogeneous micro and nanocellular polymeric films. In this sense, the use of different chemical cross-linking agents, added to the polymer matrix, can retain the CO₂ molecules during the depressurization process, thus controlling the cellular structure parameters (cell density and cell size), as a function of the cross-linking agent employed [12,13]. In our case, the use of methacrylate-based crosslinking agents is particularly interesting due to their good CO₂-philicity, thus enhancing their foamability behavior [14]. Another interesting alternative is the use of physical cross-linking process, in which the polymer is irradiated with electrons to difficult the molecular movement, stabilizing the structure during the foaming process. This research line focuses the last published works of different authors, analyzing both the physical foaming using ScCO₂ and also the use of chemical blowing agents [15–17]. On the contrary, it is well known that the use of cross-linking agents in ScCO₂ foaming can difficult the CO₂ sorption process, thus limiting the nucleation sites and the formation of the cellular structure.

The study of mechanical properties of foamed polymers is also a very interesting topic, especially when cell size is reduced down to micro and nanocellular range. In this sense, microcellular polymer foams offer improved toughness, strength, and stiffness respect to solid polymers. Thermal insulation in nanocellular materials has been extensively analyzed during decades, but on the other hand, the research associated to the mechanical properties of these materials has only increased recently. Following this investigation line, different authors have presented several works in the last years focused in the analysis of different mechanical properties (compression, tensile or impact), of micro and nanocellular amorphous polymers (mainly PMMA and PEI) obtained using ScCO₂ [18–21].

Bearing all these ideas in mind, in this work we present a procedure to obtain microcellular amorphous polymeric films using ScCO₂ as foaming agent with controlled morphological structure through the

addition of a crosslinker agent with different molecular masses. Film is placed between two steel plates during the saturation process, then confining the CO₂ during the depressurization process, allowing the formation of the microcellular structure [9,10]. The addition of different cross-linking agents, based on poly(ethylene glycol) dimethacrylates with different molecular masses (between 200 and 20,000), tunes the cellular structure, in terms of homogeneity and cell size, and also the mechanical properties. To evaluate and quantify this correlation, the Young's modulus, elongation at break and tensile strength of the microcellular films were analyzed through low-velocity tensile tests.

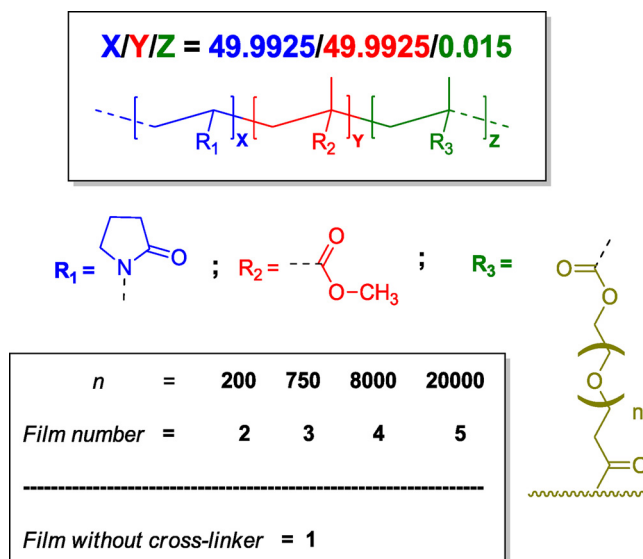
2. Experimental

2.1. Materials

All materials were used as received and were commercially available. The list includes: 1-vinyl-2-pyrrolidone (VP) (Aldrich, > 99%), methyl-methacrylate (MMA) (Aldrich, > 99%), and poly(ethylene glycol) dimethacrylate as cross-linking agent (PEGDMA) with different molecular masses (200, 750, 8000 and 20,000). PEGDMA₂₀₀, PEGDMA₇₅₀ and PEGDMA₂₀₀₀₀ were supplied by Aldrich, (> 98%), whereas PEGDMA₈₀₀₀ was supplied by Alfa Aesar (> 98%). 2,2-dimethoxy-2-phenylacetophenone was used as UV photo-initiator (Fotoi) (Aldrich > 99%).

2.2. Film preparation

Films were prepared via a simple bulk radical copolymerization process, which is extensively described in detail in one of our previous works [21]. VP was copolymerized with MMA and the corresponding PEGDMA, with proportions 49.9925/49.9925/0.015 (molar feed ratio), using Fotoi (0.16 wt.%) as UV radical photo-initiator. As a consequence, we maintained the nominal cross-linking ratio (X) value fixed to 3·10⁻⁴ mol PEGDMA/mol VP and also to 3·10⁻⁴ mol PEGDMA/mol MMA (value of X can be easily calculated as the percentage of the ratio between the moles of the cross-linker and the moles of each monomer). Then, the cross-linking density was kept constant to eliminate the influence of this parameter in the foaming behavior. Bulk radical polymerization reaction was carried out in a silanized glass mold (100 μm thick) in an oxygen-free atmosphere at RT overnight. The chemical structure of the films is presented in Scheme 1. The films were transparent, flexible and also easily manageable.



Scheme 1. Structure of the films.

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