# Effect of Molecular Modification on PCL Foam Formation and Morphology of PCL

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**Summary:** Poly($\varepsilon$-caprolactone) was chemically modified by using dicumyl peroxide from 0.25 to 2 % (w/w) and the effects of molecular architecture on the density and morphology of PCL foams were examined. The polymer was first blended with dicumyl peroxide at a low temperature (80°C), to prevent premature peroxide decomposition. The peroxide modification was then performed at different temperatures, from 110°C to 150°C. The reaction kinetic was followed by measuring the dynamical rheological properties of the melt in isothermal experiments by using a parallel plate rheometer. The evolution of the macromolecular structure during the chemical reaction was followed by analyzing the time evolution of the complex viscosity. Foams were prepared from the peroxide modified PCL with a batch foaming process using nitrogen as the foaming agent under different process conditions. As expected, the increase of the molecular modification led to a shift towards higher temperatures of the foaming window and, moreover, influenced the viscoelastic behavior of the expanding polymeric matrix so that the final foam properties are affected.

**Keywords:** chemical modification; dicumyl peroxide; foaming; polycaprolactone

## Introduction

Polymeric foams are two phase materials with unique properties which enable their use for various industrial applications, particularly when good mechanical properties and low weight need to be coupled or when specific functional properties are required. Typical examples are packaging, transport, acoustic insulation and damping, energy-absorption devices. The recent development of a variety of processes for making polymeric foams with improved properties at lower cost has led to an increased interest in their use in engineering components. For this reason, the design, control and optimization of the

physical properties of these materials are important steps in the development of final products with appropriate macroscopic properties for the particular application.[1,2]

Polymeric foams produced by physical expansion processes are based on three steps: first, the polymer is saturated with the blowing agent, at a fixed temperature ($T_{sat}$) and pressure ($P_{sat}$) so that an homogeneous mixture is obtained; the second step includes bubble formation and growth, which are induced by a change of thermodynamic conditions, generally through pressure reduction to atmospheric pressure ($\Delta P = P_{sat} - P_{atm}$). Once nucleated, a bubble continues growing as the blowing agent diffuses into it. More precisely bubble growth is influenced by the diffusion of gas molecules which inflate the bubble against the viscoelastic and surface forces that are exerted by the polymer-blowing agent mixture.[3-5] The final step relates to the stabilization of the cellular structure which is generally achieved by cooling the expanded matter to room temperature. The choice and control of suitable process parameters and the chemical modification of the material in order to change its viscoelastic properties are two possible ways to control the density and/or the morphology of polymeric foams.

Several investigations on the foaming process have indicated three fundamental process parameters that allow the control and the optimization of the cellular structures, in terms of mean cell size and cell size distribution, structure and connectivity:[6-13]

1. gas mass fraction at equilibrium ($\omega_{sat}$)

2. foaming temperature ($T_{foam}$), that is the temperature at which foaming occurs

3. pressure drop rate ($\Delta \dot{P}$), that is how fast the pressure is released

The chemical modifications affect the viscoelastic properties of the polymeric matrix[14-17] and plays an important role on the cell growth process.[18,19] An increase in viscosity is expected to affect the final foamed structure by increasing its density and decreasing the cell dimensions. But the control of cell growth is not trivial. The purpose of this paper is, therefore, to understand the relationship between rheological properties of a polymeric matrix and its cellular structure in a biodegradable foam. To this aim, the viscoelastic properties of poly(ε-caprolactone) were modified through branching and/or crosslinking of the polymeric matrix using dicumyl peroxide, which was reported to generate polymeric radicals by hydrogen abstraction reactions. Polymeric radicals immediately react to generate branching and crosslinking.[20] Samples of different degrees of chemical modification were subsequently foamed and the foams analyzed to understand the morphological effect.

# Experimental

## Materials

Poly($\varepsilon$-caprolactone) (PCL), was kindly supplied by Solvay Interox Ltd. (PCL CAPA 6800). Some characteristics of the polymer used were: weight average molecular weight = ~80000; $T_g$ = -60°C; $T_m$ = 60°C; and Young modulus = 450MPa. Dicumyl peroxide (DCP) was used for the preparation of chemically modified PCL. DCP was purchased from Aldrich and was used as received. In the foaming process, commercially pure grade $N_2$ was used as the blowing agent.

## Chemical Modification of PCL

A Haake Rheomix 600 internal mixer with two roller rotors was used for the preparation of the PCL/DCP blends, containing 0.25, 0.5, 1 and 2%wt. of dicumyl peroxide. The PCL/DCP mixing temperature was set at 80°C, so that no premature DCP decomposition started during this step. The rotating speed of the rotors and mixing time were fixed at 100 rpm and 10 min, respectively.

The peroxide modification was then performed at a different temperature, from 110°C to 150°C and the reaction kinetic was followed by measuring the dynamic rheological properties of the melt in isothermal experiments by using a parallel plate rheometer (Ares) from Rheometrics Inc., USA.

## Foam Preparation and Characterization

The chemically modified materials were foamed in a batch apparatus, a thermoregulated and pressurized cylinder. Typical experiments were conducted using the following procedure: PCL samples 5 mm thick, diameter 15 mm, were saturated at 75°C with $N_2$ at saturation pressure, $P_{sat}$ = 180 bar, for at least 6 hours. The vessel was then cooled to different foaming temperatures, $T_{foam}$, in the range 40-55 °C and finally pressure-quenched to the ambient pressure, using a fixed pressure drop rates, $\Delta \dot{P}$ = 320 bar/s. The pressure vessel for the preparation of foam samples was designed to allow a careful measurement and control of the three process parameters of interest. For the temperature control, an electrical heater as the heating element and a heat exchanger with an oil bath as the cooling element were used, both controlled by a PID thermoregulator. A pressure transducer was used to measure the pressure during the saturation step and to register pressure history using a data acquisition system (DAQ PCI6036E, National Instruments,

USA) during blowing agent discharge, which occurs through a discharge valve (HiP ball valve, model 15-71 NFB) controlled by an electromechanical actuator (HiP, model 15-72 NFB TSR8). 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 analysed by SEM. The samples were first sectioned in liquid nitrogen and then coated with gold using a sputter coater (Emscope SC500). The morphology of the fracture surface was studied using a LEICA mod. S440 scanning electron microscope, operated at 20 kV.

## Results and Discussion

### Effect of Molecular Modification on Rheological Properties of PCL

Rheological properties are affected by the molecular architecture and, even at very low branching level, their measurement allows the analysis of the branching reaction extent.[21] The kinetic of molecular modifications was followed by analyzing the time evolution of complex viscosity in isothermal experiments using a parallel plate rheometer. The results of the effect of the reaction on the rheological properties are reported in Figure 1 and Figure 2.
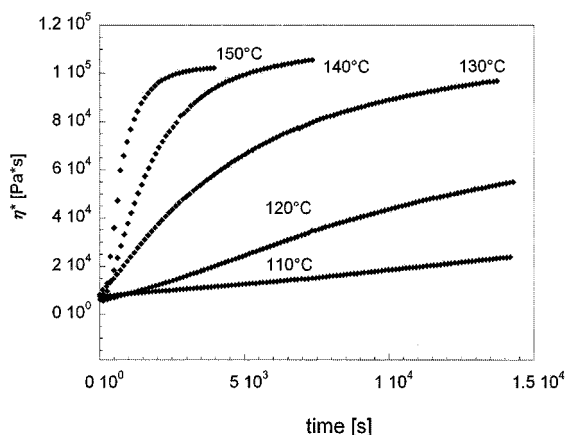


Figure 1. Effect of temperature on reaction rate and final degree of molecular modification of PCL/dicumyl peroxide (1% wt.) blend.
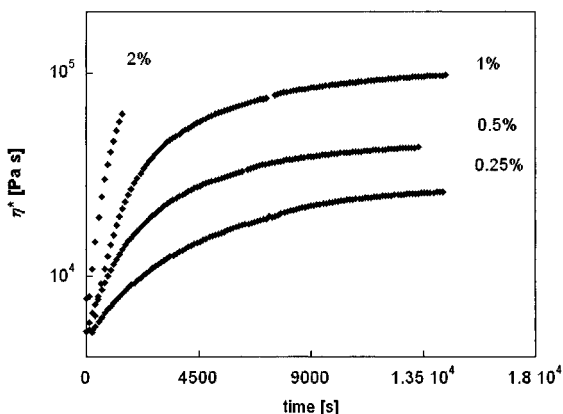
Figure 2. Effect of dicumyl peroxide concentration on reaction rate and final degree of molecular modification of blend. Temperature is set up to 130°C.

The reaction rate increases when the temperature increases, in experiments performed on PCL/dicumyl peroxide containing 1%wt of peroxide (Figure 1). Similar results are reported in Figure 2, which shows the evolution of complex viscosity in experiments conducted at the same temperature (130°C) but at different contents of DCP (from 0.25 to 2%wt.). The final degree of molecular modification increases with the increase of the DCP content. The viscoelastic properties, measured in frequency sweep tests, show the extent of the rheological modification of the material. Figure 3 reports G′ and G″ vs. frequency for selected PCL/DCP samples .

The typical dynamic moduli distributions of incipient crosslinking systems is observed (see, for instance, Winter and Mours [22]), with G′ and G″ proportional to each other at DCP composition intermediate between 0.5 and 1 % (see Figure 3). Narkis and Wallerstein reported the inception of gel formation at about 0.75% DCP, as measured by solubilizing the PCL/DCP samples in boiling benzene.

The gradual evolution of the reaction allows the careful selection of the molecular and viscoelastic modification by a proper selection of DCP concentration, reaction time and temperature.
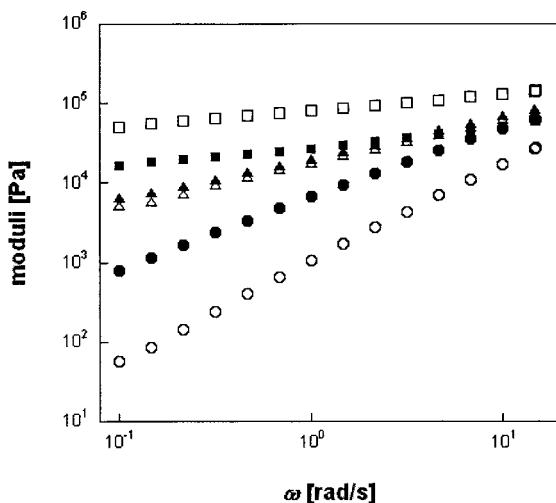
Figure 3. Dynamic moduli of neat and modified PCL (neat PCL, 0.25 and 1% DCP); G′ (○) and G″ (●) of neat PCL; G′ (△) and G″ (▲) of PCL/dicumyl peroxide (0.25 %); G′ (□) and G″ (■) of PCL/dicumyl peroxide (1%).

### Effect of Molecular Modification on PCL Foam Structure

The molecular architecture modification resulted by the peroxide decomposition reaction affects 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. These effects are herein described in relation to the final foam density and mean cell diameter. Figure 4 reports the effect of the foaming temperature on the final foam density for both neat PCL and peroxide-modified PCL. The typical behavior with a minimum is observed with the neat PCL foams. This behavior is due to several mechanisms taking place during foaming. At a high temperature, cell collapse occurs due to the decrease of the melt strength of the polymeric matter, leading to foams of higher density. At lower temperatures, higher densities are related to the increase of viscosity and/or to the occurrence of partial crystallization of the polymeric matrix. Both the increase of viscosity and the occurrence of some crystallization reduce the deformability of the expanding matter and thus the foaming efficiency. When using the peroxide cured PCL, the increase of viscosity due to the molecular modification has led to foams at higher density (see Figure 4). The chemical modified materials, on the other hand, can be foamed at higher

temperatures, since the enhanced elongational properties prevent cell coalescence. In this case, at a temperature as high as 55°C, neither coalescence, nor cell wall rupture were observed. Neat PCL foams, conversely, at the same temperature have collapsed, as evidenced by the density increase (see Figure 4) and by the poor morphology, shown in the following SEM photographs.
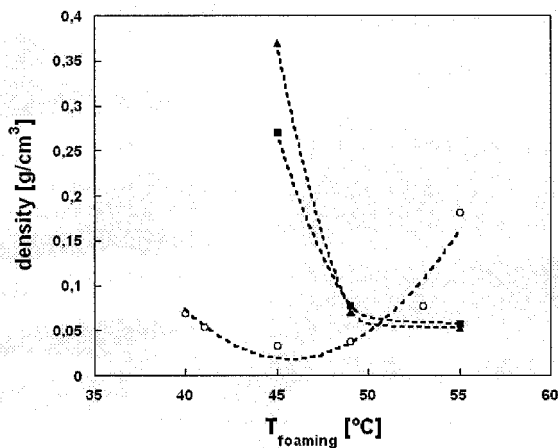


Figure 4. Effect of the foaming temperature on the final foam density of neat PCL (○); PCL/dicumyl peroxide (1%) (■);PCL/dicumyl peroxide (0.5%) (▲).

Figure 5 reports the micrographs of PCL foams obtained at 45°C for the neat polymer (Figure 5a) and the 1% dicumyl peroxide modified material (Figure 5b). The increase of the viscosity for the cured material is, in this case, responsible for the decrease of the cell size mean dimension (of the order of hundreds of microns for the neat PCL and tens microns for the cured PCL).



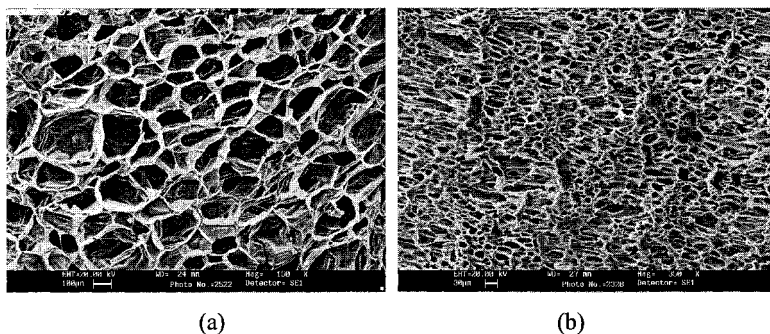(a)                                             (b)

Figure 5. SEM micrographs of pure PCL (a) and PCL/dicumyl peroxide (1%) (b), foamed at 45°C. Note: (a) is 150X magnification; (b) is 350X magnification.

Figure 6 reports SEM micrographs of the neat and modified materials expanded at 55°C. In this case, the neat PCL foam morphology is poor, indicating the foam structure collapse, which is also evidenced by the increase of the foam density, as reported in Figure 4. The morphology of the modified PCL is, conversely, characterized by a uniform cellular structure and fine cell dimensions. Another interesting point is outlined by comparing Figure 5a and Figures 6b,c: these foams are characterized by a similar density ($0.05 g/cm^3$, see Figure 4), while having different cell morphologies. In effect, the mean cell diameter of the neat PCL foamed at 45°C (Figure 5a) is 170µm, while peroxide modified PCL, foamed at 55°C (both 0.5%, Figure 6b and 1%, Figure 6c) have an average cell diameter of 50µm. This aspect is important in some technological applications, where the optimization of both mean cell diameter and foam density is crucial. Through using the modified PCL it is possible to control these parameters independently, by changing the foaming temperature and the degree of molecular modification.
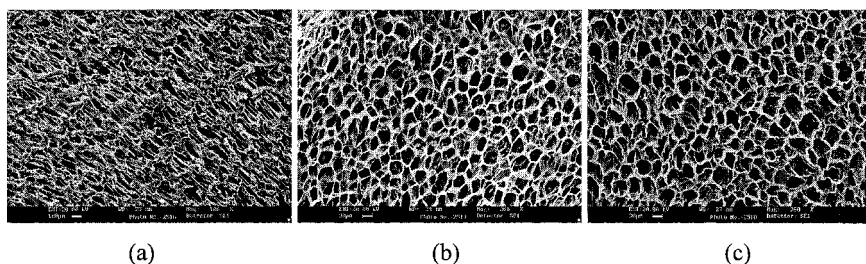


(a)            (b)            (c)

Figure 6. SEM micrographs of pure PCL (a); PCL/dicumyl peroxide (0.5%) (b); PCL/dicumyl peroxide (1%) (c), foamed at 55°C. Note: (a) is 100X magnification; (b) and(c) are 350X magnification.

## Conclusions

Poly(ε-caprolactone), a biodegradable polymer, was chemically modified using dicumyl peroxide to improve its elongational viscoelastic properties. The reaction kinetics were followed by analyzing the time evolution of complex viscosity in isothermal experiments. Results have shown that the increase of the peroxide content or the increase of the reaction temperature has led to an increase of the final degree of chemical modification and the reaction rate, respectively. Moreover the gradual evolution of the reaction allows the careful selection of the desired viscoelastic properties by a proper choice of process reaction parameters. The effects of chemical modification on the microstructure of foams

were analyzed in terms of final density and mean cell size dimensions. As expected, the foaming temperature window of branched PCL shifts towards higher values due to the viscosity increase of these materials. Another interesting result is represented by the ability to obtain foams with similar density but different cell morphologies, by tuning the molecular modification of the biodegradable polymer and the foaming temperature.

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