Heterogeneous bubble nucleation in PCL/clay nanocomposite foams

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Abstract

Nanocomposites based on biodegradable polycaprolactone (PCL) and organically modified layered silicates (organoclay) have been prepared by melt mixing. The foaming process of PCL/clay nanocomposites containing 2 and 5%wt of clay were investigated by using a batch process. The results showed that the presence of clay resulted in the increase of cell density and a reduction of cell size compared to pure PCL.

Key words: polycaprolactone, organoclay, nanocomposites, foam

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1. Introduction

Polymer nanocomposites based on nanoscale particulates of clays are receiving great interest, due to the markedly improved properties compared to pure polymers or conventional particulate composites. The improvement of modulus, strength, barrier properties, heat resistance, etc. are achieved at the very low loading of the inorganic components (1-10%) compared to conventional filled polymers (20-40%) [1-4].

Direct melt intercalation is being recognised as a promising approach because it can be performed by using a conventional polymer mixing or extrusion process. The preparation of the nanocomposites require extensive delamination of the layered clay structure and complete dispersion of the resulting platelets throughout the polymer matrix. This is readily achieved when using a high surface energy polymers, which determine a good adhesion between the polymer and the clay phase. For some low-energy materials, such as polyethylene and polypropilene, chemical modification can improve the dispersion process and the final properties of the nanocomposites. The commercial thermoplastics of interest to be hybridized with organoclay include styrenic polymers [5, 6], polyolefins [7,8], nylons [9, 10] and so on.

It has been shown that the presence of nanoclay resulted in the increase of crystallization rate and the decrease of undercooling degree required for crystallizing nucleation [11-12]. In the present study we investigated the nucleating effect of nanoclay on the crystallization and foaming process of PCL/clay nanocomposite.

2. Experimental

2.1 Materials

The PCL used was Solvay's CAPA 680, in the form of pellets and was supplied by Solvay Interox Ltd. Some characteristics of the polymer used were: Mw = 120000ca, Tg = -60°C, Tm=60°C. The organoclay used in the preparation of nanocomposites was purchased from Southern Clay Products Inc, USA, under the commercial name of Cloisite 30B (whereafter referred as 30B) and was used as received. According to the product information from producer, this 2:1 montmorillonite (MMT) contains a quaternary ammonium ion containing methyl tallow bis-2-hydroxyethyl (MT2EtOT) as the organic modifier, respectively.

2.2 Samples preparation

A HAAKE RHEOMIX®600 internal mixer with two roller rotors was used for the preparation of the PCL/organoclay nanocomposites containing 2%w (PCL2) and 5%w (PCL5) of 30B. The mixer is controlled by a measuring drive unit, HAAKE RHEOCORD® 9000. The processing temperature was set at 100 °C. The rotating speed of the rotors and mixing time were fixed at 100 rpm and 12 minutes.

Foams were prepared by using a pressure vessel thermoregulated by electrical heaters and a cooling oil bath. The experiments were conducted using the following procedure. Small samples (around 1g) of PCL were saturated at 70°C and 150 bar with a CO_2/N_2 (20/80 w/w) mixture for at least 6 hours. The vessel was then cooled to the foaming temperature, T_{foam}=40°C, and the pressure was quickly released to allow the nucleation and growing of the bubbles.

2.3 Characterization

Differential scanning calorimetry (DSC) analysis was carried out on DSC2920 (TA Instruments, USA). The samples were heated from 20 to 100°C at 10°C/min under nitrogen atmosphere. They were then kept at 100°C for 3 minutes to eliminate the previous heat history, subsequently cooled to 40°C at 40°C/min and then kept at this temperature for the isothermal crystallization experiments

Dynamic rheological measurements were carried out using an advance rheometric expansion system (ARES) rheometer from Rheometric Inc, USA. The measurements were performed in an oscillatory shear mode using parallel plate geometry of 25 mm in diameter at 70°C under nitrogen atmosphere. Specimens were placed between the preheated plates at 70°C for a complete melting and were allowed to equilibrate prior to each frequency sweep run. Frequency sweeps between 0.01 and 15 Hz were carried out at low strains (2%) that have been shown to be within the linear viscoelastic range.

3. Results and discussion

3.1 Thermal and rheological properties

The preparation and the characterization of nanocomposites based on biodegradable polycaprolactone (PCL) and organically modified layered silicates (organoclay) have been reported in a previous publication [13]. We showed that the exfoliation of organoclay could be achieved via melt mixing process in the internal mixer which also showed dependence on the type of organic modifier, organoclay contents and the processing temperature.

The thermal analysis was performed in order to verify the effect of nanoclay concentration on the crystallization temperatures of the nanocomposites during cooling and these results

were used to optimize the foaming process in the batch reactor. As shown in figure 1, the crystallization rate during the isothermal experiment increases dramatically in presence of nanoclay. The half time $t_{1/2}$ decreased from 3500s (PCL) to 700s for PCL2 and 750s for PCL5. This behaviour can be explained by the assumption that the silicate layers act as efficient nucleating agents for the crystallization of PCL matrix causing a higher crystallization rate compared to that of the neat PCL. These results are confirmed by the Avrami constant n (table 1) which decreased from 3 to 2.

The rheological properties of the nanocomposites were analyzed with the aim of understanding the effect of nanoclay concentration on the bubble growing. The viscous forces around the bubble determines the growing kinetic and, as showed below, the final density of the foams. The phenomena governing the expansion of the bubbles are related to the transport properties of the gas in the polymeric melt and to the rheological properties of the matter around the bubble and they can be described by differential equations that consider the mass balance in the bubble, the mass balance of the gas in the solution and the force balance around the bubble [14]. The latter equation (eq.1) is strongly dependant on the elongational viscosity of the polymer/gas solution and it is a function of temperature and gas concentration.

$$\rho\left(\frac{\partial v_r}{\partial t} + v_r\,\frac{\partial v_r}{\partial r}\right) = -\frac{\partial P}{\partial r} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r\tau_{rr}\right) - \frac{\tau_{\theta\theta} + \tau_{\phi\phi}}{r} \qquad (1)$$

The dynamic rheological tests, reported in figure 2 show that the complex viscosity of nanocomposites are higher than that of the neat PCL, expecially in the low frequency range where, at 5 wt% of 30B, the viscosity curve of the nanocomposite have a much steeper slope. The increase of viscosity at low frequency, at which bubble growing takes place in the final

stage, influenced the maximum expansion of the foams. The addition of 5% of clay leaded to materials of higher density, as shown below.

3.3 Foam preparation and characterization

The use of the batch process to produce the nanocomposite foams allowed the control of the amount of gas solubilized in the polymer melt and, most important, the temperature at which the foaming takes place. Moreover, the absence of extensional and/or shear stresses, usually occurring during extrusion operations, permits to evaluate the effect of process parameters and material composition on the nucleation and growing phenomena, which results in foams of different cellular morphology.

The cellular structure of the PCL and PCL/clay foams are shown in figure 3 and the morphological characteristics of these foams (density, number and size of cells), reported in table 2.

The morphology of the nanocomposite foams changed with the presence of nanoclay. In particular, PCL containing the 2% of clay has a very similar density than PCL but a higher number of cells of smaller size, suggesting the occurrence of heterogeneous nucleation. This behaviour is in agreement with the results regarding the crystallization behaviour.

As all the thermodynamic phenomena, the nucleation process involves a variation of the free energy. It is interesting to observe that, in a transformation from a liquid to a solid (crystallization) the energetic barrier ΔG_c for an homogeneous nucleation is a function of the physical properties of the solid and liquid phases (hentalpy of fusion Δh, melting temperature T_f and interfacial energy γ) and of the undercoooling ΔT:

$$\Delta G_c = \frac{16\pi}{3} \frac{\gamma^3 T_f^2}{\Delta h^2 \Delta T^2} \tag{2}$$

In a very similar thermodynamic approach regarding the bubble nucleation, a very similar equation appears for the energetic barrier [15]. In particular, if the nucleation occurs on a solid surface, the equation becomes:

$$\Delta G_c = \frac{16\pi}{3} \frac{\sigma^3}{\Delta P^2} f(\theta) \tag{3}$$

were $f(\theta)$ account for the reduction of the critical energy due to the presence of a solid surface. The expression of $f(\theta)$ is [16]:

$$f(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4} \tag{4}$$

were θ depends upon the interfacial energies of the pairs gas/solid (σ_{gs}) gas/polymer (σ_{gp}) and solid/polymer (σ_{sp}) by means of the following expression:

$$\sigma_{sp} = \sigma_{gp} + \sigma_{gs} \cos\theta \tag{5}$$

In equation 4, a reduction of the energetic barrier will occurs if the solid phase is "available" for the gas phase, i.e. if the σ_{sp} in not too high to hinder the formation of a gas phase on the solid. Even though there are evidences that the PCL molecules can interact well

with the nanoclays [13, 17], the surface of these inorganic particles are still available for heterogeneous nucleation, as occurred during crystallization phenomena.

4. Conclusions

The well dispersed organoclay 30B platelets act as effective nucleating agents in PCL matrix for both crystallization and bubble formation. Nanoclay foams prepared by using a batch process showed a higher number of cells of smaller dimension, even though the final density was increased, due to the higher viscosity of the matter.

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Table 1: Avrami parameters and crystallization time ($t_{1/2}$) calculated at Xr=0.5

Table 2: Morphological properties of PCL and PCL/clay foams

Figure 1: Relative crystallinity (X_r) during isothermal crystallization (Tc=40°C): ○ PCL, ●

PCL2, ■ PCL5

Figure 2: Rheological properties of PCL and PCL/clay nanocomposites: ○ PCL, ● PCL2, ■

PCL5

Figure 3: SEM microphotographs of PCL and PCL nanocomposite foams.