PROCESSING AND CHARACTERIZATION OF PHBV/CLAY NANO-BIOCOMPOSITE FOAMS BY SUPERCRITICAL CO$_2$ ASSISTED EXTRUSION

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Abstract
In this study, we developed a continuous sc-CO2 assisted extrusion process to prepare PHBV/clays nano-biocomposite foams by two methods: a one-step method based on the direct foaming of physical PHBV / clays mixtures, and a two-step method based on the foaming of PHBV / clays mixtures prepared beforehand by twin-screw extrusion. The structures obtained were characterized in terms of clays dispersion, matrix crystallization, porosity and pore size distribution and density, and discussed as regard to the processing conditions such as temperature, shearing/pressure, CO$_2$ mass fraction. It is shown that the prior preparation of a masterbatch and its further dilution during the foaming process is a necessary step to favour clay dispersion without extensive thermal degradation of PHBV. By controlling the sc-CO2 mass fraction in a narrow window, good clay dispersion appears to favour homogeneous nucleation while limiting the coalescence, and hence allows to obtain PHBV/clays nano-biocomposite foams with better homogeneity and porosity higher than 50 %.

1. Introduction

Bio-based polymers like polyhydroxyalkanoates (PHAs) are marketed as eco-friendly alternatives to the currently widespread non-degradable oil-based thermoplastics, due to their natural and renewable origin, their biodegradability and biocompatibility. Poly 3-hydroxybutyrate (PHB) properties are similar to various synthetic thermoplastics like polypropylene and hence it can be used alternatively in several applications, especially for agriculture, packaging but also biomedicine where biodegradability and biocompatibility are of great interest. However, some drawbacks have prevented its introduction to the market as an effective alternative to the oil-based thermoplastics. PHB is indeed brittle and presents a slow crystallization rate and a poor thermal stability which makes it difficult to process [1, 2]. In order to improve the PHB properties, several kinds of PHAs copolymers have been described in the literature such as the Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) with various hydroxyvalerate (HV) contents and molecular weights, which present better mechanical properties, lower melting temperature and an extended processing window [3]. Improved properties can be also obtained by the addition of nanoparticles of layered silicates

such as clays. Indeed, clay minerals present high aspect ratio and specific surface, and can be dispersed in small amounts in polymer matrices to prepare nanocomposites with improved thermal stability, mechanical properties or barrier properties [4]. One of the key parameters is the clay dispersion that can be controlled by the elaboration route either the solvent intercalation, the *in-situ* intercalation or the melt intercalation; the latter being preferred for a sustainable development since it limits the use of organic solvents [1]. The organomodifiers inserted in clays interlayer spaces to improve polymer / clay affinity and the polymer chains intercalation have a strong influence on the dispersion but it has been also shown to catalyse the PHBV degradation during processing [3, 5].

The use of supercritical fluids have recently appeared as an innovative way to improve clay dispersion leading new "clean and environment friendly" processes. Supercritical carbon dioxyde (sc-CO_2) has favorable interaction with polymers and it has the ability to dissolve in large quantities and to act as a plasticizer, which modify drastically polymer properties (viscosity, interfacial tension, …). In addition, the dissolved sc-CO_2 can acts as a foaming agent during processing. It is therefore possible to control pore generation and growth by controlling the operating conditions [6, 7], and to generate low density porous structures of interest for the lightening of packaging or the storage of active ingredients, e.g. for drug release applications. All these features make sc-CO_2 also able to modify the nanoparticles dispersion inside polymer matrices, which in turn has an effect on the foam structure. Improved dispersion of clays and modified porous structures of synthetic polymers have been obtained with sc-CO_2, mainly in batch processes via the *in-situ* intercalation method. Only few studies have reported on the preparation of nanocomposites systems by sc-CO2 assisted continuous processes [7], more easily adaptable for an industrial scale-up. Zhao et al. [8, 9] have recently investigated the possibility to use a supercritical N_2 assisted injection molding process to develop microcellular PLA/PHBV clay nano-biocomposites. The results showed a decrease of the average cell size and an increased cell density with the addition of clays in PLA/PHBV blends. Rheological behaviour of the PLA/PHBV/clays nanocomposites suggested good dispersion of the clays within the matrix.

In this study, we developed a continuous sc-CO_2 assisted extrusion process to prepare PHBV/clays nano-biocomposite foams by two methods: a one-step method based on the direct foaming of physical PHBV / clays mixtures, and a two-step method based on the foaming of PHBV / clays mixtures prepared beforehand by twin-screw extrusion. The structures obtained are characterized in terms of clay dispersion, matrix crystallization, porosity and pore size distribution and density, and discussed as regard to the processing conditions such as temperature, shearing/pressure, CO_2 mass fraction.

2. Materials and methods

2.1. Materials

PHBV with a HV content of 13 wt%, nucleated with boron nitride and plasticized with 10 % of a copolyester was purchased from Biomer (Germany). The weight-average molecular weight is 600 kDa. The clay used is an organo-modified montmorillonite (MMT), Cloisite C30B (C30B), produced by Southern Clay Products, Inc. (USA). To limit hydrolysis of PHBV upon processing, C30B and PHBV were dried at 80°C before use.

2.2. Preparation of PHBV / C30B extruded mixtures and physical mixtures

PHBV based nanocomposites containing 2.5% w/w C30B and PHBV based masterbatches containing 10%, 20% w/w C30B were prepared by melt intercalation using a co-rotating twin-

screw extruder BC21 (Clextral, France) having a L/D (length to diameter ratio) of 48. A parabolic temperature profile not exceeding 165°C was used to limit thermal degradation of PHBV. The mixing and the dispersion of the C30B clays within the PHBV matrix were ensured by two kneading sections. Extrudates were water-cooled at the exit of the die, and dried overnight at 50°C under vacuum. About 2.5 kg of granules were collected for each batch. All the batches were moulded by injection with a Krauss Maffei KM-50-180-CX into test specimens. The barrel to die temperature profile was 40 to 165°C. PHBV based masterbatches containing 10%, 20% w/w C30B were diluted to 2.5 % w/w C30B in the injection molding machine to analyze the effect of the dilution on the nanocomposite structures and properties. As will be shown in the following, this dilution procedure was also used to produce PHBV / 2.5% nanocomposite foams by sc-CO_2 assisted extrusion.

In addition to extruded mixtures, physical mixtures of PHBV pellets coated with 2.5% w/w of C30B were prepared with a simple manual batch mixing by placing a mixture of both components in a stainless steel rotative drum for 10 minutes (Faraday cage linked to Keithley 6514 electrometer). These physical mixtures of PHBV pellets / 2.5% C30B were then also foamed by sc-CO_2 assisted extrusion.

2.3. Foaming by sc-CO_2 assisted extrusion

Figure 1 shows the experimental set up, which has previously been described elsewhere [6, 10]. The single-screw extruder (Rheoscam, SCAMEX) has a screw diameter of 30 mm and a length to diameter ratio (L/D) of 37. It is equipped with four static mixer elements (SMB-H 17/4, Sulzer, Switzerland). Sensors allow measuring the temperature and the pressure of the polymer during the extrusion process. CO_2 (N45, Air liquide) is pumped from a cylinder by a syringe pump (260D, ISCO, USA) and then introduced at constant volumetric flow rate. The pressure, the temperature and the volumetric sc-CO_2 flow rate are measured within the syringe pump. Sc-CO_2 density, obtained with the equation of state established by Span and Wagner [11], is used to calculate mass flow rate and thus the sc-CO_2 mass fraction w_{CO2}. Once steady state conditions are reached with the chosen operating conditions, extrudates are collected and water-cooled at ambient temperature. Several samples were collected during each experiment in order to check the homogeneity of the extrudates.
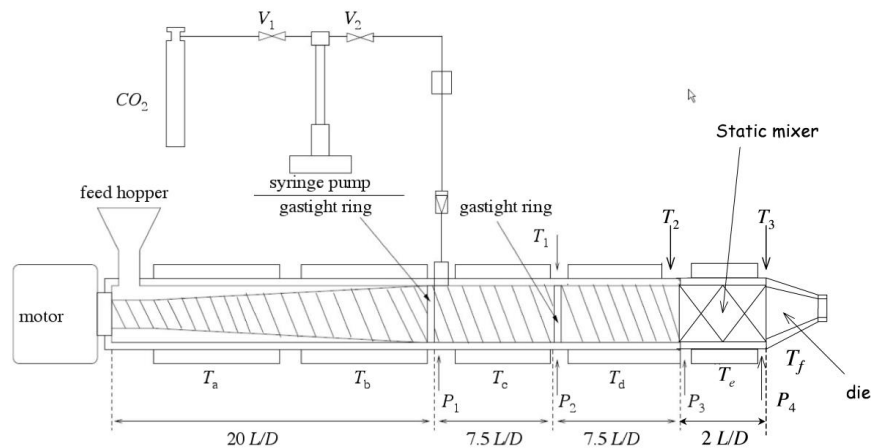

Figure 1. Experimental device used for the foaming by sc-CO_2 assisted single-screw extrusion

Experimental conditions chosen after preliminary trials (not described here) are summarized in Table 1. The lowest possible screw speed was selected to increase the residence time of the mixtures, and thus the mixing time. For all experiments, T_a, T_b and T_c were fixed at 160°C to ensure the melting of the PHBV matrix while limiting thermal degradation. Moreover, the

polymer temperature was reduced at the exit of the die in order to favour foaming. T_d and T_e were fixed at 140°C and T_f not higher than 140°C.

Series	Material	Screw speed (rpm)	T_f (°C)	w_{CO2} (mass %)	Static mixer	Die length (mm)	Die diameter (mm)
2	Neat PHBV	30	140	0 to 4	no	20	1
3	PHBV / 2.5% C30B (physical mixture)	40	140	0 to 3	yes	5	0.5
4	PHBV / 2.5% C30B (extruded mixture)	55	140	0 to 4	yes	20	1

Table 1. Experimental conditions used for the foaming by sc-CO2 assisted single-screw extrusion

2.4. Structural characterizations

The structures of nanocomposites and masterbatches were observed with a Quanta 200 FEG (FEI Company) electron microscope in transmission mode (STEM). Ultra-thin specimens of 70 nm thicknesses were cut from the middle section of moulded specimens and deposited on Cu grids. The wide angle X-Ray diffraction (WAXD) were performed using an AXS D8 Advance diffractometer (Bruker, Germany) equipped with a Cu cathode (λ = 1.5405 Å). The interlayer distance d_{001} of the C30B clays were determined from the (001) diffraction peak using Bragg's law.

Porosity ε is defined as the ratio of void volume to the total volume of the sample and can be calculated by the Equation (1):

$$\varepsilon = 1 - \rho_{app} / \rho_p \qquad (1)$$

Where ρ_{app} is the apparent density calculated from the weight of the samples and their volumes evaluated by measuring their diameter and length with a vernier (Facom, France). ρ_p is the solid polymer density, determined by helium pycnometry (Micromeretics, AccuPYC 1330), which is about 1.216.

The fracture surfaces of foamed extrudates were sputter coated with gold and observed using an Environmental Scanning Electronic Microscope XL30 ESEM FEG (Philips, Netherlands). On the basis of the images obtained, a mean diameter D_{cell} is determined and a cell density N_{cell} per volume unit of unfoamed sample were calculated according to Equation (2):

$$N_{cell} = (N^{3/2} / A) \times (\rho_p / \rho_{app}) \qquad (2)$$

N_{cell} is the number of cells on an SEM image, A the area of the image, ρ_{app} the apparent density of the foam and ρ_p the solid polymer density.

3. Results and discussion

3.1 Structure and rheology of extruded PHBV / C30B nanocomposites and masterbatches

The structures of the PHBV / C30B nanocomposites and masterbatches were investigated by two complementary methods, WAXD and STEM. The WAXD measurements allowed to determine the interlayer distance of the C30B clays within the PHBV matrix. The STEM gave a direct visualization of the clay dispersion within the matrix. As shown on Figure 2a, WAXD patterns showed a diffraction peak at 2θ = 4.6° for C30B clays, which corresponds to an interlayer distance of 18 Å. Two diffraction peaks were detected on the patterns of the PHBV

/ 2.5, 10 and 20 wt% C30B mixtures. For the PHBV / 10% and 20% C30B masterbatches, the peak at d_{001} distance of 17 - 18 Å corresponding to the initial interlayer distance of C30B, suggests that a part of the clays is still aggregated. The second peak observed at d_{001} distance of 38 Å, 36.1 Å, 34 Å for PHBV / C30B containing 2.5, 10 and 20 wt% C30B, respectively, indicates an important intercalation of the polymer chains within the interlayer space of the clays. Similar results were found by Choi et al. [12] and Bordes et al. [13] for PHBV / 2 - 3% C30B prepared by melt intercalation. The intensity of the peak at 38 Å for the PHBV / 2.5% C30B is particularly weak suggesting a possible exfoliation of the clays. Moreover, masterbatches have been diluted in a single-screw injection press to analyse the effect on the clay dispersion. The WAXD patterns are very similar for the PHBV / 2.5% C30B nanocomposite and the PHBV / 2.5% C30B nanocomposites diluted from the masterbatches. These results were confirmed by the STEM pictures, on which mostly intercalated and possibly exfoliated layered structures are observed for both PHBV / 2.5% C30B (Figure 2b) and PHBV / 2.5% C30B diluted from the 20% C30B masterbatch (Figure 2c).
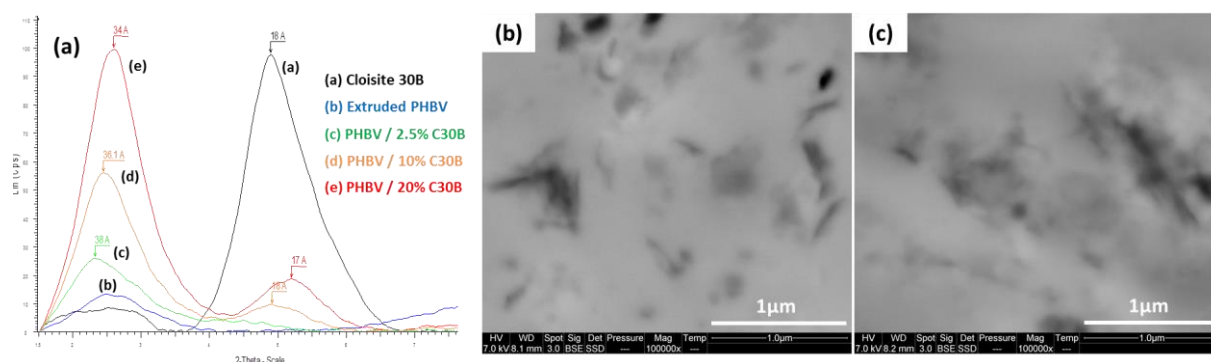

Figure 2. WAXD patterns (a) and STEM pictures of PHBV / 2.5% C30B (b), and PHBV / 2.5% C30B diluted from the 20% C30B masterbatch (c).

The rheological behaviour of extruded PHBV and PHBV / C30B nanocomposites was compared to unprocessed PHBV. The zero-shear rate viscosity of the extruded PHBV was strongly decreased after the extrusion process. This can be directly related to a decrease of the average molecular weight of the PHBV chains due to thermal degradation and shearing upon extrusion. When adding 2.5% C30B, a strong shear thinning behaviour was observed at high pulsations, highlighting the catalytic degradation effect of the clays on the PHBV matrix. The rheological behaviour at high pulsations is indeed known to be mainly determined by the macromolecular structure of the polymer matrix with little influence of the clays. When diluting the 20% C30B masterbatch to 2.5% C30B, it was interesting to observe that at high pulsations, the viscosity of the unprocessed PHBV was recovered due to the input of unprocessed and hence non-degraded PHBV in the mixture.

This preliminary study on the nanostructure and the rheological behaviour of the PHBV / 2.5% C30B nanocomposites and those produced from the masterbatches allowed to demonstrate that the dilution of the masterbatches to lower clay contents in a single-screw apparatus is a good approach to prepare PHBV / C30B nanocomposites with good dispersion and limited degradation. The good dispersion capacity of the clays is attributed to the physico-chemical interactions between PHBV and C30B that originates from strong hydrogen bonding between the ester carbonyl groups of PHBV and the hydroxyl groups in the interlayer space of C30B [12]. In the following, this dilution procedure has thus been used to prepare PHBV / 2.5% C30B nanocomposites foams, i.e. PHBV / 20% C30B was diluted to 2.5% C30B with unprocessed PHBV during the sc-CO2 assisted single-screw extrusion. The obtained foams were compared to PHBV / 2.5% C30B foams based on physical mixtures.

3.2. Processing and characterization of the PHBV / clays nano-biocomposite foams

3.2.1. Effect of the sc-CO$_2$ mass fraction on the PHBV and PHBV / 2.5% C30B foams

The effect of the sc-CO$_2$ mass fraction on the porosity ε is represented on Figure 3a. In all cases, porosity decreases with increasing sc-CO$_2$ mass fraction, which is rather astonishing since more sc-CO$_2$ is theoretically available for nucleation. This could be explained by a faster cooling of the extrudates, as sc-CO$_2$ pressure drop is endothermic. The fast cooling thus increases the stiffness of the polymer which limits the growth of the cells and hence the expansion and the porosity. A part of the sc-CO$_2$ could also be in excess [14] due to the formation of PHBV crystals upon cooling that limits the diffusion. This excess of sc-CO$_2$ diffuses to the walls of the extruder and does not participate to cell nucleation. This also decreases the processing pressures and temperatures, which in turn limits the expansion.
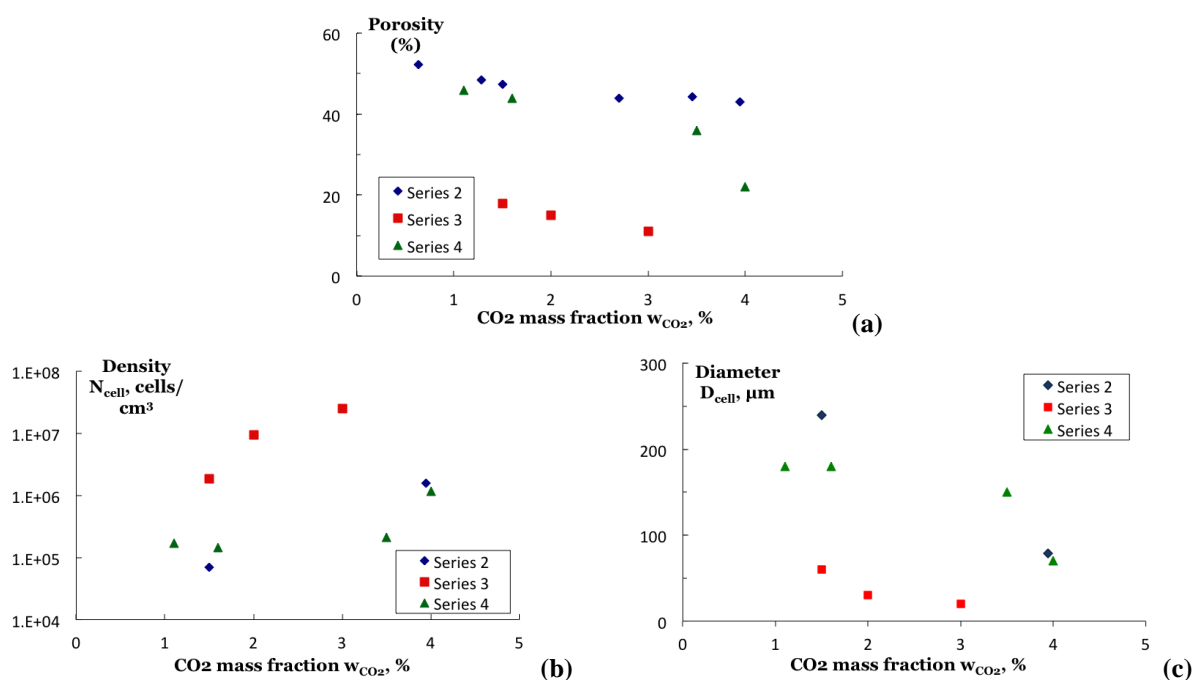

Figure 3. Evolution of (a) the porosity ε, (b) the cell density N_{cell} and (c) the mean diameter D_{cell} as a function of the CO$_2$ mass fraction for foams series 2, 3 and 4.

SEM pictures of the extrudates of neat PHBV and physical and extruded PHBV / 2.5% C30B mixtures are represented on Figure 4. When sc-CO$_2$ mass fraction increases, pores become smaller, more numerous and regular. These observations are illustrated by the evolution of the cell density and the mean cell diameter on Figure 3b and c. It confirms that the presence of more sc-CO$_2$ increases nucleation (higher cell density) but accelerates the cooling and thus limits the growth and the coalescence of the pores (lower cell diameter). The sc-CO$_2$ mass fraction must thus be optimized to promote nucleation while keeping enough growth and expansion. Generally, the PHBV and PHBV / 2.5% C30B foam structure dependency to sc-CO$_2$ mass fraction can be summarized as follows:

    (i)   Low sc-CO$_2$ mass fractions induce higher processing pressures and temperatures that promote higher pressure drop, extensive growth and higher porosity, but also less nucleation and poor homogeneity due to the coalescence of the pores.

   (ii) High sc-CO$_2$ mass fractions promote nucleation and homogeneity, but also induce lower processing pressures and temperatures, that limit the growth and porosity due to the increased stiffness of the frozen polymer.
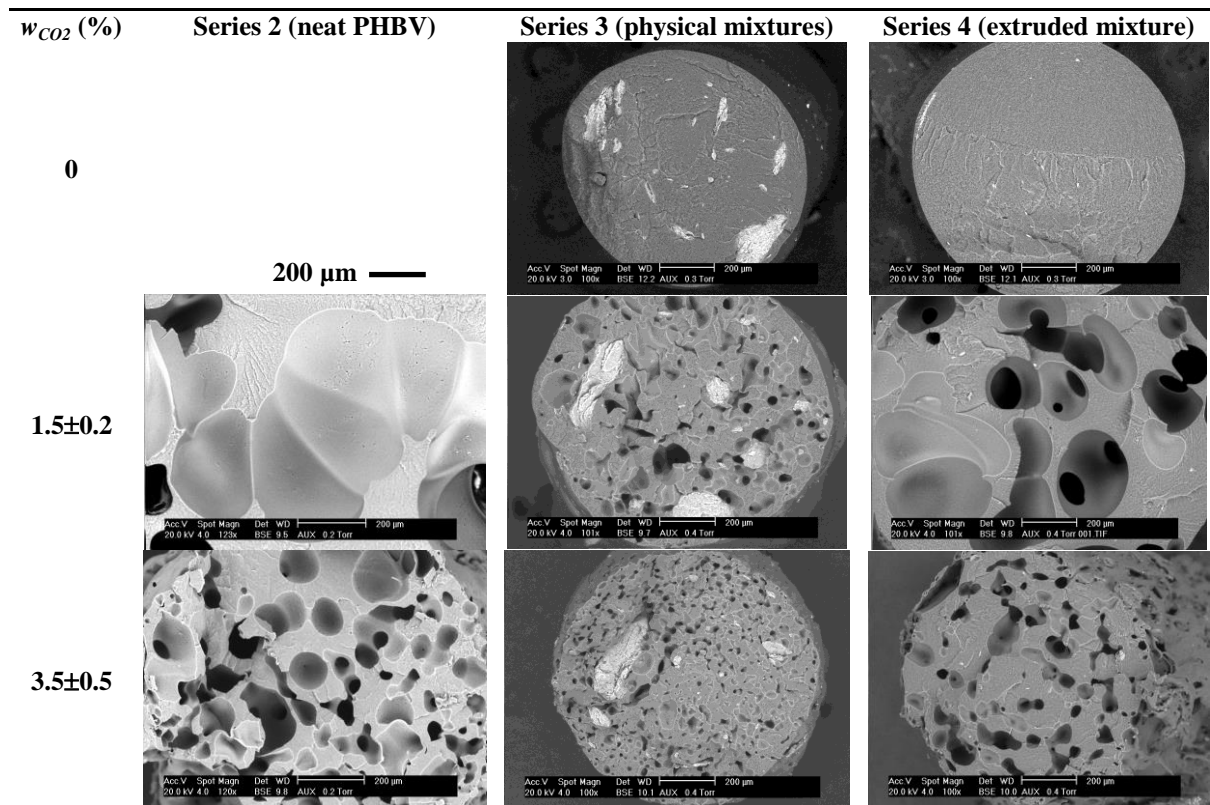
w_{CO2} (%)	Series 2 (neat PHBV)	Series 3 (physical mixtures)	Series 4 (extruded mixture)
0			
1.5±0.2	200 µm ───		
3.5±0.5			

Figure 4. SEM pictures for foams series 2, 3 and 4 at different sc-CO_2 mass fraction.

3.2.2. Clays / Foaming interrelationships and effect on the nanocomposite foams structure

As shown on Figure 4, the clay particles are inhomogeneously dispersed in the extrudates based on the physical PHBV / 2.5% C30B mixtures (series 3). Several aggregates of 10 µm to 350 µm are observed whatever the sc-CO_2 mass fraction. The effect of the sc-CO_2 on the properties of the polymer matrix and the presence of the static mixer were thus not sufficient to induce the intercalation of the polymer chains within the interlayer space of the C30B clays and their dispersion during single-screw extrusion. The static mixer indeed enhances the distributive mixing of the sc-CO_2 and the clays but only have little dispersive efficiency. Concerning the extruded PHBV / 2.5% C30B mixtures (series 4), a very good dispersion of the C30B is observed with no visible aggregates (Figure 4). This supports that the prior preparation of a PHBV / 20% C30B masterbatch and its further dilution to 2.5% C30B during the sc-CO_2 assisted extrusion process is a necessary step to obtain a good dispersion. WAXD patterns (not shown) revealed that the position of the intercalation peak at 36.2° for series 4 remains unchanged by the foaming process whatever the sc-CO_2 mass fraction, meaning that no significant enhanced intercalation occurs with the plasticization of the matrix induced by the sc-CO_2. A possible improvement of the dispersion capacity of the clays could be obtained by improving their 'CO_2-philicity' with a surfactant bearing together hydroxyl groups to conserve a good affinity with PHBV and a 'CO_2-philic' carbonyl group.

Good dispersion of the clays has been shown to favour homogeneous nucleation, limit the coalescence, and hence give porous structures with higher cell density [15, 16]. As shown on Figures 3 and 4 at low sc-CO_2 mass fraction ($w_{CO2} < 1.5\%$), extruded PHBV / 2.5% C30B mixtures based foams indeed appear less heterogeneous with rather smaller cell diameter as compared to neat PHBV foams, while showing equivalent porosity. At high sc-CO_2 mass fraction ($w_{CO2} > 3.5\%$), the presence of the clays decreases significantly the porosity. The diffusion of the sc-CO_2 within the PHBV matrix may be slightly hampered by the C30B

clays, which are known to be barrier to gas and fluid in polymeric materials [17]. Consequently, the excess of sc-CO_2 diffuses to the walls of the extruder and accelerates the cooling of the extrudate, limiting the growth of the pores and the expansion of the foams.

4. Conclusions

A continuous sc-CO_2 assisted extrusion process has been developed to prepare PHBV/clays nano-biocomposite foams. The prior preparation of a PHBV / 20% C30B masterbatch and its further dilution during the sc-CO_2 assisted single-screw extrusion process are necessary steps to obtain good clay dispersion and limited PHBV degradation. By controlling the sc-CO_2 mass fraction in a narrow window, good clay dispersion appears to favour homogeneous nucleation while limiting the coalescence, and hence allows to obtain PHBV/clays nano-biocomposite foams with better homogeneity and porosity higher than 50 %.

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