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Design of a PHB-HV/clay nanocomposite foam by using sc-CO_2 assisted extrusion

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Poly(3-hydroxybutyrate-3-hydroxyvalerate) (PHB-HV) is a biopolymer that has recently caught the attention, due to its biodegradability, biocompatibility and natural origin. However, some drawbacks have prevented its introduction on the market as an effective alternative to the currently widespread non-degradable oil-based thermoplastics. In consequence, improving the properties of PHB-HV by the addition of a small quantity of an environmentally innocuous material such as clay, may allow this class of polymers to extend their potential uses to many fields. In this context, a great deal of effort has been made to design nanocomposite systems with the aid of supercritical carbon dioxide ($scCO_2$).

Our laboratory has developed a scCO2-assisted extrusion process. Injection of $scCO_2$ into a single-screw extruder modifies the rheological properties of the polymer in the barrel and $scCO_2$ acts as a blowing agent during the depressurization when flowing through the die [1]. In the present work, this process has been used to prepare a PHB-HV/clay composite. At first, the mixing of the polymer and the clay was achieved by two methods: physical mixture and twin screw extrusion. Then, the foaming process with $scCO_2$-assisted extrusion has been applied to the PHB-HV and clay/PHB-HV mixtures obtained. The designed nanocomposite foams showed porosity up to 50 % was achieved, while having a relatively poor homogeneity. Growth and coalescence of the pores were limited by the decrease of the die temperature and the increase of the CO_2 mass fraction. In spite of a favourable kinetics of triboelectrification, the dispersion of the clay was not homogeneous in foams prepared with physical mixture. In the case of extruded mixture, DRX spectra showed that intercalation and possible exfoliation occurred and was not affected by the foaming step. The presence and the dispersion of the clay particles seemed to favour heterogeneous nucleation of the CO_2, but it was not sufficient to obtain a homogeneous and highly porous structure.

INTRODUCTION

Polymers of fossil origin are widely used in several areas. However, due to their slow degradation and the predicted exhaustion of the world petroleum reserves, significant environmental problems have arisen. Therefore, it is necessary to replace them with bioplastics that are CO_2 neutral and degrade in a short time when exposed to a biologically active environment [2].

Biopolymers like PHAs (polyhydroxyalkanoates) are marketed as the eco-friendly substitutes for common polymers, due to their biodegradability, biocompatibility and natural origin. PHAs are polyesters of various HAs which are synthesised by numerous microorganisms as energy reserve materials in the presence of excess carbon source. Poly(3-hydroxybutyrate) (PHB) is the most widely found member of this biopolymer group. It was also the first to be discovered, and has been the most widely studied PHA [3]. Its properties are similar to various synthetic thermoplastics like polypropylene and hence it can be used alternatively in several applications in the fields of medicine, agriculture, and packaging [3]. However, some drawbacks have prevented its introduction on the market as an effective alternative to the currently widespread non-degradable oil-based thermoplastics. Some of these drawbacks are its brittleness, thermal degradability at temperatures not far above the melting point, and its high price [4].

In order to improve the properties of PHB, several kinds of PHA copolymers have been described in the literature incorporating structural units such as 3-hydroxyvalerate (PHB-HV) [5]. Unfortunately, PHB-HV presents also several problems to be solved: slow crystallization rate, relatively difficult processing, low elongation at break and very high crystallinity [6]. In consequence, improving the properties of PHB-HV by the addition of a small quantity of an environmentally innocuous material such as clay, may allow these polymers to extend their potential uses to many fields. Clay minerals are commonly used in nanocomposite manufacturing because of their small particle size and layer expanding properties, especially in the application of reinforced polymers.

In this context, a great deal of attention has been given to design nanocomposite systems with the aid of supercritical carbon dioxide ($scCO_2$). Indeed, its ability to dissolve in large quantities into many polymers and thus to modify theirs properties (viscosity, interfacial tension, …) could allow the improvement of the nanoparticles dispersion inside the polymer matrix.

Extrusion is a process used to convert a raw material into a product of uniform shape and density by forcing it through a die under controlled conditions and it has extensively been applied in the plastic and rubber industries, where it is the most important manufacturing process [7]. Moreover, this technique is widely used to prepare nanocomposites by the melt intercalation process which is the preferred method in the context of sustainable development since it avoids the use of organic solvents, which are not eco-friendly as shown by their life cycle analysis [8].

Our laboratory has developed a $scCO_2$-assisted extrusion process. Injection of $scCO_2$ into a single-screw extruder modifies the rheological properties of the polymer in the barrel of the extruder and $scCO_2$ acts as a blowing agent during the depressurization when flowing through the die [11]. It has been already applied to produce foams of a pharmaceutical polymer [9] and more recently of PHB-HV [10]. In the present work, this process has been used to prepare a PHB-HV/clay nanocomposite. At first, the mixing of the polymer and the clay was achieved by two methods: physical mixing and twin screw extrusion. Then, the foaming process with $scCO_2$-assisted extrusion has been applied to the PHB-HV and clay/PHB-HV mixtures obtained. Samples of nanocomposite foams were characterized performing density measurement, X-ray diffraction, thermal analysis and scanning electron microscopy. Finally, the influence of operating conditions on the nanocomposite properties has been studied.

EXPERIMENTAL SECTION

Materials

PHB-HV (M_w=600 kDa), with a HV content of 13 % and plasticized with 10 % of a copolyester was purchased from Biomer (Germany). PHB-HV is a semi-crystalline polymer with a glass transition temperature around 94°C and a melting onset temperature of 143°C measured by DSC (DSC Q200, TA) (grey curve on Figure 1).

The clay used is named Cloisite C30B (C30B) and was purchased from Southern Clay Products (USA). It is a natural montmorillonite modified with a ternary ammonium salt, specially designed for polyester matrices.

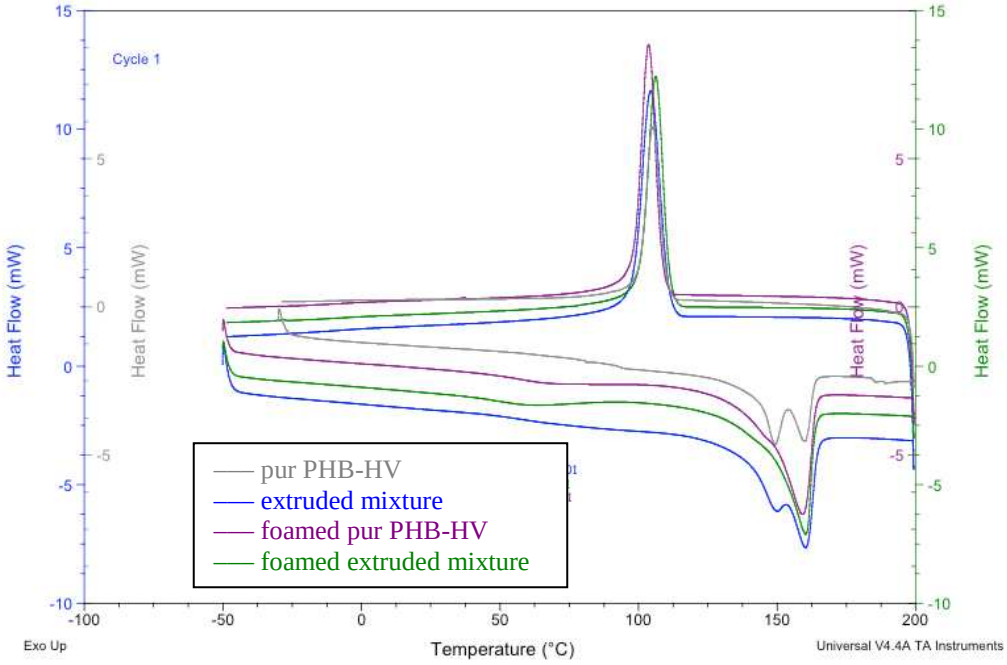


Figure 1. DSC spectra

Visualisation

The samples were observed using an Environmental Scanning Electronic Microscope XL30 ESEM FEG (Philips, Netherlands).

X-ray diffraction (XRD)

XRD spectra were obtained using a Bruker AXS D8 Advance diffractometer.

Physical mixtures preparation: mixing possibility

Figure 2 shows the kinetics of triboelectrification of PHB-HV and C30B. PHB-HV exhibits a negative electrification whereas C30B exhibits almost no electrification. When both components are mixed, the mixture behaves like C30B, which shows that PHB-HV is coated by C30B. Thus, mixtures with 3 mass % of C30B were prepared. SEM pictures confirm that C30B particles are coated on PHB-HV pellets (Figure 3 (b)).

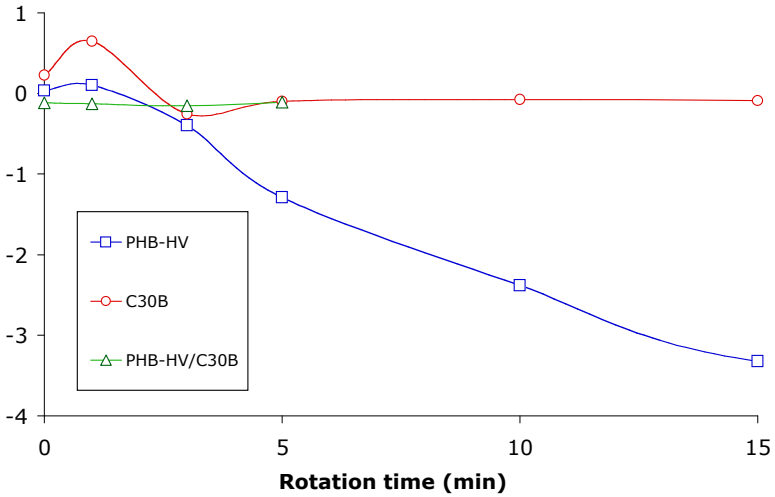
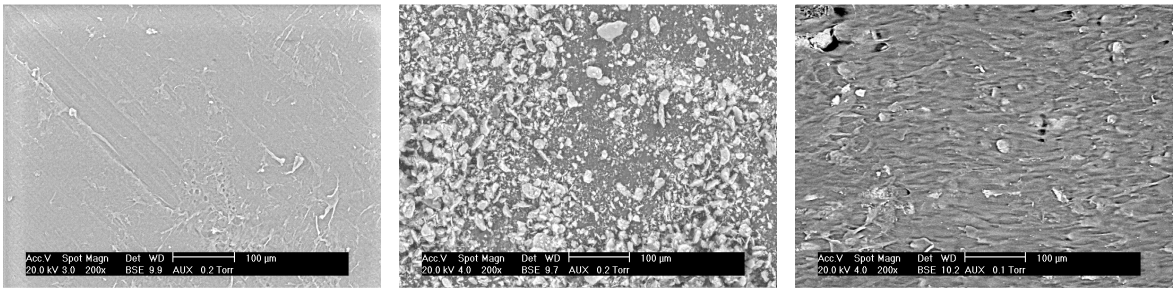


Figure 2. Kinetics of triboelectrification



(a) (b) (c)

Figure 3. SEM pictures; (a) PHB-HV;
(b) PHB-HV/C30B physical mixture; (c) PHB-HV/C30B extruded mixture

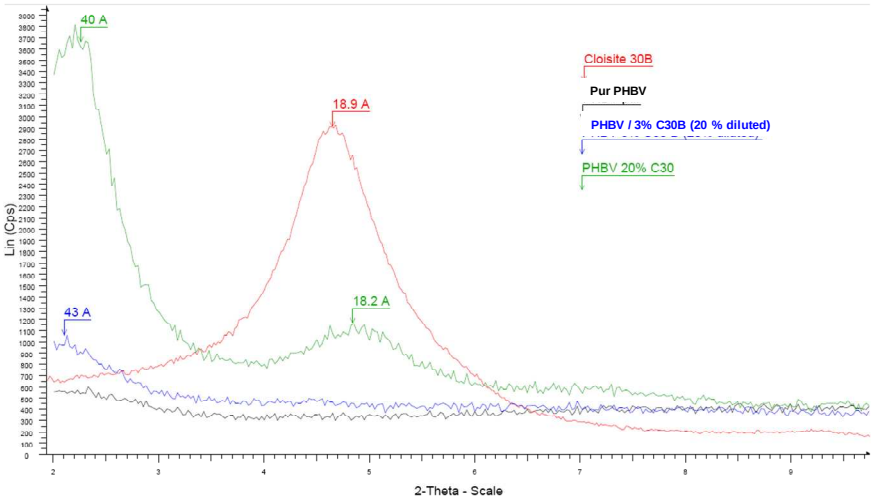


Figure 4. DRX spectra of pure components and extruded mixtures

Extruded mixtures preparation: characterisation of the dispersion state

An extruded masterbatch with 20 mass % of C30B was prepared by means of a twin screw extruder (Clextral BC21, France). Three dispersion states can be obtained with this type of clays: agglomerated, intercalated and exfoliated. The agglomerated state is the initial shape of the clays and it can be observed when the clays are not or badly dispersed in the matrix. The intercalation results from the limited insertion of the polymer chains in the interlayer spacing of the clays. The exfoliated state is characterized by the insertion of the polymer in large quantity and the delamination of the clay layers, which leads to a nanostructured composite and greater improvement of material properties.

DRX spectra are represented on Figure 4 for the pure components, the extruded mixture and the extruded mixture diluted to 3 wt% C30B in a single screw extruder. PHB-HV shows no diffraction peaks in the range 2 to 10°, whereas C30B exhibits a peak at $2\theta=4.6°$, which corresponds to an interlayer distance of about 19 Å. Two diffraction peaks are detected for the 20 wt% C30B mixture. One corresponds to the interlayer distance, whereas the other peak is observed at lower angle, corresponding to a distance of about 40 Å. This indicates that some copolymer chains are intercalated into the silicate layers, with still the presence of agglomerates. This is confirmed on the SEM picture (Figure 3(c)), on which some agglomerates can be observed. When diluting the masterbatch to 3 wt% of C30B in a single screw extruder, only a small peak at 40 Å can be observed, which is representative of an intercalation and a possible exfoliation. This phenomenon is attributed to the favourable interaction between PHB-HV and C30B that originates from the strong hydrogen bonding between ester carbonyl group of PHB-HV and the hydroxyl group in the gallery of C30B [11].

On Figure 1 (blue curve), it can be however observed that DSC spectra is modified, with a decrease of the glass transition temperature and a modification of the two fusion peaks. This could be explained by a degradation of the PHB-HV induced by either the temperature or the clays [12].

Sc-CO_2 assisted extrusion

Figure 5 shows the experimental set up, which has previously been detailed elsewhere [9,10]. The single-screw extruder has a 30 mm-screw diameter and a length to diameter ratio (L/D) of 37 (Rheoscam, SCAMEX). The screw is divided into four parts. The length to diameter ratio is of 20 for the first one, 7.5 for the two following ones and 2 for the last one. Between each part, a restriction ring has been fitted out in order to obtain a dynamic gastight, which prevents $scCO_2$ from backflowing. The first conical part of the screw allows the transport of solid polymers and then, their melting and plasticizing. Then, in the two following parts, the screw has a cylindrical geometry from the first gastight ring to the last part. The fourth part, which is removable, contains four static mixer elements with a diameter of 17 mm (SMB-H 17/4, Sulzer, Switzerland). The temperature inside the barrel is regulated at six locations: T_a and T_b before the CO_2 injection, T_c and T_d after the injection, T_e in the static mixer and T_f in the die.

There are four pressure and two temperature sensors: P_1 after the CO_2 injector, P_2 and T_1 before the second gastight ring, P_3 and T_2 before the static mixer and P_4 and T_3 by the die. This allows measuring the temperature and the pressure of the polymer inside the extruder. Errors associated to pressure and temperature measurements were about 0.2 MPa and 1°C respectively.

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 in the CO_2 pump is kept slightly higher than the pressure P_1. The CO_2 injector is positioned at a length to diameter ratio of 20 from the feed hopper. It corresponds to the beginning of the metering zone, that is to say the part where the channel depth is constant and equal to 1.5 mm. The pressure, the temperature and the volumetric CO_2 flow rate are measured within the syringe pump. CO_2 density, obtained on NIST website by Span and Wagner equation of state [13], is used to calculate mass flow rate and thus the CO_2 mass fraction w_{CO2}. Once steady state conditions are reached with the chosen operating conditions, extrudates were collected and water-cooled at ambient temperature in order to freeze the extrudate structure before its characterisation. Several samples are collected during each experiment in order to check the homogeneity of the extrudates.

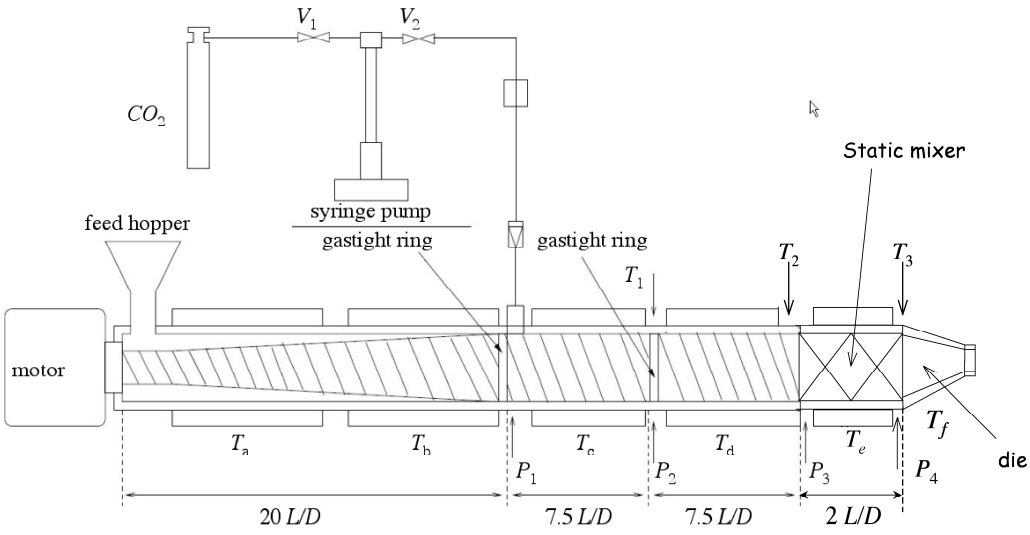


Figure 5. Foaming experimental device

Porosity

Porosity ε is defined as the ratio of void volume to the total volume of the sample and can be calculated by the following equation:

$$\varepsilon = 1 - \frac{\rho_{app}}{\rho_P} \quad (1)$$

ρ_{app} is the apparent density. To calculate this apparent porosity, samples were weighed and their volumes were evaluated by measuring their diameter and length with a vernier (Facom, France). To obtain this apparent density with a good enough precision, the mean of 9

measurements was carried out. ρ_p is the solid polymer density, determined by helium pycnometry (Micromeretics, AccuPYC 1330), which is about 1216 $kg.m^{-3}$.

RESULTS

Choice of the operating conditions

Three different cylindrical dies have been tested (Table 1). The first trials with PHB-HV were carried out with the L12 die, but pressures obtained in the extruder were too low to allow $scCO_2$ injection. In consequence, the L12 die was replaced by the L20 to increase operating pressures.

With the addition of the clays, a large decrease of operating pressures was observed. This effect could be explained by a degradation of the PHB-HV [12] and a plasticizing effect of the clays. Indeed, rheological dynamic measurements showed that the addition of 3 wt% of C30B decreases the viscosity of the polymer. This phenomenon was particularly significant at high shear rates, which usually occur during the extrusion. Thus, the die L5 exhibiting a smaller diameter was used with physical mixture to increase the pressure and allow $scCO_2$ injection. Unfortunately, it was not possible to keep this die with the extruded mixture because of its clogging.

Die	Length (mm)	Diameter (mm)
L12	12	1
L20	20	1
L5	5	0.5

Table 1. Dimensions of the dies

Experiments are summarized in Table 2. Screw speed can be varied from 30 to 80 rpm, but the lowest possible 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 fusion of the polymer without degradation. Moreover, to reduce enough the polymer temperature in order to promote foaming at the exit of the die, T_d and T_e were fixed at 140°C and T_f not higher than 140°C.

Series	Material	Screw speed (rpm)	Tf (°C)	w_{CO2} (mass %)	Static mixer	Die
1	PHB-HV	30	120 to 140	1.5	no	L20
2	PHB-HV	30	140	0 to 4	no	L20
3	Physical mixture	40	140	0 to 3	yes	L5
4	Extruded mixture	55	140	0 to 4	yes	L20

Table 2. Foaming experiments

Effect of the die temperature

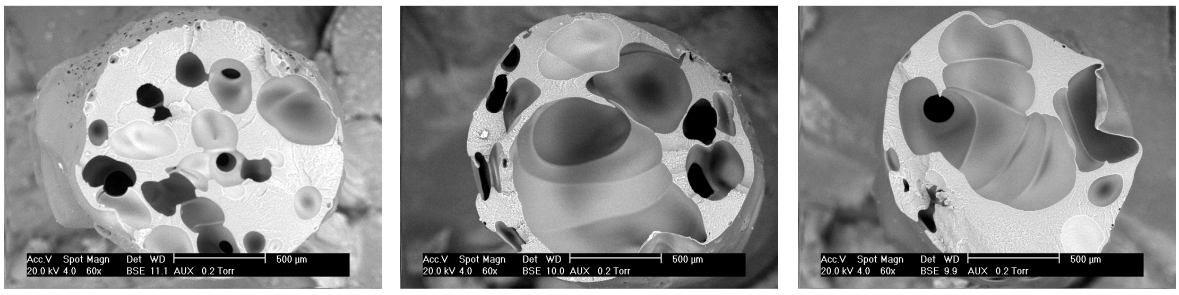
Results for series 1 are summarized in Table 3. Pressure before the die decreases with

increasing temperature, due to the lowering of the viscosity. The porosity is rather independent of the die temperature.

T_d (°C)	P_4 (bar)	ε (%)
120	233	48
130	222	46
140	192	47

Table 3. Results for series 1

However, we can observe on Figure 6 that porosity is inhomogeneous and badly dispersed in the sample. This could be attributed to a lack of mixing between the two components or to the semi-crystallinity of the polymer. Indeed, semicrystalline polymers are two-phase systems in which crystallites are dispersed in the amorphous matrix. As the crystallites hamper the solubility and diffusion of CO_2 into the polymer, the absorption and diffusion of the CO_2 take place almost exclusively through the amorphous regions and the formed polymer/gas solution is not uniform [1]. We can also observe that an increase in temperature favours growth and coalescence of the pores [14]. This could be explained by a slower cooling of the sample after the die.



120°C 130°C 140°C

Figure 6. SEM pictures for series 1 at différent T_f

Effect of the CO_2 mass fraction

The effect of the CO_2 mass fraction on the pressure P_4 is represented on the Figure 7. Pressure before the die decreases with increasing CO_2 mass fraction. This decrease is linked with a lower polymer viscosity, due to the plasticizing effect of the CO_2. This decrease, which is up to 30 %, does not seem to be influenced by the presence of clays whatever the mixture.

The effect of the CO_2 mass fraction on the porosity ε is represented on Figure 8. In all cases, porosity decreases with increasing CO_2 mass fraction, which is rather astonishing since more CO_2 is theoretically available for expansion. This could be explained however by a faster cooling of the sample, as CO_2 pressure drop is endothermic, what limits the expansion.

SEM pictures of the samples are represented on Figure 9. When CO_2 mass fraction increases, pores become smaller, more numerous and regular. It confirms that the presence of more CO_2 accelerates the cooling and thus limits the growth and the coalescence of the pores.

The DSC spectra of a pure PHB-HV sample foamed with $scCO_2$ is represented on Figure 1 (purple curve). The DSC spectra is modified by the $scCO_2$ foaming process. Indeed, it can be observed a decrease of the glass transition temperature and a modification of the two fusion peaks, with a large predominance of the second one. It seems thus that the foaming step results in a modification of the polymer, probably due to the thermal degradation of the polymer.

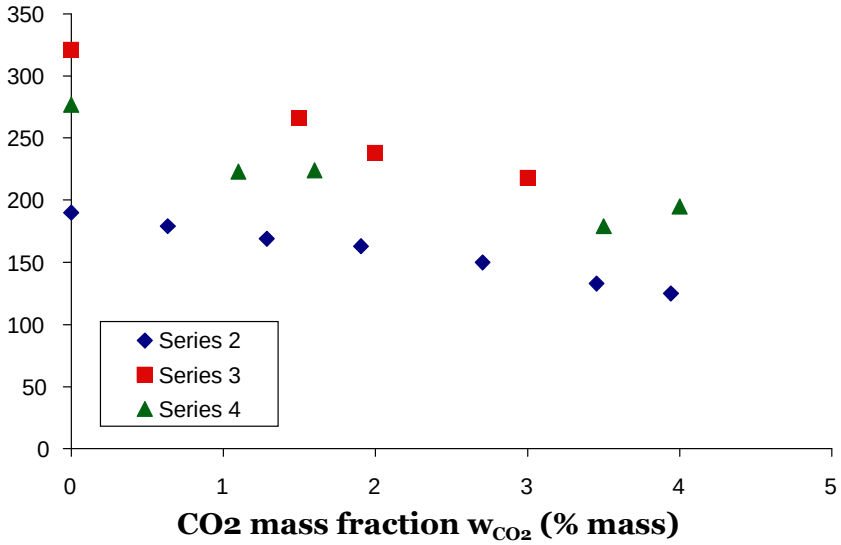


Figure 7. Evolution of the pressure P_4 with the CO_2 mass fraction

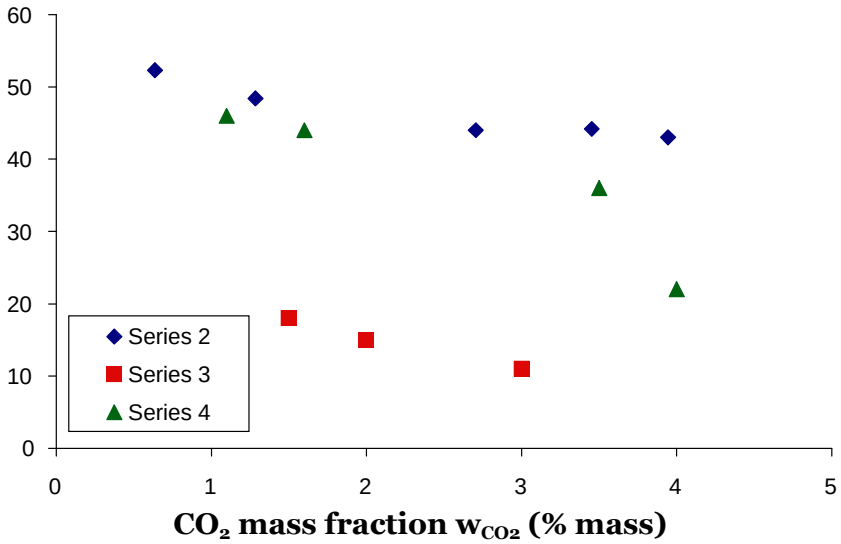


Figure 8. Evolution of the porosity ε with the CO_2 mass fraction

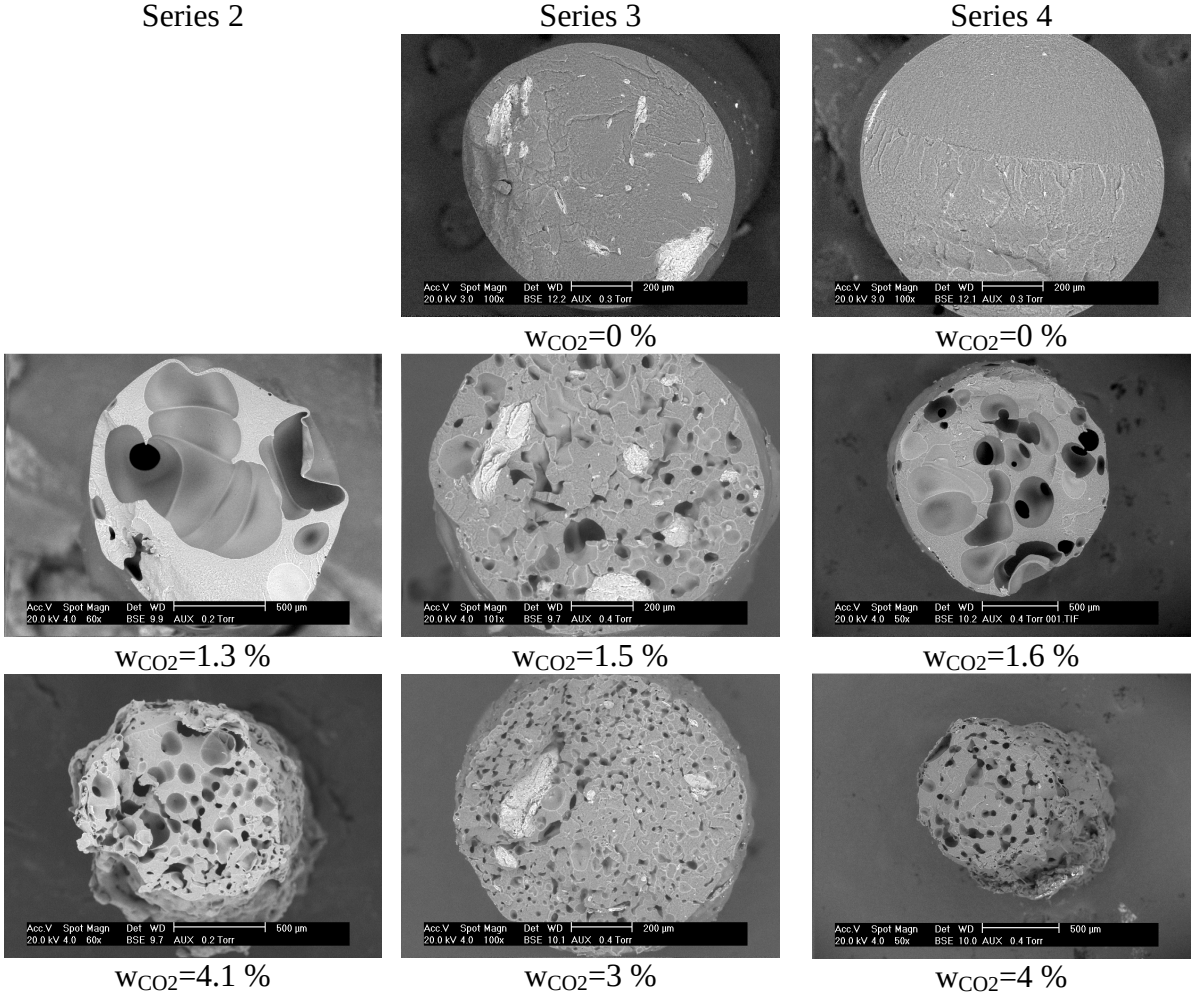


Figure 9. SEM pictures for series 2 to 4 at different CO_2 mass fraction

Effect of the die geometry

The observed porosity is much lower for the extrudates obtained by sc-CO_2 assisted extrusion of the physical mixture clay/PHB-HV. This is probably due to the shorter die used in this series of experiments, which increases the pressure drop rate $\Delta P/\Delta t$ and in turn the cooling speed of the sample and thus limits the evolution of the structure.

For the highest CO_2 concentration, we can however observe the sample for which pores are smaller, numerous and evenly distributed. This is an evidence of the homogeneous dispersion of the CO_2 in the polymer. However, growth and coalescence have then to be better controlled.

Dispersion and effect of the clays

Clearly, the clay particles are not well dispersed in the case of the physical mixing extrudates (series 3), despite the presence of static mixers and the CO_2 addition (Figure 9). These static mixers are well known to enhance rather distributive mixing than dispersive mixing. Concerning the extruded mixtures extrudates (series 4), the clay dispersion observed on the SEM pictures is the same with or without the CO_2-foaming (Figure 9). There is thus no re-agglomeration during the foaming step. It has to be noted that a study of residence time distribution, not described here, was performed by means of a Raman probe and allowed to quantify the effect of the static mixers.

The porosity of the series 4 samples is the same as the samples obtained with pure PHB-HV at low CO_2 mass fraction but, at higher CO_2 mass fraction, the presence of clay acts synergistically with the CO_2 to enhance the decrease (Figure 8). The presence of clays might have improved the heterogeneous nucleation of the CO_2, and thus the acceleration of the cooling. To conclude, a good dispersion of the clays allows to improve the porous structure, but the foams obtained were not as good as the ones obtained with pure PHB-HV.

The DSC spectra of the extruded mixture foamed with $scCO_2$ is modified in comparison with the extruded mixture before the foaming step, which confirms the modification of the material by the foaming step (Figure 1, green and blue curves). The presence of the clay does not allow limiting this modification.

CONCLUSION

In this study, we designed nanocomposite systems with poly(3-hydroxybutyrate-3-hydroxyvalerate), PHB-HV, a biopolymer that has caught the attention recently, and clay. This was carried out by using a supercritical carbon dioxide ($scCO_2$)-assisted extrusion process.

Before processing, the mixtures of the polymer and the clay were prepared by two methods: a physical mixture and twin screw extrusion. The kinetics of triboelectrification showed a favourable coating of PHB-HV pellets by clay particles for the physical blends and DRX spectra showed that intercalation occurred during extrusion. Then, the foaming with $scCO_2$-assisted extrusion was applied to the PHB-HV and clay/PHB-HV mixtures. The designed nanocomposite foams show porosity up to 50 % were obtained, while having a relatively poor homogeneity. Growth and coalescence were limited by the die temperature, which must however not be too low, and by the increase in CO_2 mass fraction. The dispersion of the clay was not homogeneous in the foams from physical mixture. In the case of extruded mixture, DRX spectra showed that intercalation has occurred and has not been affected by the foaming process. The presence and the good dispersion of the clay particles seemed to improve heterogeneous nucleation of the CO_2, but were not sufficient to obtain a high quality porous structure.

Finally, more trials have to be carried out to identify better operating conditions and in particular concerning temperatures and pressure drop evolution.

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