SYNERGISTIC ACTION OF NEW EXTRUSION PROCESS AND NANOFILLER INCORPORATION ON IMPROVEMENT OF BARRIER PROPERTIES OF A BIOPOLYMER FILM

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Abstract

Nanocomposite films were prepared from PolyButylene Succinate Adipate (PBSA) as biopolyester matrix and 5 wt% of native montmorillonite (MMT) or organo-modified montmorillonite (OMMT) as nanofillers. Nanocomposite films were melt blended using an innovative extrusion protocol. It consists in introducing liquid water into the extrusion barrel, under high pressure and high temperature, in order to optimize dispersion and exfoliation levels of nanofillers within the polymer matrix. X-ray diffraction and transmission electron microscopy testified this improvement, depending on the nanofiller used as well as a specific orientation of nanoclays in the matrix, parallel to the extrusion flow. The objective of the present work is to investigate the impacts of this new extrusion process on barrier properties of the resulting nanocomposite, by measuring permeation of water and gases (N_2, O_2, CO_2) through nanocomposite films and by correlating their barrier performances to physico-chemical properties. Our results show that water injection during the extrusion process allows improving barrier properties of nanocomposite films. As better nanofiller dispersion within the matrix is obtained, tortuosity effects induced by the presence of inorganic nanofillers, are enhanced. Besides, films with OMMT have better barrier performances than those containing MMT despite water injection. As a result, it can be pointed out that the new extrusion process contributes to increase barrier properties of nanocomposite containing MMT but no so much to substitute the filler organo-modification.

Keywords: Barrier properties, water injection process, nanocomposite, PBSA

1. INTRODUCTION

Nowadays, the development of new biodegradable films is currently receiving a great attention in scientific and industrial areas due to environmental issues. Lots of research works are also focusing on bio-polyesters [1]. PolyButylene Succinate Adipate (PBSA) is one of promising aliphatic polyester due to its good properties like processability, thermal and mechanical resistances which are found to be similar to polypropylene and its biodegradable character. However, its barrier performances are found to be insufficient which limit industrial targeted applications like packaging [2].

Incorporating inorganic nanofillers within a matrix polymer is a relevant way to improve its barrier properties, as suggested in the literature [3]. For this purpose, despite the high aspect ratio of selected nanofillers, the challenge consists in optimizing the matrix/nanofillers interfacial area and the affinity of clay towards the polymer chains. Indeed, dispersion and exfoliation levels of nanofillers within the polymer matrix are key parameters. On the one hand, the hydrophilic character of native nanofillers like montmorillonite usually limits the compatibility with polymer chains which induces aggregated structures [4]. The inorganic clay surface is thus modified by chemical treatments incorporating a hydrophobic surfactant to improve its compatibility [5]. Nevertheless, the organo-modification can generally reduce the thermal stability of

nanofillers while increasing its price. On the other hand, the choice of preparation method of nanocomposite films, combined with processing conditions plays a key role in achieving a suitable structural organization [6].

In this work, an innovative recently-reported extrusion process [7] was applied to prepare nanocomposites based on PBSA matrix in order to increase the dispersion and delamination levels of native nanofillers (MMT) within matrix. This new extrusion process consists in introducing liquid water, under high pressure and high temperature, into the barrel during extrusion process. It can be indicated that the pressure is required to break down nanofiller aggregates while water is thought to plasticize polymer matrix which facilitates the polymer chain motions and as a result, can contribute to improve nanofiller dispersion. Touchaleaume et al. [8] have already shown that nanocomposites composed of a polar matrix (polyamide 6) and MMT fillers exhibited well-exfoliated structure and similar to those elaborated with OMMT due to water injection during extrusion process, although the interlayer distance of nanofillers remained constant for nanocomposites prepared from apolar matrix (styrene-co-acrylonitrile) and MMT [9].

The synergistic action of this new extrusion process and nanofiller incorporation within PBSA matrix (having polar and apolar groups in its chemical structure) was analyzed by means of permeation kinetics and microstructural characterizations to evaluate the efficiency of this process, and thereafter the possibility to substitute the organo-modification of nanofillers. PBSA-based nanocomposites loaded with MMT were also compared to those of ones prepared with OMMT.

2. EXPERIMENTALS

2.1 Materials

PolyButylene Succinate Adipate (PBSA) was provided by Natureplast, France. Native montmorillonite and organomodified montmorillonite (referred to as CNa and C30B, respectively) were supplied by Neutrino Corporation, Iran. C30B is a methyl bis-2-hydroxylethyl tallow ammonium-exchanged montmorillonite clay.

2.2 Nanocomposite preparation

Nanocomposite films were elaborated as follows. First, PBSA pellets and 15 wt% of nanoclays were melt mixed in a Clextral BC45 twin-screw extruder, using a temperature profile from 120 to 160 °C from the feed to the die. Then, the resulting pellets were diluted with pure polymer pellets using a corotating twin-screw Krupp WP ZSK25 extruder (Figure 1) in order to obtain pellets containing 5 wt% of nanoclays. Temperature profile was from 120 to 180 °C between the feed and the die. Finally, these pellets were transformed into a film using a Haake single-screw Thermo extruder with a temperature profile from 120 to 150 °C. When water injection was used during extrusion process, the resulting films were noted with « -W » as follows PBSA+CNa(5%)-W with (5%) corresponding to the nanofiller content.
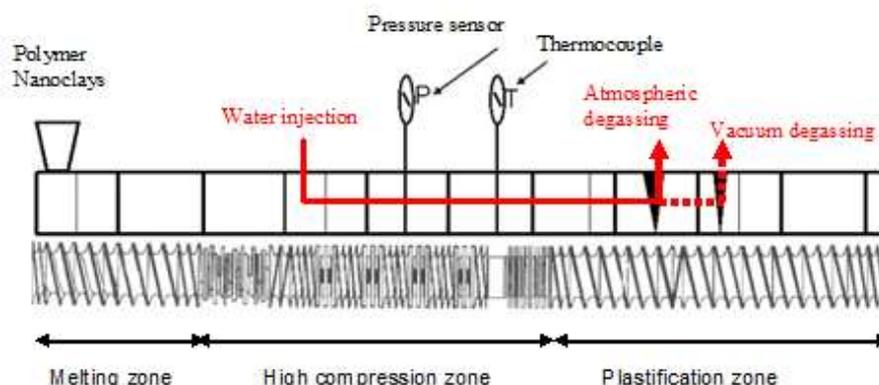

Fig. 1 Schematic representation of the new extrusion process using water injection [according to 10 with emphasis on the water flow]

2.3   Nanocomposite Characterization

2.3.1 Transmission Electron Microscopy (TEM)

Dispersion and exfoliation of platelets were observed using a transmission electron microscope LEO 922 (Zeiss) with a 200 kV acceleration voltage. Specimens were cut using a Reichert cryo-microtome (-30 °C for sample and -40 °C for knife). Ultrathin sections of approximately 95 nm in thickness were prepared with a cryo-diamond knife with a cup angle of 35° (Diatome, Switzerland) and transferred to 400 mesh copper grids.

2.3.2 X-Ray Diffraction (XRD)

To complete TEM observations, XRD analyses were performed on nanocomposite films to evaluate the exfoliation level of nanoclays in the polymer matrix. XRD was carried out with a Brucker AXS D8 Advance diffractometer equipped with a cobalt source (λ=1.789 Å) operating at 40 mA and 35 kV.

2.3.3 Gel Permeation Chromatography (GPC)

Molecular weight of film samples was calculated using a Varian PL-GPC 50 Plus spectrometer at 27.5 °C, using polystyrene standard for calibration and dichloromethane with a 1 mL.min^{-1} flow as solvent.

2.3.4 Differential Scanning Calorimeter (DSC)

Thermal behaviour of film samples was analysed with a TA Instrument Q100 DSC under nitrogen atmosphere. The first-heat curves were plotted from data resulting from the first-heating from -60 °C to 150 °C with a flow rate of 10 °C.min^{-1}.

2.3.5   Permeation measurements

Water permeation kinetics through the film samples were measured at 25 °C using a permeation cell and a chilled mirror hygrometer [11]. Each measurement was at least duplicated. First, dry nitrogen flow was flushed into measurement cell until a dew point lower than -70 °C was obtained. Then, the upstream compartment of the cell containing the sample to test was full with liquid water. Water flux *J* related to the transfer of water molecules through the film sample, was measured as a function of time until that the steady state (i.e. stable humidity value) was reached. The permeability *P* was calculated from the equation:

$$P = \frac{J_{st} \cdot L}{\Delta a}$$ (1)

Where J_{st} is the water flux at the steady state, *L* is the film thickness and *Δa* is the difference of water activity across the film sample. The permeability unit is given in Barrer; 1 Barrer = 10^{-10}.cm^3 (STP).cm.cm^{-1}.s^{-1}.cmHg.

2.3.6   Gaz permeation

Gaz permeation kinetics were performed at 25.0 °C using the variable pressure method named "time-lag" technique [12]. The measurements were repeated twice for each film sample. The film was mounted in the measurement cell composed of two compartments separated by the film – the upstream compartment and the downstream compartment. A high vacuum desorption was realized for 15 h. Then, the diffusing gas (N$_2$, O$_2$, CO$_2$) was introduced into the upstream compartment of the cell with a pressure of 3 bar. The increase of pressure in the downstream compartment was recorded using pressure sensor as a function of time to determine the quantity of diffusing molecules accumulated in the downstream compartment after transferring through the tested film. Permeability P was determined at the steady state.

3. RESULTS AND DISCUSSION

3.1 Structural characterization

Nanocomposite properties are highly dependent on the material microstructure, so that it usually required to characterize it by means of GPC, DSC and XRD experiments and TEM observations.

From GPC experiments, the change in molecular weights was evaluated for nanocomposite films, because both nanofillers incorporation and film process conditions can be at the origin of the degradation phenomenon due to chain scissions. It can be briefly indicated that 1) the C30B incorporation induced a greater degradation of PBSA chains compare to CNa. This result is already reported in the literature and explained by the action of C30B surfactant during the melt process via reactions like Hoffman elimination [13]. The resulting degradation products promote random chain scissions. 2) The molecular weights of films extruded with water injection were similar than those extruded without water injection. As a consequence, the new extrusion process can be considered as a no degradant process.

DSC measurements showed that nanocomposite films exhibit a glass transition temperature of about -44 ± 1 °C, a melting temperature of 87 ± 1 °C and possess a crystallinity degree of about 38 ± 1 %. These values are close to those of PBSA film which indicates that neither the nanofillers incorporation nor the water injection during process affect the microstructure of the matrix.

Dispersion and delamination levels of nanofillers within the matrix were analysed from TEM observations and X-ray diffraction measurements. Results showed that the water injection during process allows improving exfoliation and dispersion of nanoclays within PBSA matrix, in different manner according to the nanofillers used. This is clearly observed when incorporating CNa in PBSA matrix. Smaller aggregated and intercalated structures were observed in the case of water injection while larger aggregates were obtained without water injection. A specific orientation of CNa platelets seems also occurred with the water injection. Delamination and dispersion levels of C30B platelets were found to be very similar for films extruded with and without water injection: well-dispersed and oriented structure was obtained in both cases (Fig. 2). So, one can conclude that the delamination level of C30B platelets within matrix without water injection (film considered as a reference film) was still higher than for CNa platelets within matrix prepared with water injection (the new extrusion process).
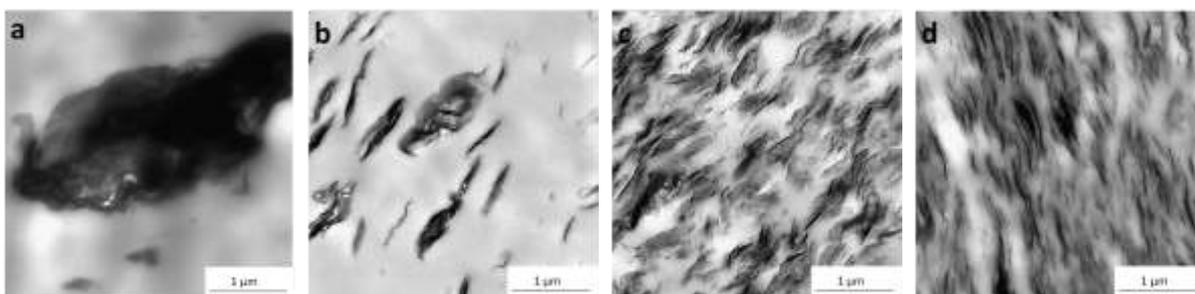

Fig. 2 TEM observations of film containing CNa (a), CNa-W (b), C30B (c) and C30B-W (d)

3.2 Evaluation of nanocomposite barrier properties

Barrier properties were examined by using liquid water and gases (N_2, O_2 and CO_2) as diffusing molecules. Results highlighted that the evolution of barrier performances were similar, irrespective of the diffusing molecule used. Only results obtain in permeation to water are also presented (Fig. 3).In all cases, the presence of fillers (CNa and C30B), with and without water injection, leads to improve the barrier properties of the loaded PBSA, as expected, with the tortuosity effect by increasing the diffusion pathway. It can be seen that 1) when incorporating CNa, permeability of films extruded with water injection is lower than those extruded without injection water; and 2) when incorporating C30B, permeabilities of films extruded with or without water injection are very similar. These results seem to be in accordance with TEM observations.

Comparing all nanocomposites, a lesser dispersion of CNa facilitates the transfer of diffusing molecules through the film, and hence, permeability is higher. This finding is an indication of the fact that the new extrusion process leads to improve the CNa delamination. In contrast, due to the surfactant presence that enhances interface matrix/filler, C30B platelets were already well-dispersed in PBSA without using injection. In this case, the new extrusion process can not improve much more the platelets delamination, and barrier properties are therefore similar.

Besides, in comparison with PBSA+C30B nanocomposite film (Fig. 3), permeability of films containing CNa extruded with water injection was still measured higher, even in the case of a chain degradation as revealed by GPC experiments. These results are in good agreement with TEM observations and X-ray diffraction measurements. Indeed, the more nanofillers are dispersed and exfoliated within the matrix, the more tortuosity effects are important. So, diffusing pathways are increased and as a result barrier performances of films were improved [11].

From the barrier properties correlated with usual physical properties, it can be stated that water injection into the barrel extruder during extrusion process allows improving barrier properties of nanocomposite containing unmodified nanofillers as CNa, but the effect is not sufficient in comparison with the organo-modification of nanoclays. One can however consider the concomitant action of melt process conditions with nanofillers incorporation inducing a visible decrease of permeability, and hence an increase of barrier behaviour of nanocomposite films.
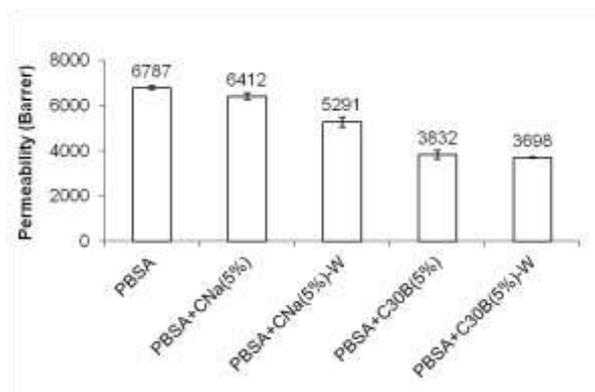

Fig 3 Water permeability of nanocomposite films

CONCLUSION

PBSA-based nanocomposite films containing 5 wt% of nanoclays (CNa and C30B) were successfully prepared by means of a new extrusion process consisting in injecting liquid water at specific pressure and temperature into the extruder barrel. It was shown that neither the incorporation of CNa and C30B nanoclays, nor the water injection affect the nanocomposite structure. Without water injection, as expected, aggregated structures were observed in films containing CNa, whereas C30B platelets, having more affinity with the matrix, were well-exfoliated. When water injection was used, smaller clay aggregates and intercalated structures were observed in nanocomposite containing CNa while C30B platelets were still well-dispersed. It has been shown that barrier performances of the nanocomposite films are directly correlated with structural properties of nanocomposite films. Indeed, without water injection, permeabilities to water and gases of films containing C30B are clearly lower than those elaborated with CNa, reflecting a better barrier performances due to increased tortuosity effects inducing longer diffusing pathways. As CNa formed aggregates within PBSA matrix when using the classical extrusion process, water injection during process helps to disrupt these aggregates, allowing them to be more oriented by extrusion, and consequently to clearly improve barrier properties of the films. In the case of C30B nanoclays, C30B platelets being already well-exfoliated within PBSA matrix, there is no benefit of using water injection. Finally, the present study

reveals that this new extrusion is suitable for improving the dispersion of nanoclays having no or few affinity with an organic matrix. This, with this process, an improvement of barrier properties of nanocomposites can be obtained when untreated clays are used. However, the synergistic impact of specific process conditions and nanoclay incorporation is indubitably demonstrated since barrier performances were improved for a system composed of an organic matrix reinforced by nanofillers.

ACKNOWLEDGEMENTS

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