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## In-situ nano-fibrillation of poly(butylene succinate-co-adipate) in isosorbidebased polycarbonate matrix. Relationship between rheological parameters and induced morphological and mechanical properties

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# This manuscript is in honor of the 50 year anniversary of the French Polymer Group (Groupe Français des Polymères – GFP).

Abstract. Multiphase systems in which 30 wt% of ductile semi-crystalline polymer, namely poly(butylene succinate-co-adipate) (PBSA), was homogeneously dispersed at the melt state in an amorphous bio-based poly(isosorbide carbonate co-cyclohexanedimethanol) (named PIC). Usually, for the manufacturing of in situ microfiber reinforced polymer composite (MFCs), the melting temperature of the reinforcing polymer must exceed that of the matrix by at least 30 °C, to allow fibril preservation during matrix consolidation step. Then, the blend is drawn at temperatures equal or slightly above the glass transition temperatures (Tg) of both components. Surprisingly, in our case, despite the low melting temperature of PBSA with respect to the (Tg) of PIC, it was demonstrated for the first time, the feasibility to create a nanosized fibrillar PBSA phase in the continuous PIC matrix. The development of a stable nanofibrillar morphology was promoted by controlling the viscosity and elasticity ratios between the dispersed and continuous phases as well as the time required for fiber breakup during processing. Interestingly, compared to the PIC matrix, the nanofibrillar PIC/PBSA composites exhibited outstanding mechanical and rheological properties. The elongation at break of the blend was increased by about 670% compared to that of the neat matrix without sacrificing the tensile strength. On the other hand, the energy to break of blends was found to be almost ten times greater than that of pure PIC matrix. Therefore, the methodology for the rheological and morphological control developed in the present study could find interesting applications in the design of novel bio-based polymer composites thin films dedicated for green packaging.

Keywords: Polymer blends; extrusion casting film process; fibrillar morphology; rheology.

## **INTRODUCTION**

Polymer blends are important industrial materials which are, still further, gaining in practical importance and scientific interest since the development of a blend is more economical than the synthesis of new functional polymers which not only involves exorbitant costs but also cannot satisfy industrial demand[1]. The great majority of useful blends are not miscible, and in these blends, physical properties can be optimized by controlling the quality of the dispersion which in turn depends on the rheological properties as well as on the mode of deformation of blend components[2]. Compared to composite materials which contain a rigid filler, polymer blends form a multiphase system with a deformable dispersed phase[3]. Due to the complex nature of deformation of the minor phase, polymer blends have the potential of generating a wide range of morphologies during melt processing[4]. These morphologies can roughly be divided in two classes; co-continuous systems and dispersion-like systems. In the latter, spherical, ellipsoidal, fibrillar or droplet-in-droplet morphologies have been reported in the scientific literature even with same composition[5]. In particular, the self-induced fibril morphology is a complex rheological as well as thermal process, in which the discontinuous phase can form a fibrous structure under certain processing conditions, which results in one polymer being reinforced or softened by the other one. Therefore, such materials called MFCs have attracted a great deal of interest and have been the subject during the last decade of several academic studies and use in various industrial applications[1].

On the other hand, the utilization of monomers originated from renewable resources for bioplastic preparation is drawing a significant interest due mainly to the growing concerns for the depletion of oil reserves and environmental challenges. Of the typical eco-friendly non-petroleum monomers, isosorbide (named ISB) is a thermally stable bicyclic diol produced from

glucose, and it is commercially available. Recently, isosorbide has been widely used for the synthesis of bio-based polyesters such as polyurethanes, poly(ethylene terephtalate) and polycarbonates[6]. As far as the polycarbonates are concerned, isosorbide is an excellent candidate to replace bisphenol A (BPA) known for its high human toxicity[7, 8]. However, isosorbide is highly hydrophilic and its reactivity is lower than that of BPA, resulting in the difficult synthesis of isosorbide-based polymers and high production cost[9]. In particular, biosourced polycarbonates produced using solely isosorbide called poly(isosorbide carbonate) have a rigid structure (Figure 1), resulting in a high glass transition that makes the polymer difficult to transform[9]. Therefore, copolymerization modification was used to solve the rigidity problem and adjust the physical properties of poly(isosorbide carbonate) polymers[10]. For example, poly(isosorbide carbonate co-cyclohexane-di-methanol) (Figure 1) obtained by polycondensation of isosorbide and diphenylcarbonate in the presence of flexible cyclohexanedimethanol (CHDM) as a comonomer was developed recently by Mitsubishi chemicals and commercialized under the name Durabio[11]. This bioplastic can be employed in a very wide range of industrial applications. Apart from injection-moulded parts, this material is currently used in the form of thin sheets, especially for the automotive as dashboard trims, touch screen, console and exterior radiator grilles and for mobile phone as front panels of smartphones[12]. However, compared to standard petroleum-based films, the amorphous bio-sourced polycarbonate could find only limited usages in packaging, due to its low thermal stability, low ductility and poor notched impact resistance[13].

To overcome these limitations, a strategy was adopted in the present study consisting in the insitu generation, during the manufacturing process, of well-aligned high aspect ratio flexible nanofibrils having strong interfacial affinity with the bio-based matrix. Discussed here are blends of bio-based polycarbonate copolyester mentioned above and a biodegradable polycondensate, particularly poly(butylene succinate-co-adipate) which was chosen to form the fibrillar phase because of its impressive ductility, as well as its excellent processability. The basis for the creation of self-induced fibril morphology is founded upon two essential conditions. The first mechanism is based upon the rheological and interfacial properties of the molten components (viscosity and elasticity ratios, and interfacial tension) which control the dispersed phase deformation mode and guarantee the droplet/fiber transition[14]. The second condition depends upon the stability of the fibrous structure throughout the manufacturing process which is closely associated with the relaxation and break-up kinetics of the fibril component[14]. Thus, under specific processing conditions, if suitable rheological and thermal conditions are satisfied, the development of fibril morphology in the melt occurs [14, 15].

Usually, for the manufacturing of Microfibrillar in-situ reinforced polymer composites (MFCs), the melting temperature of the reinforcing component must exceed that of the continuous phase by at least 30 °C, to allow preservation of the fibrillar structure during matrix consolidation step. In this case, the polymer blend is drawn at temperatures equal or slightly above the glass transition temperatures (Tg) of both components. However, in this work, the melting temperature of PBSA is lower compared to the (Tg) of PIC matrix and to the drawing temperature applied during the extrusion cast processing of the films.

The present study aims at investigating the influence of the in-situ PBSA fibrils generation during the cast film extrusion process on the rheological, crystalline structure and mechanical properties of the resulting bio-based films. The correlation between viscoelastic properties of blend components, morphological structure and ultimate properties of the in-situ polymer composites is discussed throughout this paper.



*Figure 1*: *Chemical structure of poly(isosorbide carbonate co-cyclohexane-di-methanol)* copolymer (left) and poly(isosorbide carbonate) (right).

## **EXPERIMENTAL SECTION**

#### **Raw materials**

Poly(butylene succinate-co-adipate) (PBSA) used in this study (Mw = 185 kg/mol, density =  $1.23 \text{ g/cm}^3$ , Tg = -40.9 °C and melting temperatures, Tm's = 85.6 °C (first) and 96.6 °C (second)) is a commercial product (Bionolle #3001, Showa Highpolymer, Japan).

PBSA BIONOLLE #3001 has an inherent viscosity of 1.15 dl/g and a melt-flow index (MFI) =  $1.8 \text{ g/10} \text{ min} (190 \degree \text{C}, \text{ASTM 1238})$ . The molar ratio of succinate unit to the adipate unit is ~ 4:1 and the content of the chain extender agent (hexamethylene diisocyanate) unit is ~ 0.5 mol%.

The second bio-based polymer used in this study (Mw = 100 kg/mol, density = 1.37 g/cm<sup>3</sup>, Tg = 120 °C) is a commercial product (Durabio #D7340, Mitsubishi chemical, Japan). It is a Poly(Isosorbide Carbonate co-CycloHexane-Di-Methanol) containing a minimum biobased content of 58% (Isosorbide which comes from corn) according to Japanese Plastic Federation.

The melt flow rate (MFR) of the amorphous polycarbonate (Durabio #D7340) at 230°C and 2,16 kg load is 10 g/10 min. The neat density is  $1.37 \text{ g cm}^{-3}$  and the heat deflection temperature according to ISO 75 method B is  $114^{\circ}$ C[16]. PBSA and PIC materials were dried in a vacuum oven at 60 °C and 80 °C respectively for 24 h prior to use.

#### **Preparation of Polymer Blends**

In a first step, the PIC/PBSA (70/30 w/w) blend were made by melt extrusion using a co-rotating twin screw extruder (ZSK 26, Coperion, Germany) with a screw diameter of 25mm and a length to diameter ratio of 40:1. The extruder barrel regulation was carried out on 10 zones: 9 barrel zones and the die section. Each barrel zone was heated separately from the feeder to the die to

160, 170, 180, 180, 180, 180, 180, 180, 170 and 160 °C. A specific screw profile for enhanced melt mixing was used for PIC/PBSA blends as employed in previous studies by our team [17]. The screw profile is presented in Figure 2. It included the following screw elements looking at the extrusion direction from hopper (right) to die (left): 12D-108/18D-108/KB45°D-12/12R-24/KB45°D-72/KB30°D-24/KB45°D-36/12D-72/KB45°D-36/18D-108/KB45°D-12/KB90°R-108/18D-24/12D-24/MixD-72/18D-108/12D. (D, direct conveying elements; KB, kneading blocks; Mix: mixing elements; R, reverse elements). This screw profile assured (i) homogeneous blending of PIC and PBSA at the entrance (ii) melting the two blend components completely in the stagnant flow area induced by reverse elements and (iii) conveying the molten blend to the die.



Figure 2. Screw profile for twin-screw extrusion processing of PIC/PBSA blends.

The screw speed and feed rate were set at 300 rpm and 6 kg/h, respectively. Extruded strands were cooled into a water bath and then pelletized. The resulting pellets were immediately dried in a vacuum oven at 60°C during 24 hours.

#### Extrusion of the film

The polymer blend granules were fed into the hopper of a single screw extruder (Rheomex 254, Haake Buchler, Germany) (screw diameter: 19 mm, L/D ratio: 25:1) equipped with a wide flat sheet die measuring a thickness (H) of 0.9 mm and a width (w) of 150 mm and regulated by a Haake Buchler Rheocord System 40 system (Germany). The thermal regulation was made over 4 zones. The optimal processing temperatures were determined for each sample and are listed in

Table 1. The measured residence time in the single screw extruder was 40 s and the maximum shear rate in the extruder was estimated to be  $40 \text{ s}^{-1}$  according to the equation (1).

Shear rate = 
$$\frac{\pi \cdot D \cdot N}{60 \cdot h}$$
 (Eq. 1)

where D is the screw diameter, N is the rotational velocity (RPM), h is the gap or the tolerance. The apparent shear rate  $\dot{\gamma}$  in the extrusion die estimated according to the equation (2) gives a value of 100 s<sup>-1</sup>.

$$\dot{\gamma} = \frac{6 \times Q_v}{w H^2} \qquad (Eq. 2)$$

This apparent shear rate was used in the following work to investigate the influence of viscosity and elasticity ratio on the stability of the fibrillation process in the extruded blends.

Assuming that the Cox-Merz rule is valid in this work (we consider that PBSA and PIC are thermorheologically simple which is valid as an approximation since PIC matrix is linear and PBSA is weakly branched polymer), the viscosity at an apparent shear rate (100s<sup>-1</sup>) corresponds to that at the angular frequency of 100 rad.s<sup>-1</sup>.

The melt film was extruded horizontally downwards and quenched by two water chill rolls casting unit located at about 6 cm from the die exit. The film produced was 90 mm width and its thickness was adjusted to 300  $\mu$ m by controlling the stretching occurred in the necking zone between the sheeting die exit and the contact line on the water-cooled rollers. The measured mass flow rate was 8,5 Kg/h giving a volume flow rate (Q<sub>v</sub>) of 2 cm<sup>3</sup>/s (based on a density of the polymer melt at 160 °C of 1,15 g.cm<sup>-3</sup> [18]). Melt densities at 160 °C for all the systems under study were measured using capillary rheometry according to the methodology described in our previous paper [19]. Thus, the calculated linear velocity of the extrudate was Ve = 0,91 m/min. On the other hand, the measured linear velocity of chill roll was Vr = 4,05 m/min. Therefore, the draw ratio: Vr/Ve = 4,5 and the elongational strain rate: (Vr – Ve) /  $\Delta l = \dot{\epsilon} = 0.9 \text{ s}^{-1}$ .

#### Table 1. Optimized processing temperatures for the cast films.

	Zone 1 (°C)	Zone 2 (°C)	Zone 3 (°C)	Zone 4 (°C)	Speed (RPM)	Pressure (bar)
PBSA	140	140	140	140	110	200
PIC	160	170	180	190	110	220
PIC/PBSA BLEND	160	170	165	160	110	300

#### **Characterizations and measurements**

#### Molecular weight measurements

The average molecular weight of virgin polymers and blends were determined by Size Exclusion Chromatography (SEC) using a mixture of chloroform and hexafluoro-2-propanol (95:5 vol %) on Agilent Technologies 1260 series (Santa Clara, USA) equipped with Shodex column chromatography (K-G, K803, K804 and K802.5). Samples with a concentration of 3 to 5 g/L were injected under a flow rate 1 mL/min. Signals were detected using a refractive index detector (Schambeck RI 2000, Germany) calibrated using PS standards. The incident light wavelength of the MALS detector was 658 nm.

#### NMR characterization

<sup>1</sup>H NMR spectra of the polymers were recorded on a Bruker Avance 300 MHz instrument (Bruker, Billerica, MA, USA) at 300 K using a deuterated chloroform (CDCl<sub>3</sub>). The chemical shifts were calibrated at 7.26 ppm.

#### Surface energy measurements

Surface energy of each polymer component was determined at 21 °C with the sessile drop method (DSA4 drop shape analyser, Kruss, Germany). From contact angle measurements performed with water and diiodomethane as probe liquids, the total surface energy, as well as the disperse and polar parts, of the samples were determined by using Owens-Wendt regression method. On each measurement, ten drops of each liquid were deposited and measured over the whole surface to ensure reproducibility at laboratory temperature.

#### **Morphology analyses**

A scanning electron microscope (SEM S4300 SE/N, Hitachi, Japan) was used to examine the shape and size distribution of the PBSA dispersed phase. The cast films were vitrified in liquid nitrogen, then fractured longitudinally parallel to the machine direction and coated with gold during 45 seconds at 2.4kV before SEM observations. For each sample, the average diameter of the dispersed phase was calculated using ImageJ software by measuring approximately 200 fibrils.

#### WAXD measurements

WAXD curves were recorded on a horizontal diffractometer (D8 Bruker, Germany) operating at 40 kV and 35 mA with a beam consisting of Co K $\alpha$  radiation ( $\lambda$ =1.78897 A°). Data were collected in the 2 $\theta$  region 10-90°, with a step size of 0.05° and a counting time of 0.5 s per step.

#### **DSC** analyses

DSC measurements were carried out by using DSC1 (Mettler Toledo, Swizerland) in the range of -70 °C to 160 °C at a rate of 10 K min<sup>-1</sup> under nitrogen flow of 50 mL/min. To determine the degree of crystallinity of PBSA, the melting enthalpy of 113.4 J/g was used which corresponds to the 100% theoretical crystalline polymer[20].

#### **Rheological tests**

Dynamic rheological measurements were performed using a controlled-stress rheometer (Haake Mars III, Thermo Scientific, Germany). All measurements were performed at 160°C under nitrogen atmosphere, in parallel-plate geometry with 35 mm diameter plates and a 2.2 mm gap size. Frequency sweeps were carried out at angular frequencies decreasing from 100 to 0.01 rad.s<sup>-1</sup> with a constant applied strain of 0.5%, which is within the linear viscoelastic region. The storage modulus (G'), loss modulus (G'), and complex viscosity ( $|\eta^*|$ ) were measured as function of the angular frequency. The samples were dried in vacuum at 60 °C for 12 h before measurement.

The extensional rheological behavior of neat polymers and blends was characterized using a SER tool (Sentmanat Extensional Rheometer, Thermo Scientific, Germany) in conjunction with the same rheometer (HAAKE MARS III, Thermo Scientific, Germany). The principle is based on film stretching between two revolving drums and, as the two drums turn in opposite direction, the applied deformation field is purely uniaxial. The detail of measurement of the extensional viscosity using the SER is reported in detail by Sentmanat et al [21]. The rotating drums induce a tangential elongation of the sample mounted on them, and the resulting torque M is measured by the torque transducer of the rotational rheometer, M(t)=2 R F(t) where F(t) is the instantaneous force imposed to the sample from stretching at time t.

and R is the drum radius. The Hencky stain rate  $\dot{\epsilon}_{H}$  at a constant drum rotating speed  $\Omega$  is  $\dot{\epsilon}_{H} = \frac{2 \Omega R}{L_0}$ ,  $L_0$  is the gage length between the fixing clamps. Thus, the transient elongational viscosity can be obtained by the equations (3 and 4) bellow:

$$\eta_{\rm E}^+(t) = \frac{M}{2 \, {\rm R} \, \dot{\epsilon}_{\rm H} \, {\rm A}({\rm T})}$$
 (Eq. 3) and  ${\rm A}({\rm T}) = {\rm A}_0 \left(\frac{\rho_{\rm s}}{\rho_{\rm M}({\rm T})}\right)^{2/3} \exp[-\dot{\epsilon}_{\rm H} t]$  (Eq. 4)

A(T) is the cross-sectional area which decreases exponentially with time,  $\rho_S$  is the sample density at solid state,  $\rho_M(T)$  is the melt density at temperature T, and A<sub>0</sub> is the initial cross-sectional area of the sample. The measurements were performed at 160°C and the samples were stretched at a strain rate of 1 s<sup>-1</sup>.

#### **Tensile tests**

Tensile tests were carried out according to ISO 527-1 on a tensile machine (Lloyd LR50K) using a 1 kN force sensor at a cross-head speed of 10 mm/min and at 23°C  $\pm$  2°C and 50%  $\pm$  5% relative humidity. The neat materials and blend films were cut into strips of 20 mm wide and 150 mm long with a cutting machine. The mechanical properties (mainly the elongation at break and yield strength) were determined from the recorded stress–strain curves. A minimum of five specimens for each material were tested for each reported value to estimate the precision of the reported data. Tensile energy to break (TEB) is calculated by the area under the stress-strain curve, or TEB =  $\int_0^{\varepsilon_T} S \, d\varepsilon$ , where S is the stress at any strain,  $\varepsilon$ , and  $\varepsilon_T$  is the strain at rupture. The value is in units of energy per unit volume (MJ.m<sup>-3</sup>).

## **RESULTS AND DISCUSSIONS**

#### Molecular weight measurements

The table 2 summarizes the results of SEC measurements. It was clearly shown that almost no degradation of the blend components occurred during processing. The number average molecular weight ( $\overline{M}_n$ ) of PIC/PBSA blends was 74 Kg.mol<sup>-1</sup> against 26,4 Kg.mol<sup>-1</sup> and 91,5 Kg.mol<sup>-1</sup> for PIC matrix and PBSA dispersed phase respectively. The measured molecular weight of neat components are close to the values known in the literature for the same grades of PBSA [22] and PIC[23]. Surprisingly, an unsual high molecular weight noted in the case of polymer blend which isn't in agreement with the additivity rule. This abnormal result may be due to an imperfect solubility of the high molecular weight PIC/PBSA polyesters which could affect the accuracy of SEC measurements.

**Table 2**. The weight average molecular weight  $(\overline{M}_w)$ , the number average molecular weight  $(\overline{M}_n)$ and the polydispersity index  $(\overline{M}_w/\overline{M}_n)$  for PIC, PBSA and PIC/PBSA blends.

Component	$\overline{\mathbf{M}}_{\mathbf{n}}$ (g/mol)	${ar{ m M}_{ m w}}$ (g/mol)	${ar{\mathrm{M}}}_{\mathrm{w}}/{ar{\mathrm{M}}}_{\mathrm{n}}$
PBSA	9,15. 10 <sup>4</sup>	1,85. 10 <sup>5</sup>	2.02
PIC	2,64. 10 <sup>4</sup>	1,00. 10 <sup>5</sup>	3.80
PIC/PBSA Blend	7,41. 10 <sup>4</sup>	2,10. 10 <sup>5</sup>	2.84

#### Structural analysis of virgin polymers and blends

PIC/PBSA films were prepared by extrusion casting. To verify whether during the melt blending step, no copolymer had been formed, <sup>1</sup>H–NMR spectroscopy was performed. <sup>1</sup>H–NMR spectra of the PBSA and PIC are shown, respectively in Figure 3 and Figure 4. From the <sub>1</sub>H–NMR

spectrum of the PBSA was shown: O—CH2–, from the 1,4-butanediol unit at  $\delta$  4.1; COCH2–, from the succinyl unit at  $\delta$  2.6; COCH2–, from the adipoyl unit at  $\delta$  2.3; and –CH2–, from the 1,4-butanediol unit and the adipoyl unit at  $\delta$  1.7. <sup>1</sup>H–NMR spectrum of PBSA showed a ratio of 1/0.24 between adipoyl and succinyl units which is in accordance with literature [24]. The analysis of <sup>1</sup>H–NMR spectra of PIC matrix exhibited a structure with isosorbide and CHDM units and the results were presented in table 3:

*Table 3*: <sup>1</sup>*H*–*NMR* analysis of PIC matrix.  $\delta$  is the chemical shift peak.

δ (ppm)	<sup>1</sup> H-NMR assignments
7.5-7.3	derived from terminal phenyl group
6.7-6.5	derived from terminal double bond of ISB
5.6-4.8	derived from all ISB structural units
4.4	derived from terminal hydroxy group of ISB
3.6-3.5	derived from terminal hydroxy group of ISB and derived from terminal hydroxy group of CHDM
3.5-3.4	derived from terminal hydroxy group of CHDM and derived from terminal double bond of ISB
2.6	derived from terminal hydroxy group of ISB
2.3	derived from terminal double bond of CHDM
2.2-0.5	derived from all CHDM structural units
1.7	derived from the cyclohexylene ring tertiary CH protons
1.0-1.7	derived from the CH <sub>2</sub> ring protons

The isosorbide/CHDM ratio determined was 1/0.54, and the presence of a trace of phenol is also evidenced. The <sup>1</sup>H NMR spectrum of PIC/PBSA films was shown in Figure 5. Their signals values were compared with those obtained from the <sup>1</sup>H NMR data obtained with virgin PBSA and PIC specimens as reported in Figure 6. The results showed no apparent difference between the spectra once superimposed and therefore no evidence of the formation of a copolymer. Indeed, no trace of chemical accounting with transesterification between the two polymers had appeared. Tan et al.[25] stipulated that the formation of a copolyester by transesterification between the succinate units and Isosorbide groups should induce the appearance of pics located at 3.70 ppm and 4.25 ppm. This is not the case in this study.



Figure 3 : <sup>1</sup>H NMR spectrum of PBSA



Figure 4: <sup>1</sup>H NMR spectrum of PIC matrix



Figure 5 : <sup>1</sup>H NMR spectrum of PIC/PBSA film



*Figure 6* : superposition of 1H NMR spectra of: PIC/PBSA Film (green), PIC (blue), PBSA (brown).

Interfacial tension assessment

The contact angles and surface energy of the neat materials are summarized in Table 4. The values of the disperse component of the surface energies clearly show the strong non-polar nature of the PIC compared to PBSA. On the other hand, PBSA has a polar part of the surface energy twice as large as that of the PIC matrix. Nevertheless, the total surface free energy of PBSA and PIC are very close. The interfacial tension at ambient temperature estimated using the Wu's theory[26] gives  $\gamma^{\text{PIC/PBSA}} \approx 1.5 \text{ mN/m}$ , suggesting a good initial compatibility between the two immiscible polymers. The interfacial tension at 160 °C corresponding to the mean processing temperature is 0.23 mN/m deduced from the interfacial tension at 21°C using the coefficient 0.009 mN/m°C as reported by Chapleau et al. for polar polymer blends[27].

*Table 4.* Total, polar, and dispersive components of the surface energy of PBSA and PIC at 21  $^{\circ}C$ .

Component	Contact angle (°)	γ polar (mN/m)	γ dispersive (mN/m)	Surface energy (mN/m)
PBSA	$\theta^{\text{H2O}} = 76; \ \theta^{\text{CH2I2}} = 35$	11.9	28.3	40.2
PIC	$\theta^{\text{H2O}} = 72; \ \theta^{\text{CH2I2}} = 43$	6.3	37.1	43.4

#### **Morphological** analysis

The scanning electron micrographs at low magnification (Figures 7(A,B)) give an overview of the morphology of PIC/PBSA cast films. Blends have microstructures comprised of highly elongated PBSA fibrils dispersed homogeneously in the continuous PIC matrix. The high aspect ratio nanofibrils were well-oriented preferentially parallel to the flow direction since cast films are mono-oriented in extrusion direction. On the other hand, one can clearly see that PBSA fibrils look like being intimately embedded within the PIC matrix with a good adhesion at the fibril/matrix interface. Generally, such fibrillar structure was rarely encountered in the most insitu microfibrillar reinforced materials (MFCs) where the microfibers were smoother and clearly distinguished in the matrix. In addition, higher magnification SEM images (Figures 7(C,D)) showed that the blend formed transverse matrix/fiber connections and distinct interfibrillar linkages approximately perpendicular to the fiber axis. Gupta et al. [28] found similar morphological structure in the case of HDPE/LLDPE blends where intense interfibrillar connectivity was reported. Xie et al [29] highlighted the presence of strong interfacial ligaments in the case of PLA/PBS (60/40) nanofibrillar composites prepared through "slit die extrusion-hot stretching-quenching" process. The authors found that the highly oriented semi-crystalline PLA kebabs strung by the PBS nanofibrils serve as self-reinforcing elements. Zhou et al [30] showed similar morphologies during the in situ formation of ductile PBAT nanofibrils in PLA matrix. They revealed an orderly oriented structure of interlinked networks and outstretched tie chains in amorphous phase of semi-crystalline PLA. In the presence of drawn PP/PET blends, Friedrich et al. [31] showed that the formation of transverse connections arises from the transcrystallization of PP matrix onto the PET fibrils. They reported that the highly oriented PET microfibrils act as effective nuclei for transcrystallization of the PP matrix. However, in our blend system, the biobased polycarbonate phase is amorphous; therefore the existence of transcrystalline layers is excluded. So, the reason for the interconnectivity between fibrils and matrix is not clear and more detailed investigation would be necessary. The fiber size distribution data are shown in Figure 8. It was found that the polydispersity of the PBSA nanofibrils obey the log-normal distribution. The fibril diameter varied in the range 0.07 - 0.5 $\mu$ m with a mean diameter of 0.25  $\mu$ m ± 0.10  $\mu$ m. Nevertheless, it was not possible to estimate the lengths of these fibrils from SEM micrographs since it was very difficult to extract chemically PBSA fibrils from the PIC matrix without altering the fibrillated discontinuous phase.



Figure 7: SEM observation of longitudinal fracture surfaces of PIC/PBSA blend films.



Figure 8: Fiber size distribution in PIC/PBSA blend films.

## WAXD analysis

In order to investigate the effect of nanofibrillation on the chain structure of the PIC matrix and the crystalline structure of PBSA, WAXD experiments of PBSA, PIC and PIC/PBSA blend were performed (Figure 9). PBSA film shows two strong diffraction peaks located at 20 values of  $22.8^{\circ}$  (0.45 nm) and  $26.3^{\circ}$  (0.39 nm) and two small peaks located at  $30.4^{\circ}$  (0.34 nm) and  $34.0^{\circ}$ (0.30 nm). According to Ren et al., [32] the four diffraction peaks from low to high angles are assignable to, (020), (110), (121) and (111) planes, respectively. In the case of PIC matrix, a broad scattering peak at 20 of about 21° (0.49 nm) was seen. This halo corresponds to the mean intersegmental amorphous chain spacing of the matrix. For the PIC/PBSA film, the WAXD pattern shows similar crystalline peaks with the same angle locations as the pure PBSA component. Nevertheless, the intensity of peaks was reduced and the shape of the diffraction peaks was flattened. Thus, blending polycarbonate amorphous polymer with semi-crystalline PBSA dispersed phase does not modify its ordered crystal structure but reduces its overall crystallinity degree. However, the amorphous peak corresponding to PIC became slightly broader in the blend (the full width at half-maximum changed from  $5.7^{\circ}$  to  $7.0^{\circ}$ ), and the halo position shifted slightly to a higher scattering angle from 20.9° to 21.6°. This implies that a decrease in the interchain d-spacing of amorphous polycarbonate occurred in the presence of PBSA fibers. In addition, the relative size corresponding to the largest dimension of crystallite was estimated based on the peak associated with the (110) plane according to the Scherrer equation[33].

$$D_{(110)} = \frac{0.9 \lambda}{B_{(110)} \cos(\theta)}$$
 (Eq. 5)

where  $\lambda$  is the X-ray wavelength (0.17889 nm), B<sub>(110)</sub> is the (110) diffraction peak width at half the maximum intensity, and  $\theta$  is half the scattering angle which are reported in Table 5. It was found that in the blend, the presence of PIC matrix induces the decrease of crystal thickness of PBSA from 13.7 nm to 6.0 nm. This demonstrates that polycarbonate matrix restricts the crystallization of PBSA dispersed phase in the blend.

 Table 5: The scattering angles, diffraction peaks (110) and the crystal sizes of neat PBSA and
 PIC/PBSA blend films.

	Neat PBSA	Blend
2θ (°)	26,2	26,2
B <sub>(110)</sub> (°)	0,7	1,6
Crystal size (nm)	13,7	6,0



Figure 9: WAXD patterns of PIC, PBSA and PIC/PBSA blend films.

#### **Thermal Properties**

To elucidate crystallization and melting behaviours of neat PIC, neat PBSA and both components in the blends, DSC analyses were conducted and the relative scans are shown in Figure 10. Reported data were taken from a second heating scan to overcome the effect of the thermal history and the results are summarized in Table 6. DSC curve of neat PBSA shows two distinct melting peaks located at 85.9 °C and 96.5 °C. Yoo and Im [34] from DSC and WAXD measurements for PBSA crystallized at different temperatures concluded that the multiple melting behaviour of PBSA does not originate from the different crystal modification. They confirmed that the double melting endotherms of PBSA can be explained by the melting and recrystallization model. Yasuniwa et al. [35] also found that PBSA showed double melting endotherms upon nonisothermal crystallization from the melt which was ascribed to the recrystallization and remelting mechanism. Then, Qiu et al. [36] provided a direct evidence to

support the melting and recrystallization mechanism through the study by TMDSC and conventional DSC at different cooling rates ranging from 1 to 10 °C/min. In the case of blend samples, the lowest endotherm disappeared and the highest one was shifted towards the lower temperature region resulting in a flat peak located at 94.5 °C. This observation reflects that a change in the crystalline lamellar structure of PBSA phase was occurred in the presence of polycarbonate matrix. The reason shall be the decrease in crystallite size as was previously proved using the X-ray diffraction analysis. Indeed, melting points can decrease significantly with decreasing crystallite size. The high degree of interaction of the rigid PIC chains with the PBSA fibers can restrict the mobility and the flexibility of the PBSA chains and thus act as an obstacle to the crystal growth of PBSA. Therefore, the total heat of fusion ( $\Delta H_m$ ) of PBSA decreases with the addition of PIC matrix (see Table 6) and the degree of crystallinity in the blend ( $\chi_c$  =38 %) was lowered compared to that of pure PBSA ( $\chi_c$  =51.8 %). The strong interaction between PBSA and the PIC components is further established by the depression in the enthalpy of crystallization ( $\Delta H_c$ ) as well as the crystallization temperature ( $T_c$ ). The crystallization of neat PBSA exhibits an exothermic peak at 58.4 °C (Figure 10). In the blend, the crystallization peak of the PBSA component shifted to lower temperature ( $T_c = 50$  °C). It arises from the fact that the amorphous PIC component acts as a diluent to retard the nucleation and growth of PBSA crystals. Thus, crystallization from dispersed PBSA chains becomes more difficult due to the obstacle of a large number of surrounding rigid polycarbonate chains, which is to a large extent responsible for the lower melting point of generated PBSA crystals. Furthermore, despite the high compatibility between the two phases, DSC curves revealed two distinct glass transition regions corresponding to the glass transition temperatures of the individual components. This is consistent with the presence of two immiscible phases in these materials as revealed by SEM analyses. PBSA is characterized by an apparent glass transition (Tg) of about -40 °C when measured based on the second heating step and -50 °C based on the

first cooling scan. On the other hand, Polycarbonate component presents a Tg of about 123 °C and 119°C when measured at the second heating and first cooling scans respectively.



Figure 10: Heat flow versus temperature for PIC, PBSA and PIC/PBSA blend films.

Table 6	DSC da	ta narameters	for PI	C PRSA	and PI	C/PRSA	hlend	films
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Cycle	Neat Components		Bl	end
2st Heating	PIC	PBSA	PIC	PBSA
Tg (°C)	123.5	-40.5	122.7	-40.1
Tm,1 (°C)	-	85.9	-	-
Tm,2 (°C)	-	96.5	-	94.5
$\Delta Hm (J/g)$	-	57.1	-	36.5
$\chi_{c}(\%)$	-	51.8	-	38.0
1st Cooling	PIC	PBSA	PIC	PBSA
Tg (°C)	119.1	-50.0	118.7	-51.4
Tc (°C)	-	58.4	-	50.0

ΔHc (J/g)	-	52.2	-	43.0
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#### **Rheological behaviour**

#### Investigation of chain topology of neat polymers and blends

Trinkle and Friedrich [37] proposed a rheological method for the characterization of polymer melts and chain topology, which is based on the reduced Van-Gurp-Palmen plot (rVGP) [38]. An rVGP plot is made up of the loss angle  $\delta$  against the logarithm of reduced modulus G<sub>red</sub>, and the latter was obtained by dividing the absolute complex modulus  $|G^*|$  by the value of the plateau modulus,  $G_N^0$  (the elastic modulus in the high frequency region when  $\delta \rightarrow 0$ ). For the PIC matrix and PBSA blends, the plateau modulus corresponds to 7,0  $\times 10^5$  Pa and 3,7  $\times 10^5$  Pa respectively. In the case of PBSA, the plateau modulus can hardly be attained. We take the value corresponding to  $\omega = 100 \text{ rad.s}^{-1}$  giving a plateau modulus of 7.5x10<sup>4</sup> Pa. Figure 11 shows the (rVGP) plot of the studied samples. The (rVGP) plot for the neat PIC matrix displays a classical shape that is generally matched with polymers having a linear structure. A plateau of the phase angle at 90° is observed, indicating nearly viscous behavior in the low frequency zone. At higher modulus or frequencies, the phase angle decreases. The neat PBSA displays lower values of the phase angle in comparison with the pure PIC, reflecting a general increase of the elasticity which characterizes the branched polymers [39]. According to the Trinkle model [37], the molecular structure of PBSA corresponds to an H branching type. In the case of PIC/PBSA blends, the (rVGP) plot contains a maxima corresponding to the major component (PIC matrix) and a minima reflecting the high frequency shape relaxation of the dispersed phase (PBSA). This shape of (vGP) plot is characteristic of the matrix/droplet morphology.



Figure 11. Van Gurp Palmen plot of the PIC matrix, PBSA and PIC/PBSA blends.

Another model which has been widely used in the literature in order to probe the polymer chain structure of polymers is the cole-cole model [40]. Based on the latter, Perez et al [41] developed the biparabolic model which gives an expression of the complex shear modulus G<sup>\*</sup> as a function of several parameters having a physical meaning:

$$G^* = G' + iG'' = G_c + \frac{G_{I}-G_c}{1+Q(i\omega\tau_{mr})^{-u} + (i\omega\tau_{mr})^{-u}}$$
 (Eq. 6)

where  $\omega$  is the angular frequency, G<sub>C</sub> and G<sub>I</sub> are respectively the relaxed and unrelaxed modulus and  $\tau_{mr}$  is the molecular relaxation time. The parameter u' (0<u'<1) corresponds to correlation effects at the structural scale in the sample such as nodes or entanglements. The coefficient u' increases when the crosslinking density, the impurity concentration and/or the filler fraction in the material decreases. The parameter u (0<u<u'<1) corresponds to correlation effects at the monomer scale. It governs the high frequency of the curve as presented in Figure 12.

u' will be lower than 0.7 for crosslinked resins (effect of nodes) and will be close to unity for amorphous (or melt) thermoplastic polymers [42]. Thus u' values when located in the [0.6–0.8] interval, this corresponds to the rheological behavior of branched polymers [42]. The values of u', u and Q are determined by plotting G'' versus G' according to Figure 13.



*Figure 12. Graphical determination of parameters (u, u', G<sub>L</sub>, G<sub>C</sub> and Q) from a Cole–Cole plot.* From Figure 13, u' values for the PIC matrix, PBSA and PIC/PBSA blends are reported in Table 7. It can be observed that the parameter u' is closer to unity in the pure PIC. On the contrary, in the neat PBSA, the parameter u' decreases to 0,78 which corresponds to the rheological behavior of a branched polymer. In the case of PIC/PBSA blends, u' is close to 0,9 so between that of PIC and PBSA. It's useful to mention that PBSA nanofibrils which interact at the interface with PIC chains behave like a solid viscoelastic filler. A network filler structure is formed making it possible to reduce the u ' parameter. Indeed, Van Gurp plot (Figure 11) indicates that PIC matrix remains viscous throughout the entirety of the frequency range studied. However, with the presence of PBSA nanofibrils, blends begin to show a shift towards elasticity. The decrease of the slope of the G' ~  $\omega$  at low frequencies in the case of PIC/PBSA blends supports this finding



Figure 13. Cole–Cole diagram of PBSA, PIC matrix and PIC/PBSA blends.

Table 7. u' number of PBSA, PIC and PIC/PBSA blend.

	PBSA	PIC matrix	PIC/PBSA blend
u' parameter	0,78	0,98	0,89

#### **Rheology/morphology relationships**

The development of a polymer/polymer composite with fibrillar morphology requires the satisfaction of specific rheological conditions. The viscosity ratio ( $k=\eta^{PBSA}/\eta^{PIC}$ ) should be kept below 4, otherwise the droplet breakup becomes difficult [43]. In order to promote the fibrillation, it is necessary to develop a system such as the elasticity ratio ( $k'=Wi^{PBSA}/Wi^{PIC}$ ) is lower than 1[14, 15]. Here Wi is the Weissenberg number of the droplet phase (Wi<sup>PBSA</sup>) and matrix (Wi<sup>PIC</sup>).

The Weissenberg number which is known to represent the melt elasticity [19] is defined in a shear flow by the ratio of the elastic forces to the viscous ones as  $W_i = \frac{G'}{G''}$ . In addition, the breakup of the fibers is expected afterwards. Thus, the following condition should be satisfied: The breakup time of the fiber (t<sub>b</sub>) should be significantly higher compared to the characteristic time for flow induced deformation [19]. The viscosity ratio (k) at 100 rad.s<sup>-1</sup> (based on the calculated shear rate in the extrusion die) is equal to 0.10, far below the critical value of 4 (Table 8). On the other hand, the elasticity ratio (k') is equal to 0.44, far below the unity. Therefore, very favorable rheological conditions are met for the in-situ generation of the fibril morphology in the extrusion die of melt blend films.

	η(Pa.s)			
Samples	at 100 rad/s	<b>k</b> (-)	Wi (-)	<b>k</b> ' (-)
PBSA	1000		1,15	
PIC	7450		2,62	
Blend		0,13		0,44

*Table 8. Viscosity and elasticity ratio(s) of neat polymers and blends.* 

Figure 14 shows the variation of the storage modulus with the pulsation on a log-log plot of pure PBSA, pure PIC and blends. In the case of PIC matrix, in the terminal regime, for lower frequencies (smaller than the Rouse relaxation time), the storage modulus exhibited a slope of 2, on a log-log plot. However, in the case of PBSA, this slope shift to 1.5, which is characteristic of

a branched H-polymer [37]. Furthermore, the slope of G' of the PIC/PBSA blend in the lower frequency range is 0.7, far bellow of linear polymers. This could explain the increase of storage modulus at low frequency (presence of plateau) induced by the fibrillar morphology. Similar trends were reported by Yousfi et al in the case of PP/PA6 blends filled with ionic liquids [44]. According to the authors, the observed plateau modulus in the terminal regime is a signature of the presence of a cluster three-dimensional network which is more protected against deformation. In another report, Xie et al [29] observed similar behavior in the case of PLA/PBS blends manufactured by "slit die extrusion – hot stretching – quenching" process. According to the authors, the increase of storage modulus in the low frequency region (below 1 Hz) principally lies in the shape relaxation of the discrete PBS phase in the PLA matrix. During oscillatory shear flow, PLA/PBS blends present a much longer relaxation time than that of the pure polymers due to the increased total area of the PLA/PBS interface.



Figure 14. Storage modulus G', (a) and complex viscosity  $|\eta^*|$  (b) as a function of the angular frequency  $\omega$  for the PICmatrix, PBSA and PIC/PBSA blends at 160 °C.

To elucidate the effect of PBSA nanofibrils on the shear viscosity behavior of the blend, the complex viscosity data was fitted with a Carreau- Yasuda law including an additional term of

yield stress  $\sigma_0$ . ( $\omega$ : angular frequency,  $\eta_0$ : zero-shear viscosity,  $\lambda$ : average characteristic relaxation time, n: pseudoplasticity index, a: curvature parameter).

$$|\eta^*(\omega)| = \frac{\sigma_0}{\omega} + \eta_0 \left[1 + (\lambda \omega)^a\right]^{(n-1)/a}$$
(Eq. 7)

The results presented in Table 9 don't show any apparent yield stresses  $\sigma_0$  for the pure PIC and PBSA materials. Conversely, PIC/PBSA blends exhibit a moderate yield stresses of 475 Pa. This demonstrates without ambiguity the presence of PBSA network inside the PIC matrix.

Table 9: Carreau-Yasuda parameters used to fit the viscosity data of PIC, PBSA and PIC/PBSA

Parameter	PIC	PBSA	PIC/PBSA blend
<b>5</b> 0 (Pa)	0	0	475
η <sub>0</sub> (Pa.s)	145000	19000	66000
$\lambda$ (s)	0,46	4,60	1,00
n	0,24	0,50	0,41
a	0,70	1,10	0,95

blend films.

We apply now the Palierne model [45] to investigate the interfacial tension of PIC/PBSA blends. The Palierne approach proposed an emulsion model able to predict the linear viscoelastic behavior of polymer blends. The Palierne model took into account the size of the dispersed phase, the interfacial tension between the components, and the viscoelastic property of both components following the equation bellow:

$$G^{*}(\omega) = G^{*}_{m}(\omega) \left[\frac{1+3\sum_{i} \emptyset_{i} H_{i}(\omega)}{1-2\sum_{i} \emptyset_{i} H_{i}(\omega)}\right]$$
(Eq. 8)  
$$H(\omega) = \frac{4 \left(\Gamma/R\right) \left[2 G^{*}_{m}(\omega) + 5 G^{*}_{d}(\omega)\right] + \left[G^{*}_{d}(\omega) - G^{*}_{m}(\omega)\right] \left[16 G^{*}_{m}(\omega) + 19 G^{*}_{d}(\omega)\right]}{40 \left(\Gamma/R\right) \left[G^{*}_{m}(\omega) + G^{*}_{d}(\omega)\right] + \left[2G^{*}_{d}(\omega) + 3G^{*}_{m}(\omega)\right] \left[16 G^{*}_{m}(\omega) + 19 G^{*}_{d}(\omega)\right]}$$
(Eq. 9)

where  $G_m^*$  and  $G_d^*(\omega)$  are the complex shear moduli of matrix and droplet at the frequency of the dynamic strain.  $\Phi$  is the volume fraction of the dispersed phase,  $\Gamma$  is the interfacial tension to be determined and R is the radius of the dispersed PBSA fibrils. The figure 15 shows the fit of the experimental PIC/PBSA curve by the Palierne model. The best fit was obtained with an interfacial tension of 0.4 mN/m. This prediction of interfacial tension is in good agreement with the experimental results of surface energy measurements reported above. It is useful to mention that the Palierne model is considered valid in the case of immiscible blends with nodular morphology. In this study, the morphology of cast blend films is nanofibrillar. However, during rheological dynamic shear measurements, the fibrils can relax and regain a nodular shape. This makes the fit of the data by the Palierne model work well.



Figure 15. Comparison between simulated and experimental dynamic storage modulus versus the pulsation frequency of PIC/PBSA blends.

The relaxation time of the interface ( $\lambda$ ) was estimated from the interfacial tension  $\Gamma$  (obtained by the fit by the palierne model) according to Choi–Schowalter emulsion model (Eq. 9) [46], where R is the mean radius of the PBSA fibers,  $\eta_m$  the zero shear viscosity of the PIC matrix, k the viscosity ratio and  $\Phi$  the volume fraction of the PBSA dispersed phase.

$$\lambda = \frac{(\eta_{\rm m} R) \left[ (16k+16) (2k+3-2\phi(k-1)) \right]}{(4 \Gamma) \left[ (k+1)-2\phi(5k+2) \right]}$$
(Eq. 10)

The calculated relaxation time of the interface between PIC and PBSA was estimated to be around 230 seconds. This is an indicator that PBSA nanofibrils have a greater interaction with the PIC matrix with the presence of a high surface area.

#### Uniaxial elongational behavior of neat materials and nanofibrillar blends

The rheological response in an extensional flow of a melt polymer is known to be mainly controlled by the structure of entanglement and chain topology of their macromolecules [47]. This topology in turn, depends on the type of the molecular structure which could be linear or with a macromolecular branching. Thus, polymers with linear, semirigid and short chains are known to produce poor rheological properties during the extensional flow[48].

Figure 16 depicts the transient extensional viscosity as a function of time of neat PIC, pure PBSA and PIC/PBSA films at 160 °C and under an elongational deformation at the strain rate 1 s<sup>-1</sup>. PIC matrix didn't show any strain hardening at the investigated stretching rate, which was in a good agreement with the commonly behavior of a linear polymer under elongation known as strain softening [49]. In the opposite, for pure PBSA, the extensional viscosity rapidly increased with time indicating a strong strain-hardening behavior which characterize the polymers with macromolecular branching [50]. In the case of PIC/PBSA blends, an increase in the extensional viscosity was shown and this could be attributed to an improvement in the melt strengthening of the nanofibrillar blends compared to neat PIC matrix [51] and the formation of a physical network of PBSA nanofibrils in the blend as previously discussed in the investigation of chain topology of neat polymers and blends.

It's useful to indicate that since the PBSA phase is in the molten state during the SAOS test, it wasn't excluded that the fibrillar morphology initially present in the blends could be destroyed during the dynamic rheological experiment. Indeed, the molten PBSA fibrils may relax during the time necessary to carry out SAOS tests. Whereas if PBSA nanofibrils were kept in the solid state, the strain hardening observed should been much more pronounced[52].



*Figure 16.* Uniaxial elongational responses of PIC, PBSA and PIC/PBSA nanofibrillar composites melts at a strain rate of 1 s<sup>-1</sup> and a temperature of 160 °C.

#### Stability of the nanofibrillar morphology

The criteria Ca > 4  $Ca_{(crit)}$  in both shear and elongational flows was used to predict the fibril formation in PIC/PBSA blends as reported recently by Yousfi et al [19] and Chomat et al [15]. Ca is the capillary number, which represents the ratio of the viscous stresses imposed on the droplet by the external flow field to the interfacial tension forces that tend to restore the droplet to a spherical shape. The capillary number in shear flow is defined as:

$$C_a = \frac{\eta_m \times \dot{\gamma}}{\Gamma/R} \qquad (Eq. \ 11)$$

where  $\eta_m$  is the viscosity of the matrix,  $\dot{\gamma}$  is the shear rate, R is the radius of the droplet prior to undergoing deformation, and  $\Gamma$  is the interfacial tension.  $Ca_{(crit)}$  is the capillary number corresponding to the critical shear rate ( $\dot{\gamma}_c$ ). In elongational flow, the capillary number is defined

by 
$$C_a = \frac{\eta^E_m \times \dot{\epsilon}}{\Gamma/R}$$
 (Eq. 12)

where  $\eta_{m}^{E}$  is the elongational viscosity of the matrix,  $\dot{\epsilon}$  is the stretching rate. Thus  $Ca_{(crit)}$  in elongational flow is the capillary number corresponding to the critical stretching rate ( $\dot{\epsilon}_{c}$ ). In shear flow (inside the die), the calculated capillary number *Ca* gives a value of 230. However, during the stretching of the PIC/PBSA films, the elongational capillary number is equal to 9.4.

From experimental data, De Bruijn[53] showed that the critical capillary number can be fitted with the following empirical equation (for k < 4):

$$\log \left(\frac{Ca_{(crit)}}{2}\right) = C_1 + C_2 \log(k) + C_3 (\log(k)^2) + \frac{C_4}{\log(k) + C_5}$$
(Eq. 13)

where  $C_i$  values for shear and extensional flows are given in Table 10.

	<b>C</b> <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	$C_4$	C5
Shear flow	-0.5060	-0.0994	0.1240	-0.1150	-0.6110
Elongational flow	-0.64853	-0.02442	0.02221	-0.00056	-0.00645

*Table 10.*  $C_i$  coefficients for the equation  $C_a(crit) = f(k)$  [43].

The critical capillary numbers obtained were 0,56 and 0,42 in shear and elongational flow respectively. Thus, the capillary number ratios were 400 in shear flow and close to 23 in elongational flow far above the recommended value of 4. As reported previously, the transition from droplets to stable filaments is achieved when Ca > 4 Ca<sub>(crit)</sub>. Therefore, favorable conditions of the fibrillation were met to obtain the in-situ nanofibrillar PIC/PBSA blends as confirmed by the SEM analysis.

#### Fiber breakup time

The stability of a fibrillar structure can be evaluated by the time required for fiber breakup.

When the fiber is being deformed under flow, an additional deformation due to flow superposes to the one due to Rayleigh instabilities. Assuming the following assumption: i) the fiber deforms affinely with the matrix (*Ca/Ca(crit)*≥2), ii) the fiber breaks up when the local diameter reduction rate due to the instability is greater than that produced by the fluid deformation, iii) the instability wavelength is independent of flow. Based on these assumptions, fiber breakup time was predicted from the work of Huneault et al. [5] using the equations (14, 15 and 16), where  $\varepsilon_0 \approx 10^{\circ}$ <sup>9</sup> m corresponds to the initial amplitude of the distortion of the fiber [54] and  $\Omega(k,X_m)$  is a complex function calculated from Tomotika's original equation [55].

In shear flow, the fiber breakup time was calculated using the equation 14:

$$\mathbf{t}_{\mathbf{b}} = \left[\frac{\eta_{\mathrm{m}} \ln(\varepsilon_{\mathrm{b}}/\varepsilon_{0})}{\Gamma \,\Omega(\mathbf{k}, \lambda_{\mathrm{m}})\dot{\gamma}^{1/2}} \,\mathbf{R}\right]^{2/3} \qquad (\text{Eq. 14})$$

For  $0.01 \le k \le 10$ , [56] used the following equation to fit the function  $\Omega(k, \lambda_m)$ :

$$\Omega(k,\lambda_m) = \exp[b_0 + b_1 \log k + b_2 (\log k)^2 + b_3 (\log k)^3 + b_4 (\log k)^4]$$
(Eq. 15)  
where  $b_0 = -2.588$ ,  $b_1 = -1.154$ ,  $b_2 = 0.03987$ ,  $b_3 = 0.0889$ , and  $b_4 = 0.01154$ 

According to Huneault et al. [5],  $\ln(\epsilon_b/\epsilon_0)$  is equal to 20 for polymers and  $\Omega(k, \lambda_m)$  is therefore equal to 0,2. Thus, the resulting fiber breakup time  $t_b$  was 8 s.

In elongational flow, the fiber breakup time was estimated to be 14 s using the equation 16 :

$$t_b = \left(\frac{2}{\dot{\epsilon}}\right) ln \left(\frac{\eta^E_m ln(\varepsilon_b/\varepsilon_0)\dot{\epsilon}}{\Gamma \Omega(k,\lambda_m)} R\right) \quad \text{(Eq. 16)}$$

The breakup time (t<sub>b</sub>) of PBSA phase is 8 s at shear flow and 14 s in elongational flow are far above the process characteristic time  $\dot{\gamma}^{-1}$  (0,01 s) and  $\dot{\epsilon}^{-1}$  (1,1 s), which explains the stability of the fibrous structure of PIC/PBSA blend (see SEM micrograph, Figure 7).

#### **Mechanical properties**

The mechanical performance, especially strength, ductility and toughness, are likewise crucial for practical application in thin packaging films [30]. Figure 17 describes the stress-strain curves for pure PIC, PBSA and PIC/PBSA nanofibrillar in-situ composites. Compared to PIC matrix, a drastic improvement in mechanical properties is observed in the nanofibrillar PIC/PBSA composites (Table 11). The elongation at break is increased by about 670% compared to that of the PIC neat matrix. On the other hand, a minor reduction (~ 4.3 MPa) in the yield strength is observed. The strong adhesion between the PBSA phase and the matrix observed by SEM, and the significant orientation of PBSA nanofibrils allow a suitable stress transfer between ductile PBSA and PIC matrix, thereby improving the ductility of the blend. Similar results were obtained by Ojijo and Sinha Ray [57] in PLA/PBSA blends prepared by compression moulding. They found that the fibrillation of the dispersed phase induced a brittle to ductile transition in the investigated blends.

It's useful to mention that in the case of PIC/PBSA blends, a strain-hardening occurred at high strain values. The increase in stress with continued straining is associated with the presence of the well oriented PBSA nanofibrils in the PIC matrix. At ambient temperature, PBSA is in the rubber state (Tg <-40°C). Since PBSA nanofibrils are well bonded to the PIC matrix and its content is high (30wt%), the strain hardening observed is due to the stretching to high strains of the PBSA rubber phase inside PIC matrix during the tensile test. Indeed, at a very high strain, the rubber PBSA nanofibrils stretch, expanding the yield zone and strain hardening occurs.

On the other hand, compared to neat PIC matrix, a dramatic increase in the tensile energy to break (TEB) was noticed in PIC/PBSA nanofibrillar films. Since the TEB represents the amount of energy per unit volume that the film can absorb before rupturing, the formation of PBSA nanofibrils in the PIC matrix seems to be in the origin of this increase in breaking energy. Thus, the tensile energy to break (TEB) of blends is more than nine times greater than that of pure PIC films. The increase of energy to break in the PIC/PBSA blends is largely due to the excellent ductilily and toughness of PBSA. The latter exhibits greatly interfacial interactions with the PIC matrix. Thus, the creation of ductile nanofibrils permits the effective transfer of external deformation under an applied stress as could be evidenced by SEM analyses.



*Figure 17: Tensile stress versus tensile strain of neat PIC, neat PBSA and PIC/PBSA blend films.* 

 Table 11. Tensile properties of the neat polymers and PC/PBSA blend films. Between

 parentheses are the standard deviations. TEB designates the Tensile Energy to break in

	PIC	PBSA	PIC/PBSA
σ <sub>max</sub> (MPa)	45.5 (1.9)	16.0 (1.4)	41.2 (4.2)
E (%)	15 (5.5)	550 (75.0)	115 (32.0)
E (MPa)	1375 (124.0)	213 (21.0)	1293 (89.0)
TEB (MJ.m <sup>-3</sup> )	5,4 (0,9)	107,4 (10,4)	51,9 (10,7)

MegaJoule per m3.

#### CONCLUSIONS

PIC/PBSA films with outstanding mechanical and rheological properties have been successfully prepared by the melt extrusion cast technology using the in-situ nanofibrillar polymer-polymer composites concept. The nanofibrillar morphology was successfully obtained by a careful control of the viscoelastic properties of the blend components.

1H-NMR results demonstrate the absence of the transesterification reaction between the two polyester components. DSC and WAXD analyses demonstrated the influence of nanoscale confinement of PBSA nanfibrils by the surrounding amorphous PIC chains on the overall crystallinity of PBSA. The rheological modeling using the Cole-Cole and VanGurp Palmen theories showed that the nanofibrillar morphology affects the relaxation behavior of the blends.

As evidenced by SEM analyses, the strong interfacial adhesion between the well-aligned semicrystalline PBSA nanofibrils and the amorphous PIC matrix as well as the resultant chain topology and fine morphology were found to be responsible for the improved melt strength, ductility and breaking energy of the blends. Thus, the rheological and morphological control methodology shown in this study should find uses in the design of novel polymer composites based films for packaging-related applications.

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