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New Reactive Formulations For Polypropylene Foams

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Abstract

This work focuses on reactive extrusion to design polypropylene chains with long and short branching to obtain a non-linear behaviour for the synthesis of low-density foams ($<100\text{kg/m}^3$) using batch scCO_2 foaming process. From a maleic anhydride grafted PP (PP-g-MA), the long-branched chains are performed using [MA]/ [OH] reaction (with Sorbitol alcohol). On the other hand, short branched chains are made from hydrolysis/condensation of amino-alkoxysilane (3-Aminopropyl-triethoxysilane, APTES) in situ grafted onto PP chains through the ([MA]/ NH_2) reaction). Both long and short branching are considered separately and then combine. Our results show the need to combine both systems to reach the optimum of the rheological behaviour to obtain a low-density foam. This also demonstrate that the rheological behaviour under linear and non-linear conditions is relevant to determine the best formulation in terms of critical impact on the foaming behaviour.

On the other hand, the foaming behaviour of PP/PA6 polymer blends at $T=180^\circ\text{C}$ was also investigated as another way to control the rheology and the foamy behaviour. At this temperature, $T=180^\circ\text{C}$, the PA6 phase behaves as solid dispersed particles in a viscoelastic liquid PP matrix. Finally, this study shows the influence of PA6 concentration on the foaming and foam morphology correlated to a rheological study (shear and extensional) and to the mechanical compressive properties.

Introduction

Polymer foams belong to the family of solid foams which are versatile materials widely used in a wide range of applications such as automotive, packaging, sports products, thermal and acoustic insulation, or tissue engineering. Polymer foams are then extremely used in our daily lives today. Among the large variety of polymer foams, polypropylene (PP) foams have been developed much more recently [1],[2]. Due to the melting temperature of PP ($T_m=165^{\circ}\text{C}$) these derivatives foams can be used in temperature conditions up to 120°C . Furthermore, from an environmental point of view, polyolefin foams have the advantage of being fully recyclable due to their thermoplastic nature compared with foams based on crosslinked network.

In terms of foaming, processes using CO_2 and more particularly supercritical CO_2 are under strong developments in academic labs with scale up to the industry. Many articles in the literature deal with the polymer chains structures that a polymer must have to control the cell growth. Branched structures of PP chains [3] are then recommended as they give strain hardening properties under melt elongation flow (high melt strength) that lead to the stabilization of growing cells and thus prevents cell coalescence [4]. As a result, different strategies have been developed for branching PP chains, the best known of which is the one starting from PP grafted with anhydride maleic (PP-g-MA). The PP-g-MA is then modified to obtain branching by reaction with amino-silane [5], amines [6],[7], or by ionic interactions [8]. In our last paper [9], we have shown that the branched structure of polymer chains can be designed from a rheological criterion based on the notion of fractal behavior (coupling of relaxation modes), which polymer chains must have for nonlinear behavior (strain hardening). This criterion has been defined by analogy with the sol-gel transition ($\tan \delta = 1$). While the linear criterion makes possible to specify the structure of the polymer chains, it cannot describe the non-linear behavior such as, for example, the maximum deformation that the polymer can undergo under elongation stress.

Furthermore, the cell morphology in terms of close or open structures is of importance regarding the foam properties. Inorganic fillers are generally added [10][11][12] in order to modify the foaming behaviour with the objective to control cell morphology from close cell to open cell. Another way of controlling the morphology is to control the crystallinity during the foaming process and the foaming temperature [13][14][15]. By controlling the crystallinity

and/or the foaming temperature, the viscosity and the rigidity of the polymer from close-cell to open-cell can be adjusted. The increase of crystallinity is directly linked to an increase of open-cell content, nevertheless, by modifying the temperature of foaming, the rheological behaviour is changed accordingly.

The objective of this work is to study the foaming, using a CO₂ batch process, of new branched PP formulations based on reactive modification of PP-g-MA. Compared with our previous work [9], we intend to focus this study on a non-linear criterion (strain at break under transient extensional experiment). For this, we use a reactive system for PP-g-MA branching based on a combination of diol and amino silane chains extenders. In addition, and still with the objective of controlling the final properties of the foam by controlling the morphology of the open/closed cells, a new formulation based on a compatible PP/PA6 mixture is developed. The PP phase is based on the branched system (PP-g-MA combined with a triamine) developed in our previous study [9]. The shear and extensional rheology, the blend morphology and finally the compressive properties of these new foams are investigated.

Materials

PP-g-MA: A commercial PP-g-MA from Exxon was used for this study, trade name PO1020. It contains 1.1wt% of anhydride maleic and has a molar mass $M_w=10^4$ g/mol. Its rheological behaviour is Newtonian, with a viscosity of 70 Pa.s at $T=180^\circ\text{C}$.

Chain extenders, branching of PP chains: In our previous work [9] we studied the foaming of PP branched structures from the chemical modification by reactive extrusion of PP-g-MA with a primary tri- amines (MA/ NH_2 reaction, triamine: Jeffamine T-403). In the present paper, the branching strategy of PP-g-MA is based on the use of multi-alcohols, amino-silane and a combination of both. As multi-alcohols, sorbitol provided from Aldrich was used. In terms of functionality this molecule is characterized by two primary alcohols and four secondary alcohols, the 3-Aminopropyl-triethoxysilane (APTES), frequently used in the functionalization of surfaces with alkoxy-silane, was selected. The reaction leading to the branching of the PP chains is expected from the hydrolysis condensation of the alkoxy-silane after grafting of this molecule on the PP chains by the reaction between the anhydride and the amine of APTES. The molar ratio ($[\text{NH}_2]/[\text{MA}]$ or $[\text{OH}]/[\text{MA}]$) of the different samples is reported in Table 1.

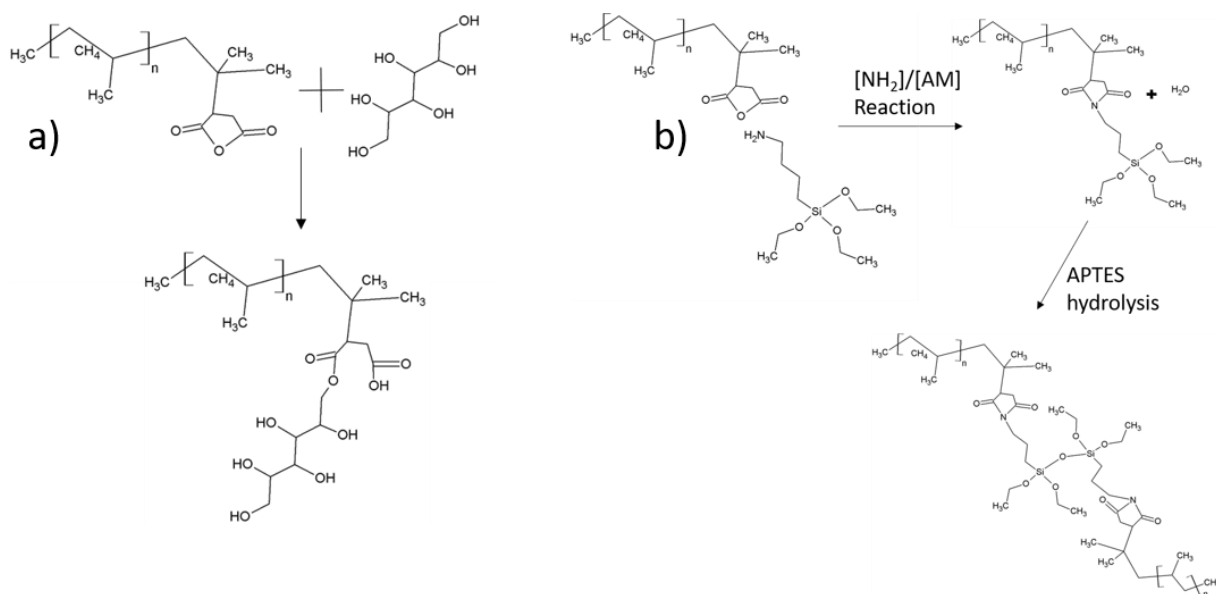


Fig 1: chemical reaction of a) PP-g-MA/Sorbitol and b) PP-g-MA/APTES

In order to study the impact of the PA6 dispersed phase on the foamability, the branched PP synthesized from the chemical modification of PP-g-MA with a triamine (T403 at the concentration of 4.4%wt) was used accordingly to our previous study ([9]). The PA 6 reference is Akulon f223d provided by DSM Engineering Materials.

Table 1: Formulations for the preparation of the branched PP samples from chemical modification of PP-g-MA. Molar ratio ($[\text{NH}_2]/[\text{MA}]$ or $[\text{OH}]/[\text{MA}]$)

Branching precursors	$[\text{NH}_2]/[\text{MA}]$ or $[\text{OH}]/[\text{MA}]$	Concentration (%wt)
Sorbitol	4.1	4
Sorbitol	6.3	6
Sorbitol	8.6	8
Amino-silane	0.53	1.2
Amino-silane	0.62	1.4
Amino-silane	0.73	1.65
Sorbitol/Amino-silane	6.31/0.26	6/0.61

Table2: Formulations for the preparation of PP/PA6 blend

Polypropylene (%wt)	PA6 (%wt)	Name of the blend
100	0	PA0
90	10	PA10
80	20	PA20
70	30	PA30

Reactive extrusion: Every branched system was prepared by reactive extrusion using a corotative twin-screw extruder (D=18mm) with a L/D=60 ratio and under the following processing conditions: mass flow rate: Q=3 Kg/h and screw rotational speed N= 300 rpm. The

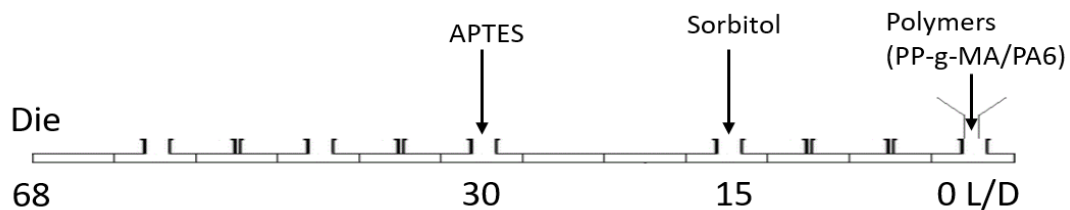


Fig 2 : scheme of the extruder zones (L/D) with the position of the feeding zones of Polymers and reactive agents

extruder temperature was fixed at 200 °C excepted for the first two feeding zones (50 °C and 110 °C). The extrudate is cooled using air and then pelletized. With the objective to favour the reaction $[OH]/[MA]$ firstly, the multi-alcohol is added at $L/D=17$ and the APTES is added at $L/D=32$ according to Fig 2. The PP/PA6 blend was processed using the same screw profile with a barrel temperature of 230°C to melt the PA6 crystalline phase.

Shear rheology: Rheological measurements were performed using a rotational rheometer G2 (TA-ARES instruments). The rheometer is used under dynamic oscillatory using a parallel-plate geometry (Diameter=25mm and gap= 1.5 mm). The strain applied is 5% (linear domain of the viscoelasticity). The frequency sweep test start at 100rad/s to 0.1 rad/s at the stabilized temperature of 180°C.

Elongational rheology: The samples for extensional rheology experiments were prepared using a plate press at $T=230^{\circ}\text{C}$ under 100 bars for 10 minutes then relaxed for 20 minutes. This protocol avoids any stress relaxation during the rheological experiments. Extensional rheological measurements were performed on G2 (TA-ARES instruments) at 180°C under constant strain rate.

Foaming: Batch CO₂

To perform the foaming of samples, a batch process was used with the use of Anton Parr system (reference: mini bench reactor 4567). Sample of 25 mm of diameter and a thickness of 2mm is saturated with CO₂ for 30 min at 180°C under the pressure of 150 MPa. Then, the rate of depressurization is about 1.5 MPa/s until the pressure reaches ambient pressure.

Density and cell diameter: The measurement of the foam density was made with a densimeter (Mettler Toledo ML-DNY-43). Then the foaming ratio is v_f which is the ratio of the density of the polymer unfoamed (ρ_0) by the density of the polymer foamed (ρ_f).

$$v_f = \frac{\rho_0}{\rho_f} \quad (1)$$

Measurement of the cell diameters was done by optical microscopy (magnitude of 40 and 100) observation after cutting sample with a high sharp blade (for those foam there was

not a need for cryofracture). Foam images were then digitally analysed to get the mean cell diameter.

Scanning Electronic Microscopy (SEM): The characterisation of the PA6 phase was realised using a S 400M microscope (Hirachi) after marking the PA6 nodule by letting Phosphotungstic acid dilute at 2% infuse after cryofracture for 24h.

Compressive properties: Compressive measurements were carried out with a Shimadzu AG X equipped with a sensor of 500N. For each formulation, five tests are performed on cylindrical foam samples (Diameter: 25mm, thickness 10mm). The compressive speed is set at 6mm/min.

Open/close cell characterisation: A sample is cut of the centre of the foam then weighed and subsequently put in water. After 10 minutes on water the sample is weighed again. We assume additional weight is only due to water inside the open cell. (eq 2)

$$\varphi_{\%open-cell} = \frac{m_{water} / \rho_{water}}{V_{total}} \quad (2)$$

Results and discussion

Extended chains from anhydride/alcohol reaction The anhydride/alcohol reaction is a well-known reaction used in the field of chemical modification of polymers ([16], [17]). However, it is much slower than the anhydride/amine reaction and most of the time leads to side reactions at processing temperatures ($T > 200^{\circ}\text{C}$). As expected, **Fig 3** shows that the anhydride/alcohol reaction leads to a strong modification of the rheological behaviour of PP-g-MA due to the coupling of the PP chains induced by this reaction. However, whatever the alcohol concentration, $\tan\delta$ is always greater than 1, thus describing an overall viscoelastic liquid behaviour of the branched PP. It is clear that this system cannot lead to a viscoelastic solid behaviour due to the low reactivity of the alcohols and their plasticizing effect of PP matrix. In this present case, we rather obtain an extended structure of the PP chain. However, for the concentration close to 6% alcohol, $1 \leq \tan\delta \leq 3$ in the studied frequency range, showing a viscoelastic behaviour close to the gel point and whose behaviour is therefore favourable according to this criterion to a controlled growth of the cells. Unfortunately, due to the low viscosity of these formulations, they could not be characterized in extensional rheology

because of sample sagging problems above the melting temperature. Finally, the foams obtained are not exploitable because their morphology is not homogeneous with a large cell size distribution.

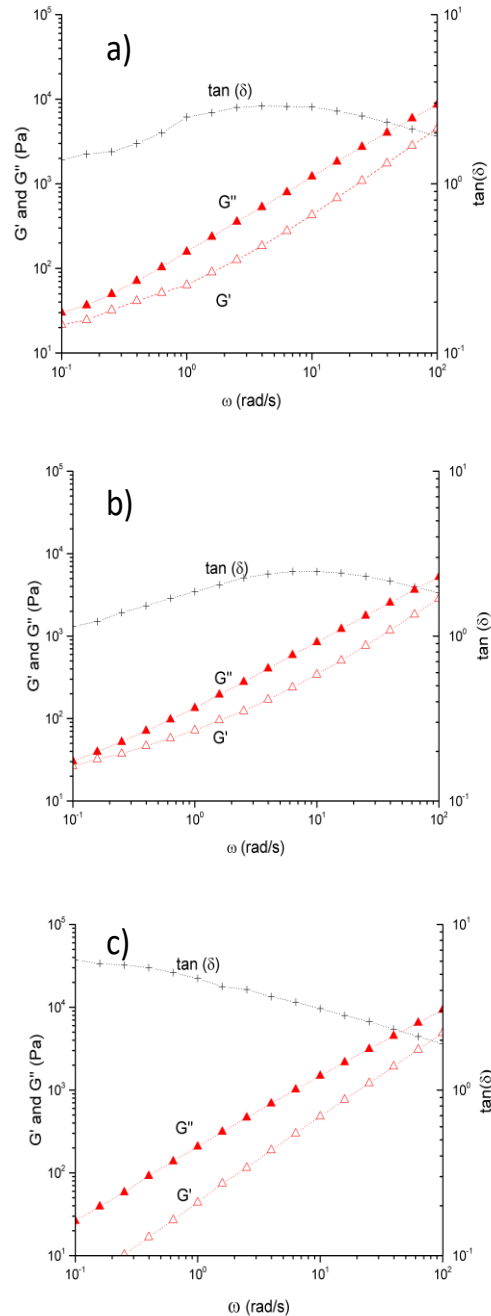


Fig 3: Branched PP from PP-g-MA/sorbitol systems. Variations of the complex shear modulus $G^*(\omega)$ and $\tan \delta (\omega)$ for three different sorbitol concentrations, **a)**: 4wt%, **b)**: 6wt% and **c)**: 8wt%. $T=180^\circ\text{C}$

Short chain branching from anhydride/aminosilane reaction. This system is probably more complex compared to anhydride/amine ([9]) system or anhydride/alcohol system. Indeed, it is first expected a grafting reaction of APTES on the PP chains via the anhydride/amine

reaction followed by the hydrolysis-condensation reactions of the alkoxysilanes which will lead to the PP branching (see Fig 1). The principle of this chain branching mechanism was reported and discussed in our previous paper ([18]). We have shown that hydrolysis-condensation can take place in the extruder due to high process temperatures. In fact, the water generated by imide formation may promote the hydrolysis of the alkoxysilane and thus condensation reactions of the silanol created leading to the formation of siloxane bonds. Finally, branched structure of the polymer chains can be observed from a rheological behaviour point of view.

Actually, **Fig 4** shows the variations of the complex shear modulus and $\tan\delta$ versus frequency for 3 APTES concentrations. The closest concentration of APTES to the criterion $\tan\delta\approx 1$ is 1.4% ($[\text{NH}_2]/[\text{MA}]=0.62$) for which the variation of $\tan\delta$ depends on the frequency in the range $0.8 < \tan\delta < 2$. Furthermore, the variation of the extensional viscosity versus the Hencky deformation is shown in **Fig 5**. It is observed that the strain and the viscosity at break do not exceed 1 and 10^6 Pa.s respectively. This viscoelastic behaviour is less favourable for the stability of growing cells and consequently foams with a less well-defined morphology are expected.

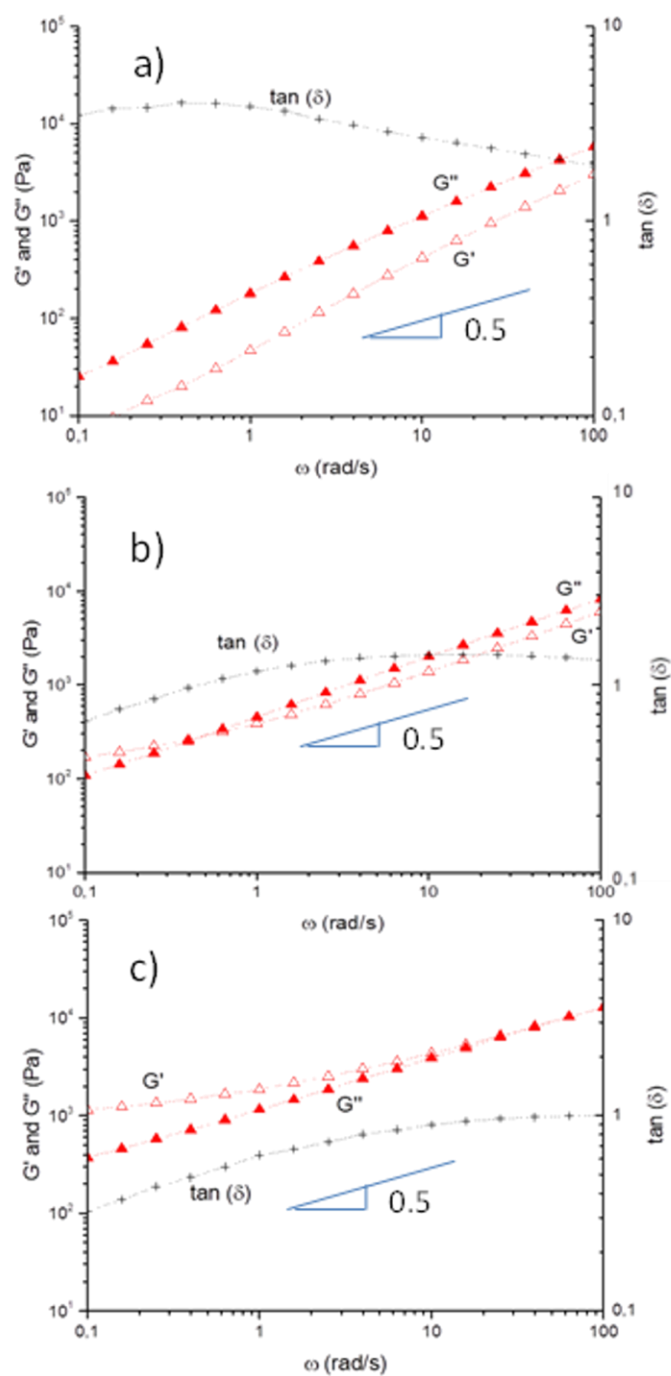


Fig 4: Branched PP from PP-g-MA/APTES systems. Variations of the complex shear modulus $G^*(\omega)$ and $\tan\delta(\omega)$ for three APTES concentrations, **a):** 1wt%, **b):** 1.4wt% and **c):** 1.65wt%. $T=180^\circ\text{C}$.

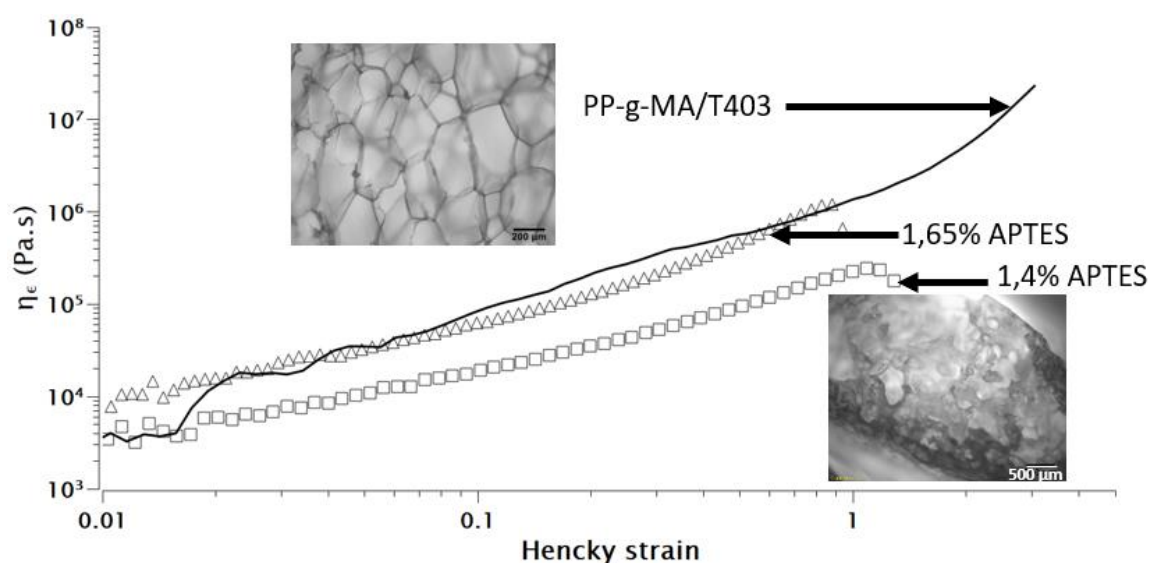


Fig 5: Variation of the extensional viscosity $\eta_E^+(t)$ for two APTES concentrations, 1.40 and 1.65 wt%. $T=180^\circ\text{C}$, extensional rate: 0.01 s^{-1} . The solid curve corresponds to the formulation PP-g-MA/Triamine developed in our previous work [9]

Indeed, the foams obtained show a coarse morphology as shown in **Fig 5** with a density 300 Kg/m^3 . As a result, PP branched structures from APTES chain modification is not a relevant strategy to obtain foam of low density. Furthermore, there is an extreme sensitivity of the aminosilane-based system to the concentration of APTES. In fact, from a technological point of view, it is difficult to control such small variations in concentration. Furthermore, this chemistry leads to short and dense branched structure. On the other hand, we have seen that the sorbitol-based system does not lead to the right rheological criterion because only the primary OH react and their reactivity is less than that of the amines. The idea is then to combine these two PP chains branching chemistries in order to modify their rheological behaviour and to tend towards the criterion of $\tan \delta \approx 1$. For this, we report the results obtained for a concentration of 6% sorbitol and 0.6% amino silane. Compared to the result of the PP-g-MA/sorbitol system **Fig 3**, the addition of 0.6% APTES makes it possible to decrease the overall $\tan \delta$ values and bring them closer to our $\tan \delta \approx 1$ criterion as shown in **Fig 6a**. Furthermore, the extensional behavior **Fig 6b**, compared with that of the aminosilane formulation, also shows a much more pronounced strain hardening behavior reaching higher stresses and Hencky deformations. Furthermore, it must be pointed out that these critical values at break cannot be reached due to the limitation of our experimental setup.

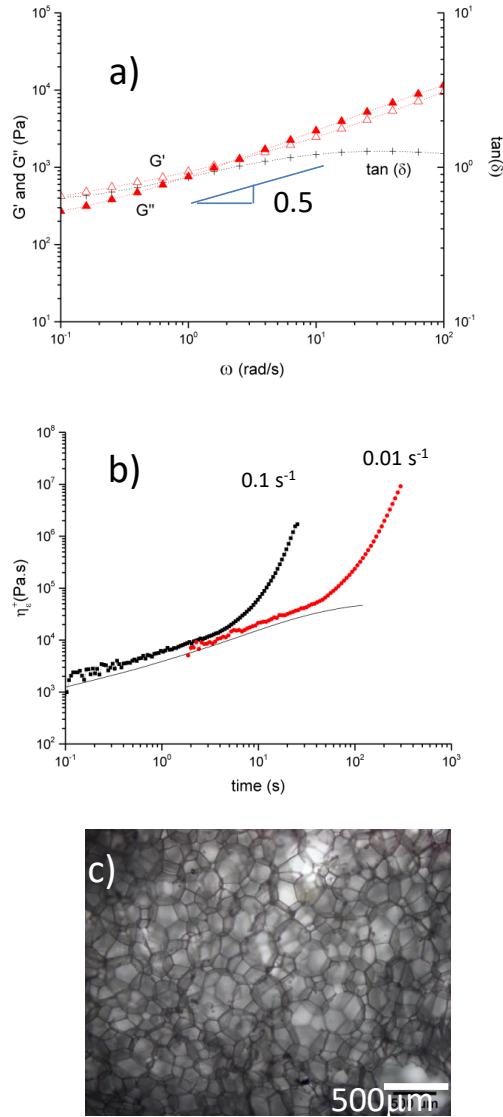


Fig 6 : PP-g-MA/(6% sorbitol+0.6% APTES): **a)** Variation of $G^*(\omega)$ and $\tan\delta(\omega)$, **b)** Extensional viscosity $\eta_{E^+}(t)$ and **c)** Foam morphology. $T=180^\circ\text{C}$

To clarify this non-linear criterion, the PP-g-MA/Sorbitol/Aminosilane extensional viscosity is compared in Fig 7 with polymer from our previous work [9] which has a great ability to foam. Actually, these formulations are characterized at the end of the experiment by a viscosity greater than 10^7 Pa.s and a Hencky strain at break greater than 3. Finally, this non-linear criterion ($\varepsilon_b > 3$) is relevant to predict foamability for obtaining foams with extremely low density ($\rho \sim 20 \text{ kg m}^{-3}$ for the present system).

However, in terms of formulations, these results also show that the structure of the polymer chains can be adjusted from a judicious balance between chain extensions and short branched structures as schemed in **Fig 8**. Indeed, the formulation PP-g-MA / (6% sorbitol+0.6% aminosilane) gives remarkable results according to the linear criterion ($\tan \delta = 1$) and the non-linear criterion (Hencky strain > 3) and therefore in terms of foam morphology and density.

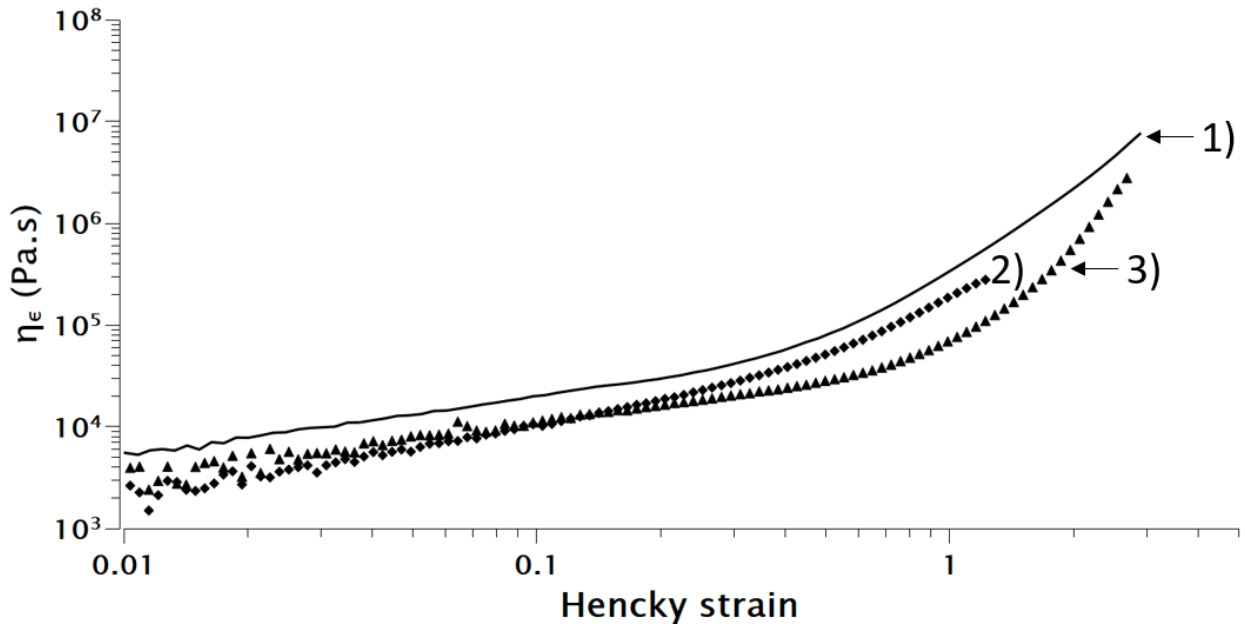


Fig 7 : Variation of the extensional viscosity versus the Hencky strain for the different PP formulations. **1):** Triamine (solid line, from our previous work [9]), **2):** Amino-silane, **3):** Sorbitol/amino-silane. Extensional rate: 0.1 s^{-1} .

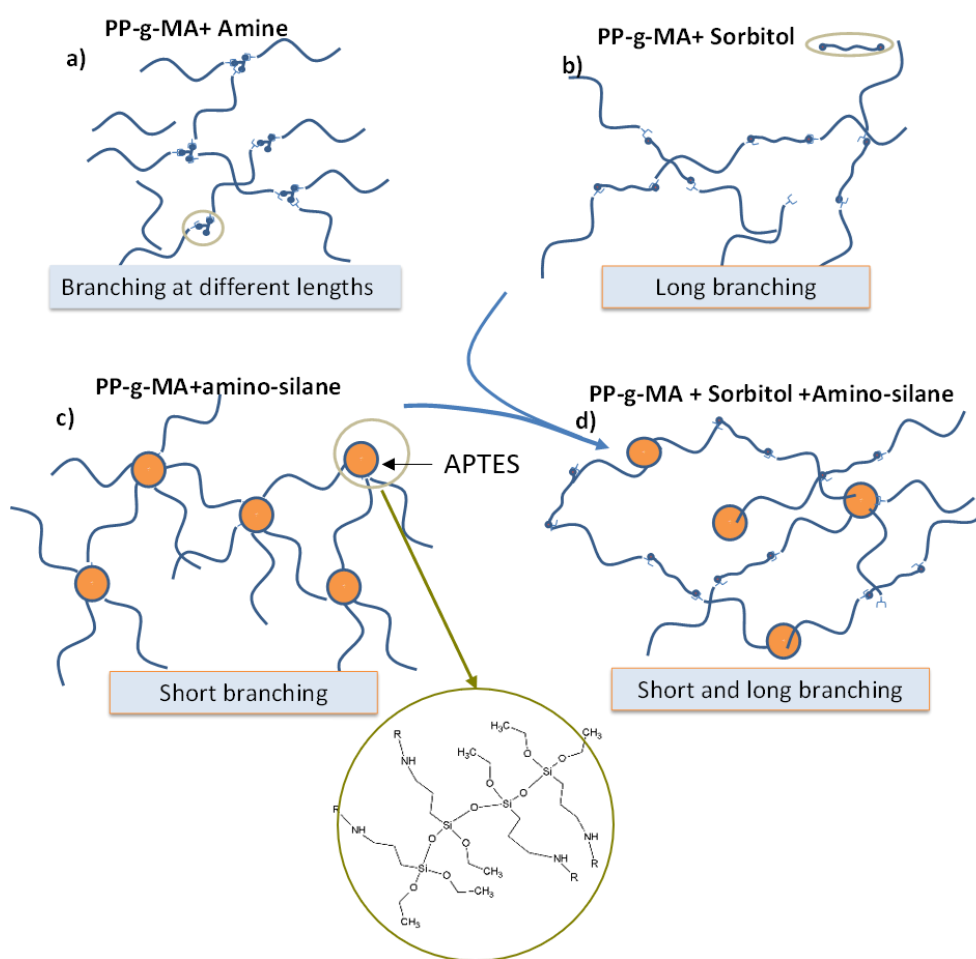


Fig 8: Scheme of PP-g-MA chains branching imagined from viscoelastic experiments. **a)** Chain branching at different lengths from imide formation **b)** Long chain branching from sorbitol (primary alcohols), **c)** short chain branching via the reaction of anhydride with amine of 3-aminopropyltriethoxysilane followed by hydrolysis condensation, **d)** Short and long chain branching by combination of reactions used in b) and c).

Foams from PP/PA6 blend

This part is focused on the foaming of PP/PA6 blends. We used the branched PP developed in our previous work [9] through anhydride/amine reaction. From a chemistry point of view, the compatibilization of this blend is expected from the imide formation though the reaction between the anhydride maleic and the terminal primary amine of the PA6 [19,20]. First, the linear viscoelastic behaviour of these blends at different PA6 concentrations has been studied at the temperature $T=180^{\circ}\text{C}$ as shown in **Fig 9**. It must be pointed out that, at this temperature, the PA6 phase is in solid state and consequently behaves as a filler (solid particles). As expected, a reinforcement of the PP phase is observed from the variation of the storage modulus ($\tan \delta < 1$). However, we are still close to the rheological criterion ($\tan \delta \approx 1$), which suggests that these samples could present a good foamability.

Moreover, the morphology of the blends is shown in **Fig 10**. It can be observed that the PA6 phase is composed of nodules of submicronic size which increases with its concentration (radius of 60nm for 10% PA6 to 330nm for 30% PA6).

The extensional viscosity curves (**Fig 11**) at 0.1s^{-1} and 1s^{-1} strain rate for low concentration of PA6 (10% of PA6) show strain hardening behaviour like the branched system PP/amine ([9]) or the PP-g-MA/Sorbitol/APTES (present study, **Fig 6**). However, at high concentrations (20% to 30%), a strain softening behaviour appears with a strong decrease of the Hencky strain at break ($\varepsilon_b=0.6$ compared to 3 without PA6). This softening behaviour has been already described in the case of polymer blends, named organic composites ([21]). This behaviour is due to the inhomogeneous elongation flow near the solid phase.

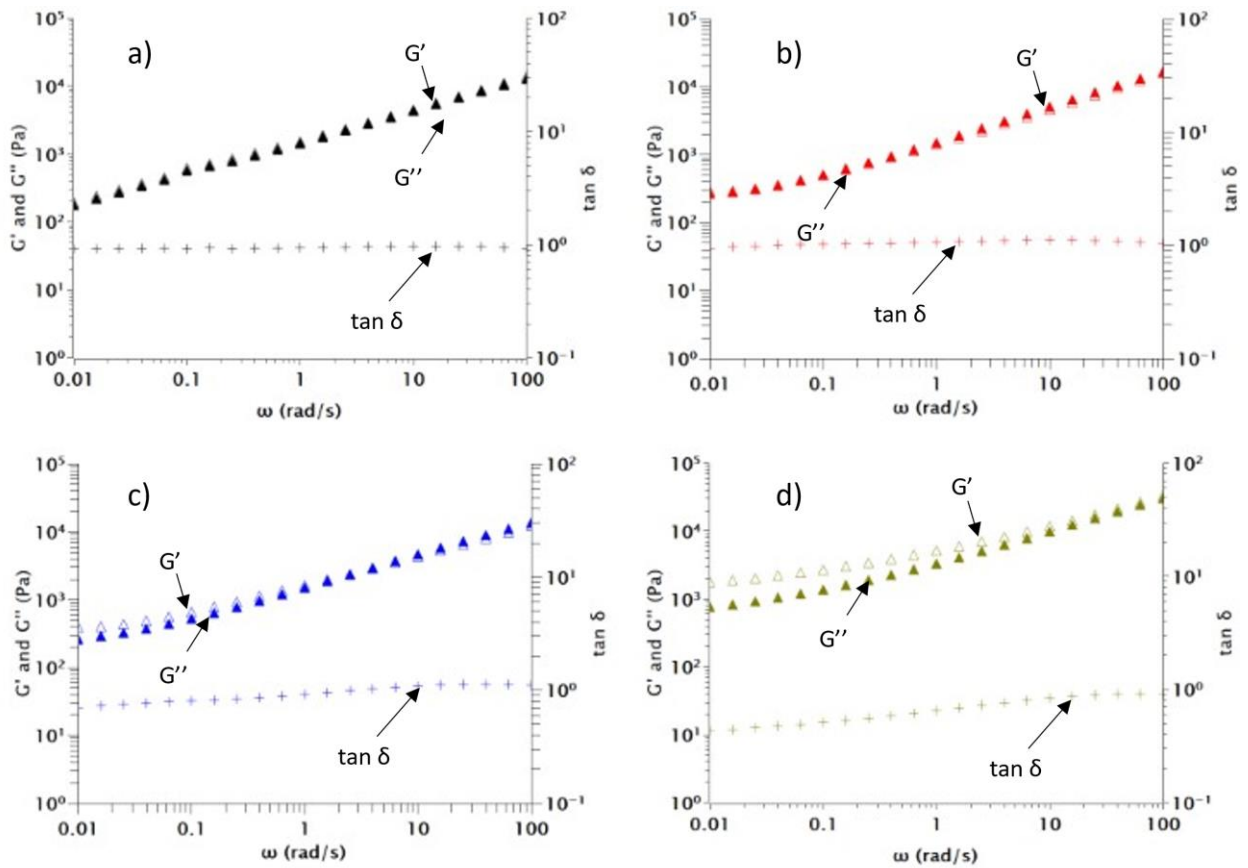


Fig 9 : PP/PA6 blends, variation of the complex shear modulus and $\tan \delta$ for 4 concentrations of PA6 **a)** 0%; **b)** 10%; **c)** 20% and **d)** 30%, $T=180^\circ\text{C}$

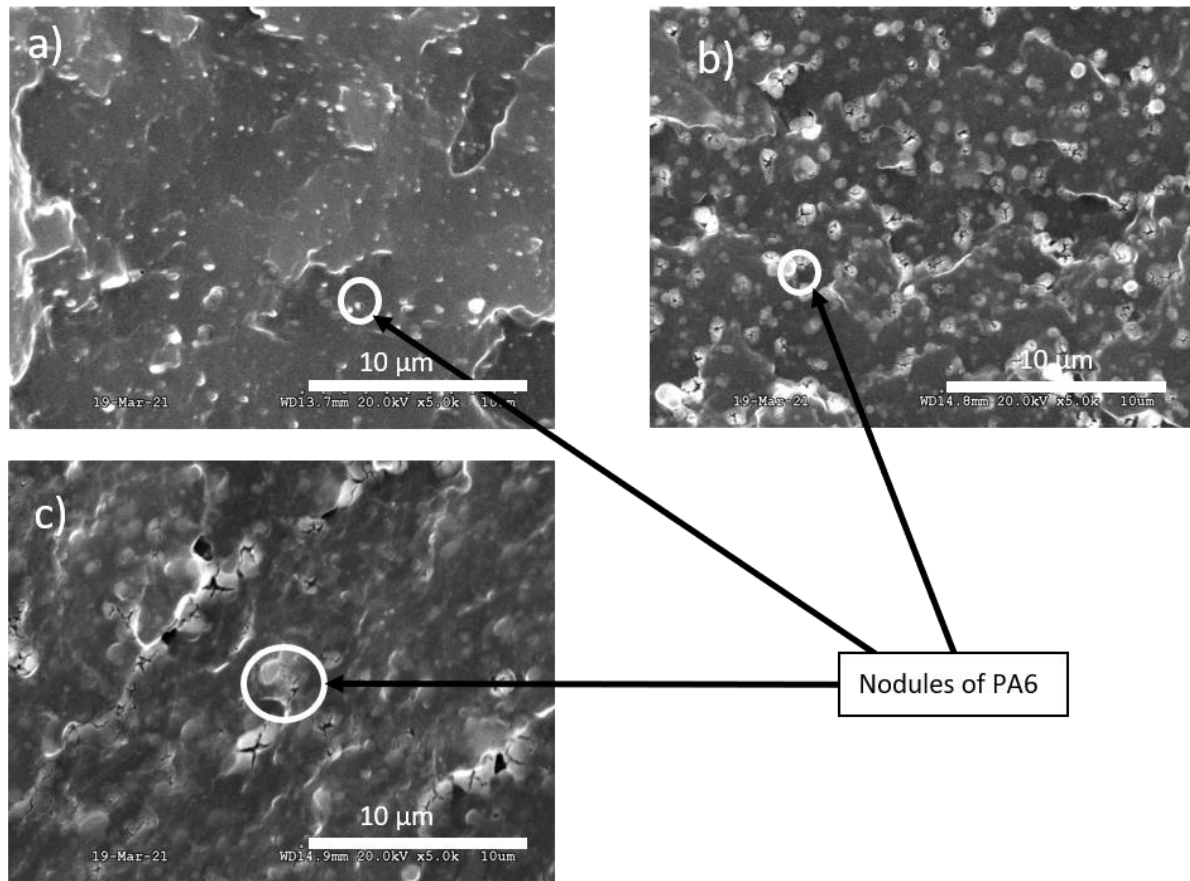


Fig 10: SEM observation after cryofracture of PP-g-MA/PA6 samples **a)**: 10%, **b)**: 20%, **c)**: 30%,

So, the addition of PA6 leads to a divergence from the criteria developed on our previous work([9]) also the addition of PA6 implies a transition from strain hardening to strain softening which reduces the foamability of the blend (apparition of coalescence) for high content of PA6 (30%) and so heterogeneity of the resulted foam. Although the foams appear to be identical in morphology regardless of PA6 concentration (**Fig 12**), increasing the PA6 concentration tends to reduce the fraction of closed cells as well as the average cell radius. This means that by increasing the amount of PA6 we can control the type of cells (open or closed), their sizes and ultimately the density of the foam.

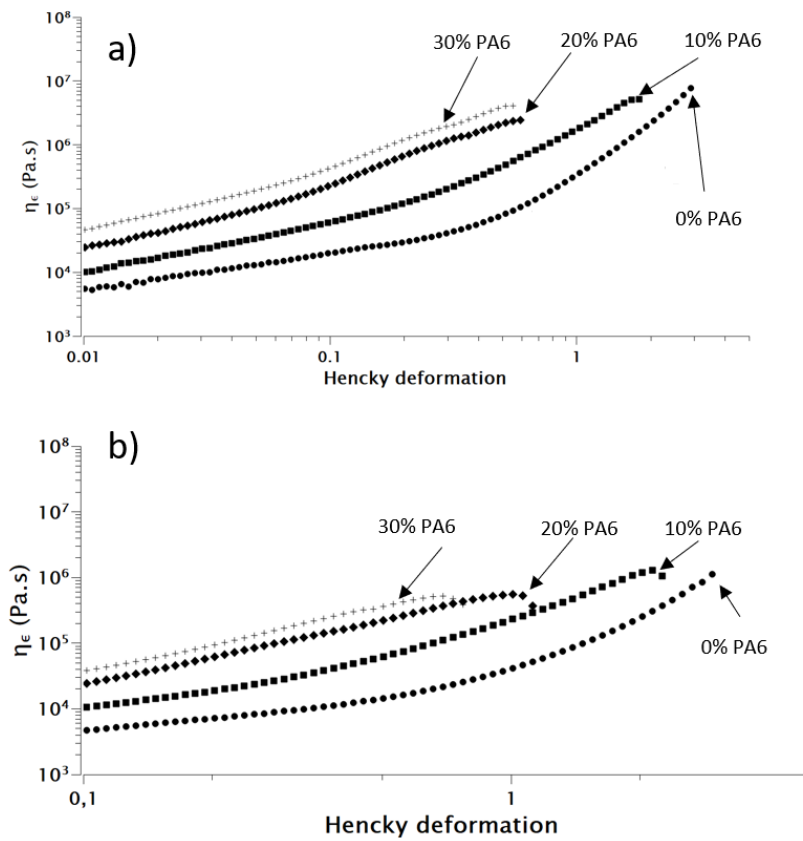


Fig 11: Variation of the extensional viscosity versus Hencky strain at various content of PA6 for 2 strain rates, **a)** 0.1 s^{-1} and **b)** 1 s^{-1} .

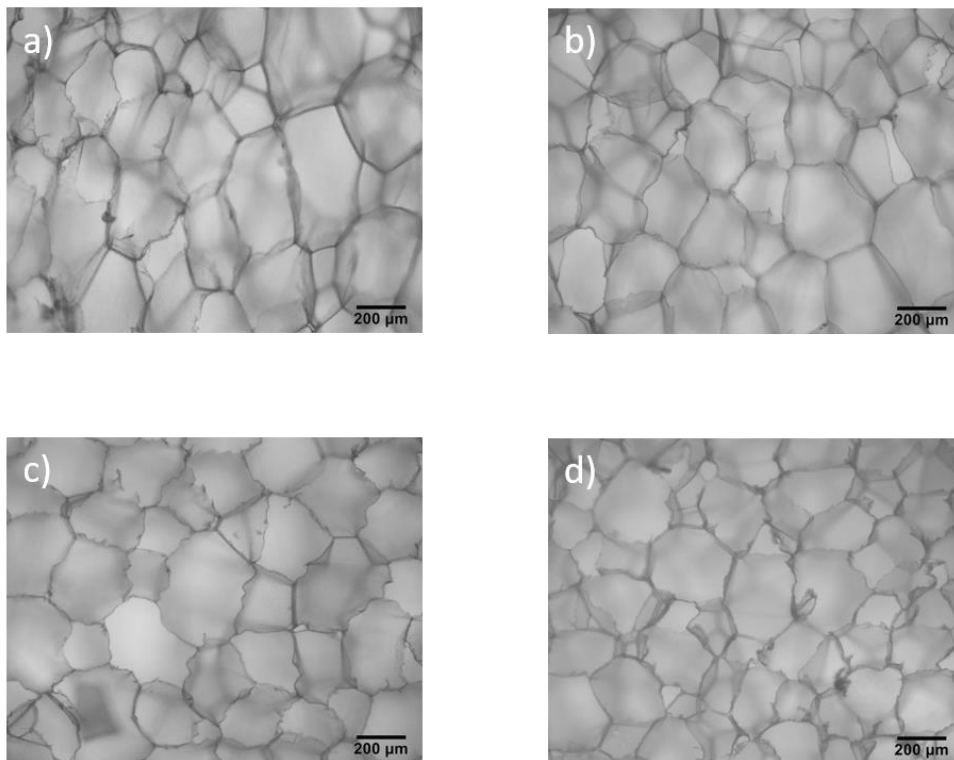


Fig 12: Foam morphology for 4 different content of PA 6, **a)** 0% ; **b)** 10% ; **c)** 20% and **d)** 30%). Foaming conditions $T=180^\circ\text{C}$ and $P=150 \text{ bars}$

This implies that the addition of PA6 can be used to control the cell type (from closed to open) but with an increase in density. Moreover, the increase of open-cell fraction demonstrates the importance of the maximal Hencky strain at break to achieve a closed cell foam. So the importance of adding a non-linear criteria to our previous foaming criteria ([9]) to predict the foamability (defined as a close cell foam) was necessary as proved in the present work.

The impact of the PA6 concentration (from 0% to 30%) on the mechanical compressive property has been investigated. To compare theses foams, the specific compressive stress ($\sigma_{\text{specific}} = \sigma/\rho$) is more relevant from a discussion point of view. The compressive resistance of the foam decreases drastically with increasing the PA6 concentration as shown in **Fig 14**. This behaviour can be explained by a difference of foam structure which changes with the PA6 concentration (from closed-cell to open-cell morphology). The apparition of open-cell morphology is more likely to happen due to the reduction of the foamability induced by the reduction of the maximal Hencky strain (**Fig 11**).

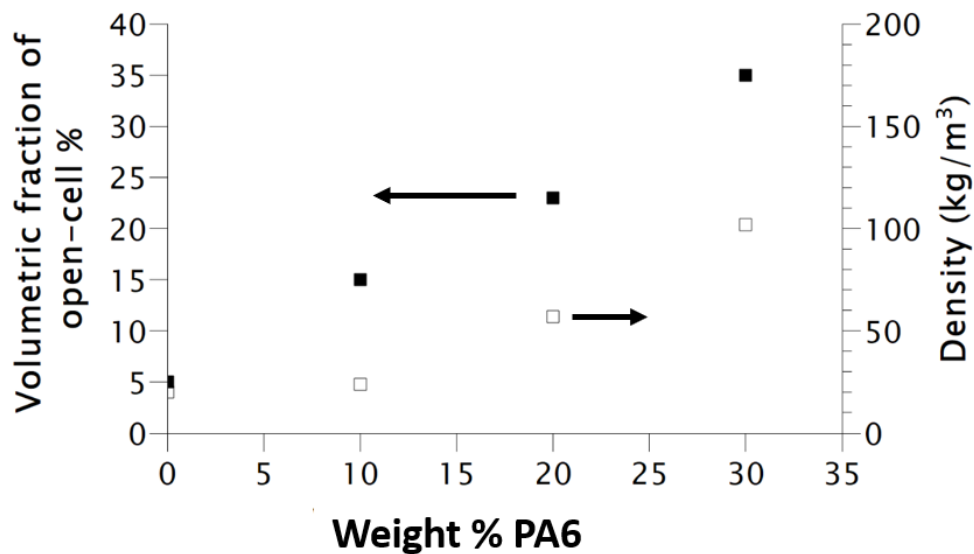


Fig 13: Variation of the volume fraction of open-cell (close symbol) and density (open symbol) versus the weight fraction of PA6

The influence of PA6 on mechanical properties of the un-foamed material has been studied by others [22][23][24]. These studies showed an improving of mechanical properties as the content of PA6 increases. Yet the addition of PA6 increases the tensile properties of PP/PA6 blend even for low content of PA6. [22] [24]. In our case the improvement of the intrinsic mechanical properties of PP/PA6 blend at low content of PA6 described in the literature (using a PP-g-MA as a compatibilizer) does not lead to any reinforcement of the foam. Indeed Ru et

al [25] has shown the importance of close cell on compressive strength, an increase from 6% to 15% of open cell content induces a strong decrease of 2 time of the stress at 50% strain. This explains the diminution of the compressive mechanical properties even though the blend of polymer has better mechanical property. In other words, regarding the mechanical properties, this result means that the morphology (open/closed structure) of the foam is the first order parameter compared with the intrinsic mechanical properties of the dense material.

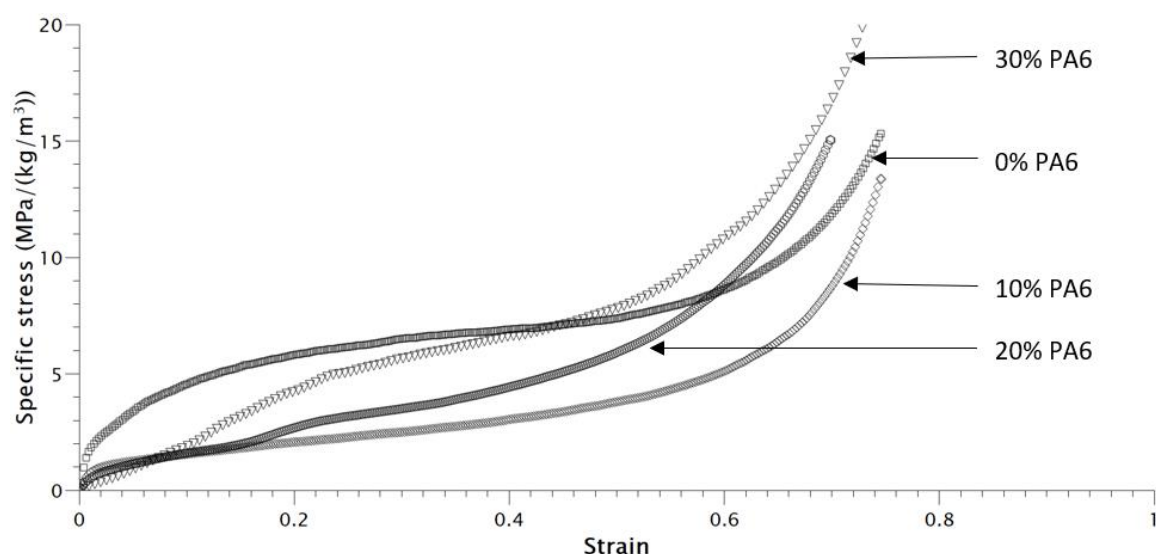


Fig 14 : Stress/strain curve for compressive test for different concentrations of PA6, at room temperature

Conclusion

To carry out this study, two reagent systems were selected, based on chemical reactions with maleic anhydride: MA/OH (Sorbitol) and MA/NH₂-(OR)₃ followed by a hydrolysis condensation reaction (aminosilane, APTES). Regarding the second system, the aminosilane molecule is grafted by the MA/NH₂ reaction onto PP chains subsequently followed by the hydrolysis-condensation of the alkoxysilanes. These systems have shown that it is possible to obtain branched PP structures that are favourable for foaming under CO₂ conditions. Based on our previous work [9] and our present results on chemically modified PP chains, we have demonstrated that there are two relevant rheological criteria defining the adequate branched structure. The first one criterion, from linear viscoelasticity, defines the sol-gel transition of

cross-linking systems, i.e $\tan \delta = Cte = 1$. According to the present work, we propose a second criterion based on the variation of the extensional viscosity versus the Hencky strain. Actually, to obtain foam of very low density with close cell morphology, the intercellular film must be stable at high Hencky strain. From our observations, the Hencky strain at break must be higher than 3. So, this branched PP chains allowed us to prepare low density foam ($\rho \sim 20 \text{ kg m}^{-3}$) with a close cell morphology.

In addition, we developed a compatibilized blend based on a PA6 phase finely dispersed phase in a PP branched matrix (PP-g-MA/triamine) in order to control the final properties of the foams. The rheological and foaming experiments were performed at $T = 180^\circ\text{C}$, i.e below the melting temperature of the PA6 phase so that the PA domains behave as solid fillers. With the increase of the concentration of solid PA6 phase, a strong modification of the rheological behavior was observed as shown by the appearance of a plateau of the storage modulus at low frequencies and a strain softening behavior under non-linear conditions (extensional viscosity).

Finally, the addition of PA6 is a way to control the final density and the porosity, from a closed-cell structure at low content of PA6 to an open-cell structure for high content of PA6.

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