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Switching from brittle to ductile isotactic polypropylene-g-maleic anhydride by crosslinking with capped-end polyether diamine

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ABSTRACT:

Ductile functionalized polypropylene is of great interest in multi-layer composites development. A capped-end triblock polyether diamine (H₂N-PO₂-TMO₉-PO₃-NH₂) was used as a linker of two different maleated isotactic polypropylenes (iPP-g-MAH, at 1 and 3 wt%) by twin-screw reactive extrusion. The molecular architecture, the semi-crystalline microstructure and the mechanical properties of the resulting polymers were analysed as a function of the molar ratio of NH₂:MAH (0:1, 0.33:1, 0.5:1, 0.66:1, 1:1, 1.5:1, 2:1). At the molecular scale, the chemically modified polymers were characterized by FTIR and by the determination of gel content following the ASTM D2765-84 standard method. Differential Scanning Calorimetry, Wide Angle X-rays Scattering and Self Successive Auto-nucleation techniques showed the impact of the crosslinking: a decrease of the melting temperature as compared with the unmodified iPP-g-MAH polymer, as well as a decrease of the crystallinity ratio for the iPP-g-MAH at 3 wt% of MAH. Interestingly, Dynamic Mechanical Analysis and video-controlled uniaxial tensile tests showed that the polymers obtained in stoichiometric NH₂:MAH molar ratio exhibit the best mechanical properties enlightened by a switch from brittle to ductile mechanical behaviour with few differences between the two iPP-g-MAH.

KEYWORDS: *isotactic polypropylene grafted maleic anhydride, polyether diamine, crosslinking, microstructure, molecular architecture, mechanical properties.*

1. Introduction

Environmental impact became nowadays of paramount importance to material production, in both fundamental research and industry. For example, transport accounts for 25% of global CO₂ emission, which has a direct influence on climate change. Reducing fuel consumption and thus CO₂ emission in transport could be gathered by engineering efficient combustion engines and/or by lighter transporters structures. Composite materials, such as multi-layered steel/polymer composites, appear as good candidates for lighter structures. Among polymers, isotactic polypropylene-maleic anhydride (iPP-g-MAH) combines properties of iPP, such as low cost, low density and easy processing ability with the ones of anhydride moiety that ensures a good compatibility with the metal surfaces.

The grafting of MAH onto iPP, firstly reported by Minoura *et al.*, can be carried out in the melting state [1-5], but also in solid state or in solution [6-10]. The grafting undergoes undesirable side reactions, like chain scission, that modifies the average molecular weight of the material [1-11]. For instance, Shi *et al.* reported a reduction of about 76% of the weight-average \overline{M}_w of an iPP-g-MAH made by reactive extrusion (with 0.78 wt% of MAH) [11]. This is the major drawback of this reaction, since it affects the final mechanical properties of the polymer characterized by a brittle

46 fracture. As a result, it becomes inefficient in shock absorption due to the absence of
47 plasticity and in particular volume damage. The MAH grafts also affect the
48 microstructure of the material. Seo *et al.* and Harper *et al.* reported a good miscibility
49 between the graft and the unmodified polymer chains, as well as a decrease of the
50 melting temperature range with the MAH weight fraction inside the material [12, 13].

51 To improve the mechanical properties, we proposed in this work to increase the
52 crosslinking within the polymer, by using a polyether diamine. As a matter of fact,
53 different crosslinking methods have been developed in the last ten years. For example,
54 Kubo *et al.* used hydrogen donating hydrocarbons stabilizer to prevent β -scission
55 degradation during the irradiation with an electron beam [14]. Other authors used
56 polyfunctional monomers as crosslinking agent [15], or dicumyl peroxide molecules as
57 a chemical initiator, to trigger a crosslinking reaction with a
58 peroxide/sulphur/accelerator system [16-19]. Those different crosslinking reactions
59 show an important impact on the microstructure [14-19]. A decrease of the crystallinity
60 ratio and the crystal sizes could be observed. This evolution was correlated with an
61 increase of the viscosity due to the loss of the polymer chain mobility.

62 The crosslinking reaction proposed in this work (Scheme 1) is based on the
63 reaction between maleic anhydride (MAH) and amino groups (NH_2) [20, 21]. This
64 kind of reaction, implying NH_2 in excess, has already been used and it lead to a chain
65 extension of iPP-g-MAH [22-24], and thus to new reactive sites (e.g. amino groups) in
66 the polymeric material [25, 26]. The reaction and those new functionalities could be
67 used as a coupling agent for copolymers like PP/PE [27] or PP/PA6 [28]. It could also
68 allow an enhanced dispersion of nano-fillers inside polymers [29, 30]. The wide
69 variety of the reaction applications make it particularly suitable for composites
70 production, and provide new properties to iPP. An interesting result, obtained by Lu *et*
71 *al.* [26], was the evolution of the mechanical properties of an iPP-g-MAH
72 functionalized with a large excess of diamine. Their material, an iPP-g-MAH with
73 0.55wt% of MAH grafts, was functionalized with small diamine molecules at a
74 NH_2 :MAH molar ratio of 3:1. It was observed that a significant raise of strain and
75 stress at break occurred. However, in the particular case of diamine excess, the reaction
76 only induced a polymer chain extension without creating a three-dimensional
77 macromolecular network. In this work, the evolution of the microstructure and the
78 mechanical properties of iPP-g-MAH with respectively 1 wt% and 3 wt% of MAH,
79 functionalized with a polyether diamine for different NH_2 :MAH molar ratios were
80 investigated. The objective was to determine the optimal formulation (weight fraction
81 of MAH and NH_2 :MAH molar ratio) having the best mechanical properties. Molar
82 ratios below and above equimolarity (from 0.33:1 to 2:1) were tested. The impact of
83 the reaction on the molecular architecture was characterized by FTIR and the gel
84 content standard method. The modifications of the semi-crystalline microstructure
85 were investigated by the self-successive auto-nucleation technique (SSA) and X-ray
86 scattering. The close relationship with the true mechanical behaviour was highlighted
87 by VidéoTraction™ system, after taking into account or not the volume strain.

88 2. Materials preparation

89 2.1 Materials

90 Two different maleated isotactic polypropylenes were studied in this work. The first
91 one is an isotactic polypropylene grafted with 1 wt% of maleic anhydride (noted CA
92 100). The polymer is supplied by Arkema under the commercial name Orevac®

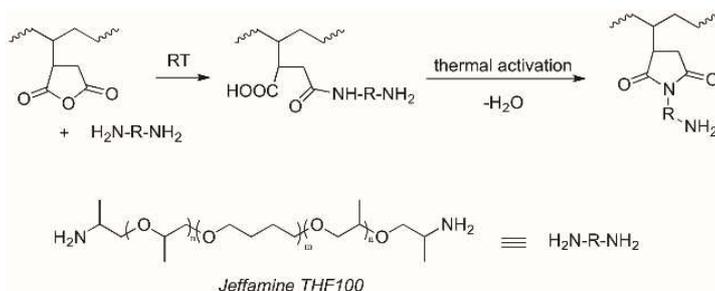
93 CA100. According to the technical specification sheet provided by Arkema [29], the
 94 yield strength is 22 MPa, and the engineering elongation at break is 12%. Its average
 95 molecular weight is estimated at $\overline{M}_n = 25\,000\text{ g}\cdot\text{mol}^{-1}$ [30, 31]. Prior to our experiments,
 96 conventional experiments have been done to determine the nature of the crystalline
 97 phase and the crystallinity ratio of CA 100. The main melting temperature, after the
 98 thermomechanical history erasing, was measured at 162°C by differential scanning
 99 calorimetry (DSC) at 10°C/min. This temperature is consistent with the melting of α -
 100 phase crystals, which were also revealed by wide angles X-rays scattering analysis
 101 (WAXS). The crystallinity ratio was determined by DSC and WAXS measurements
 102 and was of $55 \pm 3\%$ and $62 \pm 3\%$ respectively.

103 The second polymer used in this work is also an isotactic polypropylene grafted by
 104 maleic anhydride units, but in a larger amount of 3 wt%. It was supplied by Eastman™
 105 under the commercial name Eastman™ G-3015 (noted G 3015). The technical
 106 specification sheet informed us about the average molecular weights that are $\overline{M}_n =$
 107 $24\,000\text{ g}\cdot\text{mol}^{-1}$ and $\overline{M}_w = 47\,000\text{ g}\cdot\text{mol}^{-1}$ [32-34]. No more information about the
 108 mechanical properties is given. As for the CA 100, the melting temperature of 162°C
 109 revealed by DSC and the WAXS measurements confirmed the presence of crystals in
 110 the α -phase. The crystallinity ratio of G 3015 was estimated to be around $55 \pm 3\%$ by
 111 DSC and $61 \pm 3\%$ by WAXS. The MAH weight fractions of the two starting polymers
 112 were precisely determined by elemental analysis to be of 1.16 wt% for the CA 100 and
 113 of 2.9 wt% for the G 3015, respectively (see Table S1 in SI).

114 The crosslinking agent used in this work is a capped-end triblock polyether diamine
 115 ($\text{H}_2\text{N-PO}_2\text{-TMO}_9\text{-PO}_3\text{-NH}_2$), commercialized as Jeffamine® THF 100 by Huntsman
 116 [7] and used as received. Jeffamine® THF 100 (noted THF100) is a capped-end
 117 diamine copolymer of poly(tetramethylene ether glycol) (PTMEG) and polypropylene
 118 glycol (PPG), with a molecular weight of $1000\text{ g}\cdot\text{mol}^{-1}$. THF100 is liquid at room
 119 temperature and atmospheric pressure. The Jeffamine® was mostly chosen because the
 120 reactivity of aliphatic primary amines on maleic anhydride group is higher compared to
 121 aromatic amines [27]. Moreover, the high molecular weight of polyether diamine with
 122 a melting point at 9°C and a flash point at 238°C prevents any evaporation or
 123 degradation of the crosslinker during the reactive extrusion process.

124 2.2 Materials Preparation

125 The reaction between the MAH and the diamine, shown on Scheme 1, is divided in two
 126 steps. First, one amino group reacts with the anhydride, which leads to an amide and a
 127 carboxylic acid. This reaction takes place at room temperature. The second step, the
 128 cyclization one, is much slower and undergoes at the melting temperatures of the iPP-
 129 g-MAH [25-27].



130
 131 **Scheme 1.** Reaction pathway affording to the crosslinking between THF-100 and iPP-g-MAH through
 132 either amide or imide bonds.

133 The chemical reaction process was run either at the CINI Company or at the LRGP
 134 laboratory (CNRS - University of Lorraine, Nancy, France), using a 10 mm barrel
 135 extruder (Twinscrew Benchtop Compounding Line developed by Rondol Technology
 136 Ltd). Its L:D ratio is 40:1. Seven different intermediate temperature areas (Table 1)
 137 composed the extruder barrel between the pellet feed hopper and the rod shaped outlet
 138 die. The rotation speed was fixed at a specific value of 20 rpm in order to maintain a
 139 reaction time between 5 and 7 min (reaction time inside the extruder barrel after adding
 140 the THF 100), depending on the NH₂:MAH molar ratio and the material viscosity.

141 **Table 1.** Temperature profile of the extruder barrel

Extruder area	Input	Temperature Areas							Die plat
		1	2	3	4	5	6	7	
Temperature (°C)	150	170	190	190	190	190	180	170	170

142 iPP-g-MAH was introduced with a mass flow of 0.6 g·min⁻¹ for the CA 100 and 1
 143 g·min⁻¹ for the G 3015. The diamine was added in the area 3 of the extruder barrel (at
 144 190°C), and the mass flow rate was adapted to rich the targeted molar ratios
 145 NH₂:MAH (ranging from 0:1 to 2:1). The crosslinked iPP-g-MAH materials were
 146 shaped into 3 mm plates by injection moulding using a Micro 12cc Injection Moulding
 147 Machine commercialized by DSM Xplore. The material pellets were molten at 200°C
 148 and injected at 100°C under 10 bars. 2D WAXS patterns analysis confirmed the
 149 isotropic distribution of the macromolecular chains in the plane of the injected plates.
 150 Surface irregularities and microstructural heterogeneities (skin-core structure gradient)
 151 were removed by polishing the samples.

152 **3. Experimental set up**

153 **3.1. Gel Content measurements**

154 The gel content of the two iPP-g-MAH and the functionalized materials were
 155 determined following the ASTM D2765-84 standard method. The test was carried out
 156 with boiling xylene as an extraction solvent inside a copper pouch. The measurements
 157 were performed in triplicate.

158 **3.2. Fourier Transform Infrared (FTIR) spectroscopy and band assignments**

159 FTIR analyses were performed at room temperature using an IRAffinity-1S
 160 spectrophotometer commercialized by SHIMADZU. Spectra were recorded in
 161 transmission mode in the wavenumbers range of 400 to 4000 cm⁻¹ using a 4 cm⁻¹
 162 resolution and accumulating 64 scans. Before analysis, the samples, taken from the
 163 injected plates, were compressed to obtain films, with a thickness of 50 to 200 μm. The
 164 spectra were treated with the Fityk software. To compare the spectrum of each
 165 material, a reference band at 998 cm⁻¹ (methyl groups rocking) was used to normalize
 166 the overall spectral intensity. This vibrational band was chosen since it is not a
 167 vibrational band that could change with the reaction such as those associated with
 168 imide, amide, MAH or amine groups.

169 **3.3. Wide angles X-rays Scattering (WAXS)**

170 WAXS analyses were performed with a tension and an intensity of 30 kV and 40 mA,
 171 respectively. The wavelength used was the copper radiation K_{α1} (λ= 0.154 nm). A
 172 parabolic multilayer mirror (Osmic) and a cylindrical capillary selected the wavelength
 173 and shaped the incident beam. The sample used were 1cm x 1 cm square cut in the

174 middle of the injected plates, and polished from both sides to obtain a 1 mm thickness.
175 Using a rotating sample holder, the analyses represent the average crystal diffraction in
176 the plane of the sample free of any crystalline texture. The 1D diffractograms were
177 deconvoluted using the Hermans and Weidinger method [36]. The contributions of
178 amorphous and crystalline phases were fitted with a series of Gaussian and Lorentzian
179 functions [37, 38]. The crystallinity ratio was calculated as the ratio of the crystalline
180 peaks areas over the total area corresponding to the sum of the areas of the crystalline
181 peaks and the amorphous halo. The 2D analyses were performed with a photosensitive
182 plane film at a distance of 75 mm from the sample that were scanned using a
183 FUJIFILM scanner BASF 5000.

184 3.4. Differential Scanning Calorimetry analysis (DSC)

185 The DSC experiments were performed using a Q200 TA Instruments apparatus. The
186 samples, weighing around 10 mg, were taken from the WAXS samples and were
187 encapsulated in aluminium pans and analyzed under an inert flux of nitrogen. To
188 characterize the sample microstructures, the thermal cycle performed at $10^{\circ}\text{C}\cdot\text{min}^{-1}$
189 consisted in a first heating ramp from 30°C to 200°C at $10^{\circ}\text{C}\cdot\text{min}^{-1}$ to characterize the
190 initial microstructure of the sample, a controlled cooling ramp to 30°C and a second
191 heating ramp to 200°C to study the standard thermal behaviour. The crystallinity ratios
192 of the materials were estimated as follows:

$$193 X_c = \frac{\Delta H_m}{\Delta H_m^0} \quad (1)$$

194 where ΔH_m is the melting enthalpy, and $\Delta H_m^0=165 \text{ J}\cdot\text{g}^{-1}$ is the enthalpy of a 100%
195 crystalline isotactic polypropylene [39]. The main crystalline lamellar thickness
196 population (L_c) of the polymer was derived from the Gibbs-Thomson equation:

$$197 T_m = T_m^0 \left(1 - \frac{2 \sigma_e}{\rho_c \Delta H_m^0 L_c}\right) \quad (2)$$

198 where T_m is the melting peak temperature measured at the maximum of the
199 endotherms, T_m^0 is the melting temperature of a 100% crystalline isotactic
200 polypropylene, σ_e is the surface free energy of iPP crystalline lamellae and ρ_c the
201 crystalline phase density. T_m^0 is given by the literature at 460 K, σ_e at $0.0496 \text{ J}\cdot\text{m}^{-2}$, and
202 ρ_c at $0.9361 \text{ g}\cdot\text{cm}^{-3}$ [39, 40].

203 3.5. Successive Self-Nucleation and Annealing (SSA)

204 SSA experiments were performed to characterize the thickness distribution of the crystallites
205 [41, 42]. This thermal fractionation technique is used to study the semi crystalline polymers
206 with linearity defects in their macromolecular chains (co-monomers, stereo-defects, chains
207 branching, crosslinking...) [43]. For instance, Ogier *et al.* [44] previously used this method to
208 characterize the important decrease of the main lamellar thicknesses of PE orthorhombic
209 crystals as a function of the crosslinking degree of an ethylene-co-vinyl acetate polymer. This
210 method could also be used to study the length distribution inside a polymer like
211 polypropylene [45, 46]. The SSA protocol is initiated at a specific temperature, called ideal
212 self-nucleation temperature T_s , which was previously determined by a self-nucleation (SN)
213 analysis. In case of comparison of the thermal fractionation behaviours of chemically
214 modified semi-crystalline polymers, the material used to identify T_s is the one that presents
215 the highest melting temperature, which is neat CA 100 for the CA 100 materials, and neat
216 G3015 for the G 3015 materials [46]. The SN protocol and its application is presented in the
217 supporting information.

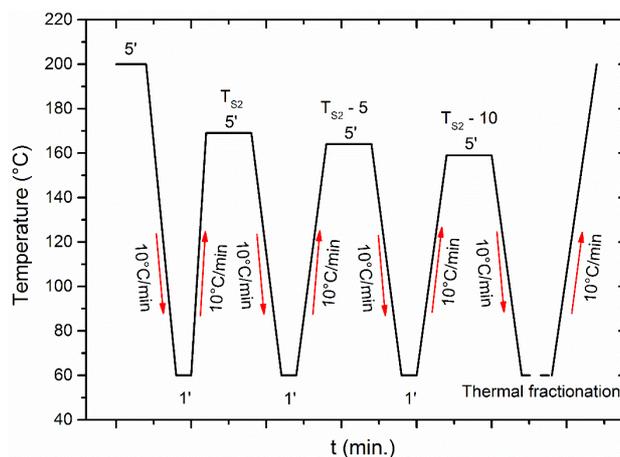


Fig.1. Temperature profile of the SSA crystal fractionation method.

218
219

220 Once the T_s was determined, the SSA protocol illustrated in Fig.1 can be carried out as
221 follows:

- 222 • The thermomechanical history of the elaborated samples is firstly erased by a rapid
223 heating ramp above the melting temperature at 200 °C for 3 min. then followed by a
224 controlled cooling ramp to 60 °C at 10 °C/min to ensure for all materials the same
225 thermal history.
- 226 • Heating up to T_{s2} , and holding this temperature for 5 min.
- 227 • Cooling down to 60 °C at 10 °C.min⁻¹.
- 228 • Heating up to a new temperature T_s , 5 °C lower than the previous one and remaining 5
229 min.
- 230 • Repeating the two last steps until the achievement of seven different T_s temperatures.
- 231 • Carrying out a final heating, up to 200 °C to melt all the fractionated crystals.

232 3.6. Dynamic mechanical analysis (DMA):

233 The dynamic mechanical properties of the materials were determined using a DMA
234 242C commercialized by Netzsch. Rectangular bar shaped samples of dimension 20 x
235 4 x 3 mm³ were machined out in the injected plates. Measurements of the complex
236 modulus were performed in three points bending mode at three different frequencies
237 (1, 5 and 10 Hz) in the temperatures range from -150 °C to 130 °C and at a constant
238 heating rate of 2 °C.min⁻¹. The complex modulus is composed of the storage modulus
239 E' (real part) and the loss modulus E'' (imaginary part). E' represents the storage
240 modulus material and is proportional to the energy stored during a loading cycle. It
241 corresponds to the elastic Young modulus. E'' represents the loss modulus from the
242 viscous part of the polymer. The loss factor $\tan \delta$ is then defined as the ratio of the loss
243 modulus to storage modulus. Results of i) storage modulus (E'), and ii) loss factor
244 ($\tan \delta = E''/E'$) are represented as a function of temperature for three frequencies.

245 3.7. Mechanical testing:

246 The true mechanical behaviours of the different materials were determined using the
247 VidéoTraction™ system [47-51]. This method gives access to the true mechanical
248 behaviour of polymers at a constant true strain rate. A geometrical defect is machined
249 out in the middle of the gauge length of the dumb-bell shaped specimen to ensure the
250 localization of the plastic deformation (necking). Seven ink markers are printed in this
251 specific region, called Representative Volume Element (RVE). The axial true strain,
252 ϵ_{33} , is obtained by a polynomial interpolation of partial strains measured from the
253 displacement of axial markers using Lagrange Transform and following Hencky's

254 definition. For uniaxial tensile testing, the transversal strains in the RVE, ϵ_{11} and ϵ_{22} ,
255 are equal if the strain field is transversally isotropic in the center of the neck [52-56].
256 Lastly, the volume strain in the RVE, ϵ_v , is simply computed from the trace of the true
257 strain tensor:

$$258 \quad \epsilon_v = \epsilon_{11} + \epsilon_{22} + \epsilon_{33} \quad (3)$$

259

260 The volume strain can be positive, null or negative. In particular, when it is superior to
261 zero it is called volume damage (since the “reversible” elastic part can be neglected),
262 and in the opposite case (when it is negative) it is considered that a compaction
263 mechanism is active.

264 The axial true stress, or Cauchy stress, is determined in the RVE, as the load per unit
265 actual cross-section:

$$266 \quad \sigma_{33} = (F/S_0) * e^{-2\epsilon_{11}} \quad (4)$$

267 where S_0 is the initial cross-section at the RVE of the sample.

268 All the mechanical tests were performed at room temperature and at a constant true
269 strain rate of 5.10^{-3} s^{-1} . This rate was chosen to ensure the control loop of the testing
270 machine actuator, and it is slow enough to avoid self-heating of the sample [55, 56].

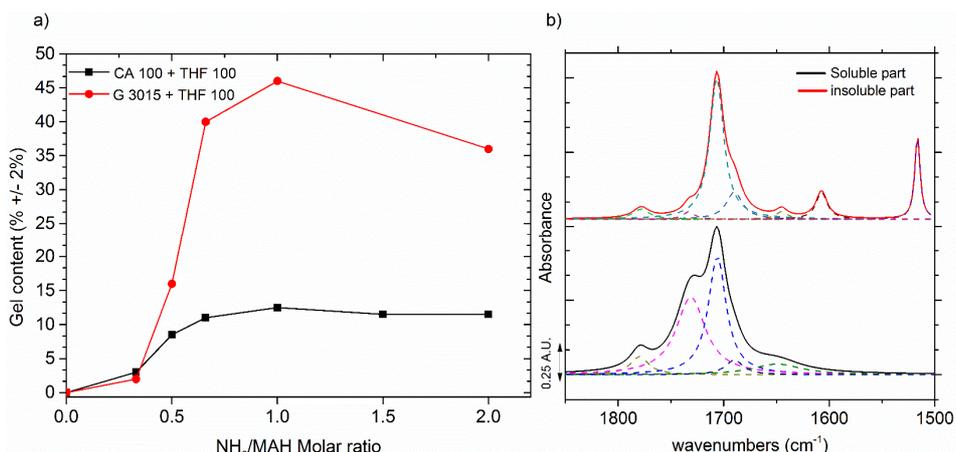
271 **3.8. Scanning Electron Microscopy**

272 Scanning electron microscopy (SEM) is used to observe the fracture surface of the
273 different materials and then to enlighten the differences between the mechanical
274 behaviours. To this end, *post mortem* micrographies are recorded using an
275 environmental Quanta FEG 650 electron microscope from the FEI Company. The
276 microscope parameters selected are a water vapor pressure of 100 Pa and an
277 acceleration voltage of 4 kV.

278 **4. Results and Discussion**

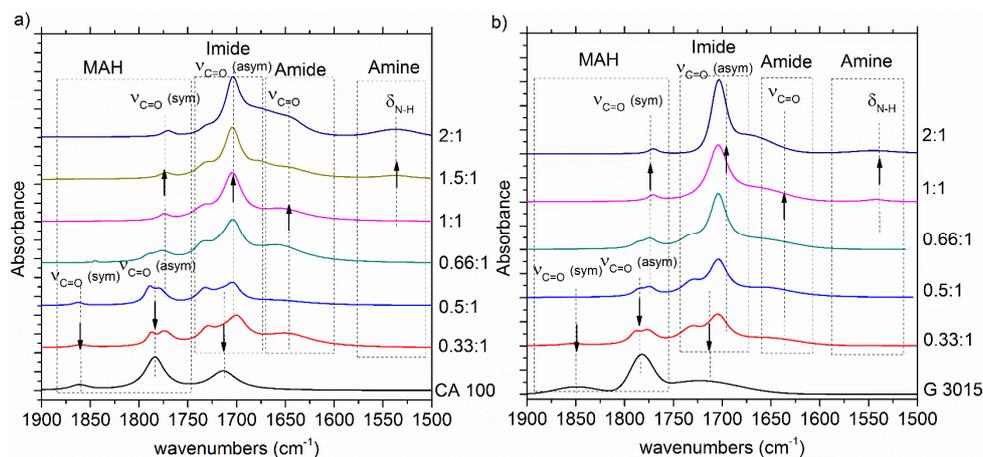
279 **4.1 Chemical analysis**

280 Fig.2 a) shows the evolution of the gel content as a function of NH_2 :MAH molar ratio
281 between Jeffamine THF 100 and iPP-g-MAH polymers. Whatever the wt% of MAH,
282 the gel content continuously increases with the amount of Jeffamine THF100 from 0,
283 for the unmodified iPP-g-MAH polymers (0:1 molar ratio) to 12% and 46% for the CA
284 100 1:1 and G 3015 1:1 molar ratios, respectively. The null gel content values of the
285 unmodified iPP-g-MAH polymers came from their low molecular weights induced by
286 the MAH grafting reaction [1-11].



287
 288 **Fig.2.** a) Gel Content evolution of CA 100 and G 3015 based materials after reaction with Jeffamine
 289 THF 100 at various molar ratio NH₂:MAH and b) FTIR spectra of the CA 100 1:1 soluble and
 290 insoluble parts.

291 The G 3015 1:1 gel content is three times higher than the one of CA 100 1:1. This
 292 difference could be explained by the difference of the grafted MAH weight fractions
 293 between both iPP-g-MAH, which vary from 1 to 3wt%. Between 0:1 and 1:1 molar
 294 ratios the gel content increases similarly for both materials. This could be explained by
 295 the crosslinking of the iPP-g-MAH chains that produces a 3D molecular network. For
 296 molar ratios higher than 1:1, an important difference between the two series of
 297 materials is observed. Whereas a plateau is reached for CA 100 at a gel content value
 298 of about 12%, there is a decrease from 46% to 36% gel content for G 3015 at a 2:1
 299 molar ratio. The important excess of diamine in this last material (three times higher
 300 than in case of CA 100 for the same molar ratio) could be responsible for the decrease
 301 of the gel content value. As a matter of fact, when it is in excess, some molecules of
 302 diamine might only react with one MAH moiety, promoting thus a chain extension
 303 rather than a crosslinking. This was already observed with other diamines at high
 304 NH₂:MAH molar ratios [22-26].



305
 306 **Fig.3.** FTIR spectra of a) the CA 100 based materials and b) the G 3015 based materials as a function
 307 of the NH₂:MAH ratio.

308 In order to follow the evolution of the reaction as a function of molar ratio of the
 309 reactive species, FTIR analyses were performed and the spectra are presented in Fig.3.
 310 The spectroscopic vibrational band positions with respect to the chemical groups
 311 present in iPP-g-MAH polymers and in modified materials are given in Table S2 in SI.
 312 In the case of iPP-g-MAH polymer, the two characteristic vibrational bands at 1860
 313 and 1780 cm⁻¹ can be assigned to the symmetric and asymmetric ν_{C=O} vibrations of the

314 maleic anhydride group (MAH). The band at 1715 cm^{-1} could be assigned to $\nu_{\text{C=O}}$
315 vibrations associated to carboxylic groups formed by hydrolysis under wet storage
316 conditions. By adding the Jeffamine THF 100, the intensity of the characteristic
317 vibrational bands of the maleic anhydride group decreases to finally disappear when
318 the 1:1 NH_2 :MAH molar ratio is reached. In the meantime, one can observe the
319 appearance of four new vibrational bands, among which the ones at 1770 and 1700 cm^{-1}
320 ¹, are assigned to the symmetric and asymmetric $\nu_{\text{C=O}}$ vibrations of the imide group,
321 respectively. Indeed, upon the reaction of the diamine with the maleic anhydride two
322 consequent addition-elimination reactions might take place to produce five-ring
323 imides. The other two vibrational bands located at 1735 and 1650 cm^{-1} can be assigned
324 to associated carboxylic acid/amide bonds, respectively. The amide bonds result from
325 both reactions between carboxylic acid and Jeffamine THF100 and from the
326 incomplete imidization reaction (opening of the anhydride ring without cyclization).
327 The intensity of the band at 1700 cm^{-1} remained strong up to the 2:1 CA 100 material,
328 but falls for the G 3015 2:1, with a raise of the imide bands, indicating a more
329 complete reaction.

330 Finally, a broad bending vibration assigned to N-H bond can be observed at around
331 1550 cm^{-1} and could be due to the overlap of secondary amide and primary amino
332 groups. The imide and amide/carboxylic acid bands describe the reaction between the
333 primary amine brought by the THF 100 and the MAH groups grafted onto the
334 polymers. The MAH bands evolutions indicate a complete consumption of the MAH
335 groups by the reaction from the 1:1 equimolar molar ratio since they totally disappear.
336 The absence of the primary amine band also confirmed the complete use of the amine
337 groups for those materials. This evolution is in agreement with the gel content
338 evolution from the 0:1 to the 1:1 sample for the CA 100 and the G 3015, which is
339 maximum for the 1:1 molar ratio. In agreement with the gel content results, for this
340 particular formulation, each MAH group reacts with one amino group, crosslinking
341 thus iPP-g-MAH chains.

342 The presence of characteristic FTIR bands of the primary amine at molar ratios above
343 1:1 indicates indeed that the crosslinking agent is in excess or has not fully reacted.
344 This might explain the stabilization for CA 100 based materials and the decrease of the
345 gel content for the G 3015 based materials at molar ratios above stoichiometry. The
346 peculiar decrease observed in case of G 3015 based materials is due to the excess of
347 diamine, three times higher than in case of the CA 100 based materials. Some diamine
348 molecules may only react with one MAH graft and that could be responsible for a
349 chain extension instead of a crosslinking between the iPP-g-MAH macromolecular
350 chains.

351 **4.2. Microstructural characterization**

352 It is well known that the crosslinking of a semi-crystalline polymer can change its
353 microstructure because of the three-dimensional network, which may modify the
354 macromolecular mobility and the chain segments length available for crystallization
355 [17-22]. Those effects are thus investigated by performing one-dimensional WAXS
356 and DSC experiments. The results are given in Fig.4, Fig.5 and numerically gathered in
357 Table 2.

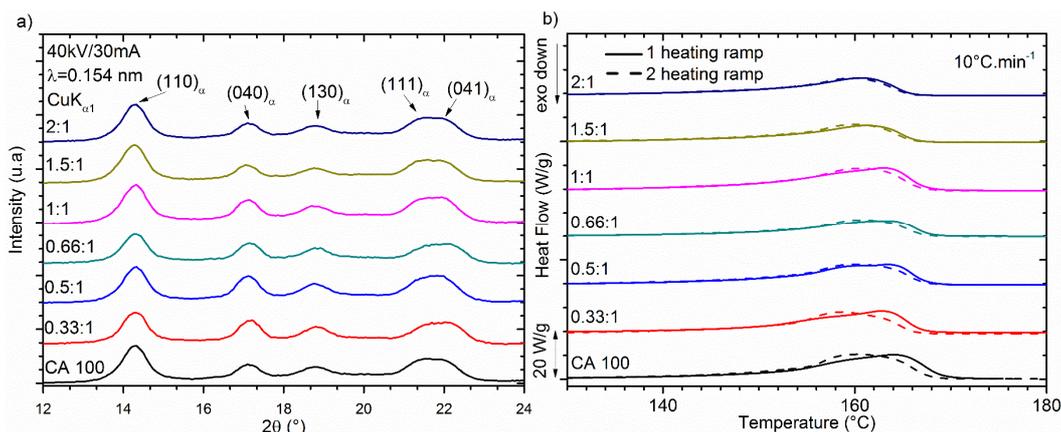


Fig.4. a) 1D WAXS diffractograms and b) DSC thermograms of CA 100 and its modified materials prepared at variable NH₂:MAH molar ratios.

The 1D WAXS diffractograms of CA 100 based materials (Fig.4 a)) exhibit characteristic peaks of a monoclinic α crystalline phase of iPP [44, 45]. The crosslinking reaction using THF 100 do not induce any modification of the crystallinity ratio, which remained of about 62%, as in the starting polymer. One can only observe some variations of the shape of the peaks and the values of the melting temperature range depending on the NH₂:MAH molar ratio and on the thermal history of the sample. In the case of the first heating endotherms, a decrease of the main melting temperature is observed with the increase of the NH₂:MAH molar ratio (from 165°C to 160°C between 0:1 and 2:1 molar ratios, respectively). On the second heating endotherms, small shoulders appear around 160°C up to a molar ratio NH₂:MAH of 1:1. Below NH₂:MAH equimolarity, this effect disappears probably due to the presence unreacted Jeffamine, in excess, which tends to facilitate the chains mobility. The decrease of the main melting temperatures and of the crystallinity ratios between the first and the second heating ramp would suggest an influence of the injection molding process on the semi-crystalline microstructures.

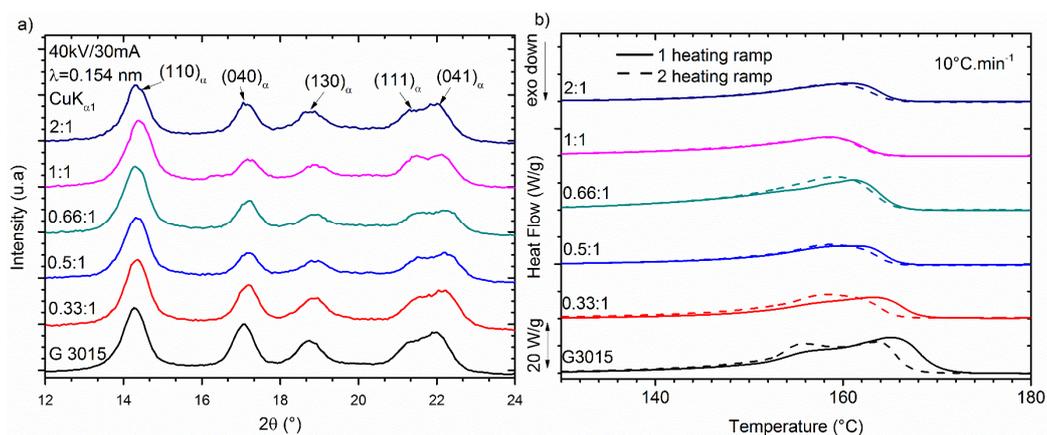


Fig.5. a) 1D WAXS diffractograms and b) DSC thermograms of G 3015 and the modified materials prepared at variable NH₂:MAH molar ratios.

Fig.5 shows the 1D WAXS diffractograms (Fig.5 a)) and the DSC thermograms (Fig.5 b)) of G 3015 based materials. Numerical values are reported in Table 2. Similarly to CA 100 based materials, the monoclinic α crystalline phase of the iPP can be identified on all WAXS spectra. However, a noteworthy difference can be distinguished since a decrease of the crystallinity ratio from 62% to 58% is observed and particularly for the highest NH₂:MAH molar ratio, of 2:1. Fig.5 b) shows the thermograms of the G 3015 based materials during the first heating revealing again the thermal history induced by

386 the injection molding process and a second heating resulting from a controlled cooling
387 in the DSC apparatus at $10^{\circ}\text{C}\cdot\text{min}^{-1}$. The melting temperatures ranges also confirm the
388 presence of the monoclinic α crystalline phase of iPP. As previously observed with CA
389 100 based materials on their first heating thermograms, double shoulder shaped
390 endotherms appear, but only until the ratio of 0.66:1. Again, in the case of the first
391 heating, a decrease of the main melting temperature as a function of the increase of the
392 $\text{NH}_2:\text{MAH}$ ratio is also noticed from 165°C to 158°C for the ratios 0:1 and 1:1. Beyond
393 that, the high quantity of THF 100 could be responsible for a unique crystalline
394 lamellae thickness population. With large excess of diamine (ratio 2:1), T_m seems to
395 increase beyond 160°C . The second heating thermograms show that the main melting
396 temperatures are quite similar (close to 159°C) whatever the modified G 3015. Only a
397 change of their melting temperature ranges is observable with a decrease of the
398 minimum and maximum temperature values as a function of the increase of the
399 $\text{NH}_2:\text{MAH}$ molar ratio. G 3015 shows a double melting peak demonstrating its ability
400 to generate two main crystallites size populations using a controlled cooling rate of
401 $10^{\circ}\text{C}\cdot\text{min}^{-1}$. Focusing on the crystallinity ratios determined from the first and the
402 second heating ramp, it can be assumed that they are equal for a given $\text{NH}_2:\text{MAH}$
403 molar ratio. Their trends to decrease are also similar as a function of the reaction
404 degree, which is in good agreement with the previous WAXS result. The WAXS
405 diffractograms and the DSC thermograms of the CA 100 and G 3015 based materials
406 allow to characterize the impact of the new three-dimensional molecular network on
407 the semi-crystalline microstructure of the different materials.

408 In the case of the matrices based on CA 100, the decrease of the melting temperatures
409 implies, by using the Gibbs-Thomson relation equation (2), a decrease of the
410 crystalline lamellae thicknesses, but without any modification of the crystallinity ratio.
411 The three-dimensional molecular network presents here a direct influence on the
412 crystallization ability of the materials. On the opposite, the G 3015 based materials
413 which present a more complex three-dimensional network with a gel content three
414 times higher than in case of CA 100's, shows a more significant impact of the
415 crosslinking reaction. The obtained networks affect the melting temperatures and so
416 the crystalline lamellae thicknesses of the polymers, but also the polymer chain
417 mobility since a decrease of the crystallinity ratios is mentioned. To better describe the
418 evolutions of the melting temperature ranges for the modified samples for both CA 100
419 and G 3015 based materials, SN/SSA studies were performed. The results of the SN
420 protocol applied on the CA 100 polymer (polymer that exhibits the highest melting
421 temperature of its series), are shown in supporting information. With those results, T_S
422 temperatures were determined respectively at 169°C for the CA 100 and 167°C for the
423 G 3015.

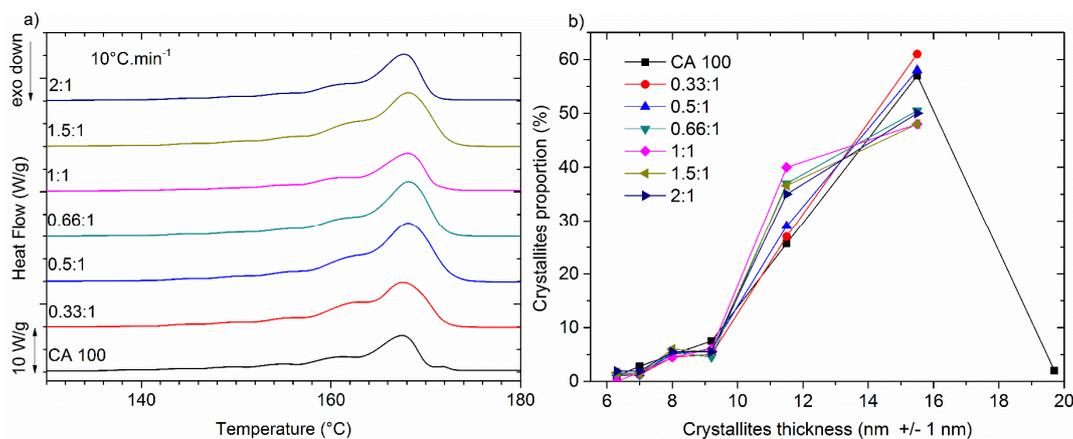
424 Fig.6 shows the last heating ramps of the SSA protocol for various CA 100 samples
425 (Fig.6 a)) and the crystallite size distributions after deconvolution with the Fytik®
426 software (Fig.6 b)). As expected, the unmodified CA 100 shows seven populations of
427 crystalline lamellae thicknesses. Tightening of the crystallite size distribution towards
428 smaller lamellae sizes is observed with the increase of the $\text{NH}_2:\text{MAH}$ molar ratio. The
429 thickest population of CA 100 ($L_c = 19.8$ nm) represents 2% of the overall crystallinity
430 ratio. This population is provided from the crystallization of the longest polymer chain
431 segments of the sample. The second thickest population ($L_c = 15.5$ nm) is the most
432 important and represents 56% of the crystallinity ratio. The first population disappears
433 from the 0.33:1 sample in favour to the second population proportion. This comment is
434 also true, but in a lower intensity, for the 0.5:1 material. From the 0.66:1 molar ratio, it

435 is the second population that decreases in favour to the third one ($L_c = 11.5$ nm), which
 436 corresponds to even smaller chain elements. The crosslinking reaction, leading to a 3D
 437 network, disturbs thus the crystallization process of the longest chain elements. This
 438 leads to the disappearance of the thickest crystalline population followed by a decrease
 439 of the second one from the 0.66:1 NH_2 :MAH molar ratio. This evolution of the
 440 crystallization ability of the longest chain elements explains the decrease of the melting
 441 temperatures range enlightened from the previous DSC results. The network building
 442 prevents the crystallization of the materials in favors of thinnest lamellae.

443 **Table 2.** Crystallinity ratio and melting temperatures of the different materials determined by
 444 DSC and WAXS analyses.

Materials		unmodified	0.33:1	0.5:1	0.66:1	1:1	1.5:1	2:1
CA 100	$X_c (\pm 3\%)$ (1 st heating)	45	45	45	44	43	44	43
	$T_m (\pm 1^\circ\text{C})$ (1 st heating)	160/165	159/163	160/163	160/163	159/162	161	160
	$X_c (\pm 3\%)$ (2 nd heating)	47	46	47	47	47	45	45
	$T_m (\pm 1^\circ\text{C})$ (2 nd heating)	161	159	160	161	160	161	159
	$X_c (\pm 3\%)$ (1D WAXS)	62	60	63	62	62	61	62
G 3015	$X_c (\pm 3\%)$ (1 st heating)	50	48	47	47	44	--	42
	$T_m (\pm 1^\circ\text{C})$ (1 st heating)	157/165	159/163	159/162	157/161	158	--	160
	$X_c (\pm 3\%)$ (2 nd heating)	50	48	47	47	46	--	42
	$T_m (\pm 1^\circ\text{C})$ (2 nd heating)	157/164	159	159	158	158	--	159
	$X_c (\pm 3\%)$ (1D WAXS)	62	62	61	61	60	--	58

445



446
 447
 448

Fig.6. a) SSA last heating thermograms and b) distribution of the lamellae thickness populations according to T_s temperatures for CA 100 and its crosslinked materials.

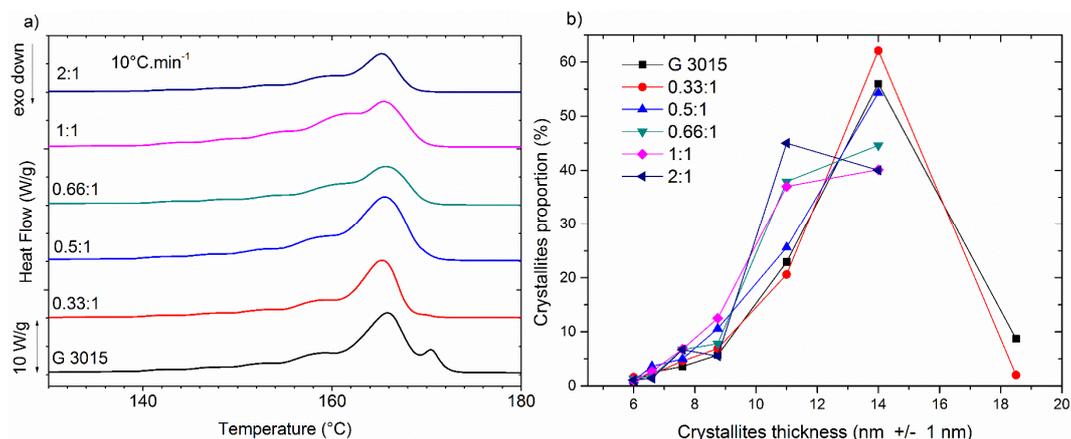


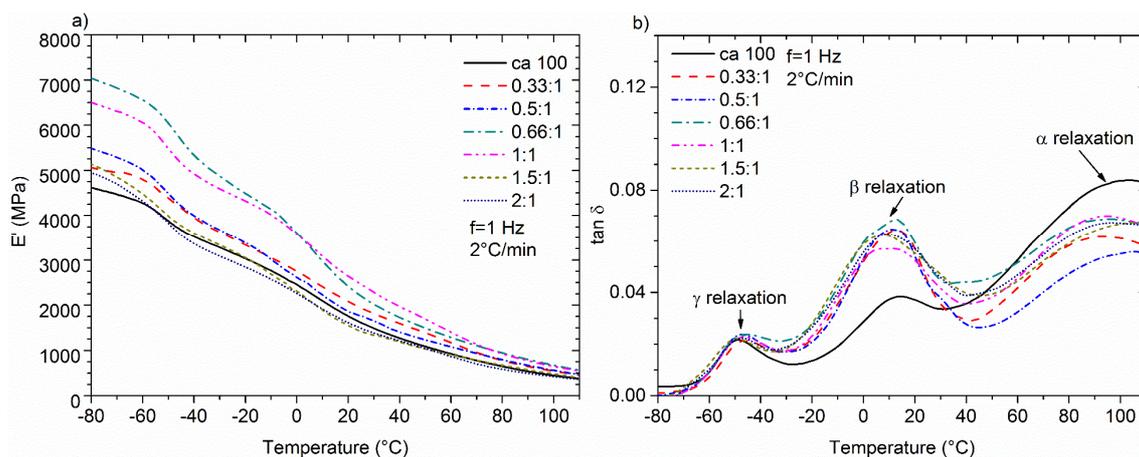
Fig.7. a) SSA last heating thermograms and b) distribution of the lamellae thickness populations according to T_s temperatures for G 3015 and its crosslinked materials.

449
 450
 451
 452 Similarly to CA 100, G3015 shows seven sizes of crystalline populations (Fig.7).
 453 However, the thickest population ($L_c = 18.5$ nm) observed in the case of G 3015 and
 454 0.33:1 material is 1 nm thinner than in case of CA 100. This difference could be
 455 explained by the higher MAH weight fraction and the smaller molecular weight of G
 456 3015 [11, 29-34]. This population represents 9% of the overall crystallinity ratio for the
 457 G 3015 and only 2% for the 0.33:1 molar ratio and it disappears completely for the
 458 other materials. At the same time, the second thickest population ($L_c = 14.5$ nm) first
 459 raises from 56% for the unmodified G 3015 to 62% for the 0.33:1 sample and then
 460 decreases to 54% for the 0.5:1 and to 40% for the 1:1 samples. From the 0.66:1 to the
 461 2:1, the third population ($L_c = 11$ nm), which corresponds to smaller chain segments,
 462 raises from 21% to 37% for the 1:1 material and finally to 45% for the 2:1. In the case
 463 of the CA 100 based materials, the second population remains the most important, but
 464 for the G 3015-based materials, the third population becomes equal in proportion to the
 465 second one. The three-dimensional networks of the G 3015 polymers are denser than
 466 the ones of materials based on CA 100. Then they exhibit a greater influence on the
 467 polymer crystallization ability, as discussed for DSC thermograms.

468 The three-dimensional network created by the chemical reaction shows here another
 469 difference between the two iPP-g-MAH. In the case of CA 100, the network affects the
 470 crystallization ability of the different samples, with a slight decrease of the melting
 471 temperatures range, as pointed out by SSA results. In the case of G 3015, with three
 472 times more MAH and gel content at equimolarity, the materials show a slight decrease
 473 of the melting temperatures range, but also a decrease of the crystallinity ratio. This
 474 second microstructure evolution is similar to that observed for other crosslinked
 475 polymers in the literature [17-22].

476 4.3. Mechanical properties

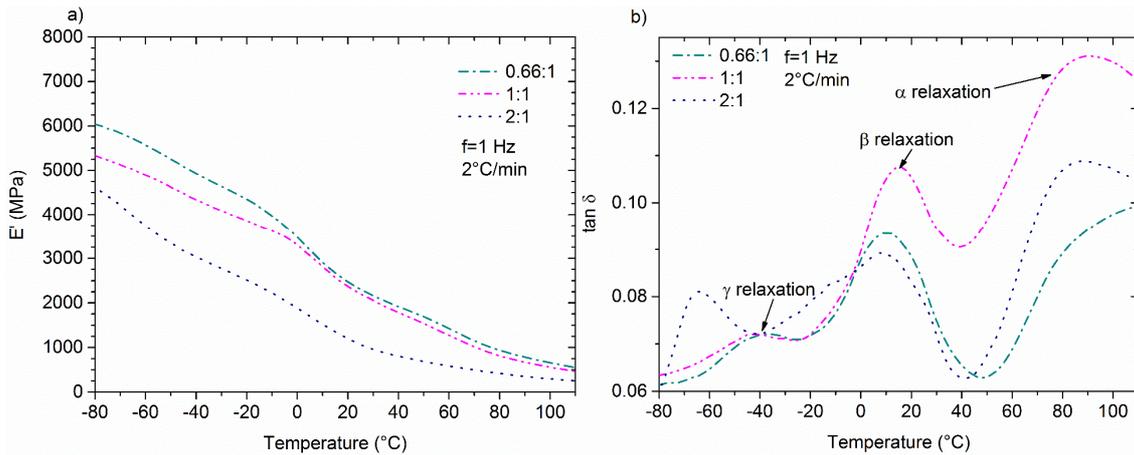
477 Fig.8 a) depicts the comparison of the DMA signals recorded for the storage Young
 478 modulus at a unique frequency of 1 Hz as a function of temperature for all the
 479 materials based on CA 100.



480
481 **Fig.8.** a) Evolutions of the storage Young modulus and b) the loss factor of CA 100 based
482 materials.

483 The storage modulus values pointed out at low temperatures below 0°C tend to
484 increase from the unmodified CA 100 to the 0.66:1 material. The increasing excess of
485 diamine molecules may explain this phenomenon. Above 0°C, the elastic mechanical
486 behaviour is stronger as long as the NH₂:MAH molar ratio increases until the
487 equimolarity. This mechanical resistance improvement is clearly a consequence of the
488 crosslinking reaction put in evidence by the FTIR analyses and the gel content results.
489 When the crosslinking agent is introduced in excess, the elastic properties decrease
490 progressively which means that THF 100 acts like a plasticizer. Fig.8 b) gives the
491 evolutions of the loss factor at the same 1 Hz frequency as a function of temperature
492 for all the materials based on CA 100. They all present the three relaxations already
493 found for iPP [48]. The γ -relaxation associated with the motions of the methyl groups,
494 has the same amplitude for all materials and occurs at around -40°C. The β -relaxation,
495 associated with the glass transition of the iPP, stays close for the different materials at
496 about 11°C, but presents different amplitudes. The crosslinking reaction during
497 reactive extrusion, issued from the introduction of the THF 100 involves a change in
498 the material architecture, which increases the amorphous phase contribution to the β -
499 relaxation associated with the glass transition of iPP. Indeed, even without crystallinity
500 ratio alteration, the amorphous phase disorder increases. This has resulted from an
501 increase of the loss factor amplitude of the β -relaxation for the modified materials by
502 the THF 100, compared with starting CA 100. The α -relaxation, associated to local
503 motions within the crystalline phase, is located around 90°C for the various materials.
504 The variations of amplitude of this relaxation could be explained by the weakest ability
505 of modified matrices to crystallize in thickest lamellae in comparison to the
506 unmodified CA 100.

507 In the case of the G 3015 materials it should be noted that due to heterogeneities inside
508 the molded plates, mechanical analyses could be performed only on materials obtained
509 at molar ratios higher than 0.66:1 (Fig.9 a)). The 0.66:1 and 1:1 corresponding
510 materials exhibit close Young modulus, and the same decrease for the 2:1 material is
511 observed due to the same reasons as those discussed previously for materials based on
512 CA 100. Fig.9 b) gives the evolutions of the loss factor for only the injectable materials
513 based on G 3015.

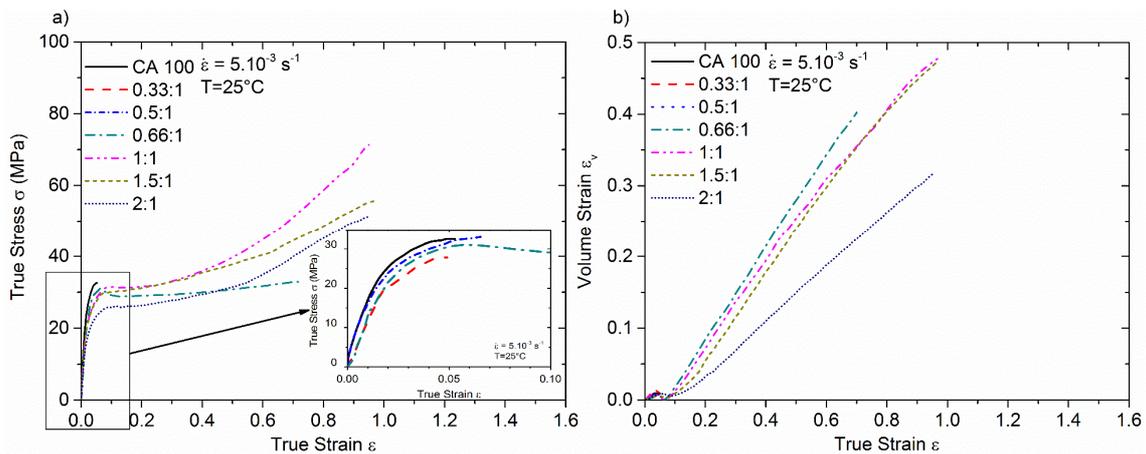


514 **Fig.9.** a) Evolutions of the storage Young modulus and b) the loss factor of G 3015 based
 515 materials
 516

517 Materials G 3015 0.66:1 and 1:1, as materials based on the CA 100, present the three
 518 well-known relaxations found for iPP, while the material 2:1 presents several changes
 519 at low temperatures. The γ -relaxation associated with the motions of the methyl
 520 groups, has the same amplitude for materials 0.66:1 and 1:1 near -40°C . The
 521 temperature of the β -relaxation, associated with the glassy transition of the iPP,
 522 increases from 12 to 15°C between the ratios 0.66:1 and 1:1, then decreases by 8°C
 523 for the material 2:1. The increase of the temperature associated with the glassy transition is
 524 logical in view of the crosslinking occurring which decreases the mobility of chains;
 525 this is highlighted by the chemical analysis of the materials. The decrease of
 526 temperature between the ratios 1:1 and 2:1 can be explained by the presence of
 527 molecules of diamine THF 100 in excess, which behaves as a plasticizing agent thus,
 528 they increase the mobility of chains and lower the temperature of the relaxation
 529 associated with the glassy transition. The more the material is crosslinked, the more the
 530 amplitude of the β -relaxation decreases being in agreement with a decrease of the
 531 mobility of chains. The α -relaxation, associated with local motions within the
 532 crystalline phase, is located close to 90°C for the various materials; however, the
 533 variations of amplitude of this relaxation are more difficult to explain. The material 2:1
 534 presents important changes around the γ -relaxation and the β -relaxation at low
 535 temperatures compared to the two other materials. Besides the absence of the γ -
 536 relaxation typical of the iPP, a new relaxation between -65 and -60°C can be noticed,
 537 as well as a change of the shape of the β -relaxation at 8°C . This new relaxation can be
 538 associated with the glassy transition of the chains of poly (tetramethylene ether
 539 glycol) / PPG (polypropylene glycol) copolymer composing THF 100 [35, 57-60].
 540 Furthermore, the THF 100 in excess crystallizes at low temperatures. Its melting
 541 occurs at 8°C what could explain the appearance of a shoulder superimposed on the γ -
 542 relaxation of this material at low temperatures.

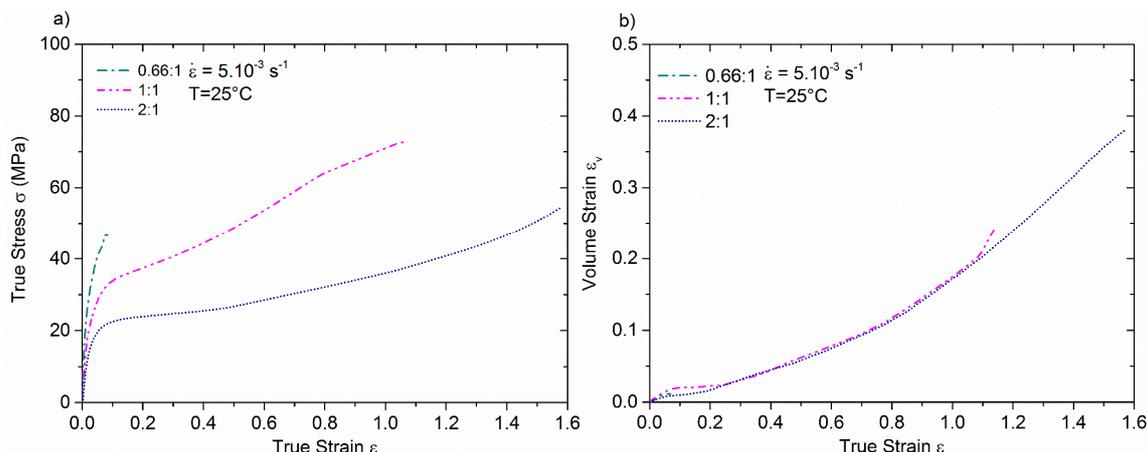
543 For further mechanical analysis at high true strain values, all the materials tested by
 544 DMA were studied with the VidéoTraction™ system in uniaxial tension deformation
 545 path. Fig.10 a) shows the true mechanical behaviours of the different CA 100 based
 546 materials. As expected, CA 100 presents a brittle mechanical behaviour with no
 547 plasticity due chains breaking induced by MAH grafting. The two materials with the
 548 lowest molar ratios (0.33:1 and 0.5:1) have also brittle mechanical behaviours similar
 549 to the one obtained for CA 100. The three-dimensional network in these cases is not
 550 sufficiently developed to improve the mechanical properties of the materials at high
 551 strains. The first significant change appears only from the 0.66:1 material which breaks

552 at a true strain value 15 times more important than in the case of the unmodified CA
 553 100 ($\epsilon_{b \text{ CA100}} = 0.05$ and $\epsilon_{b \text{ 0.66:1}} = 0.75$). The molar ratio of this material is close to the
 554 one corresponding to the complete reaction, when NH_2 groups consume all MAH
 555 grafts. This next molar ratio 1:1 achieves the best mechanical properties in terms of
 556 resilience and ductility. The true stress at break is more than twice higher than in the
 557 case of the unmodified CA 100 ($\sigma_{b \text{ CA100}} = 33 \text{ MPa}$ and $\sigma_{b \text{ 0.66:1}} = 71 \text{ MPa}$). Moreover,
 558 the stress hardening is clearly stronger than in case of the previous molar ratio that
 559 could be explained by a higher level of molecular chains orientation towards the
 560 stretching direction. This result highlights that the optimum crosslinking degree that
 561 has been previously found regarding the gel content and the FTIR analyses and that
 562 does not induce important impact on the semi-crystalline microstructure (only a weak
 563 decrease of the crystalline lamellae thicknesses) is consistent with the material that
 564 presents the best mechanical properties. The two others materials, 1.5:1 and the 2:1,
 565 show also ductile behaviours, but with a significant decrease of the stress level
 566 compared to the 1:1 molar ratio material. Nevertheless, the amplitude of their stress
 567 hardening is not so much affected. This result can be explained by the excess of
 568 diamine molecules which acts here as a plasticizing agent as identified by the DMA
 569 results that promotes macromolecular chains mobility and then orientation.



570 **Fig.10.** a) True mechanical behaviour laws and b) evolutions of the volume strain of the
 571 modified CA 100 based materials in uniaxial tension
 572

573 Regarding the evolutions of volume strain as a function of true strain, uncompleted
 574 crosslinking encourages volume damage whereas diamine molecules excess decreases
 575 it, which is in good agreement with the shape of the stress hardening discussed in
 576 Fig.10 a).

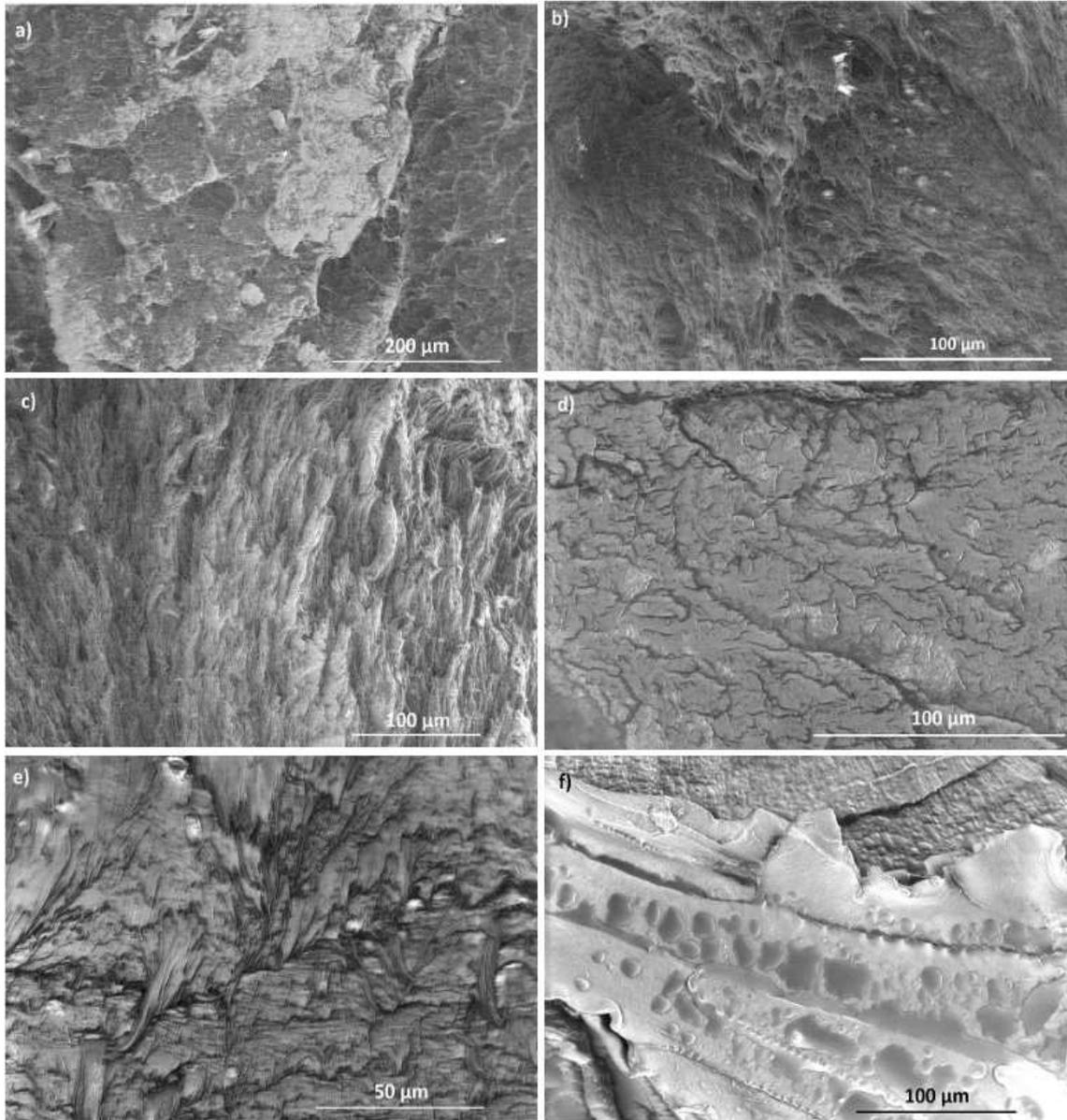


577 **Fig.11.** a) True mechanical behaviour laws and b) evolutions of the volume strain of the modified G
 578 3015 based materials in uniaxial tensile tests.
 579

580 Fig.11 a) shows the true mechanical behaviour of the G 3015 based materials. Like for
 581 the DMA analyses, only three materials were studied, the 0.66:1, 1:1 and 2:1 samples.
 582 In opposition with the CA 100 0.66:1 material, the G 3015 0.66:1 still present a brittle
 583 mechanical behaviour. The improvement of the mechanical properties occurs only
 584 from the 1:1 molar ratio. This material exhibits mechanical properties close to those of
 585 the CA100 1:1, with a ductile mechanical behaviour, and an important raise of true
 586 strain and true stress at break. The G 3015 2:1 samples also show a ductile mechanical
 587 behaviour, but with a raise of true strain at break, and a decrease of true stress level.
 588 Similar to the CA 100 2:1, this material presents the effect of the large excess of
 589 diamine molecules that act like a plasticizing agent. However, in this particular case of
 590 G 3015 2:1, the diamine molecules excess is three times higher than in case of CA 100
 591 2:1 and so it induces in addition to a weaker stress resistance, the raise of true strain at
 592 break. This observed excess improves the deformation ability of the sample. These
 593 conclusions drawn from the true mechanical behaviours of modified G 3015 materials
 594 are corroborated by the evolutions of the volume strain depicted on Fig.11 b) since
 595 similar low volume damage is undergone during stretching.

596 To highlight such switch of true mechanical behaviour at large strains, SEM
 597 observations were performed on the fracture surface of the various samples.
 598 Micrographies are gathered in Fig.12. Fig.12 a) illustrates the unmodified CA 100
 599 fracture surface and shows a classical brittle one in conformity with the determined
 600 true mechanical behaviour. The topography begins to change from the CA 100 0.66:1
 601 material (image b)) with the development of a fibrillary microstructure on the most part
 602 of the sample surface. This morphology is complete with the CA 100 1:1 material
 603 (image c)) that exhibits the best true mechanical behaviour, with an important plastic
 604 deformation. It has to be noticed that fibrils were oriented along the stretching
 605 direction (perpendicular to the micrographies plane) and result from the creation of
 606 elongated voids. This evolution between the different CA 100 materials is in good
 607 agreement with the previous mechanical analysis. In case of the G 3015 materials, the
 608 d) micrography which corresponds to the fracture surface of the 0.66:1 material shows
 609 a brittle surface with some small regions where some fibrils can be observed. This
 610 indicates the beginning of the three-dimensional network influence on the mechanical
 611 properties. However, the network here is not sufficiently enhanced to induce the
 612 expected ductility. In case of G 3015 1:1 (image e)), a complete fibrillary
 613 microstructure is revealed, proof of the switch of true mechanical behaviour. A
 614 particular attention could be drawn on Fig.12 f) which shows an interesting zone of the

615 G 3015 2:1 fracture surface, it reveals the presence of some round elements on the
 616 fracture surface. They could be identified as THF 100 diamine molecules drops
 617 resulting of the large excess, which did not mix well with the polymer matrix. The
 618 same thing was not observed for the CA 100 2:1 material since the diamine excess is
 619 three times lower. Thus, these SEM observations confirmed really well the switch from
 620 brittle to ductile of the true mechanical behaviour from the 0.66:1 molar ratio in the
 621 case of CA 100 based materials and from the 1:1 molar ratio in the case of G 3015
 622 based materials.



623 **Fig.12.** SEM observations of the fracture surfaces of a) unmodified CA 100, b) CA 100 0.66:1,
 624 c) CA 100 1:1, d) G 3015 0.66:1, e) G 3015 1:1, and f) and G 3015 2:1 materials.
 625

626 Finally, to resume and to compare the real mechanical behaviours of all the materials
 627 of the study at large strain values (it means of the matter only without considering
 628 voids), intrinsic true mechanical laws were determined using the theory developed by
 629 Ponçot *et al.* in 2013 [51].

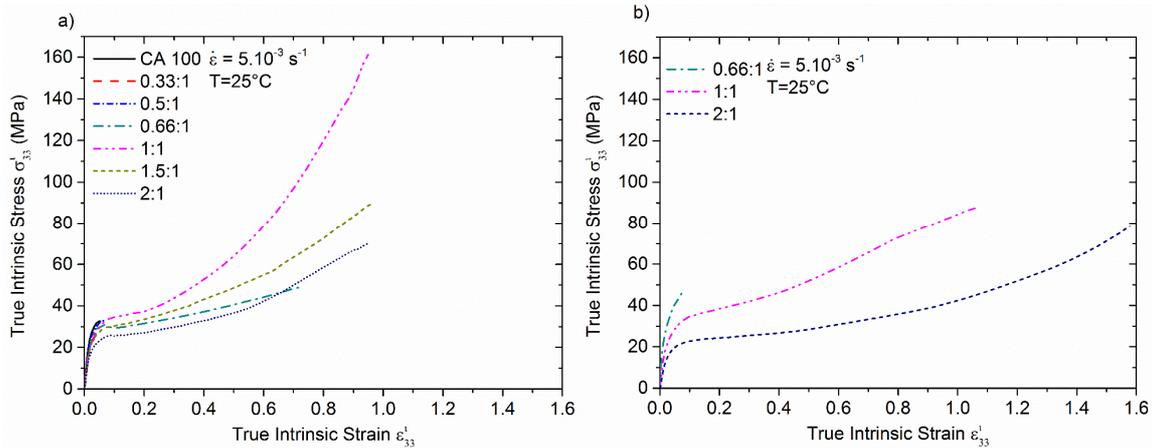
630 The remarkable shape of cavities in case of isotactic polypropylene is tube-like shape
 631 from the moment that volume strain intensity is high enough to have an influence on

632 the true mechanical parameters without significant change of shape. Thus, the intrinsic
 633 true strain in the axial direction can be expressed as follows:

$$634 \quad \varepsilon_{33}^i = \varepsilon_{33} \quad (5)$$

635 The expression of the intrinsic true stress may be given by:

$$636 \quad \sigma_{33}^i = \frac{F}{S^i} = \sigma_{33} \frac{S}{S^i} = \sigma_{33} e^{\varepsilon_v} \quad (6)$$



637 **Fig.13.** Comparison of the true intrinsic mechanical behaviours of a) the modified CA100 and
 638 b) the modified G 3015 based materials.
 639

640 Fig.13 compares the intrinsic true mechanical behaviours of materials based on CA
 641 100 (Fig.13 a)) to those of materials based on G 3015 (Fig.13 b)). By correcting the
 642 volume damage that occurs in such materials during uniaxial stretching, it can be
 643 observed that mechanical resistance increases as a function of the increase of
 644 crosslinking with a maximum for the 1:1 formulation for both iPP-g-MAH. The excess
 645 of diamine molecules decreases significantly the mechanical resistance due to its
 646 plasticizing effect. This phenomenon is extreme in case of the G 3015 2:1 material, but
 647 results to a large increase of the strain at break.

648 5. Conclusion

649 In-situ crosslinking of iPP-g-MAH bearing two weight fractions of anhydride (1 wt%
 650 for CA 100 and 3 wt% for G 3015) was performed through a twin-screw reactive
 651 extruder with a primary end-capping diamine, the polyether Jeffamine®THF-100. The
 652 crosslinking reaction had a direct impact on the microstructure of the polymer,
 653 resulting in a decrease of the crystalline lamellar thicknesses for both maleated iPP
 654 with an additional effect on G 3015, namely a slight decrease of the crystallinity ratio.

655 The most crosslinked networks and equivalent mechanical properties were reached at
 656 equimolar ratio of NH₂:MAH for which, interestingly, the gel content was three times
 657 lower for the CA 100 materials. In other words, one needs three times less Jeffamine to
 658 crosslink the 1 wt% iPP-g-MAH polymer to reach better mechanical properties such as
 659 resilience, yield and stress at break as with the richest MAH polymer. This could be
 660 due to the fact that the crystalline microstructure is poorer in the case of G 3015, while
 661 for both materials, the β-scission induced by the MAH grafting is counterbalanced by
 662 the formation of the 3D network.

663 More important, at a certain molar ratio (0.66:1 for CA 100 materials and 1:1 for G
 664 3015 materials) the mechanical behaviour of the materials switched from brittle to
 665 ductile. When used in excess, the Jeffamine acts rather as a plasticiser, as the

666 crystallinity ratio and mechanical properties, such as Young modulus or stress level
667 decreased.

668 Finally, it should be noted that the formulations presented herein are of particular
669 interest for the design of composite materials, especially those that address structure-
670 lightening topics. This is especially the case for CA 100-derived material
671 functionalised at a 0.66:1 ratio and which exhibits a ductile behaviour while bearing
672 reactive anhydride moieties available for further interact with other surfaces (i.e.
673 carbon, metallic or metal oxides).

674 **Acknowledgements**

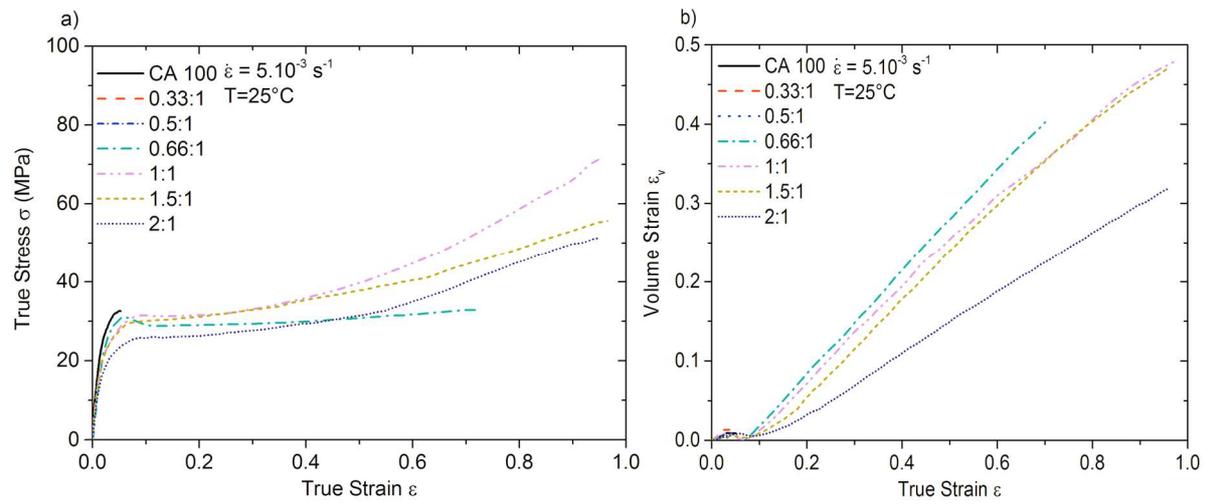
675 The authors thank the CINI Company for the extruder facilities and assistance in the
676 process development, Huntsman, Eastman and Arkema for providing chemicals and
677 polymers and Provisys Engineering Company for facilities with the VidéoTraction™
678 system. AL and MP thank the French Ministry for the PhD grant and the LabEX
679 DAMAS for the financial support.

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A slight crosslinking enables maleated isotactic polypropylenes to switch from brittle to ductile mechanical behavior with higher resilience than the most conventional one.