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Impact of the *in situ* creation of an epoxy based thermosetting minor phase on the physical properties of a PP based blend

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ABSTRACT

As an alternative to inorganic fillers based composites which present high density, an epoxy based thermosetting (TS) phase was *in situ* created in a polypropylene (PP) matrix and compatibilized by a polypropylene grafted maleic anhydride (PP-g-MA). The aim of this study is to scrutinize the chemistry and establish a relation between the morphology, the mechanical properties and the crystalline structure of this thermosetting/thermoplastic system. Depending of the components concentration, dispersed phase of around 0.5 μm diameter (even with smaller nodules) are created with the presence of PP-g-MA. Moreover, an increase up to 24 % of the Young's modulus of the system is observed and the resilience is maintained. The evolution of the PP crystallinity by Wide Angle X-rays scattering (WAXS) evidenced that TS is a β nucleating agent at the origin of an excellent toughness and impact strength.

1. INTRODUCTION

Polypropylene (PP) is a widely known and used polymer and its production represents 20 % of the total production¹ of plastic in Europe in 2016. Its use covers almost all types of industries, from food packaging to automotive parts passing by bank notes. PP is an attractive polymer due to its low cost, high macromolecular diversity, low density and it is inert to other chemicals. Even though, it has a fair good mechanical strength at room temperature and becomes brittle at low temperature since its glass transition is around 0 °C. To benefit of the qualities of PP and to replace expensive polymers, physical and chemical modifications are required in order to reinforce PP. Among those modifications, three were widely studied.

Polymer blends²⁻⁴ are very complex and have been studied for almost 30 years. Indeed, in some cases it is possible to merge the best properties of each polymer, by increasing the performance of the final material. In addition, they generally have a lower impact than developing completely new materials. However, almost all polymers with different chemical structures are immiscible, thus causing phase separation, which is problematic for the final properties of the material.

Several studies also discuss the effects of the incorporation of inorganic fillers⁵⁻⁷ such as glass fiber, talc, silica, etc. A very positive impact on mechanical and viscosity is observed without compromising the feasibility and the cost of these fillers is usually very low. Although, incorporation of inorganic fillers is very attractive, its limitation is the impact on the density of the material depending of the inorganic filler concentration usually quite high^{8,9}.

In order to overcome this limitation, the addition of organic fillers into thermoplastics has aroused increasing interest and experimentation during the last years. This technique has been widely used to improve certain intrinsic properties of conventional matrices (PS, PE, EVA) such as barrier properties¹⁰, tensile strength properties¹¹ or even viscosity¹². This type of modification was chosen in the present work, more precisely the *in situ* creation of epoxy based thermosetting (TS).

However, as PP is chemically inert, the *in situ* creation of a new polymer can have the opposite effect and decrease some properties such as resilience if any chemical bond has been created between both phases. Therefore, using a compatibilizer seems essential. The introduction of a di-block copolymer¹³ in the blend is commonly used to compatibilize two immiscible polymers. Indeed, this copolymer composed of two blocks, each miscible or of the same nature of the components of the blend, will assure the link between the immiscible polymers. Another possibility is the *in situ* formation of a copolymer^{14,15} by chemical reaction at the interface between the phases during the preparation of the blend. The type of compatibilizer used in this work is a polypropylene grafted with maleic anhydride (PP-g-MA), a modified homopolymer¹⁶, often used as coupling additive for filled polypropylene and polymer blends¹⁷, as pigment dispersant, etc. This compatibilizer introduced in not classical concentration will be an important point in our study in order to understand its influence and its role in the creation of epoxy based thermosetting (TS) in the PP matrix.

Besides, in semi-crystalline polymers, such as polypropylene, the crystalline structure is very sensitive and its modification can have an important impact on macroscopic properties. The lamellar orientation¹⁸, the lamellar thickness¹⁹ and the degree of crystallinity can have a direct effect on the Young's modulus and resilience.

In the case of polypropylene, another parameter has to be considered, since different types (α -monoclinic, β -hexagonal, γ -triclinic and smectic) of crystalline forms can be encountered. Each structure can lead to PP with quite different mechanical properties. Actually, β -polypropylene²⁰ is known to have excellent toughness and impact strength, in comparison with the α -PP, the most common crystalline form. Cascone and Fulchiron²¹, showed that a β -polypropylene can be obtained by a squeeze flow from an isotactic polypropylene (iPP) initially containing only an α -phase. This phenomenon is generally developed in specific conditions such as the presence of nucleating agents. The influence of these agents has been widely studied in the literature. Papageorgiou et al. described a non-exhaustive list of different β -nucleating agents which mostly are inorganic fillers, for example calcium derivates are often described as really performant^{22,23}. Nevertheless, some organic fillers can play the role of β -phase promoter as studied by Zhang²⁴ et al. with the use of an acylamino-nucleating based-agent. Indeed, the isotactic PP studied presented at first no hexagonal form but with the addition of 0.3wt% of nucleating agent, 87% of the crystallization of iPP was found to be with β -form. The appearance of this hexagonal modification increased the elongation at break (from 150% without nucleating agent to 500 % with 0.2 wt% of filler) and doubled the impact strength.

The main objective of this work is to investigate chemical, structural and morphological parameters initiating the mechanical properties improvement with the *in situ* creation of an epoxy based thermosetting phase TS in a PP matrix. The first part of this paper will discuss the chemical interaction between the PP matrix, the compatibilizer and the TS phase *in situ* created as well as its morphology. The second part will focus on the impact of the creation of the TS phase in the amorphous phase mobility and crystallinity of the

PP. Eventually, the third part will try to establish a relation between the morphology, the crystalline structure modifications and the mechanical properties improvements.

2. MATERIALS AND FORMULATIONS

2.1. Materials and reagents

Polypropylene (PP) PPH 3060 was supplied by Total. The melt flow index is $1.8 \text{ g} \cdot 10 \text{ min}^{-1}$ (in the following conditions: $2.16 \text{ kg}/230^\circ\text{C}$.) and the zero shear viscosity $\eta_0 = 700 \text{ Pa} \cdot \text{s}$ at $T = 200^\circ\text{C}$. The density of this polymer is $0.90 \text{ g} \cdot \text{cm}^{-3}$ at room temperature and the melting point at $T_m = 165^\circ\text{C}$ was measured by differential scanning calorimetry (DSC) analysis.

Maleic anhydride functionalized polypropylene, PP-g-MA, produced by Exxelcor (PO 1020) was used as a compatibilizer since the PP is chemically inert. The maleic anhydride mass grafting rate was determined by acid-base titration and it was found at 0.7 wt% after purification (1.2 wt% before purification). Its number-average molar mass was evaluated at $36200 \text{ g} \cdot \text{mol}^{-1}$ by size exclusion chromatography (SEC) in trichlorobenzene (TCB) at 110°C .

The DER 671, a low molar mass epoxy based-resin developed by Dow Chemicals, was used for both formulations in this study (DER 671/NBDA and DER 671/DEH 84). In order to create an epoxy based thermosetting phase, a cycloaliphatic diamine was chosen for one of the formulations, the norbornane diamine (NBDA) was provided by MitSui Chemicals in liquid state. For the second formulation, DEH 84, an epoxy curing agent which is a phenolic harder, as well from Dow Chemicals, was used to create the second epoxy-based thermosetting network. All the formulations were prepared under stoichiometric conditions (an epoxy function for one amine proton or hydroxy proton)

with regard to the creation of thermosetting (**Table 1**). All reagents and matrix are commercial products that were used without any further purification, their structure and the main characteristics are showed in **Table 2**.

Table 1 : Epoxy based thermosetting systems studied

Epoxy	Amine/phenolic hardener	Mass proportions at function stoichiometry (Epoxy : Amine/Hydroxyl)
DER 671	DEH 84	1 : 2
DER 671	NBDA	13 : 1

Table 2 : Main characteristics of the materials used

Products	Chemical Structure	Supplier	T _m /T _g (°C)	M (g.mol ⁻¹) and MFI
Polypropylene PPH3060 (PP)		Total	T _m = 165 °C	M _w = 384 000 g.mol ⁻¹ * MFI = 1.8 g. 10 min ⁻¹ (2.16 kg/230°C)
Polypropylene grafted maleic anhydride, PP-g-MA PO1020		Exxon Mobil	T _m = 167 °C	Grafting rate MA = 0.7 %* M _n = 36 000 g.mol ⁻¹ * MFI = 125 g.10 min ⁻¹ (1.2 kg/190 °C)
Epoxide resin DER671	with n = 1,6	Dow Chemicals	T _g = 57°C	M _n = 795 g.mol ⁻¹

Products	Chemical Structure	Supplier	$T_m/T_g(^{\circ}\text{C})$	M (g.mol ⁻¹) and MFI
Epoxide resin DEH84 (70wt% of DER671 contained in this hardener)	<p>70wt%</p> <p>30wt%</p> <p>with $n = 1,6$ <1wt%</p>	Dow Chemicals	$T_g = 43^{\circ}\text{C}$	$M_n = 630 \text{ g.mol}^{-1*}$
Norbornane diamine (NBDA)		TCI Chemicals	Liquid at room temperature	$M = 154 \text{ g.mol}^{-1}$

* Experimental values characterized in our laboratory by ^1H NMR, by steric exclusion chromatography (SEC) and by acid-base titration

2.2. Samples preparation

Samples were synthesized by melt blending in a co-rotating twin-screw extruder (Leistritz LSM Model, L/D = 60, D = 18 mm) at 200 °C. In order to ensure sufficient shearing and mixing, the screws profile contains two reverse conveying elements. The screw profile is shown in **Figure 1**.

Figure 1 : Twin-screw profile with two reserve conveying elements.

Screw speed was fixed at 800 rpm and the matrix was added by the hopper at a flow rate of 3 kg.h⁻¹ with the compatibilizer PP-g-MA and the reagents DER 671 and DEH 84 (solid state for both reagents). The liquid NBDA amine was incorporated with an external liquid pump at L/D = 17D of the extruder. For specific discussion as reported in the paragraph 4.1, the NBDA will be respectively injected at L/D = 32D and L/D = 42D. The different formulations prepared are listed in **Table 3**. It is important to point out that all the formulations were carried out under stoichiometric conditions (an epoxy function for one amine proton or hydroxy proton) and that the number of moles of maleic anhydride (originating from PP-g-MA) is always in default relatively to the number of moles of -[NH₂] / -[NH] / -[OH]. At the die of the extruder, the samples were cooled with air and granulated. The residence time in the extruder was estimated around 80 s from Ludovic Software®.

Table 3 : Mass fraction (wt%) for each formulation

Samples	PPH3060	PP-g-MA	DER671	DEH84	NBDA
PP+20wt%PP-g-MA	80	20	-	-	-
PP+20wt% PP-g-MA+26wt%(DER671+DEH84)	54	20	8.7	17.3	-
PP+26wt%(DER671+DEH84)	74	-	8.7	17.3	-
PP+20wt%+ PP-g-MA+12wt% (DER671+DEH84)	68	20	4	8	-
PP+9 wt% PP-g-MA+12wt% (DER671+DEH84)	79	9	4	8	-
PP+15wt% PP-g-MA+10wt% (DER671+NBDA)	75	15	9.3	-	0.7
PP+10wt% (DER671+NBDA)	90	-	9.3	-	0.7

2.3. Soxhlet procedure

In order to study the structures and chemical bonds created during the *in situ* synthesis of the epoxy based thermosetting phase in the PP by reactive extrusion, around 2 g of finely ground sample powder was placed in a thimble and then put in the Soxhlet apparatus. In the case of PP^{25,26}, xylene is often adopted as the dissolution solvent under boiling conditions. In our experiment we used 250 mL of p-xylene (boiling point at 140 °C). Once the first cycle began the reflux was maintained for at least 48 h. Both the solid extracted and the soluble fraction were dried and weighed and further analyzed by DSC and Fourier-Transform Infrared Spectroscopy (FTIR).

3. CHARACTERIZATION

3.1. Tensile tests

The formulations were injected into dumbbell specimens using a Babyplast 6/10P machine with a piston diameter of 14 mm and a clamping force of 62 kN. The temperature of the injection chamber was set between 200 and 220 °C and the pressure between 80 and 100 bars depending on the viscosity of the formulation. At least five specimens from each sample were tested with an initial distance between the grips of 50 mm. A speed of 5 mm.min⁻¹ was used to strain the specimens in order to record the Young's modulus and 100 mm.min⁻¹ for the elongation at break.

3.2. Charpy Impact

The impact strength of the different formulations was studied by means of a Charpy Impact test at room temperature. The formulations were injected into pieces with a width of 20 mm, a length of 60 mm and a thickness of 10 mm using the same injection machine and conditions described above. A notch was realized at the center of the specimen 45° wide and 2 mm deep. The impact test parameters were: mass = 0.917 kg, pendulum length = 225 mm, speed = 2.93 m.s⁻¹, fall angle = 150 ° and fall height = 302 mm.

3.3. Transmission Electron Microscopy (TEM)

Injected samples as described in section 3.1 were immersed in 1 wt% RuO₄ solution (water/sodium hypochlorite 50/50 : v/v) for 48 h. Ultrathin samples (around 70 nm thick) were obtained by microtomy with an oscillating diamond knife at room temperature. The samples were placed in a copper grid and then positioned under vacuum into the column of the

microscope (TEM PHILIPS CM120, CT μ Lyon, camera Gatan Orius200 2Kx2K) with an accelerating voltage of 120 kV.

3.4. Differential Scanning Calorimetry (DSC)

Melting temperature, melting enthalpy and degree of crystallinity were measured with a Differential Scanning Calorimetry (DSC) Q2000 machine (TA Instruments). In a hermetic aluminum capsules, 10 mg of the different samples were placed and a temperature ramp was applied: a first heating step from 25 °C to 250 °C at 10 °C.min⁻¹ and a cooling step until room temperature at the same speed, the same procedure was repeated at least twice. It is possible to determine the degree of crystallinity of a polymer by differential scanning calorimetry by calculating the melting enthalpy (ΔH_m) and comparing this value to the melting enthalpy of a theoretical 100% crystalline PP ($\Delta H_{m\infty}$), as showed in the equation that follows:

$$\%Crystallinity = \frac{\Delta H_m}{\Delta H_{m\infty}} \times 100$$

With $\Delta H_{m\infty} = 200 \text{ J.g}^{-1}$ ²⁷

3.5. X-rays Measurement (WAXS)

X-rays scattering at wide angles (WAXS) were performed on 1 mm slices of a dumbbell specimen, injected such as described for the mechanical properties. The measurements were carried out at the Centre de Diffractométrie – CLEA in Lyon in transmission mode with an Oxford Gemini A Ultra diffractometer using a nickel filtered copper radiation (wave length = 0.154 nm). The WAXS analyses allow us to study the different crystalline phases present in the PP. The PP used here presents at first only α form crystals.

3.6. Fourier-Transform Infrared Spectroscopy (FTIR)

The infrared transmission spectra of solid samples were obtained thanks to Smart OMNI transmission (Thermo Fischer Scientific, 64 scans). A film (with a thickness between 30 and 40 μm) was prepared under hot press at 200°C for each sample.

RESULTS AND DISCUSSION

4.1. Epoxy based thermosetting synthesis and chemical mechanisms

Figure 2 shows the morphology of the reactive blend PP+26wt%(DER671+DEH84) (A) and PP+20wt%PP-g-MA+26wt%(DER671+DEH84) (B). The aim here is to evidence the important role of the compatibilizer in the final morphology.

Actually, the importance of a compatibilizer^{28,29} and its consequences on the final morphology in non-miscible polymer blends has been demonstrated in numerous publications. **Figure 2-A**, without PP-g-MA, shows a larger TS size dispersion with nodules with diameters up to 5 μm . In **Figure 2-B**, the TS domains are almost not identifiable because of low magnification applied. Thanks to complementary TEM analysis, we observe that for the sample without PP-g-MA (TEM A), the diameter of the TS particles is superior to 3 μm . However, on the micrograph for the compatibilized sample (TEM B) we can clearly identify smaller TS domains. We have a narrower distribution, several nodules of 0.5 μm diameter and even smaller nodules with the presence of PP-g-MA as compatibilizer are observed. The creation of these small domains thanks to PP-g-MA decreases the interfacial tension between the nodules and the PP matrix and tends towards a more stable and finer morphology. Note that the same type of morphology is observed for the blends with NBDA [SI-1].

Figure 2 : SEM micrograph of PP+26%wt(DER671+DEH84) (A) and PP+20wt%PP-g-MA+26%wt(DER671+DEH84) (B) and respective corresponding TEM micrograph (formulations stained with RuO_4)

Mazidi³⁰ et al., studied the impact of EPDM grafted with maleic anhydride (mEPDM) as a compatibilizer in a PP (matrix)/PA6 blend. The microstructure of the ternary blend is very similar to the one observed for our system, with a dispersed phase with a diameter inferior to the micron and with a thin interface between the two polymers, and they were able to measure the interfacial tension between PP/PA6, PP/mEPDM and PA6/mEPDM. The values at 230°C are around 5 mN.m^{-1} for the blends with mEPDM and almost three times higher for pure PP/PA6 blends. Thus, the presence of a compatibilizer significantly reduces the interfacial tension between two immiscible polymers.

Hu³¹ et al. also demonstrated the importance of a compatibilizer in the final morphology. In fact, during *in situ* synthesis of a PA6 in a PP matrix by reactive extrusion, 3-isopropenyl-R,R-dimethylbenzene isocyanate (TMI) grafted onto PP (PP-g-TMI) is introduced. PP-g-TMI initiated the creation of a copolymer PP-g-PA6 created simultaneously with the PA-6 synthesis and leads to its nanostructuration, with 80 nm diameter PA6 nodules.

In our case, this compatibilization can be explained by the creation of a chemical bond between PP-g-MA and the epoxy based thermosetting phase (one possible reaction is reported on the **Figure 3**). In order to qualify and quantify the nature of the minor phase/interface created, a Soxhlet extraction was carried out to separate the matrix from the TS based-phase.

Figure 3 : One possible chemical reaction between PP-g-MA and the amine reactant for DER671/NBDA system

First, we evaluated the Soxhlet efficiency on the systems without PP-g-MA. Therefore, the PP from non-compatibilized formulations PP+26wt%(DER671/DEH84) and PP+10wt%(DER671/NBDA) were selectively extracted by xylene. For both formulations, 95 wt% of the PP was extracted evidencing the efficiency of the solvent chosen³² with uncertainty estimated to be 5%. This same uncertainty was observed by Bream and Hornsby³³ during a Soxhlet extraction of PP/PP-g-MA in xylene.

These results were confirmed by DSC analysis as shown in **Figure 4** for PP+26wt%(DER671/DEH84) before (black curve) and after extraction (red curve). In both cases, we can observe a signal at 165°C corresponding to the PP melting and a signal at 75°C on the red curve corresponding to the T_g of the TS created. The melting signal corresponding to the

insoluble fraction after extraction has a lower intensity, confirming that the amount of PP was drastically reduced after extraction. The soluble part was also analyzed after solvent evaporation and the mass balance showed that almost all the PP was solubilized in the xylene.

Figure 4: DSC analysis of the initial sample PP+26 wt%(DER671+DEH84) (black) and of the insoluble fraction after Soxhlet extraction (red)

Infrared analyses were also carried out. In **Figure 5**, we can observe the FTIR spectra for the sample PP+26wt%(DER671+DEH84) before (black) and after (red) Soxhlet extraction and the DER671+DEH84 based-TS system (blue). Signals corresponding to the aromatic cycles vibrations from the DER 671 and DEH84 can be observed between 1450 and 1750 cm^{-1} . We can also observe signals corresponding to the stretch of C-O bonds visible at 1060 and 1220 cm^{-1} . Finally, the spectra present signals at 3000 cm^{-1} corresponding to the -CH, -CH₂ and -CH₃ elongations vibrations, therefore corresponding to the carbon chain of the DER 671 and the PP. These signals are more intense on the spectrum for the sample before extraction than on the one

the corresponding to the sample after the Soxhlet procedure due to the fact that most of PP was extracted. The spectra also show the corresponding signals of the pure TS system (blue). As we can notice, the signals corresponding to the $-CH$, $-CH_2$ bonds are even less intense on the spectrum for this sample than on the one for the sample after extraction, showing that a small amount of PP is trapped in the insoluble part and not only the $-CH$, $-CH_2$ corresponding to the TS are present in the sample.

Figure 5 : FTIR spectra of PP+26wt%(DER671+DEH84) before (black), after (red) Soxhlet extraction and the TS system DER671+DEH84 (blue), standard calibration with the peak at 1400 cm^{-1} .

The same procedure was applied to the formulations containing PP-g-MA: PP+20wt%PP-g-MA+26wt%(DER671/DEH84) and PP+15wt%PP-g-MA+10wt%(DER671/NBDA). Thanks to the mass balance (**Table 4**) we observe that, for the sample containing the DEH 84, 60 wt% of the total mass of the sample is insoluble and could not be extracted by the xylene. In fact, assuming that all PP-g-MA was consumed in order to create the interface component with the TS, we should theoretically obtain only 46 wt% of insoluble fraction (TS+PP-g-MA). Therefore, not all the PP was extracted. In **Figure 6**, both DSC thermograms for the samples before and after Soxhlet extraction present a melting signal associated to PP/PP-g-MA at 165°C. The T_g of the TS at 65°C is only visible on the thermogram for the sample after extraction since it is more concentrated in TS. We can then conclude that the TS, the PP-g-MA and a part of the PP could not be dissolved in the xylene. The DSC of the soluble part, which is mainly composed of PP after evaporation of the solvent, was realized. As expected, the curve obtained for this sample is exactly like the one for the single PP [**SI-2**] but with crystallinity degree around 35% instead of 42% for pure PP. For the sample composed of NBDA, the same scenario is observed but with 45wt% of insoluble fraction instead of 25% in theory (PP-g-MA+TS). Consequently, 20% of the PP could not be extracted in our experimental conditions and it is trapped in the thimble (**Table 4**).

Table 4: Mass balance (wt%) after extraction of PP by Soxhlet in a ternary blend PP/PP-g-MA/TS

Samples	PP-g-MA	TS	Insoluble (theoretical)	Insoluble (experimental)	PP trapped
PP+20wt%PP-g-MA+26wt%(DER671/DEH84)	20	26	46	60	14
PP+15wt%PP-g-MA+10wt%(DER671/NBDA)	15	10	25	45	20

Figure 6 : DSC analysis of PP+20wt%PP-g-MA+26wt%(DER671+DEH84) before (black) and after Soxhlet extraction (red)

The FTIR spectra for the sample PP+20wt%PP-g-MA+26wt%(DER671+DEH84) before and after Soxhlet extraction was also realized. As described before, the signals corresponding to the TS phase with the -C-O stretch (at 1060 and 1220 cm^{-1}) and the aromatic cycles vibrations (between 1450 and 1750 cm^{-1}) are visible. We can also observe the signals corresponding to the -CH, -CH₂, -CH₃ around 3000 cm^{-1} . As expected, these peaks are less intense on the spectrum for the sample after extraction. In fact, since most of PP was extracted the peaks corresponding to the -CH, -CH₂, -CH₃ bonds are mostly from the TS sample, therefore are less intense [SI-3].

The Soxhlet extractions and the chemical analysis carried out allowed us to conclude that a covalent bond between the TS and the matrix PP/ PP-g-MA was created. In fact, thanks to the mass balance we can see that after extraction not only the mass of PP-g-MA + TS was insoluble but also around 25 wt% (**Table 4**) of the total mass of the PP. We can then assume that all the

maleic anhydride from the PP-g-MA was consumed in order to create the interfacial component PP-g-TS.

The role of the compatibilizer was proved to be essential in the morphology of the blend and to have great influence in the chemical bonds of the material. It is now important to analyze how the TS was created in the PP molten state.

This part is dedicated to understand how the epoxy based thermosetting is *in situ* created in the PP matrix during the reactive extrusion and the role of the quite high concentration of the PP-g-MA. In order to argue this point, a complementary experiment was carried out, where the amine (NBDA) was introduced at respectively at $L/D = 17D$, $32D$ and $42D$ (**Figure 1**). TEM micrographs were observed to understand the evolution of the morphology.

In **Figure 7-A**, the morphology of PP+15wt%PP-g-MA+10wt%(DER671+NBDA) where NBDA is injected at $L/D = 45D$ is observed. Therefore, the reaction time between DER671 and NBDA will be quite short, around 10 s only. Even though the reaction time is limited, the conversion in TS can be considered to be complete. Actually, the kinetics' reaction of the TS (DER671+NBDA) was measured and the gel point is obtained at 200°C in less than 1 s. In **Figure 7-A**, we observe TS domains of 0.5 μm diameter with a thin interface between the two phases, smaller domains are also observed and are, for most of them, scattered in the matrix (blue circle). The **Figure 7-B** depicts the morphology obtained for the same formulation as A, but with NBDA injected at $L/D = 32D$. Once more, we observe TS nodules of on average 0.5 μm of diameter and well dispersed in the matrix, though the domains are less visible in the matrix and seem to be in small aggregates. In this case, the reaction time in the extruder is around 30 s. **Figure 7-C** depicts the morphology for the same formulation as before but with NBDA injected at the beginning of the extruder, at $L/D = 15D$, so in this case the reaction time between DER671 and the NBDA will be around one minute. The morphology of the sample is

very similar to the two previous one, the nodules have an average diameter of 0.5 μm and the interface seems thin and clear between the two domains. Nevertheless, smaller domains are also observed and are aggregated around the bigger nodules (blue circle). By comparing the **Figure 7-A and 7-C**, we can conclude that the repartition of the domains in the matrix is different and can be analyzed as the evolution of the morphology versus times of reaction. In the **Figure 7-A**, the smaller domains are dispersed in the matrix whereas in the **Figure 7-C**, they are aggregated around the bigger nodules. In fact, the earlier the NBDA is introduced, the more packed around the TS nodules the domains seem to be, letting us imagine that for a longer residence time in the extruder the domains are aggregating to the TS nodules. On the micrograph reported in the **Figure 8** at a smaller scale, this phenomenon is clearly evidenced, where small domains are all around the bigger TS nodules in the sample PP+10wt% PP-g-MA+15wt%(DER671+NBDA) with NBDA injected at 15D.

The DSC analyses of the three formulations were carried out and the point of injection of the NBDA has no influence in the crystallinity, melting point nor T_g of the sample [SI-4].

Recently, Oyama³⁴ et al. observed similar phenomenon for a blend composed of PP matrix, with poly(ether sulfone) (PES) nodules with a PP grafted with glycidyl methacrylate as compatibilizer (mPP). In fact, the smaller nodules were found to be mPP/PES copolymers that avoid the coalescence between the PES nodules.

This experiment allowed us to conclude that the reaction time between NBDA and DER 671 has an impact in the final morphology of the blend. We observed two populations of domains corresponding to the minor phase: large nodules and small domains which are aggregating to the larger ones with longer residence times in the extruder.

Figure 7: TEM micrographs of PP+15 wt% PP-g-MA+10 wt% (DER671+NBDA) with NBDA injected at (A) 45D, (B) 30D and (C) 15D.

Figure 8 : TEM micrograph of PP+10 wt% PP-g-MA+15wt%(DER671+NBDA) with NBDA injected at L/D = 15D

4.2. Degree of crystallinity and crystalline structure

DSC analyses allow us to calculate the crystallinity of the blends thanks to the melting signal. The PP pure has crystallinity degree of 42% and this amount is increased with the presence of PP-g-MA. In order to obtain the crystallinity related to the amount of matrix present in the sample, the crystallinities listed on **Table 5** refer directly to the mass of PP+ PP-g-MA. The crystallinity of the matrix decreases in the presence of TS. For the PP+20wt%PP-g-MA +26wt%(DER671+DEH84) blend, the crystallinity is of 30%, the lowest crystallinity degree for the highest amount of PP-g-MA and TS. This phenomenon is observed for the both nature of TS created and could be correlated to its concentration.

Table 5 : Crystallinity degree of the polyolefins part determined by DSC

Samples	% Crystallinity
PPH3060	42
PP+20wt%PP-g-MA	46
PP+20wt% PP-g-MA +26wt%(DER671+DEH84)	30
PP+9wt% PP-g-MA +12wt%(DER671+DEH84)	36
PP+15wt% PP-g-MA +10wt%(DER671+NBDA)	35

A specific study by WAXS was carried out in order to understand the influence of the creation of TS on the PP crystalline structure. **Figure 9** shows the WAXS patterns for the samples PP, PP+20wt% PP-g-MA, PP+15wt% PP-g-MA +10wt%(DER671+NBDA) and PP+20wt% PP-g-MA+26wt%(DER671+DEH84). The peaks are assigned to the α and β crystalline phases of the PP³⁵. The samples containing only PP and PP-g-MA evidenced peaks corresponding to α phase, the crystals in these samples are 100% under α form, the most stable phase. We can observe the characteristics α peaks corresponding to the plans (110) at 15° and 22°, (040) at 18° and (130) at 20°. In the presence of TS, we can observe a new peak around 17°corresponding to the appearance of the β -phase (300) of PP²¹. In fact, in **Figure 9-A**, we can observe that the

peak corresponding to the β -phase appears as a shoulder, the sample containing 10wt% of TS. In **Figure 9-B** the peak is more intense and clearer as the sample contains 26wt% of TS. By comparing both systems, it is clearly shown that its intensity is related to the concentration of TS created.

Recently, Liu³⁶ et al. showed that the amount of β -nucleating agent and the quantity of β -phase is related for PP matrix and poly(Acrylonitrile–Butadiene–Styrene) (ABS) as a minority phase. In fact, the more β -nucleating agent is introduced; the more β -phase crystals will appear. However, at some point a maximum is reached (1wt% for ABS in PP). Our results confirm this tendency.

Figure 9 : XRD patterns of PP (black), PP+20wt%PP-g-MA (red) and PP+15wt%PP-g-MA+10wt%(DER671+NBDA) (A-blue) and PP+20wt%PP-g-MA+26wt%(DER671+DEH84) (B-blue)

The presence of PP-g-MA as a compatibilizer will not only have an influence on the morphology and on mechanical properties, but also on crystalline structure which will itself

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3 have an influence on the mechanical properties. **Figure 10** reports WAXS diffractograms
4 obtained for two samples with and without PP-g-MA. The black curve corresponds to the
5 response for the PP+26wt%(DER671+DEH84) sample. It can be seen a light shoulder around
6 17° where the plan (300) corresponding to a β -form should be. On the other hand, the red curve,
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8 obtained with the sample containing 20wt% of PP-g-MA, we have a distinguished peak at this
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10 angle, letting us believe that not only the presence of TS generates a β -phase but also the
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12 compatibilization between the TS nodules and the PP matrix, therefore the presence of the
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14 interface component PP-g-TS. The same behavior was observed for the samples with NBDA
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25 This same phenomenon was observed by Lin³⁷ et al. for a PP/Polyamide 6 (PA6) blend. This
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27 study was carried with a PP with high content of β -phase, since it was nucleated by calcium
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29 carbonate (CaCO_3). WAXS patterns show that β -PP/PA6 blends have less β -form than β -
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31 PP/PA6/PP-g-MA blends. In fact, the absence of a compatibilizer will increase the interfacial
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33 tension between the two polymers, decrease the package effect and inhibit the β -crystallization
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35 effect on PP. Thus, it was possible to have high content of β -crystals in a β -PP/PA6/PP-g-MA
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37 by controlling the proportions of PP-g-MA.
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42 The compatibilizer will therefore play an important part in the amount of β phase generated
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44 during the synthesis by reactive extrusion of PP/PP-g-MA/TS blends.
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Figure 10 : XRD patterns of PP+26wt%(DER671+DEH84) (black) and PP+20wt%PP-g-MA+26wt%(DER671+DEH84) (red)

3.3. Mechanical properties

The mechanical properties are intimately related to the morphology and the crystallinity structure of a polymer blend. Indeed, since most of polymers blends are immiscible, the presence of nodules of different nature of the matrix can lead to defects that can have negative impacts in the tensile and impact strength and in the elongation at break. In this part we intend to elucidate the role of the creation of the epoxy based thermosetting phase, the PP-g-MA and the modification of crystalline structure on the mechanical properties.

In order to understand the effects of the compatibilizer in a macroscopic point of view, the tensile properties for both formulations studied before were investigated.

The tensile properties for the all the formulations are listed in **Table 6**.

Table 6 : Mechanical properties for PPH3060, PP+26 wt%(DER671+DEH84), PP+20wt% PP-g-MA+26wt%(DER671+DEH84), PP+10wt%(DER671+NBDA) and PP+15wt% PP-g-MA+10wt%(DER671+NBDA)

Samples	Young's Modulus (MPa)	σ_{break} (MPa)	Elongation at break (%)	Re (kJ.m ⁻²)
PPH3060	1640	20	40	6.5± 0.6
PP+20wt%PP-g-MA	1600	18	120	4.2± 0.8
PP+26wt%(DER671+DEH84)	2000	30	2	2.5± 0.6
PP+20wt%PP-g-MA+26wt%(DER671+DEH84)	2030	18	50	7.5± 0.4
PP+10wt%(DER671+NBDA)	1700	20	22	3.8± 0.5
PP+15wt%PP-g-MA+10wt%(DER671+NBDA)	1850	20	50	9.4± 0.7

As we can see, the Young's modulus of the four formulations with TS are increased, 23% for the formulation PP+20wt% PP-g-MA+26wt%(DER671+DEH84) and 14% for PP+15wt%PP-g-MA+10wt%(DER671+NBDA); the epoxy based thermosetting created *in situ* therefore affect positively this property. The introduction of thermosets in a thermoplastic matrix tends to create materials with good mechanical properties. Fine and Pascault³⁸ showed the increase of mechanical properties for poly(phenylene ether) (PPE) and a thermoset reactive blend which is controlled by the compatibilizer, a triblock poly(styrene-b-butadiene-b-methyl methacrylate) (SBM) and the morphology that is consequently created.

The role of PP-g-MA in the morphology was described before. Its presence also has a positive impact in the elongation at break.

In fact, as we can see **Table 6**, the elongation at break decrease drastically depending of the presence of the compatibilizer or not, going from 50% for the PP+20wt%PP-g-MA+26wt%(DER671+DEH84) sample down to 2% for PP+26wt%(DER671+DEH84) sample.

The poor interface between the TS nodule and the PP matrix in this last case is classically at the origin of such observation.

Another characteristic that will have an important role in the mechanical properties is the crystallinity structure of the blend. It is well known that β -phase has important consequences in mechanical properties, especially in reinforcing the resilience of the material^{20,21}. In fact, Xu³⁹ et al. showed that the spherulites in PP due to the β -phase were intercrossed by several fibrils, letting us believe that molecules intra and inter spherulite are linked. In our case, the presence of interface component PP-g-TS will reinforce this behavior.

Table 6 also shows the results of impact tests for samples with and without compatibilizer. We can see that the resilience increases for samples with PP-g-MA, therefore with PP-g-TS, going from 2.5 to 7.5 KJ.m⁻² for the samples with DER 671+DEH 84, for example.

Two main factors contribute to these results:

- With the compatibilizer the blend presents improved mechanical properties due to the control of interfacial adhesion²⁹
- The presence of PP-g-MA and the TS will also lead to a β -phase in the sample, major factor in the improvement of the resilience^{20,21}

In order to prove that the increase of the resilience is mostly due to the β -phase created by the formation of the TS, a last test was carried out. In fact, the samples that presented an important quantity of β -phase (PP+20wt%PP-g-MA+26wt%(DER671+DEH84) and PP+15wt%PP-g-MA+10wt%(DER671+NBDA)) were annealed at 135 °C for 12 h in an oven. In fact, the melting temperature of the β -PP is known to be lower than the α -PP³³(around 135°C instead 165°C for the α -PP). The goal is to melt only the β -phase of the matrix, so that it can

recrystallize into an α conformation, so that only α -phase will be present in the sample⁴⁰. The complete elimination of the β -crystallinity was observed by WAXS (**Figure 11**), as we can see the black curve does not present anymore shoulder or peak at 17° , whereas for the same sample without thermal treatment a shoulder is clearly visible (red curve).

Once the crystalline structure was defined, the resilience tests were carried out. The mechanical properties associated to the annealed samples are listed in **Table 7** and compared to the ones for the initial samples.

Figure 11 : XRD patterns of PP+15wt%PP-g-M +10wt%(DER671+NBDA) (red) and PP+15wt%PP-g-MA+10wt%(DER671+NBDA) annealed at 135 °C for 12 h (black).

Table 7 : Mechanical properties and crystalline conformations for different samples (annealed or not)

Samples	Phase	Re (kJ.m ⁻²)
PPH3060	α	6.5 ± 0.6
PP+20wt%PP-g-MA	α	4.2 ± 0.8
PP+20wt%PP-g-MA+26wt%(DER671+DEH84)	α + β	7.5 ± 0.4
PP+15wt%PP-g-MA+10wt%(DER671+NBDA)	α + β	9.4 ± 0.7
PP+20wt PP-g-MA+26wt%(DER671+DEH84 24h at 135 °C	α	3.2 ± 0.3
PP+15wt%PP-g-MA+10wt%(DER671+NBDA) 24h at 135 °C	α	3.8 ± 0.4

As we can see, the resistance to an impact decreases importantly for the annealed samples, going from 7.5 to 3.2 kJ.m⁻² for the sample with DEH84. We can therefore conclude that the appearance of the β-phase is responsible for the improvement of the resilience.

The same observations were noticed by Chen⁴¹ and al. with a homopolymer PP. The PP presenting only α-phase presents fracture energy of 6.2 kJ.m⁻² and the one with 100% β-phase 9.3 kJ.m⁻². The β-phase is therefore at the origin of the important increase of the resilience in PP reinforced by TS nodules.

4. CONCLUSION

First, the synthesis of the TS in the molten PP matrix was studied, showing the creation of a covalent bond between the TS and the PP via the use of PP-g-MA. We also observed the morphology presented by the TS as nodules of 0.5 μm diameter but equally the presence of “domains” which should be composed of TS/ PP-g-MA and are an interface component PP-g-TS. The synthesis of TS in a polyolefin matrix has an impact not only on the morphology and

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3 mechanical properties but also on the crystalline structure. Actually, this work evidenced that
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5 there is an intimate relation between morphology, compatibilization, mechanical properties and
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7 evolution of crystalline structure.
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11 The mechanical properties analyzed strengthened once more the role of PP-g-MA. The
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13 *in situ* formation of PP-g-TS created at the PP/TS interface via PP-g-MA improves the
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15 elongation at break and the resilience. Young's modulus is improved by the presence of TS. In
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17 fact, the PP-g-MA not only ensure a better compatibility between TS and PP but will also refine
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19 the nodules distribution creating a more homogenous material. There is therefore an important
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21 relation between morphology, mechanical properties and bond between the two phases.
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27 Nevertheless, the important increase for some samples of the resistance to an external
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29 impact was not expected since the presence of TS creates a default that leads to the propagation
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31 of cracks but the appearance of interface component PP-g-TS tends to reduce this aspect.
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33 Another phenomenon is therefore at the origin of this reinforcement. An investigation of the
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35 crystalline structure was carried out and the presence of a new crystalline form was detected on
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37 the presence of high amount of TS, the β -phase. The influence of PP-g-MA was once more
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39 proved since its presence induced the increase of β -phase. The epoxy based thermosetting
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41 created *in situ* is not only able to reinforce the tensile properties but will also be a β -nucleating
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43 agent, promoter of the crystallization under β -form and not under α -form.
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ABBREVIATIONS

ΔH_m	Melting enthalpy
$\Delta H_{m\infty}^\circ$	Melting enthalpy of a theoretical 100% crystalline PP
σ_{break}	Tensile at break
DEH 84	Epoxyde resin DEH 84
DER 671	Epoxyde resin DER 671
DGEBA	Bisphenol A diglycidyl ether
DSC	Differential Scanning Calorimetry
FTIR	Fourier-Transform Infrared Spectroscopy
MFI	Melt flow Index
M_n	Number Average Molecular Weight
M_w	Weight Average Molecular Weight
NBDA	Diamine norbornane
PP-g-MA	Polypropylene grafted maleic anhydride
Re	Resilience
T	Temperature
TS	Epoxy based thermosetting
TEM	Transmission Electron Microscopy

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2		
3	T_m	Melting temperature
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5	T_g	Glass transition temperature
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7	TP	Thermoplastic
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9	WAXS	X-rays scattering at wide angles

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Supporting informations consisting in five figures (S1 to S5 respectively) are dealing with TEM Images of PP+15wt%PP-g-MA+10wt%(DER671+NBDA) (**Figure S1**), DSC of the soluble part of the sample PP+20wt%PP-g-MA+ 26wt% (DER671+DEH84) after Soxhlet extraction in xylene (**Figure S2**), FTIR spectra of PP+20wt%PP-MA+26wt%(DER671+DEH84) before (black) and after (red) Soxhlet extraction in xylene (**Figure S3**), DSC of PP+15wt%PP-g-MA+10wt%(DER671+NBDA) with NBDA injected at L/D = 17D (black), L/D = 32D (red) and L/D = 42D (blue) (**Figure S4**) and XRD patterns of PP+26wt%(DER671+NBDA) (black) and PP+20wt%PP-g-MA+26wt%(DER671+NBDA) (red) (**Figure S5**).