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Melt radical grafting of diethylmaleate and maleic anhydride onto oligoamide-11 (OA11) and polyamide-11 (PA11) in presence of acyloxyimide derivatives: toward the compatibilization of PA11/EVOH blends

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ABSTRACT

For the first time, the **melt radical** grafting of diethylmaleate (DEM) and maleic anhydride (MA) onto oligoamide-11 (OA11) and polyamide-11 (PA11) was performed in presence of new acyloxyimide derivatives in the temperature range 190°C-250°C in an autoclave and a mini-extruder, respectively. The DEM grafting degree was studied as a function of reaction temperature, the DEM concentration, the acyloxyimide concentration and its chemical structure. The degree of grafting of DEM was determined by ¹H NMR and we obtained a DES (diethylsuccinimate) functionalization degree (FD) as high as 9 mol% onto OA11 when using tBu-NAPI as H-abstractor at 230°C. **However**, the transposition of this grafting reaction

at a pilot scale did not permit to obtain such a high DES FD while the morphological study of PA11/EVOH blends with the grafted copolymer did not significantly improve the adhesion between the two phases.

Keywords

Melt Radical grafting ; polyamide-11 ; H-abstractors

1. Introduction

The melt radical addition of monomers such as maleic anhydride, diethylmaleate and vinyltrialkoxysilanes to saturated polymer chains yields functional derivatives that are valued for the layer in co-extrusion, blend compatibilization and filler reinforcement applications [1-7]. In this way, the reactive extrusion technique has proved to be an effective way to introduce a variety of functional groups in macromolecular chains without the use of any solvent [1, 8]. In the latter case, peroxides are usually used to abstract hydrogen atoms onto the polymer backbone at high temperature ($T > 160^{\circ}\text{C}$ to reach convenient viscosity of the polymer under shearing) leading to the formation of radical sites on the polymer backbone that may initiate the graft copolymerization of a monomer [9, 10]. However, the use of peroxides does not permit to control the final macromolecular structure because it leads to side reactions such as B-scission (polypropylene) and coupling reactions or cross-linking among macroradicals (polyethylene) [11-16]. In contrary, when using diethylmaleate (DEM) as monomer, crosslinking and coupling reactions are totally prevented in presence of PE as polymer matrix because hydrogen transfer reactions between DEM-based macroradicals and PE chains [17, 18]. Thus, nitroxyl ethers (NORs) based radical generators were developed and their activity is based on their thermolysis which leads to the formation of either alkoxy and aminyl radicals or alkyl and nitroxyl radicals, as discussed by Pfaender [19, 20]. For example, the

nitroxyl ether Irgatec 76 (CIBA) was used for the free radical modification of polyolefins by maleic anhydride with a very high efficiency at processing temperatures above 250 °C [19]. Recently, a new family of radical initiators based on the N-acetoxyphtalimide (NAPI) was designed and these compounds are supposed to produce acyl and cyclic amidinyl radicals upon heating at high temperature ($T > 190$ °C) and the latter species are claimed to be a good alternative to peroxides molecules [21-24]. In particular, we have shown that NAPI was a better hydrogen abstractor than di-cumyl-peroxide in presence of polyethylene at 200°C and permitting us to keep under control the undesired polyethylene crosslinking reactions [24].

In case of polyamide-based materials, the melt surface modification of polyamides is not usual to prepare grafted copolymers which may be useful as compatibilizing agents for polymer blends and may improve physical and chemical properties such as weather and heat resistance [25]. Indeed, most of the work is based on the chemical modification of polyamides with different initiator systems and using solvent such as ethanol and dioxane [25-28].

Nevertheless, a few years ago Passaglia et al [29, 30] described the in situ-free radical grafting of polyamides in the melt by using functional agents in the presence of peroxides. However, it was shown that the active free radicals produced by the thermal decomposition of peroxides are responsible for branching [29].

Herein, for the first time we have studied the melt functionalization oligoamide-11 and polyamide-11 with dethylmaleate in presence of new grafting agents producing very efficient cyclic amidinyl radicals toward H-abstraction. Indeed, it is expected that this new grafting agents will produce new functionalized polyamides with a high functionalization degree that can be used as compatibilizing agent in PA11/EVOH blends. We have studied grafting reactions in regards to hydrogen abstractor chemical structures, their concentration, the reaction temperature and the monomer concentration and using an autoclave for oligoamide-11 and a microextruder for polyamide-11. The modified oligomers and polymers were

analysed by nuclear magnetic resonance (NMR) spectroscopy. Finally, the effect of the incorporation of DEM-grafted-PA11 in PA11/EVOH blends at different concentrations was evaluated by the use of scanning electronic microscopy.

2. Experimental

2.1. Materials

The oligoamide-11 (3-4 units) and the Rilsan® polyamide 11 were provided by Arkema. Diethylmaleate (99%, Aldrich) and Dicumyl peroxide (DCP, Aldrich) were used without any further purification. All other solvents were used as received.

The phthalimide-based H-abstractors (NAPI-, NANPI-, NASI-derivatives) were easily prepared according to procedures described in the literature [31-33].

2.2. Methods

2.2.1. Grafting of diethylmaleate (DEM) onto oligoamide-11 (OA11) and polyamide-11 (PA11) in an autoclave and a mini-extruder in presence of acyloxyimide derivatives

For the chemical modification of OA11, the reaction is carried out in a 450 mL autoclave (Parr) equipped with temperature and pressure devices. In a typical process, 50 g of OA11, DEM (4.6 mL, 11.5mol%), NAPI- or NANPI- or NASI-derivatives (0.74-0.95g, 1.46 mol%) were added simultaneously in the autoclave at temperatures of 190°C for 60 min and 230°C for 7.5 min to ensure fully decomposition of NAPI-, NANPI- and NASI-derivatives. The unreacted products (DEM and decomposition products) were extracted from the modified materials with boiling acetone.

For the chemical modification of PA11, 5 g of PA11, DEM (0.5 mL, 11.5mol%), NAP- or NANP- or NASI-derivatives (0.074-0.095g, 1.46 mol%) were added in a preheated mini-

extruder (Thermo Scientific HAAKE™ MiniCTW micro-conical twin screw compounder, 7 ml) at a screw speed of 60 rpm and a temperature of 110°C. This type of extruder allowed us to control the processing residence time from the recirculation of the molten polymer in the chamber. After 20 min., the temperature was increased to 190°C (or 230°C) for 60 min or 7.5 min, respectively. The unreacted products (DEM and decomposition products) were extracted from the modified materials with boiling acetone.

2.2.2. Grafting of diethylmaleate (DEM) and maleic anhydride (MA) onto polyamide-11 (PA11) in an extruder in presence of acyloxyimide derivatives

The grafting reaction of DEM and MA onto PA11 in the molten state was performed in an intermeshing co-rotating twin-screw extruder (LEISTRITZ LSM 30-34) at a rotor speed of 250 rpm and a processing temperature of 290°C. The concentration of DEM and MA was 3wt% while the H-abtractor one was 1.60wt%. Then, the corresponding material was dried under vacuum at 120°C for two hours to eliminate the residual monomer.

2.2.3. Polymer blends

The preparation of the polymer blends (Table 5) was performed at 230°C for 5 min in a preheated mini-extruder (Thermo Scientific HAAKE™ MiniCTW micro-conical twin screw compounder, 7 ml) at a rotor speed of 60 rpm.

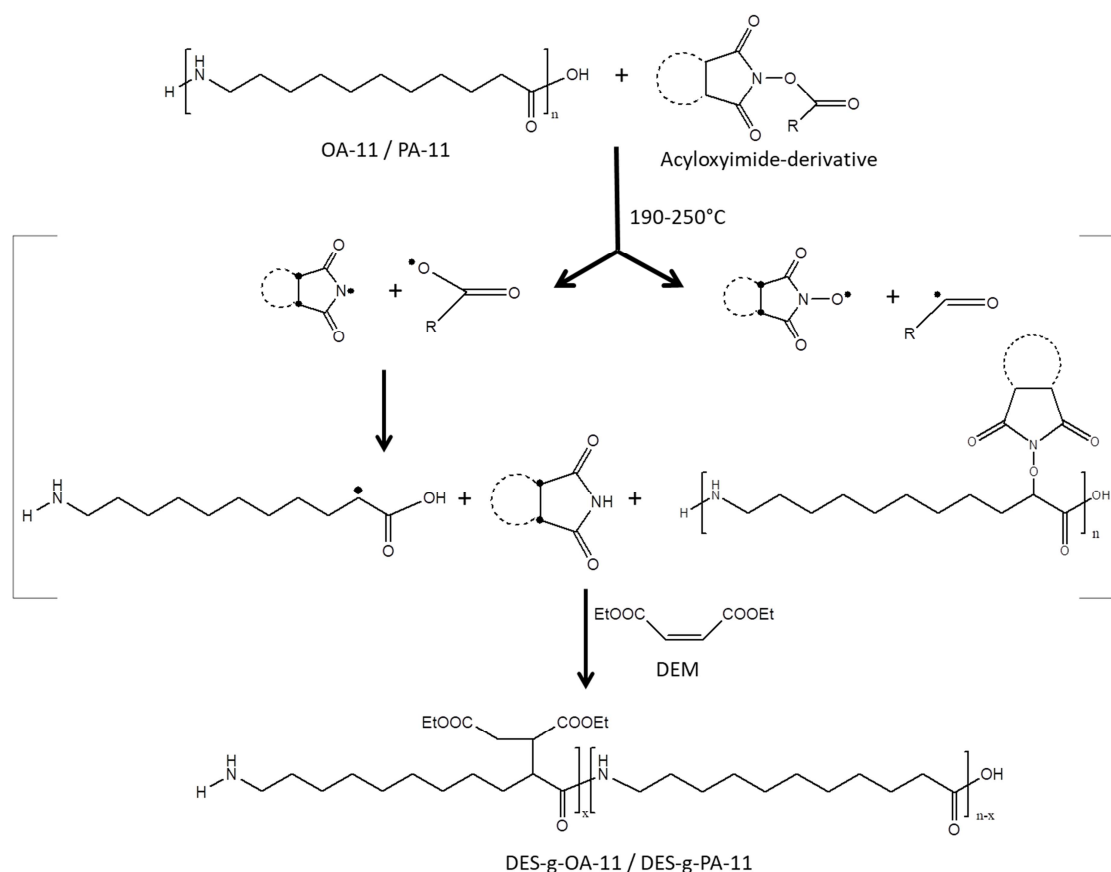
2.3. Characterizations

H NMR spectra for polymeric samples were recorded on a Bruker ALS 300 spectrometer, operating at magnetic field of 9.4 T. The experiments were performed at room temperature using 5 mg of polymer diluted in 1 mL of in D₂SO₄. A spectral width of 6410.3 Hz was used with a relaxation delay of 1.5 s and 512 scans per point.

Scanning electron microscopy (SEM) images were taken by a commercial FEI Quanta 250 FEG. The polymer blends were fractured in liquid nitrogen and deposited on carbon tape. The observation was made at 15 kV. In a typical experiment, each sample was cut in 1 mm thick band, cooled in liquid nitrogen and fractured inside a cryotransfer GATAN Alto 2500 at -150 °C using a scalpel. The observation was done in cryo mode at -150 °C with an accelerating voltage of 2 kV.

3. Results and discussion

The original biosource PA (PA11, Rilsan) are becoming increasingly popular in many application areas such as in automotive, electronics and sports. Since PA11 displays good processability, high impact strength at low temperature and low moisture absorption, it has been developed for various applications including fuel lines in automotive, pipe for oil and gas applications, air break hoses for truck and medical appliances. However, to design new applications, it may be desirable to develop novel PA11-based alloys and blends. In this context, scanning the factors influencing the selectivity toward hydrogen abstraction on nylon 11 and other side reactions is of particular interest. Hence, amidinyl-based molecules so-called acyloxyimide have been selected to generate radicals in presence of a commercially available OA11 and PA11 from Arkema (Scheme 1).



Scheme 1. Mechanism of DEM grafting onto OA11 and PA11 in presence of acyloxyimide compounds.

Indeed, the thermal homolytic decomposition temperatures of acyloxyimide affording potential hydrogen abstractors are in the range of temperatures close to the ones expected during reactive extrusion of polyamides, typically few minutes at 190-250°C. As shown in scheme 1, the DEM grafting position benefiting from the electron attractive $\text{C}=\text{O}$ group is preferred [29]. Passaglia et al. [30] studied the grafting of DEM onto PA-6 in presence of dicumyl peroxide as H-abstractor and they obtained the higher DEM grafting degree (4.3 mol%) when using 0.73 mol% of DCP and 11.5 mol% of DEM at 230°C.

3.1. Grafting of DEM onto OA11: optimization of the experimental conditions

Herein, considering that one mole of dicumyl peroxide generates two moles of radicals at full efficiency, OA11 was first modified in presence of 1.46 mol% of NAPI (two fold order of DCP, Fig. 1) as H-abstractor and 11.5 mol% of DEM at 230°C.

After reaction, the resulting polymeric sample was extracted with boiling acetone to remove the unreacted DEM and analysed by ^1H NMR (Fig. 1).

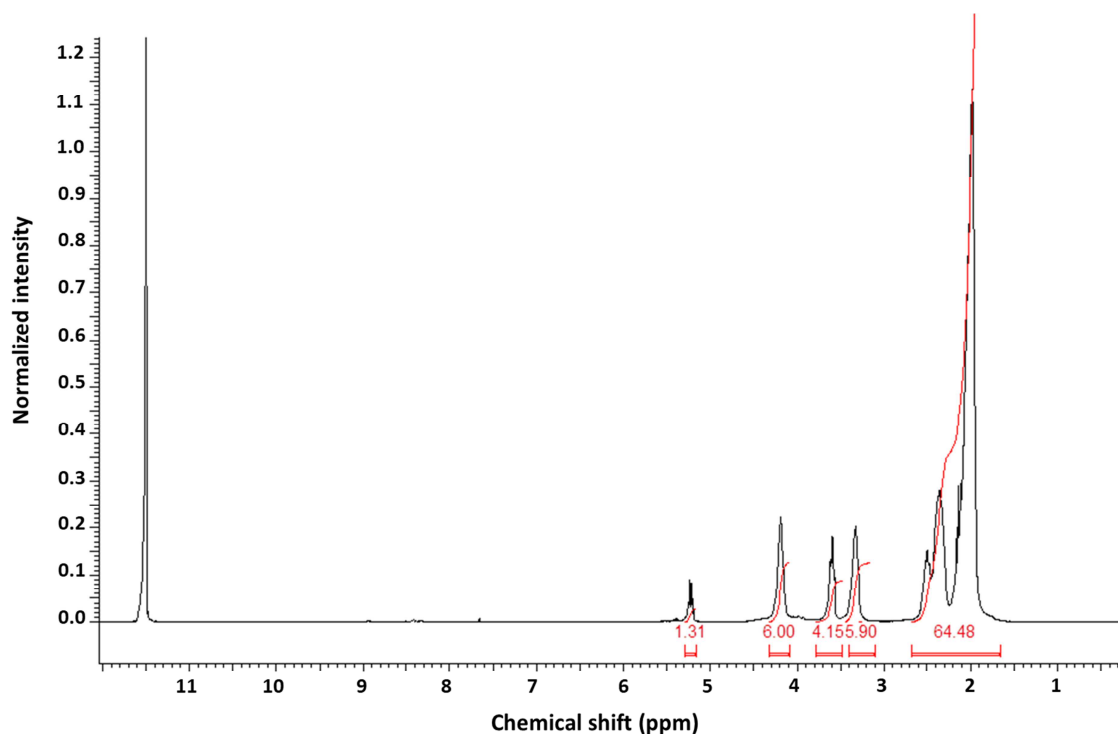


Fig. 1. ^1H NMR of DEM-g-OA11 in D_2SO_4 , as solvent.

Fig. 1 confirms the grafting of diethylsuccinate (DES) groups onto the oligoamide backbone with the presence of a characteristic resonance located at 4.2 ppm ($\text{O}-\underline{\text{CH}_2}-\text{CH}_3$, ethoxyl groups of DES) [30]. Considering the integral value of the latter peak, we have calculated the degree of functionalization (FD), as the number of DES groups per hundred OA units and we obtained a value of 8, corresponding to a grafting yield of 70%. A similar functionalization degree was obtained by using DCP at temperatures of 190°C and 230°C. Then, we have checked the optimal experimental conditions for the grafting of DEM onto OA11 by varying

the reaction temperature, and both the DEM and the NAPI concentrations. The results are summarized in Table 1.

Table 1. DES functional degrees and their corresponding grafting yields as a function of NAPI concentration, DEM concentration and temperature.

Entry	NAPI (mol%)	DEM (mol%)	T (°C)	FD (%) ^a	Grafting Yield (%)
1	1.46	11.5	230	8.4	70
2	1.46	11.5	250	7.4	65
3	0.73	11.5	250	4.9	45
4	0.73	11.5	230	3.8	35
5	0.37	11.5	230	3.8	35
6	2.92	11.5	230	8.4	70
7	1.10	11.5	230	7.0	65
8	1.46	23.0	230	11.8	50
9	1.46	17.5	230	10.2	60
10	1.46	6.2	230	5.9	95

^aDegree of functionalization calculated from ¹H RMN spectra in D₂SO₄

Regarding entries 1 to 4, we can conclude that increasing the temperature from 230°C to 250°C leads to a decrease of the DES functionalization degree (about 7%) while the presence of by-products is detected by ¹H NMR. On the other hand, the use of a lower NAPI amount (0.73%) dramatically reduces both the DES functionalization and the grafting yield whatever the temperature is (230°C or 250°C). For clarity, all the results reported in Table 1 have been plotted on graphs (Fig. 2) allowing us to determine the optimal grafting conditions.

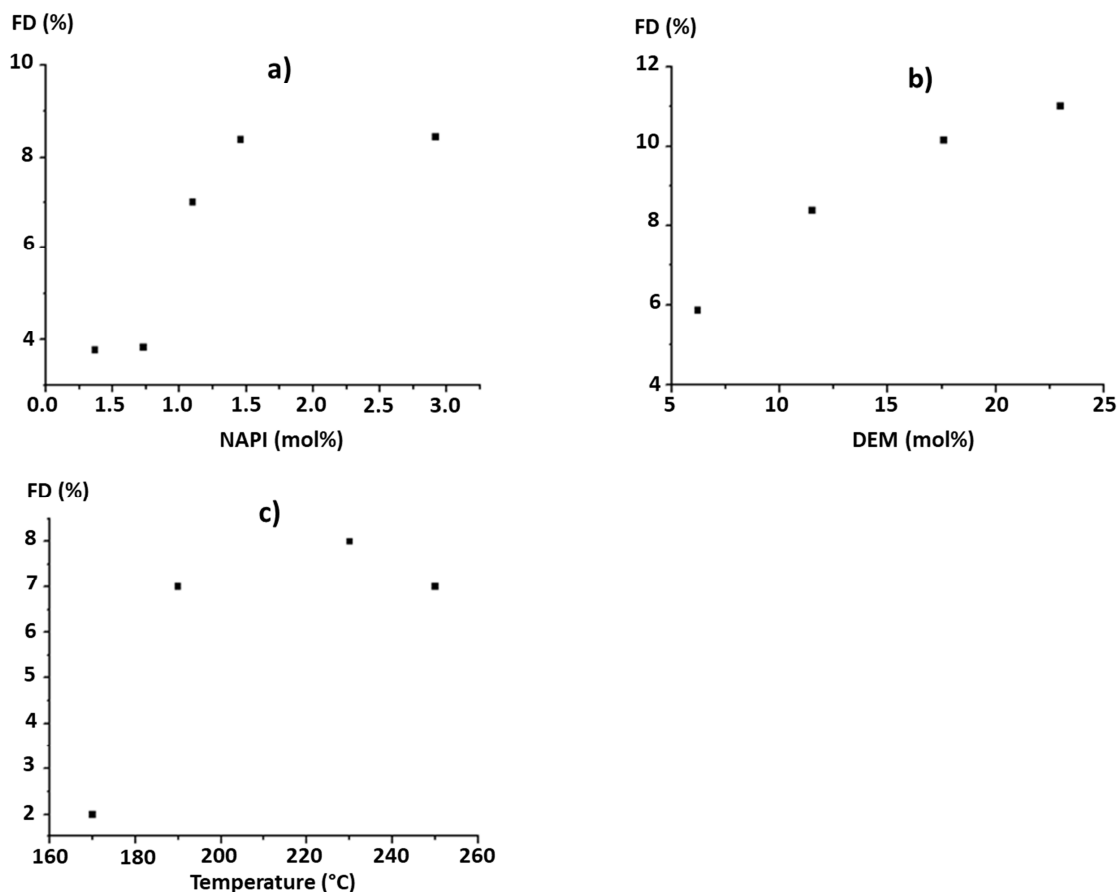
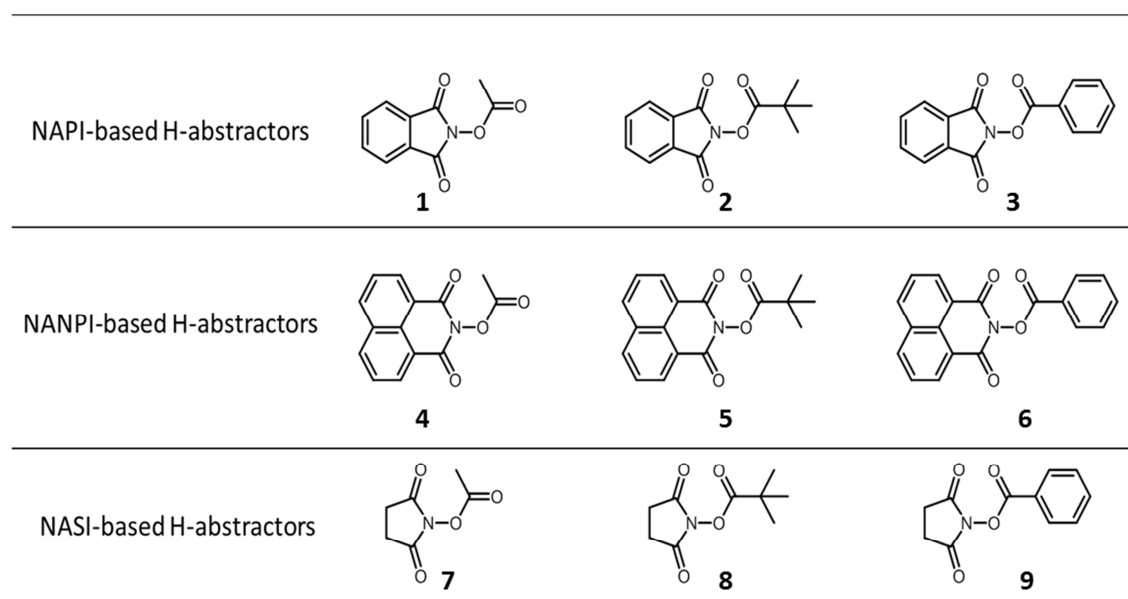


Fig. 2. Effect of a) NAPI concentration at 230°C, b) DEM concentration at 230°C and c) reaction temperature onto the FD of DES onto OA11.

Indeed, Fig. 2a clearly shows that the use of low amounts of NAPI (between 0.37 mol% and 0.73 mol%) do not permit to obtain a DES functionalization degree higher than 5% at 230°C. Moreover, a plateau is obtained from a NAPI concentration of 1.46 mol% with a functionalization degree of 8% (Fig. 3a). In addition, it can be observed from Fig. 2b that the DEM concentration may tailor the DES FD at 230°C with DES FD varying from 5.9% to 11.8% by increasing the DEM concentration from 6.2 mol% to 23.0 mol% while the higher grafting yield (95%) is obtained for the lowest DEM amount (6.2 mol%). The influence of temperature onto the DES FD has also been studied (Fig 3c) and it confirms that the optimum temperature is 230°C when using NAPI and DEM amounts of 1.46 mol% and 11.5 mol%,

respectively. Considering these results and in order to enhance the hydrogen abstraction ability of NAPI onto OA11, novel NAPI-derivatives were designed (**Scheme 2**). In particular, we investigated the use of phthalimide- (structures 1-3), naphthalimide- (structures 4-6) and succinimide- (structures 7-9) derivatives in the OA11 molten state at processing temperatures of 190 °C and 230°C and residence times of 1h and 30 min, respectively, to ensure their complete thermal decomposition.



Scheme 2. Acyloxyimide H-abstraction agents based on N-acetoxy-phtalimide structure.

The results are summarized in Table 2 and it is observed a similar DES functionalization degree for all de H-abtractors at 230°C (7-9%) close to the value obtained with DCP (8%) while the use of a lower reaction temperature (190°C) leads to a huge decrease of the DES FD for most of the H-abtractors.

Table 2. DES functional degrees at 230°C and 190°C as a function of the H-abtractor chemical structure and using a DEM concentration of 11.5 mol%.

H-abstractor (1.46 mol%)	*FD (%) at 230°C for 7.5 min	*FD (%) at 190°C for 1h
NAPI (1)	8.4	7.0
tBu-NAPI (2)	8.1	4.2
Phe-NAPI (3)	8.9	5.3
NASI (4)	8.0	5.1
tBu-NASI (5)	9.0	8.1
Phe-NASI (6)	8.1	7.9
NANPI (7)	7.0	2.1
tBu-NANPI (8)	8.1	2.2
Phe-NANPI (9)	7.2	3.0
DCP	8.0	7.9

*Degree of functionalization calculated from ^1H RMN spectra in D_2SO_4

The melting points of NAPI-derivatives and NASI-derivatives are about 130°C and 190°C, respectively, while NANPI-derivatives do not exhibit any melting point before their degradations at temperatures above 250°C which may explain their similar reactivity at a temperature of 230°C. Moreover, the results obtained at 190°C suggest that each H-abstractor may tailor the DES FD at 190°C that is related to their different rate of decomposition in the corresponding reaction media.

From Table 2, it was concluded that the most efficient H-abstractors at both reaction temperatures 190°C and 230°C are NAPI (1), tBu-NASI (5) and Phe-NASI (6) which allow a DES FD similar to the one obtained with DCP.

3.2. Grafting of DEM onto PA11

Then, the grafting of DEM onto the PA11 was studied in the molten state using an intermeshing co-rotating twin-screw mini-extruder at a processing temperature of 190 °C for 1h to avoid too much DEM evaporation. It should be mentioned that the volatility of NAPI- and NASI-derivatives powders can be neglected during the grafting reaction because their

melting points are about 130°C and 190°C, respectively, suggesting very high corresponding boiling points. The results for some NAPI- and NASI-based H-abstractors are gathered in Table 3.

Table 3. DES functional degrees at 190°C for the grafting of DEM onto PA11 as a function of the H-abstractor chemical structure.

H-abstractor (1.46 mol%)	FD(%) ^a at 190°C
NAPI (1)	5.0
tBu-NAPI (2)	6.1
NASI (4)	1.5
tBu-NASI (5)	1.5
Ph-NASI (6)	1.5

^aDegree of functionalization calculated from ¹H RMN spectra in D₂SO₄

Surprisingly, it is observed that the NAPI derivatives are much more efficient than the NASI ones allowing a higher DES FD (approximately by a factor 4). It may be attributed to the lower solubility and/or a lower diffusion coefficient of NASI derivatives in the molten PA11. Indeed, as discussed before, the melting points of NAPI-based derivatives are about 130°C while the NASI-based derivatives ones are about 190°C. This behavior will be confirmed in a future work.

These operating conditions were finally partly used to make a pilot scale test in a twin-screw extruder at a temperature of 290°C and a flow rate of 1 kg/h (required experimental conditions for Arkema, CERDATO) with maleic anhydride (MA) and DEM as monomers. From the ¹H NMR analyzes (figures S2 and S3), we calculated a MA FD of 5.3mol% and a DES FD of 2.3 mol%. The latter low DES FD in comparison with the one obtained at 190°C in a mini-extruder (i.e. 5 mol%) may be attributed to high DEM evaporation during the grafting reaction at 290°C and we were not able to compare this value with the one obtained

in a presence of a peroxide such as luperox 101 (2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane) or DCP because of their too low half time life at this temperature (less than 1 s). Even if the FDs are lower than the lab experiments, acyloxyimide derivatives allowed to prepared unprecedented functionalized PA11 using industrial conditions.

3.3. Effect of the incorporation of MA-g-PA11 and DEM-g-PA11 into PA11:EVOH blends

The grafted copolymers synthesized at a pilot scale (MA-g-PA11 and DEM-g-PA11) grafted DEM) were finally used as compatibilizing agents at different weight content in PA11/EVOH (ethylene-vinyl alcohol copolymer) blends (Table 4).

Table 4. Compositions of the PA11/EVOH-based blends.

Entry	PA11 (wt%)	EVOH (wt%)	MA-g-PA11 (wt%)	DEM-g-PA11 (wt%)
1	65	30	5	-
2	65	30	–	5
3	65	25	10	-
4	65	25	-	10
5	80	15	5	-
6	80	15	-	5

For the use of MA-g-PA11, it is also expected that it reacts with EVOH producing *in situ* a grafted EVOH-based copolymer. In addition, in order to probe the impact of the presence of the grafted copolymers on the rheological behavior and morphology of the studied polymer blends, we first carried out complex viscosity measurements on the homopolymers and the MA-g-PA11 compatibilizing agent (Fig. 3).

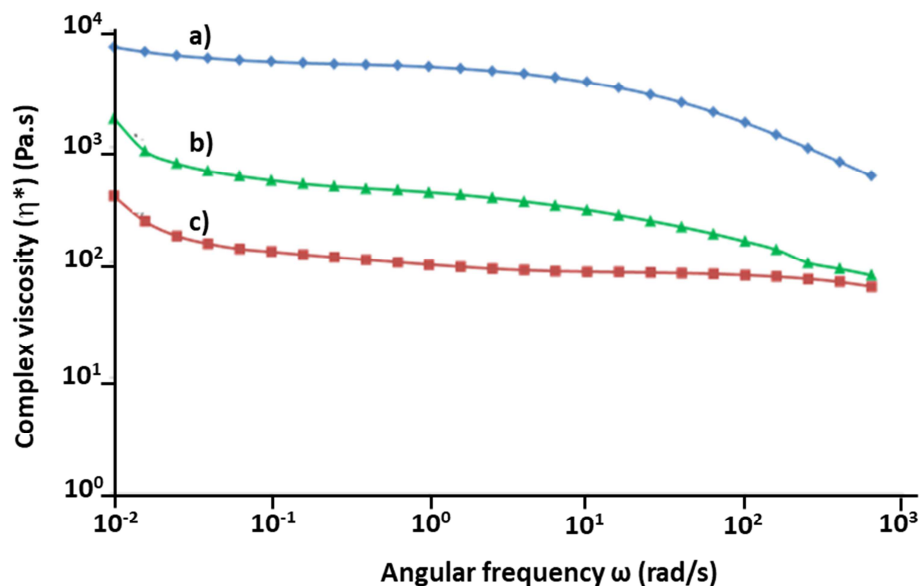
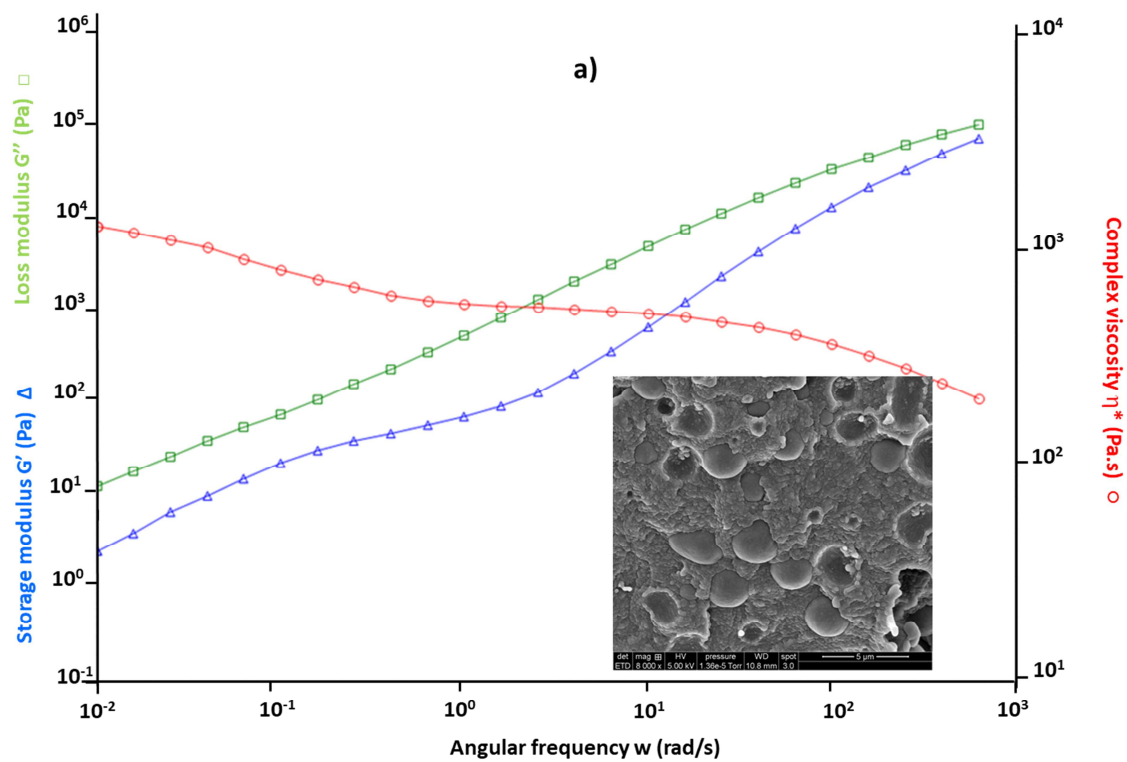


Fig. 3. Comparison of the complex viscosity behaviours of a)EVOH, b)MA-g-PA11 and c)PA11 as a function of the angular frequency.

At low frequency (0.1 rad / s), it can be observed that the complex viscosity of EVOH is 5500 Pa.s while PA11 displays a complex viscosity of 365 Pa.s. Moreover, it can be observed that the grafting of MA onto the PA11 increases its viscosity by a factor 5. Nevertheless, the rheological behavior of the various studied blends (Table 4) (with or without the grafted copolymers) are nearly the same so that it was not possible to demonstrate any significant influence of the presence of the grafted copolymer (Figure 4). For clarity, only the rheological behaviours and the SEM images of PA11/EVOH (65/35) and PA11/EVOH/MA-g-PA11 (65/30/5) (sample 1, Table 4) blends are presented.



Herein, it was shown that the grafting of monomers such as diethylmaleate and maleic anhydride onto oligoamide-11 and polyamide-11 is efficient when using acyloxyimide derivatives as H-abstractors. Under optimal experimental conditions, the DES FD was high as 9 mol% onto OA11 with tBu-NAPI as H-abstractor at 230°C in an autoclave reactor. The latter radical grafting reaction was then transposed to the grafting of DEM on PA11 at 190°C in a mini-extruder and we obtained a lower DES FD (6 mol%). Moreover, the grafting reaction at an industrial scale did not permit to reach such high DES FD (by a factor 2, below). This difference may be mainly attributed to extrusion rates and setpoint temperatures much higher than those used in the mini-extruder model study. Finally, the use of MA-g-PA11 and DEM-g-PA11 as compatibilizing agents for PA11/EVOH blends was not successful enough with both the presence of EVOH particles diameters ranging from 1µm to 2µm and EVOH particle footprints suggesting poor adhesion between the two phases. Future work will consist in optimizing the flow rate, the temperature and the amount of H-abstractors in order to obtain higher FD at a pilot scale and consequently a higher compatibilizing effect.

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SUPPORTING INFORMATION

Melt radical grafting of diethylmaleate and maleic anhydride onto oligoamide-11 (OA11) and polyamide-11 (PA11) in presence of acyloxyimide derivatives: toward the compatibilization of PA11/EVOH blends

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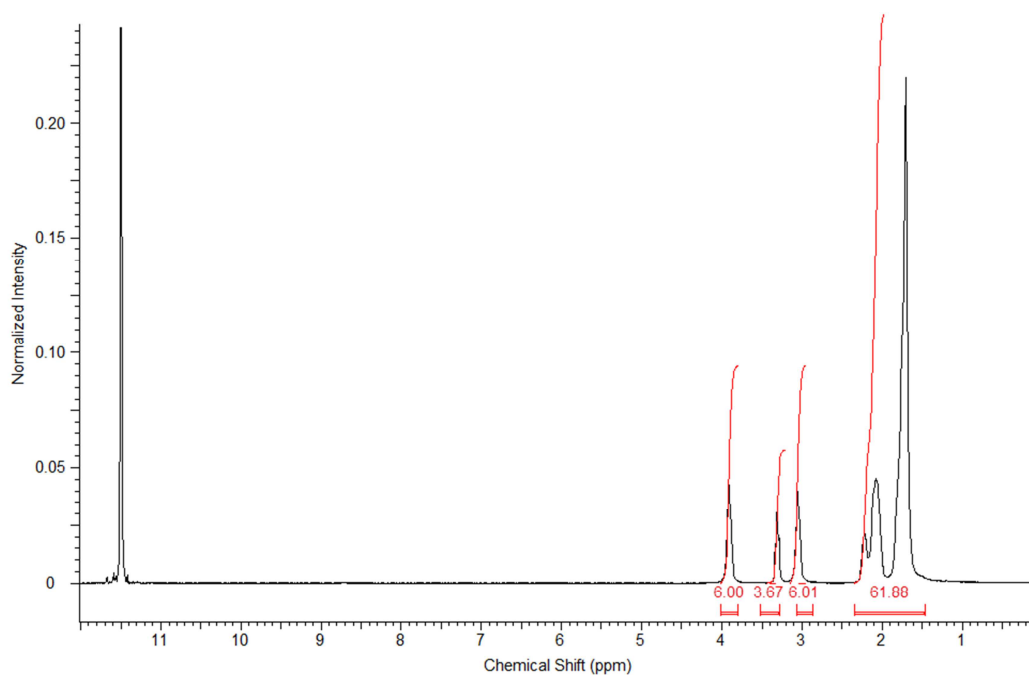


Fig. S1. ^1H NMR spectra of neat OA11 in D_2SO_4 , as solvent.

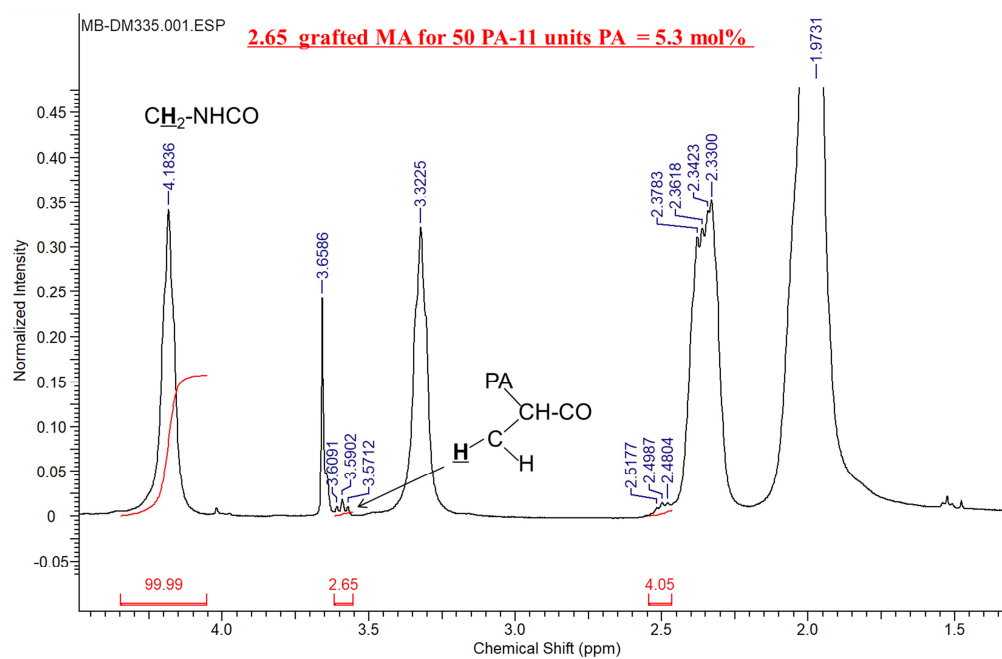


Fig. S2. ^1H NMR spectra of MA-g-PA11 in D_2SO_4 , as solvent.

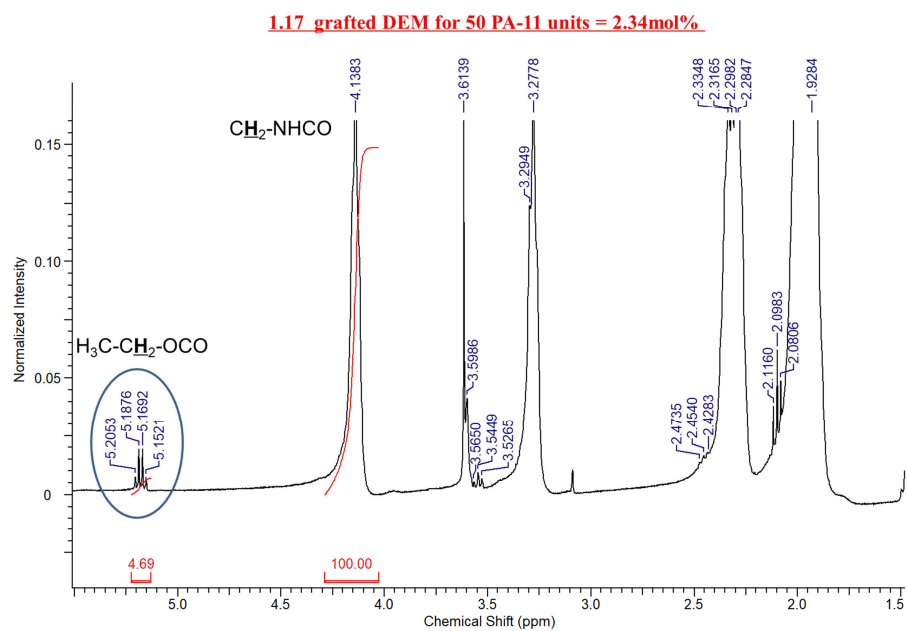


Fig. S3. ^1H NMR spectra of DEM-g-PA11 in D_2SO_4 , as solvent.

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