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Use of reactive polyetherimide to modify epoxy thermosets. I. Synthesis of an amino-grafted polyetherimide

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Abstract

The use of a nonreactive thermoplastic (TP) that is initially miscible and which phase separates during reaction has often been used to improve the toughness of epoxy networks. Most of the time no real improvement in fracture properties is obtained due to poor adhesion between phases. In this work the grafting of amino groups on the backbone of a polyetherimide (PEI) is studied. In order to avoid too high a degree of grafting and crosslinking of PEI, a synthesis in a dispersed medium is considered. Three amines are used: ethylene diamine (EDA), 1-2 aminoethyl-piperazine (AEP) and *n*-butylamine. The grafting reaction was characterized by FTIR, SEC and NMR. The influence of the drying and washing processes of the powder is shown. The degree of grafting is determined using both titration and nitrogen microanalysis and is in the range 1–5%. The glass transition temperatures of the amino grafted PEI decrease, almost linearly with the degree of grafting.

Keywords: Polyetherimide; Grafting; Pendant functionalization

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1. Introduction

High-temperature epoxy systems are widely used for composite materials in industry where properties such as high modulus, thermal stability, solvent resistance are required but the high level of crosslinking leads to brittle materials [1]. The incorporation of a nonreactive thermoplastic (TP) initially miscible which phase separates during epoxy reaction has often been used as a way to improve the toughness of thermosets (TS) since the early eighties [2]. Depending mainly on the initial composition and reaction temperature, the resulting thermoplastic-toughened epoxies may exist as TP-rich particles dispersed in TS matrix, bicontinuous or phase inverted morphologies. However, thermoset fracture toughness is significantly improved by adding a thermoplastic only when bicontinuous or inverted structures are generated [3]. When phase separation leads to thermoplastic-rich particles dispersed in a continuous epoxy–thermoset matrix, no improvement of fracture properties is obtained mainly due to poor adhesion and also mechanical stresses between thermoplastic and thermoset-rich phases

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[3,4]. To overcome such limitations different approaches to compatibilize thermoset/thermoplastic blends have been considered in existing literature.

The most developed approach consists in using a thermoplastic with reactive endgroups to improve interfacial adhesion [4]. This method allows to increase the initial miscibility between epoxy and thermoplastic products but no significant toughness improvement is found when the final blend morphology consists in thermoset-rich matrix [4]. Moreover, Auschra et al. [5,6] demonstrated that an improvement of interfacial adhesion does not imply an increase in the fracture strength. Another approach has been used by Girard-Reydet et al. [7] using a polyphenylene ether as thermoplastic and an epoxy–amine network. They extended the concept of compatibilization of immiscible thermoplastic blend to a thermoplastic–thermoset blend by using an emulsifying agent whose structure is a copolymer. The structure of the copolymer is composed of three blocks: one block miscible with the thermoplastic-rich phase, one block miscible and/or reactive with the thermoset-rich phase and one central block containing an elastomer not miscible with any of these two phases and which is located at the interface. Use of triblock copolymers was found to significantly improve fracture toughness of an epoxy–amine system [7]. The limitation of such an interesting process is that the efficient emulsifier is not always available or does not always exist.

An alternative approach involves the incorporation of pendant functionalized thermoplastics [8–12], which can react with thermoset precursors by covalent bonding. In the literature encouraging results on toughness improvement were obtained by Pak et al. [8] using as thermoplastic a polyethersulfone whose chains are grafted with amino groups, by Shin and coworker [10,11] using a polyetherimide, and by Yun et al. [12] using a polyimide, both modified by hydrolysis [10] or by amination [11,12]. All these authors found that an optimum degree of modification is needed to get a significant improvement of thermoset toughness. Too large compatibilization of the system decreases the toughness of the TS network [13] and it was demonstrated that phase separation between thermoset and thermoplastic compounds is necessary to have a reinforcement [3,13]. The thermoplastic grafting of reactive groups with thermoset can be realized either by synthesis of the pre-functionalized monomers and then their subsequent polymerization [8,10] or by direct modification of the thermoplastic [10–12]. However, concerning the grafting itself, the literature [10,12] does not give any information about the important parameters to be used to control it and it is far from obvious to obtain reproducible results in an heterogeneous medium. The initial miscibility and kinetic studies of such a PEI-modified epoxy system were already published [14–16].

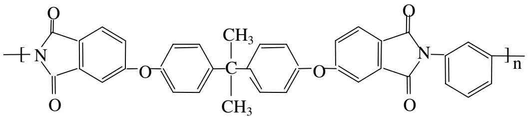
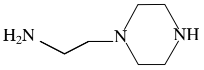
In part I of this present work, we describe the heterogeneous amination of PEI and the parameters influencing the grafting reaction and characterizations of modified PEI are presented. In part II, the amino modified PEI will be used as a toughening agent for an epoxy/amine thermoset system and the mechanical properties compared with the unmodified PEI.

2. Experimental

2.1. Materials

The thermoplastic to be grafted is a polyetherimide (PEI, ULTEM 1000 from General Electric) having a glass temperature transition of 210 °C and an average molecular weight $\overline{M}_n = 26\,000$ g/mol and $\overline{M}_w = 50\,000$ g/mol. PEI is used as a micronised powder whose average diameter is under 300 μm. Grafting agents used are amines with different functionality: ethylene diamine (EDA) supplied by Fluka, 1-(2-aminoethyl)-piperazine (AEP) and *n*-butylamine supplied by Aldrich (cf. Table 1). The dispersion media considered are acetone and ethanol because of their relatively low boiling point (respectively 56 and 78 °C) and because both are nonsolvent of PEI but solvent of the grafting agents, EDA, AEP and *n*-butylamine.

Table 1
Reagent formulae

Polyetherimide (PEI)	
Ethylene diamine (EDA)	$H_2N–CH_2–CH_2–NH_2$
n-Butylamine	$CH_3–CH_2–CH_2–CH_2–NH_2$
1-(2-Aminoethyl)-piperazine (AEP)	

2.2. Synthesis of pendant amino groups on the PEI backbone

PEI is not very reactive because its chemical structure is stabilized by mesomeric effect. It is however possible to have a reaction on imide groups with strong bases as polyamines which produces two amide groups as shown in the reaction 1 of Fig. 1, the unreacted amino group being then available as a pendant chain.

A synthesis in homogeneous or heterogeneous media is possible. The modification of PEI should not be complete and should not form a polyamide–amide resulting in a crosslinking as shown in reaction 2 of Fig. 1, and the degree of the grafting reaction should be low. The synthesis in dispersed medium is thus chosen, also to prevent the possible PEI crosslinking reaction [12,13].

The synthesis in dispersed media consists in making a dispersion of PEI in a PEI nonsolvent but which solubilizes the amine. Many of the parameters (initial size distribution of PEI powder, nature of dispersion medium and of grafting agents, concentration of reactants, time of reaction, temperature…) involved in the experiments are studied and allow the reaction to be controlled. The PEI is micronized into a powder and one of the drawbacks in the choice of synthesis in a dispersed media of PEI is that the modification can be superficial and unequally distributed. This problem is taken into account and influences the choice of the reactants.

One hundred (or 50) grams of PEI are dispersed in 2 l of acetone or ethanol at 60 or 80 °C with mechanical stirring. Amine (0.25 mol) is added to this mixture using a dropping funnel. The amination reaction time is fixed between 0.5 and 18 h to change the extent of modification. The mixture is filtered and dried *in vacuo* at 50 °C for 24 h [11]. Modified PEI is washed with 3 l of acetone divided into portions of 250 ml. After filtration, one drop of bromocresol green is added to the last portion of acetone to check that there is no residual amine. The PEI–NH_2 purified is dried *in vacuo* at 50 °C for 1 day. The amination is done with 14.95 g (0.25 mol) of ethylene diamine (EDA) or with 32.13 g (0.25 mol) of 1-(2-aminoethyl)-piperazine (AEP).

2.3. Techniques

Aminated PEI characterization is realized with FTIR spectroscopy (Nicolet), ^1H and ^{13}C nuclear magnetic resonance (Brucker AC 400MHz) (NMR) and size

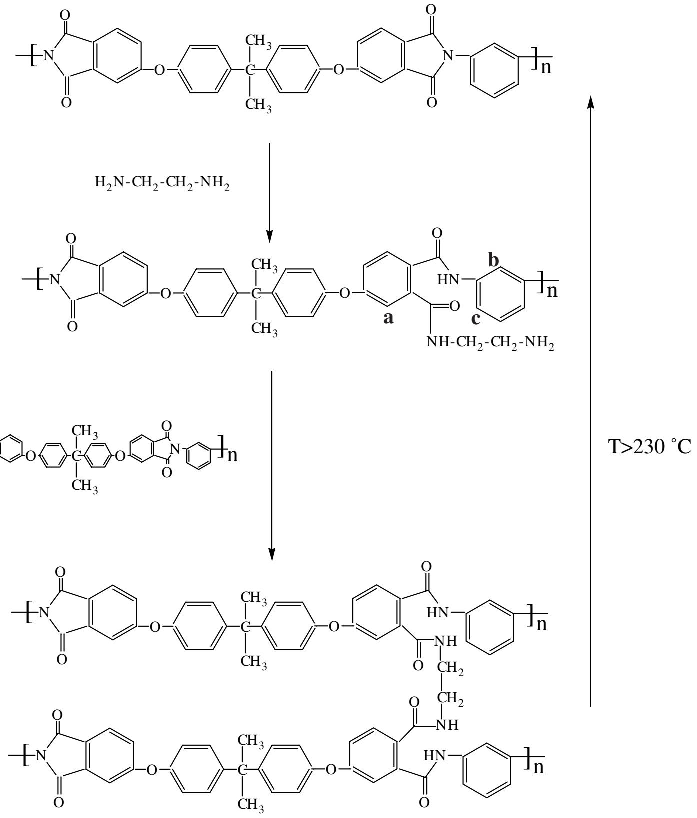


Fig. 1. Reactions between PEI and a strong base (ethylenediamine).

Table 2
Comparison of two methods to determine the degree of grafting of various PEI–NH_2 with EDA

Degree of grafting (%)	
By titration	By nitrogen microanalysis
0	–
2.6	1.6
1.9	0.3
3.4	3.3
4.7	5.1
3.0	3.3
10	8.0
4.5	4.5

exclusion chromatography (SEC) in chloroform (WATERS). A differential scanning calorimeter (METTLER TC 10A) is used to determine the glass transition temperature of modified PEI in the scanning mode at 10 °C/min under argon in the temperature range from 0 to 280 °C. Microanalysis of nitrogen element and direct amino titration are both performed to determine the degree of grafting of the amination reaction. For titration, modified PEI is dissolved in dichloromethane, one drop of crystal violet is added to the solution. Perchloric acid (0.098N) in acetic acid is used as the titration agent. We have checked that the imide group of PEI does not affect the titration. In the present work, the degree of grafting represents the average number of aminofunctions grafted per one hundred of imide functions of PEI, if no crosslinking of PEI is taking place. Amido groups formed during grafting reaction are also titrated so the degree of grafting represents only one third of total nitrogen atoms if secondary crosslinking reaction of PEI is neglected.

Table 3
Titration of PEI grafted by EDA under various conditions

Time of reaction	Experimental procedure	Amount of PEI (g)	Degree of grafting (%)
30 min	Dry/wash/dry	100	0.8
1 h	Dry/wash/dry	100	3.0
2 h	Dry/wash/dry	100	1.9
2 h	Dry/wash/dry	100	2.2
2 h	Dry/wash/dry	100	2.6
2 h	Dry/wash/dry	100	3.4
2 h	Dry/wash/dry	100	4.7
2 h	Wash/dry	50	2.3
2 h	Dry/wash/dry	50	4.6
4 h	Wash/dry	50	2.0
4 h	Dry/wash/dry	50	3.3
6 h	Wash/dry	50	2.3
6 h	Dry/wash/dry	50	5.4
6 h	Wash/dry	100	2.2
15 h	Wash/dry	100	4.2

Experimental determination of degree of grafting is realized by direct titration of amino groups in modified PEI and nitrogen microanalysis. Results are presented in Table 2. Both methods give similar results thus validating the determination of the degree of grafting.

3. Results and discussion

In the first place, it is very important to define a degree of grafting that is necessary to establish the grafting efficiency and for further use with epoxy–amine mixtures, to consider the reactive functions resulting from the grafting reaction and which can react with epoxy groups. Due to the fact that the grafting reaction is real-

Table 4
Titration of PEI grafted with AEP

Time of reaction	Experimental procedure	Amount of PEI (g)	Degree of Grafting (%)
3 h	Wash/dry	100	3.6
3 h	Dry/wash/dry	100	4.0

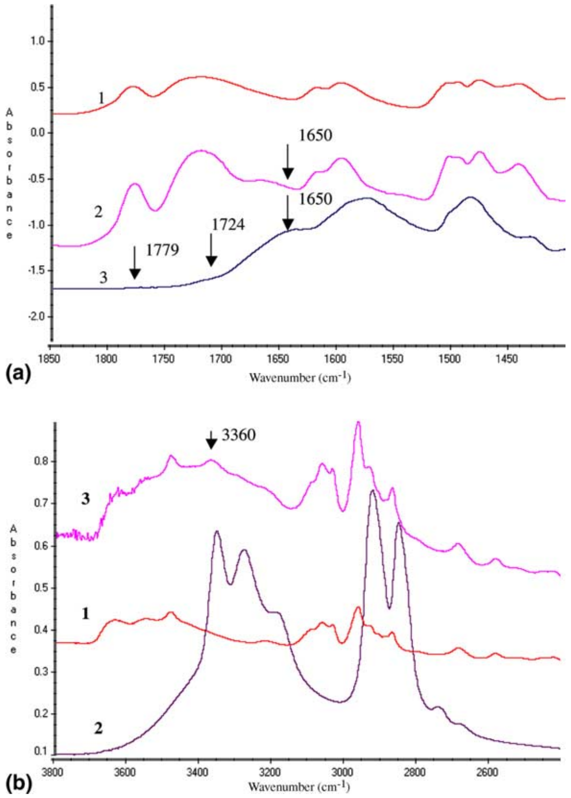


Fig. 2. Comparison of FTIR spectra of (a) PEI (1), PEI–NH_2 (2) and PAA (3); (b) PEI (1), EDA (2) and PEI–NH_2 (3).

ized in a dispersed medium, the PEI powder can be modified superficially and the modification can be distributed unequally on the macromolecules. The experimental conditions are chosen in order to prevent PEI crosslinking thus an excess of amino functions are used and acetone was preferred to ethanol as dispersion medium because insoluble parts were obtained when synthesis was performed in ethanol. The presence of insoluble parts means that ethanol can favor PEI crosslinking. As explained before, grafting reaction is realized in order to obtain pendant amino groups on PEI backbone that will be able to react with epoxy groups. A complete grafting of PEI must be avoided so as not to turn it into PAA, therefore the extent of grafting is chosen in the range of 1–5% (see Table 2).

As the amination of PEI is realized in a dispersed medium it depends on various parameters such as stirring rate, reaction time, PEI quantity, modifying agent concentration, dispersion medium... These parameters are optimized in order to obtain a degree of grafting of 4.5% meaning that an average of two units is modified per PEI chain. An important parameter that has been found is the drying stage. It was established that PEI amination can continue during the drying stage in the

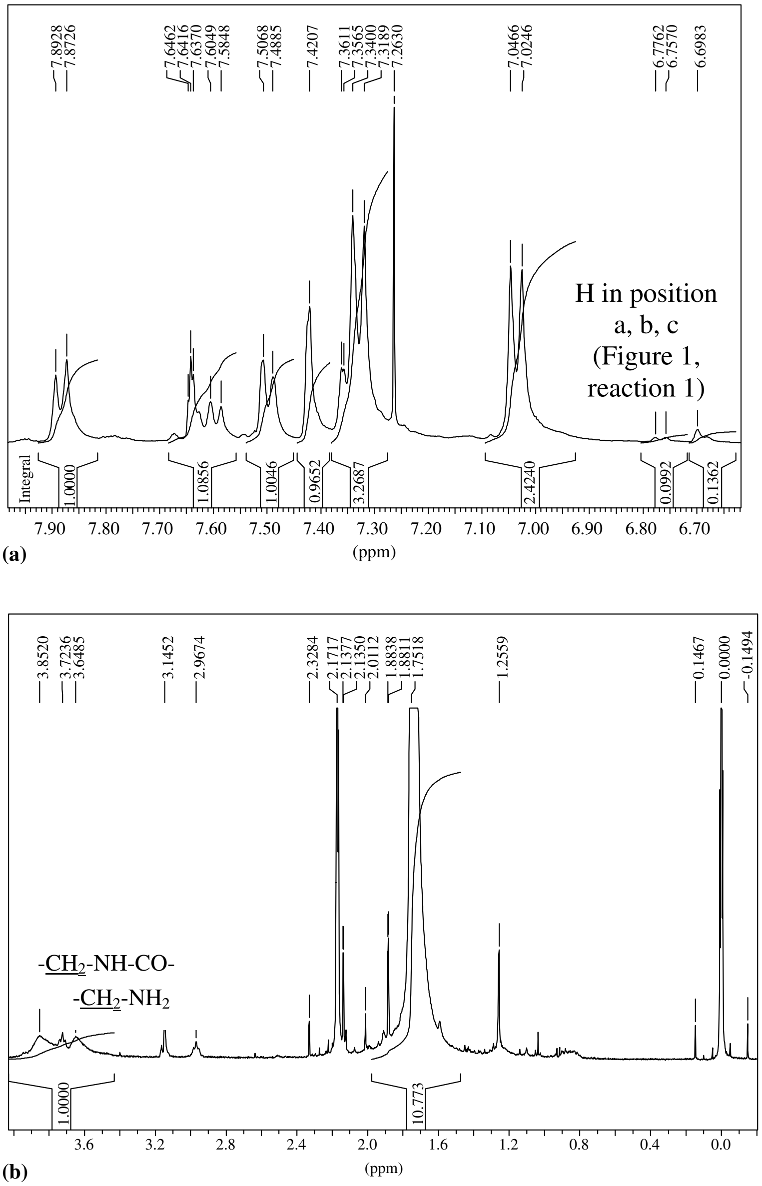


Fig. 3. ^{1}H NMR spectra of PEI–NH_2 with EDA (4.7%).

case of EDA because EDA is a solvent of PEI, so it can penetrate into the PEI particles and even after many washes, some EDA can still be trapped in PEI particles and can further react during the drying step unlike when AEP is used. As AEP is a very poor solvent of PEI, after washing, unreacted AEP is totally removed and no further reaction can take place.

To determine the quantitative importance of the drying stage in the case of EDA, products resulting from PEI modification with EDA are divided into two parts. The first one is immediately washed then dried for 24 h under vacuum whereas the second one is dried for 24 h under vacuum then washed and dried again. Results presented in Table 3 clearly indicate that when EDA is used, half of the reaction takes place inside the reactor then half of it happens in the dryer. On the contrary, when AEP that is a poor solvent of PEI is used, the reaction does not go on during the drying stage as shown in Table 4. These results indicate that EDA can diffuse in the PEI particles unlike AEP and we can state that the modification of PEI particles is more uniform when EDA is used.

3.1. Characterization of modified PEI

Because the samples used in the study have different thicknesses, the spectrograms of Fig. 2 cannot be compared quantitatively. However qualitatively, the infrared spectra of fully modified and unmodified PEI shows that the imide bands of PEI at 1779 and 1724 cm^{-1} disappear. In the modified PEI samples, a new band at 1650 cm^{-1} is identified as an amide band indicating that amination reaction takes place. When PEI amination is realized with EDA, another new band appears at 3360 cm^{-1} that characterizes primary amine stretching mode. These data indicate that only one of the two amino functions of EDA has reacted with imide function of PEI, so amino function is grafted as a pendant function on PEI backbone.

The ^{1}H NMR spectra of PEI and 4.7% grafted PEI indicate the presence of methylene groups coming from EDA at 3.7 ppm. Moreover at 6.7 ppm signals from the hydrogens belonging to hydrogen in ortho position of amido functions confirm that the grafting reaction has taken place (Fig. 3). However as the grafting rate of PEI is low, signals corresponding to the grafted groups cannot be observed in ^{13}C NMR.

In addition to FTIR and NMR analysis, size exclusion chromatography is used to characterize the PEI modified by EDA. The solvent used in the SEC study is chloroform so PEI can be totally dissolved. As EDA is a solvent of PEI, the amination process is homogeneous and we can consider that each chain of PEI is modified in the same way. This fact is confirmed by the chromatograms that show no modification in the width of the distribution (Fig. 4). However a translation of the distribution in the time scale is observed indicating that grafted PEI is another product with a different hydrodynamic volume (Fig. 4).

The DSC thermograms of modified PEI indicate a decrease of the glass transition temperature with an increase of amination (Fig. 5). It can be easily explained by the fact that addition of EDA or AEP to PEI leads to the opening of a rigid imide ring and thus to an increase in chain mobility of PEI.

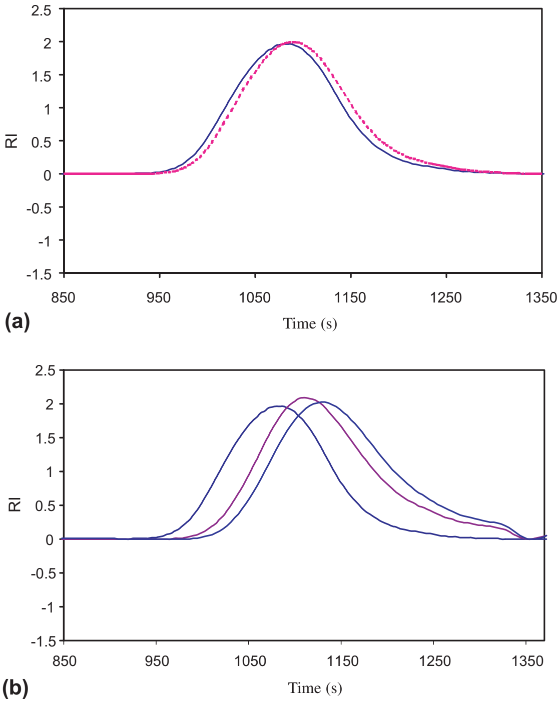


Fig. 4. S.E.C. chromatograms of PEI–NH_2 (a) PEI (full line) and PEI–NH_2 with *n*-butylamine (dotted-line); (b) from left to right: PEI, PEI–NH_2 with EDA (3.0%) and PEI–NH_2 with EDA (4.7%).

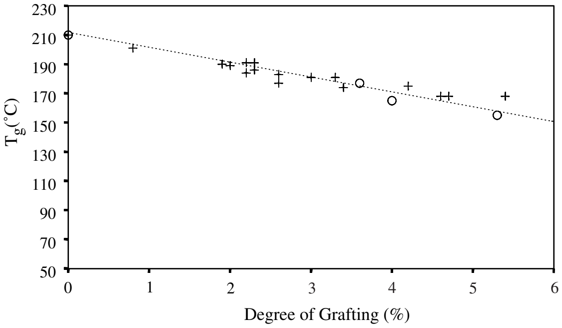


Fig. 5. Evolution of T_g versus degree of grafting of PEI modified with EDA (+) and AEP (○).

4. Conclusions

An experimental procedure was established to obtain grafted amino groups on a PEI chain by dispersion of the PEI powder in a nonsolvent. AEP can be used successfully without noticeable reaction during the drying stage. When the grafting agent used is EDA, the modification of PEI is more homogeneous due to a good impregnation of the PEI powder. The drying stage was found to be the important parameter as the grafting reaction can go on forward during that stage.

In both cases it was established that a degree of grafting up to 5% could be obtained in these conditions.

The amino-modified PEI was characterized by FTIR. A decrease in the imide function band and the appearance of amido and amino functions were observed. ^{1}H NMR spectra confirm that EDA was successfully grafted to PEI. Size exclusion chromatography indicated that amino-modified PEI did not undergo any fragmentation nor crosslinking reaction. It was found that the T_g of the amino-modified PEI linearly decreases with the degree of grafting.

These amino grafted PEI will be used in a forthcoming paper (part II) as toughening agents for epoxy thermosets.

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