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Crosslinking of PET through solid state functionalization with alkoxysilane derivatives

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Abstract

A new way for crosslinking poly(ethylene terephthalate) (PET) films and fibers is described using solid state functionalization of the PET end groups (alcohol and acid) with two reagents, respectively, 3-isocyanatopropyltriethoxysilane (IPTESI) or/and 3-glycidoxypropyltrimethoxysilane (GOPTMSI). This functionalization is then followed by hydrolysis–condensation reactions of PET–alkoxysilane end groups leading to the PET crosslinking.

First of all, the functionalization reactions were investigated on model compounds by ^{1}H NMR spectroscopy in a range of temperature 80–160 °C. Furthermore, the diffusion of reagents in solid PET, depending on the initial degree of PET crystallinity, was characterized in the same temperature range through the variation of sample mass. On the other hand, this method allowed us to determine the diffusion coefficients and the solubility of the reagents in solid PET at different temperatures and initial crystallinity degrees.

End groups functionalized PET films and fibers by alkoxysilane were then crosslinked by immersion of the samples in hot water. The crosslinking density was characterized by measuring the insoluble fraction of PET in good solvent constituted by a mixture of trifluoroacetic acid and dichloromethane (50/50 vol.). An insoluble fraction close to 70% was obtained by the functionalization treatment of amorphous PET film (8% crystallinity) by a mixture of GOPTMSI + IPTESI (50/50 M) at 155 °C for 1 h followed by hydrolysis–condensation reactions at 80 °C for 72 h. Thermomechanical and thermal properties of films and fibers were observed and found to be considerably enhanced in comparison to the untreated samples. The tensile properties of these partially crosslinked samples were maintained up to 320 °C.

Keywords: Poly(ethylene terephthalate) crosslinking; Solid state modification (diffusion-functionalization); Alkoxysilane hydrolysis–condensation

1. Introduction

Several approaches have been developed to modify PET during the synthesis or by post-modification in order to increase its viscosity and elasticity [1,2]. To overcome flowing of polyesters over their melting temperature, different chemical modifications were carried out either at high temperature or in solid state. Usually chemical modification at high temperature in presence or not of chain extenders leads to crosslinking or branching but also to degradation of polymer. In our previous study devoted to melt modification of PET with alkoxysilane derivatives [3], we succeeded to increase the melt viscosity by creating branching but also by generating shorter chains due to ester–alkoxysilane exchange reactions. Another approach for chemical modification and to limit the degradation is to carry out the reactions at lower temperature in the solid state [4–7]. However, it is well known that this approach has the disadvantage of slow reaction rate due to a diffusion-controlled process. For example, during

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postcondensation, which means without any additive, esterification and transesterification are observed [8] leading to an increase of the molar mass [9]. Maier and Chawla [10] carried out this postcondensation between 210 and 255 °C on PET pellets. Karayannidis et al. [5,11] transposed this principle to PET industrial scraps recycling.

Solid state modification by diffusion of multifunctional reagents represents an interesting approach for a controlled functionalization at low degradation levels. For example, in order to reduce the deformation of different articles during their manufacture by extrusion, Gantillon et al. [12] produced high molar mass polyesters with high melt viscosity after solid state diffusion and reaction of polyols.

The diffusion of reagents into PET fibers was studied for its dyeing behavior [13,14]. The phenomena of diffusion are limited because of the high degree of crystallinity and T_g of PET. The diffusion is carried out in the amorphous phase and the orientation of the macromolecules during the drawing of the fibers increases the tortuosity and thus modifies diffusion [15]. To improve the diffusion of pigments in PET fibers, Simal and de Araujo [16] used the benzoic acid as a conveying agent (carrier effect). Chidambaran et al. [13] modified the crystalline phase and T_g of PET fibers by incorporating solvent molecules in it which fulfill the function of plasticizer during a later heat treatment. Agarwal et al. [17] modified PET pellets chemically and physically by a process carried out in the solid state after ethylene diamine vapor diffusion during 5 min at 125 and 190 °C (where the penetration of the reagent is more important).

Dearnaley and Herk [18] introduced into PET in the solid state 1–5 wt% of saturated reagents such as cyclopropane and ethylene oxide or unsaturated molecules such as propylene and 1,3-butadiene to carry out crosslinking by irradiation.

Baker et al. [19–21] partially crosslinked polyester fibers by incorporating a solution of disulfonyl azide in the solid state PET. Thermal treatment under 230 °C promotes the decomposition of this compound and leads to crosslinking. Significant improvements in thermomechanical and creep properties were observed between the standard fibers and those produced by crosslinking.

The aim of this work is to enhance the thermomechanical properties of PET fibers by end-group crosslinking (by hydrolysis–condensation reactions of trialkoxysilanes) after the functionalization in solid state of the alcohol and acid extremities with bifunctional reagents. This is based on the Sioplas process for poly(ethylene) crosslinking [22,23] in cable-making and on laboratory work on PVC fibers crosslinking [24] and on polyamide adhesives [25]. The hydrolysis–condensation reactions of the alkoxysilanes $X_nSi(OR)_m$ are well-known [25–29]. These reactions are catalyzed by the acids and the bases but can also be carried out by immersion of polymer in boiling water without catalyst [30]. Numerous parameters have an influence on these reactions such as the nature and concentration of the ligands' alkoxide (OR), water concentration, pH of the reaction medium, the temperature and possibly the nature of the solvent. In the Sioplas process [22,23,28,31], alkoxysilane groups are grafted on the PE chain during the polymerization with a vinylalkoxysilane, and then the crosslinking is carried out by immersion of the material in water with a catalyst such as the dibutyltin dilaurate (DBTL). In the Monosil process [22,31], this functionalization is carried out using peroxides and vinylalkoxysilane during the extrusion processing (radical grafting). Several techniques of hydrolysis were studied. A tin-based catalyst can be introduced into material during processing, thus condensation can be done with the air or in hot water.

The grafting of alkoxysilane groups was also studied on PVC using aminosilane [31]. The reaction takes place between the amino group of the alkoxysilane and the chlorine of the PVC chain. There is release of HCl that is neutralized by calcium carbonate incorporated in the reactional mixture. The crosslinking takes place by immersion of the samples in water added with 5% of DBTL during 4 h at 80 °C. As the grafting reactions through radicalar process are unrealizable on the PET main chain because of the brittleness of the ester function, our choice was made on the grafting of trialkoxysilanes by modification of the end groups.

A first approach was published in a patent of Duan [32], which asserts the incorporation of crosslinking agents such as $(OR)_mSi(X)_nZ_p$ in the PET polymerization reactor. By this way, the authors obtained temporarily crosslinked polyester molecules which increase the viscosity and so improve the spinning performance.

On the other hand, we recently described studies of the branching of PET by chemical modification in melt state with alkoxysilanes [3]. During melt modification at high temperatures (higher than the melting temperature of PET at 256 °C), many degradation and side reactions were observed and no crosslinking occurred after hydrolysis–condensation reactions. Indeed, the functionalization of PET in melt conditions with either 3-(triethoxysilyl)propylsuccinic anhydride (ASSI) and/or 3-glycidoxypropyltrimethoxysilane (GOPTMSI) results in a broadening of the mass distribution. Shorter PET chains and a tail of higher molar mass characterize this distribution. The formation of branched PET chains embedded in shorter linear PET chains was coherent with the rheological behavior of this "blend" which was drastically modified in comparison with neat PET one resulting in an important increase of the zero shear viscosity.

To succeed in the PET crosslinking reaction, the solid state functionalization of PET by diffusion of reagents such as 3-isocyanatopropyltriethoxysilane (IPTESI) or/and 3-glycidoxypropyltrimethoxysilane (GOPTMSI) is studied in the present work. Indeed the isocyanate and epoxide functions are well known to react with the OH and COOH groups, respectively. On the other hand, the alkoxysilanes, widely studied in the sol–gel chemistry [33–35], are susceptible to react with both the OH and COOH groups but also in the presence of water leading to siloxane bonds. An approach on PET chain-end model compounds was carried out in conditions as close as possible to those in solid state (temperature below 200 °C, without solvent). The mechanistic aspects were investigated by ^{1}H NMR spectroscopy. Diffusion of the reagents in samples with different degree of crystallinity was studied.

Insoluble fraction according to the quantity of diffused reagents and in function of temperature and degree of crystallinity was evaluated. In addition, the thermal and thermo-mechanical behavior of PET samples modified by IPTESI and GOPTMSI, or by a mixture of both are discussed in the present paper.

2. Experimental

2.1. Materials

Benzoic acid (BA), monomethylterephthalate (MMT), triethylene glycol monomethylether (TEGMME), trifluoroacetic acid (TFA) and dichloromethane were purchased from Aldrich. The two reagents 3-isocyanatopropyltriethoxysilane (IPTESI) and 3-glycidoxypropyltrimethoxysilane (GOPTMSI) are commercial products from ABCR. All these products were used without further purification. The chemical structures of these compounds are represented in Table 1. The attributions reported in this table were used for NMR analysis.

PET 92 K homopolymer (Viscosimetric Index = 92 mg/l, end groups' proportions are, respectively, 48% and 52% in COOH and OH) was supplied by Rhodia-Tersuisse (Emmenbrücke, Switzerland). Number average molar mass (M_n = 30,000 g/mol) and weight average molar mass (M_w = 75,000 g/mol) were measured by size exclusion chromatography with a Ultrastyragel Waters column ($L = 30$ cm, $D = 5$ µm, stationary phase = PSDVB, $T = 35$ °C, feed rate = 1 ml min^{-1}) and Waters R410 refractometer detector in a mixture of 1,1,1,3,3,3-hexafluoroisopropanol/chloroform (2/98 vol.) using a polystyrene calibration and then corrected with the Mark-Houwink parameters for the PET ($a = 0.726$, $k = 0.000192$ dl/g) [36]. Thus the carboxyl and hydroxyl contents of PET sample are, respectively, 32 and 35 mmol/kg.

PET pellets were dried under vacuum at a temperature of 150 °C for 10 h in order to have very low moisture content. Films and fibers, respectively, with low (amorphous) and with high degree of crystallinity (crystalline) were used for diffusion analyses. The film samples were discs of 25 mm diameter and 150 µm thickness, prepared by compression molding at 280 °C for 2 min.

Amorphous samples were prepared by rapid cooling (after tempering, residual crystallinity $X_c = 8\%$) and crystalline films ($X_c = 62\%$) were obtained by a further thermal treatment at 170 °C for 3 h. Amorphous (non-drawn, 280 dtex, 48 filaments each one of 35 µm diameter, residual crystallinity $X_c = 8\%$) and crystalline fibers (1100 dtex, 192 filaments each one of 23 µm diameter, $X_c = 43\%$) were supplied by Tersuisse (Emmenbrücke, Switzerland).

2.2. Diffusion of reagents

We referred to the Ficks' laws [37,38] to understand the sorption phenomena of the reagents into the PET. The translational diffusion coefficient D is defined by:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

for the one-dimensional case (diffusion of the liquid in the direction of the film thickness x). C is the substance concentration in g l^{-1}.

Experimentally, diffusion coefficients can be determined with the mass evolution protocol [39]. Samples are immersed in the reagent(s) to be studied (in a closed container). The mass uptake of the sample is then raised regularly by simple weighting of the wiped sample until solubility equilibrium in a range of temperature from 25 to 180 °C for films of 150 µm thickness.

From the one-dimensional Ficks' law, we can determine the mass uptake of the penetrant at time t (M_t), knowing that when the equilibrium is reached at long times (M_∞).

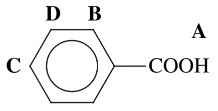
$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\frac{\left(-(2n+1)^2\pi^2 Dt\right)}{l^2} \tag{2}$$

The diffusion coefficient D is calculated in the Fickian case for: $M_t/M_\infty = 1/2$.

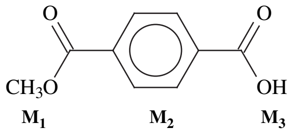
Table 1

Chemical structures of the PET end-group models and reagents, and proton labels

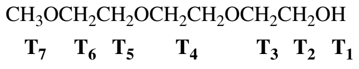
Benzoic acid (BA)



Monomethylterephthalate (MMT)

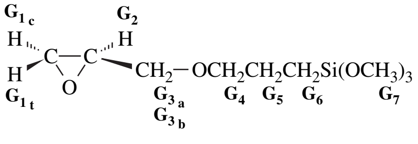


Triethylene glycol monomethylether (TEGMME)

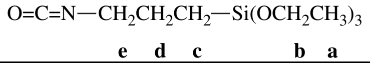


$$\underset{T_7}{CH_3}\underset{T_6}{O}\underset{T_5}{CH_2}CH_2O\underset{T_4}{CH_2CH_2}O\underset{T_3}{CH_2}\underset{T_2}{CH_2}\underset{T_1}{OH}$$

3-Glycidoxypropyltrimethoxysilane (GOPTMSI)



3-Isocyanatopropyltriethoxysilane (IPTESI)



$$O{=}C{=}N{-}\underset{e}{CH_2}\underset{d}{CH_2}\underset{c}{CH_2}{-}Si(\underset{b}{OCH_2}\underset{a}{CH_3})_3$$

$$\left(\frac{t}{l^2}\right)_{1/2} = -\frac{1}{\pi^2 D}\ln\left(\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9\right) \tag{3}$$

The coefficient D can be evaluated from the following relation:

$$D = 0.04939\left(\frac{l^2}{t}\right)_{1/2} \tag{4}$$

where l is the thickness of the film (in cm) and t is the time (in s).

To validate this method, it is necessary to check that the transport mechanism is Fickian by the linearity of the sorption curve ($M_t/M_\infty = f(\sqrt{t})$) until 0.5. So graphically with the curves showing the mass uptake of the samples according to time, we extrapolated the M_∞ value when that was possible (reached), to evaluate the $t_{1/2}$ and then calculate the diffusion coefficient D by Eq. (4).

From these experiments it is also possible to calculate the time and so the quantity of reagent necessary to functionalize all the end groups for a given mass of PET. Knowing that PET 92 K average number molar mass is equal to 30,000 g/mol, and considering the initial proportion of alcohol and acid end group, the equimolarity with the reactive end groups is reached by a diffusion of 0.008 g/g for both GOPTMSI and IPTESI in the PET in a solid state.

This value will be used to determine the time necessary to reach the equimolarity ($t_{\mathrm{equimolar}}$). However, it cannot be demonstrated that homogeneous repartition of reagents is reached when equimolarity is obtained.

2.3. Reactions on model compounds

Model compounds of PET–OH and –COOH end groups were TEGMME and MMT or BA, respectively. Equimolar amounts of IPTESI and GOPTMSI reagents were added and the closed medium was mixed at 80 and 160 °C and analyzed by ^{1}H NMR before and after reaction.

2.4. Characterization

High resolution liquid NMR spectroscopy was carried out with a Bruker AC 250 instrument working at 250 MHz for ^{1}H. Deuterated chloroform, $CDCl_3$, was used as solvent for analysis. Chemical shifts values (δ) are in ppm with reference to internal tetramethylsilane (TMS).

Insoluble fraction (IF) was determined after dissolution of PET samples (1 wt%, 24 h, 25 °C) in trifluoroacetic acid–dichloromethane (TFA/CH_2Cl_2 50/50 vol.) [10], filtering and drying. It was checked that TFA does not induce PET chain scissions in these conditions. IF was calculated from: IF (%) $= 100(w_d/w_0)$, where w_0 is the mass of the sample before dissolution (g) and w_d the mass of the insoluble fraction after dissolution of the sample and drying (g).

Thermomechanical analyses were carried out with a DMA 2980 TA Instruments. Two types of tests were performed depending on the sample shape:

- On the fibers, the experimental protocol was in tensile mode with application of a constant force of 0.01 N under a temperature ramp of 10 °C/min from 50 °C up to the break-up of the fibers. This test is a creep experiment under a constant normal stress $\sigma_0 = 5.5 \times 10^4$ Pa.
- On the films, the experimental protocol was in tensile mode with an application of a deformation amplitude of 10 μm at a frequency of 5 Hz under a temperature ramp of 3 °C/min. This test is a linear viscoelastic experiment under an elongation dynamic deformation $\varepsilon_0 = 0.05\%$.

Differential scanning calorimetry (DSC) was performed from 0 to 320 °C with a modulated DSC 2920 TA Instruments at a heating and cooling rate of 10 °C/min under nitrogen atmosphere.

3. Results and discussions

3.1. Diffusion and solubility of reagents into PET

The main limit to the solid state modification is the competition between reaction and diffusion of the liquid reagents. Parallel to the chemical aspect of modification in the solid state, it is thus initially advisable to evaluate the capacity of the reagents to diffuse in a PET samples.

According to the solubility parameters (Table 2) of the reagents calculated from group methods [40,41], GOPTMSI and IPTESI have solubility parameters lower than PET one. It can be then expected low solubility of these reagents in PET. Furthermore, it can be pointed out that the calculation methods of these parameters are based on particular conditions (room temperature, amorphous polymer). Consequently, quantitative solubility data cannot be obtained from such methods. Although the mass evolution method is simple from an experimental point of view, the solubility of GOPTMSI and IPTESI in PET can be easily calculated as it is explained here below. According to Table 3, it can be seen that the solubility of IPTESI is lower than the solubility of GOPTMSI at $T = 150$ °C (PET sample).

Table 2
Solubility parameters calculation for the PET and the diffusion reagents according to different methods: direct experimental measurement or empirical tables [39]

	Hildebrand solubility parameters δ ($J^{1/2}\,cm^{3/2}$) according to different methods or authors				
Product	Experimental	Hoftyser and Van Krevelen	Fedors	Hoy	Hansen
GOPTMSI	–	–	17.7	19.1	19.8
IPTESI	–	–	19.2	–	–
PET	$19.9 < \delta < 21.9$	20.5	23.3	23.2	–

Table 3
Evolution of the equimolar time ($t_{\text{equimolar}}$) and the diffusion coefficients versus the temperature of diffusion for the GOPTMSI, IPTESI and water in, respectively, crystalline and amorphous PET films of 150 μm thickness

Reagent	PET crystallinity (%)	Diffusion temperature (°C)	$t_{\text{equimolar}}$ (min)	Mass uptake at long times M_∞ (%)	Diffusion coefficient D (10^{10} cm^2/s)
GOPTMSI	62	80	>20 days	–	–
GOPTMSI	62	110	30	–	–
GOPTMSI	62	135	13	7.8	3.6
GOPTMSI	62	150	3	8.3	14
IPTESI	62	150	15	3.9	5.3
GOPTMSI + IPTESI 50/50	62	155	15	5	7.4
GOPTMSI + IPTESI 60/40	62	155	14	6.5	6.2
GOPTMSI	8	80	15	45	0.021
IPTESI	8	90	16 days	–	–
GOPTMSI + IPTESI 50/50	8	80	28	9	0.039
GOPTMSI + IPTESI 50/50	8	155	9	9	4.6
Water	62	80	–	1.22	5.6
Water	62	90	–	1.57	5.8
Water	62	100	–	2	8.8

3.1.1. GOPTMSI

The evolution of GOPTMSI mass uptake for PET films of 150 μm thickness as a function of time at different temperatures of diffusion is shown in Fig. 1. As expected, the diffusion of GOPTMSI is faster when temperature is increased. For crystalline samples ($X_c = 62\%$), an equilibrium plateau is reached in less than 4 h and 20 h at temperatures 150 °C and 135 °C, respectively. This plateau corresponds roughly in both cases to 0.08 g/g solubility of GOPTMSI, which diffused at the equilibrium in the PET films. This diffusion is speeding up with amorphous sample. From these curves, it is possible to determine the time of diffusion, $t_{\text{equimolar}}$, with regard to the concentration of PET acid end groups as previously defined (Table 3). It is evidenced that $t_{\text{equimolar}}$ decreases with the temperature for the crystalline samples. At 135 °C, equilibrium is reached within 13 min against 3 min at 150 °C. For the amorphous sample, this equimolar time is obtained within 15 min at 80 °C. However, tests realized on this last sample at a temperature above 80 °C pointed out a crystallization occurring during the diffusion process.

The coefficients of diffusion of the GOPTMSI reagent in the crystalline PET samples are 3.6×10^{-10} cm^2/s and 1.4×10^{-9} cm^2/s at $T = 110$ and 135 °C, respectively. For amorphous PET films, the diffusivity is very low at temperature close to T_g and is in the same order of magnitude with that of the crystalline samples at higher temperatures due to the development of the crystallization during the diffusion experiment.

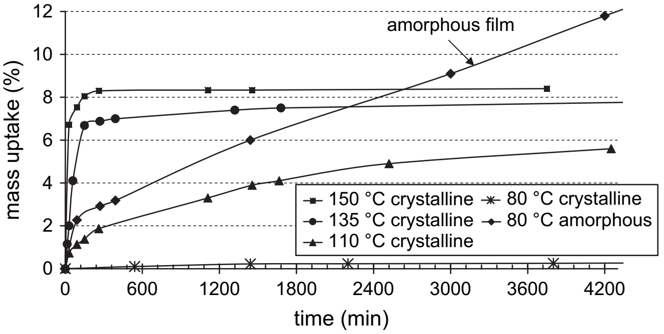


Fig. 1. Evolution of GOPTMSI mass uptake for PET films of 150 μm thickness versus time and temperature of diffusion, according to the initial degree of crystallinity.

3.1.2. IPTESI

The diffusion of IPTESI (Table 3) in the amorphous film of PET is very slow just above the glass temperature ($T = 90$ °C, $D \ll 10^{-12}$ cm^2/s) and the solubility is around 0.01 g/g. On the other hand, the time of diffusion necessary to reach the equimolar amount in IPTESI with regard to the concentration of PET alcohol end groups for crystalline film that corresponds to 0.008 g/g is equal to 15 min at 150 °C. These data evidenced the difficulty of IPTESI to diffuse by comparison with the GOPTMSI.

3.1.3. GOPTMSI/IPTESI

Other tests were carried out with a mixture of IPTESI + GOPTMSI (50/50 M) at 60, 80 and 155 °C (Table 3). The curves in Fig. 2 clearly show that the diffusion of the

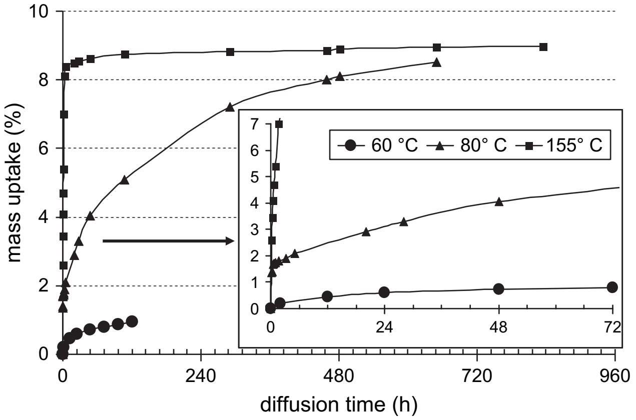


Fig. 2. Evolution of GOPTMSI + IPTESI (50/50 M) mass uptake for amorphous PET films of 150 μm thickness versus time and temperature of diffusion (60, 80 and 155 °C).

mixture at 60 °C ($T < T_g^{PET}$) is very slow and less than 0.01 g/g of reagents has diffused after 72 h. On the other hand, the solubility increases to 0.09 g/g within 30 days and 5 h at the temperatures 80 °C and 155 °C, respectively. In that last case, as already pointed out before, the degree of crystallinity increases during this test to reach 55%.

The time to reach the theoretical amount necessary to functionalize all the end groups (0.016 g/g) is obtained within 15 min at 155 °C. Nevertheless, this quantitative approach did not augured of homogeneous (or non homogeneous) repartition of reactants in PET sample.

3.2. Reactions on model compounds

3.2.1. Reaction between TEGMME and IPTESI

The isocyanate–alcohol addition can take place at room temperature [42]. The reaction between the alcohol model and the isocyanate function of the IPTESI leads to the formation of a carbamate or urethane [43–46] according to Fig. 3(a). The ^{1}H NMR spectrum of the medium after 30 min at 160 °C was compared with the spectrum of the initial mixture (Fig. 4). The quantification of this new urethane specie was obtained through the evolution of the area of signal e at 3.30 ppm and the appearance of the signal T_{2u} at 4.20 ppm and e_u at 3.17 ppm. Therefore the area of signal e_u is more important than the one of signal T_{2u}, both corresponding to the contribution of two protons. As known [47] and already shown in our previous paper [3], an exchange reaction between the alcohol and the alkoxysilane is observed. This results in the formation of a new alkoxysilane specie (Fig. 3(b)). This alkoxysilane was identified by the signal T_{2e} at 3.90 ppm. On the other hand, the ethanol formed in turn is expected to induce urethane formation (Fig. 3(c)) from its reaction with isocyanate function (measured by area of signal b_u at 4.10 ppm and which is the complementary part in the area e_u). The total area corresponding to signal $T_{2u} + b_u$ is close to 2, pointing out that all the ethanol formed by the previous reaction in our conditions reacted with isocyanate function. By setting the area c to 2, corresponding to one initial IPTESI mole, these two urethane species may be quantified by, respectively, $T_{2u}/2$ and $b_u/2$. So after 30 min at 160 °C, 80% of the urethane specie comes from the reaction TEGMME–IPTESI and 20% from the reaction ethanol–IPTESI. The reaction between alcohol and isocyanate is complete within 20 min at 160 °C and 15 h at 80 °C (Fig. 5). This reaction leads mainly to the functionalization of the TEGMME–OH end groups by alkoxysilane function. Thus PET–OH end-group functionalization by alkoxysilane group can be expected in the absence of ester–alkoxysilane exchanges as it will be evidenced in Section 3.5.

3.2.2. Reaction between BA and IPTESI

The reaction between an acid and an isocyanate group leads to an amide after decarboxylation [48–52] (Fig. 6(a)). However, under our conditions and due to the presence of alkoxysilane groups, other side-reaction products are expected. In our previous work [3], the substitution of an alkoxide by an acyloxide group on the silicon atom was evidenced leading, in the present case, to acyloxysilane and ethanol (Fig. 6(b)). Thus, ethanol created may contribute in turn, as above discussed, to the formation of urethane (Fig. 6(c)). By comparing the ^{1}H NMR spectrum of the medium after the reaction at 160 °C during 1 h to the spectrum of the initial mixture (Fig. 7), we can evidence these species through the following observations.

- Appearance of the signal e_u at 3.20 ppm and b_u at 4.10 ppm corresponding, respectively, to the CH_2 in α-position of the urethane function CH_2NHCOO and CH_2OCONH.
- Appearance of the signal c_e at 0.97 ppm corresponding to the CH_2 in α-position of the silicon atom of an acyloxysilane [3] concomitant to the observation of the signal b_e at 4.00 ppm associated to the CH_2 of an ethoxy group of the acyloxysilane.

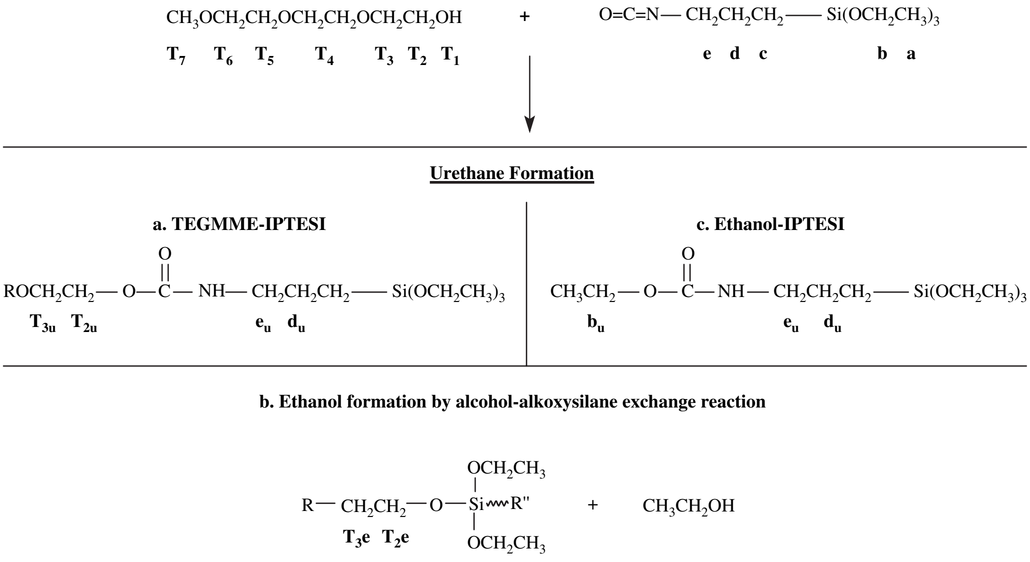


Fig. 3. Reaction scheme between TEGMME alcohol group and IPTESI.

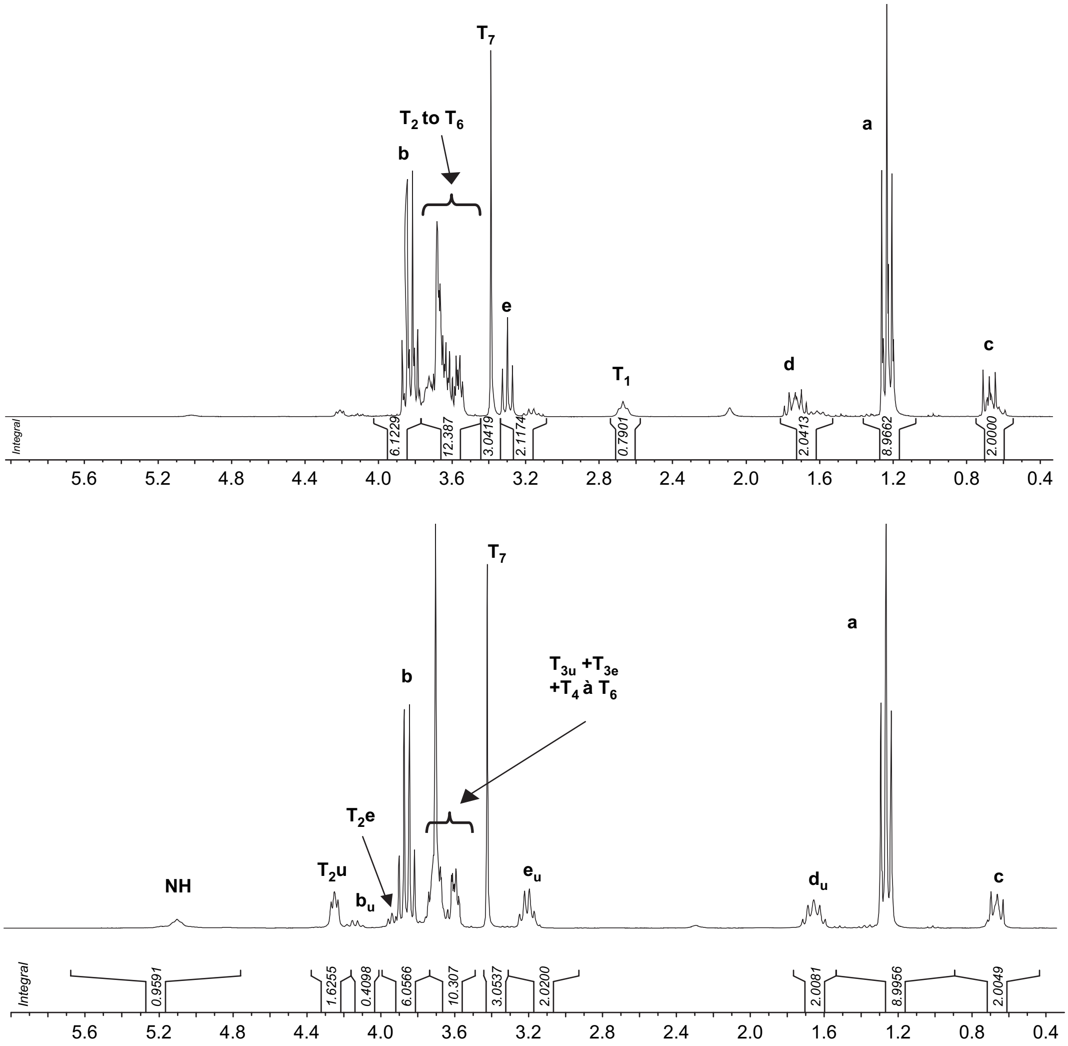


Fig. 4. TEGMME–IPTESI ^{1}H NMR spectra: the initial mixture (top) and the reaction medium after 30 min at 160 °C (bottom) – both were diluted in CDCl$_3$.

- Other typical signals are also observed such as e_a at 3.50 ppm characteristic of the CH$_2$ in α-position of an amide function, and b_b corresponding to a slight formation of ethyl benzoate by esterification reaction between BA and ethanol (Fig. 6(d)).

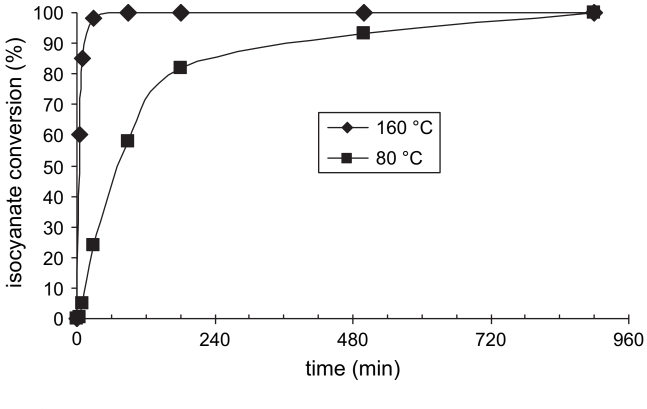


Fig. 5. Isocyanate conversion into urethane versus time of reaction, from TEGMME–IPTESI reaction at 80 and 160 °C.

The quantification of these species allows us to conclude that the isocyanate reacts rapidly at 160 °C giving 80% conversion to urethane within 1 h. Acyloxysilane (68%) is formed within 15 min at 160 °C and only 7% of amide is observed within 1 h at 160 °C. No reaction is observed after 200 h at 80 °C. This characterization evidences the possibility to functionalize the PET acid end group by alkoxysilane through mainly the formation of acyloxysilane, which can be represented as PET–COOSi(OR)$_{n-}$.

3.2.3. Reaction between MMT and GOPTMSI

In our previous work [3] devoted to the modification of PET by GOPTMSI in molten state, we pointed out on model compounds' studies the following phenomena.

At 290 °C, the classical reaction between the COOH group and the epoxy function leading to primary and secondary alcohols were evidenced after 1 min only at 290 °C. In addition, 65% of the epoxide groups were converted after 10 min at 290 °C. It was also shown three reactions involving the alkoxysilane function, respectively, alcohol–alkoxysilane exchange reactions, acyloxysilane formation and hydrolysis–condensation

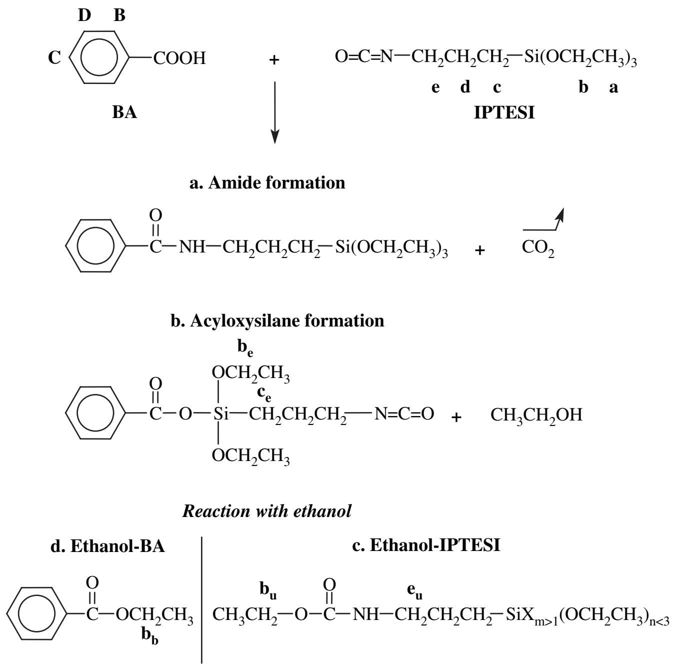


Fig. 6. Reaction scheme between BA and IPTESI.

reactions of alkoxysilane. In the present range of temperature, 80 and 160 °C, the disappearance of the epoxy function is maximal after 3 h at 160 °C (75%) and only 75% is converted after more than one week (184 h) at 80 °C (Fig. 8). The transposition of this reaction to the PET acid end-group functionalization leads to the formation of PET−alkoxysilane end group [PET−Si(OR)$_3$].

3.2.4. Reaction between TEGMME and GOPTMSI

The reaction of etherification between an epoxide and an alcohol can take place at high temperature [44]. This experiment was carried out by mixing equimolar amounts of TEGMME and GOPTMSI at 80 and 160 °C. The epoxy function is unchanged evidencing that no reaction of etherification is observed. Moreover, as already pointed out before, the exchange reaction between alcohol and alkoxysilane function is complete after 3 h at 160 °C and very slow at 80 °C (70% of exchange after 200 h). Through this exchange reaction, alkoxysilane end group such as PET−OSi(OR)$_n$ can be formed.

By combining previous data of diffusion of the reagents and the reactivity of the PET end-groups model compounds with both IPTESI and GOPTMSI, we can conclude to the possibility of functionalization of the PET end groups by alkoxysilane in the solid state in a range of time from few minutes to 3 h at

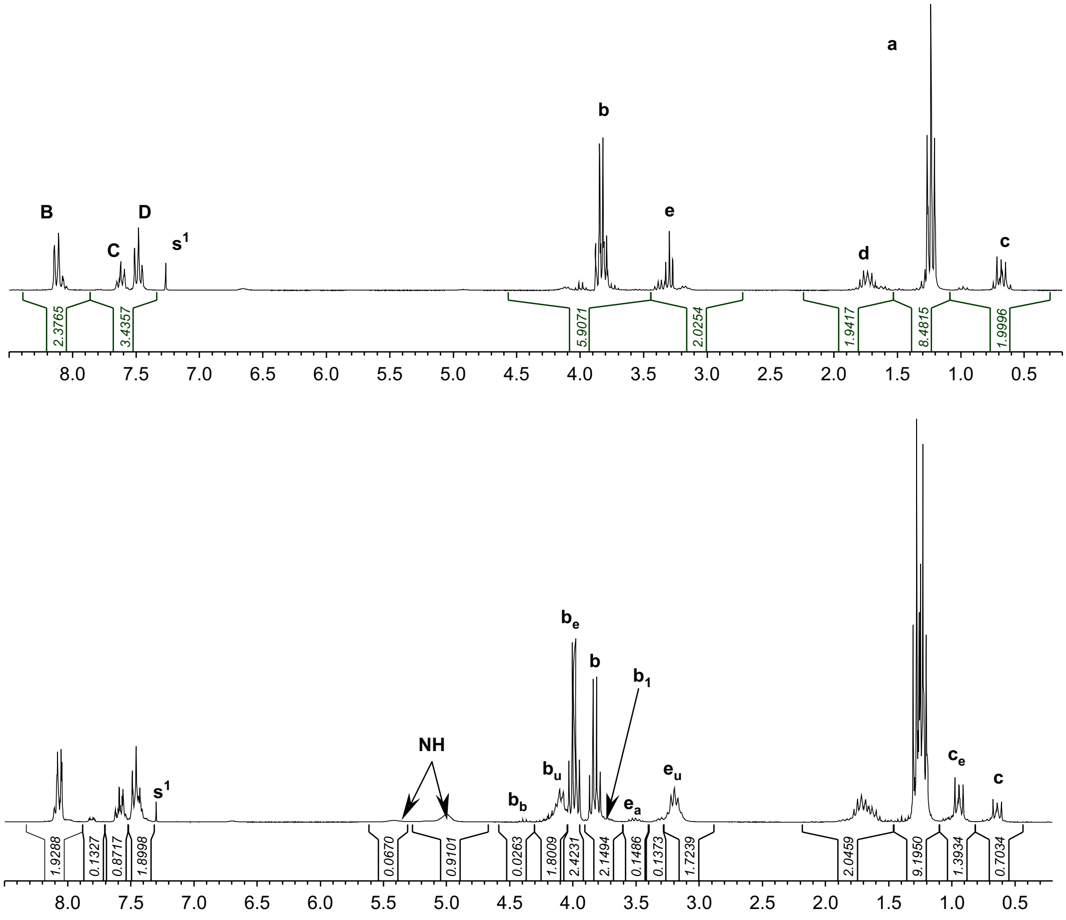


Fig. 7. BA−IPTESI ^{1}H NMR spectra: the initial mixture (top) and the reaction medium after 1 h at 160 °C (bottom) − both were diluted in CDCl$_3$ (s^1 is the protonated residue of CDCl$_3$).

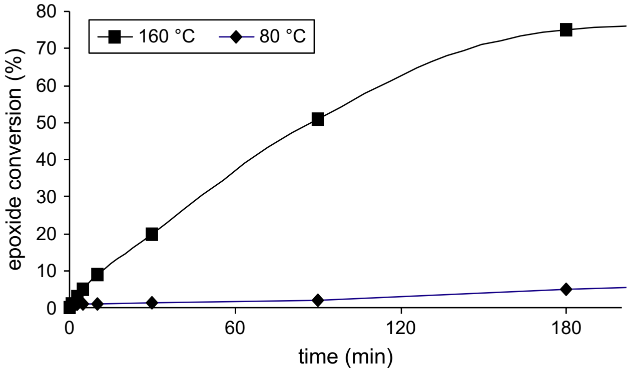


Fig. 8. Conversion of the epoxide versus time in the MMT/GOPTMSI reaction at 80 and 160 °C.

a temperature under 160 °C. These modifications should allow enhancement of the crosslinking reaction in a later stage.

3.3. Crosslinking by hydrolysis–condensation reactions

From a chemical point of view, it is far complicated to follow the degree of functionalization in solid state due to the low reagents' concentrations and the difficulty to solubilize the PET (nature of solvent and high temperature) without probably modifying the reaction advancement. Hence the homogeneous repartition of reagents cannot be easily quantified. So, the degree of crosslinking through the hydrolysis–condensation reactions of alkoxysilane PET end group (Fig. 9) was an indirect way to reach the degree of PET end-group functionalization.

To apply such crosslinking process, it was first important to check the water diffusion in crystalline PET films of 150 μm thickness in the temperature range 80–100 °C. Analysis of Table 3 and Fig. 10 evidence that the diffusion of water is fast and its solubility (equilibrium time ≈ 1 h) is in the range between 1 and 2% with a limiting value depending on the temperature. It was also checked that unmodified PET and samples after diffusion of reagents (but before the hydrolysis treatment that induces crosslinking) were soluble in a mixture of TFA/CH_2Cl_2 (50/50 vol.) at room temperature.

In the case of functionalization by the GOPTMSI alone, very low insoluble fraction was measured (<15%) whatever the hydrolysis–condensation conditions. This is consistent with the creation of PET–O–Si bond through the alkoxysilane–alcohol exchange reaction (maximal rate after 3 h at 160 °C), which is water sensitive and so cannot lead to a polymer network.

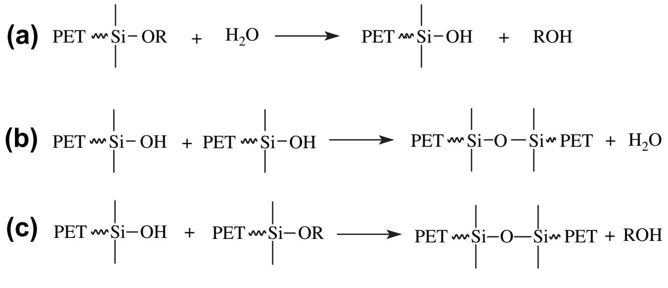


Fig. 9. Reaction scheme of the PET end-groups' grafted alkoxysilane: hydrolysis (a) and condensation (b, c).

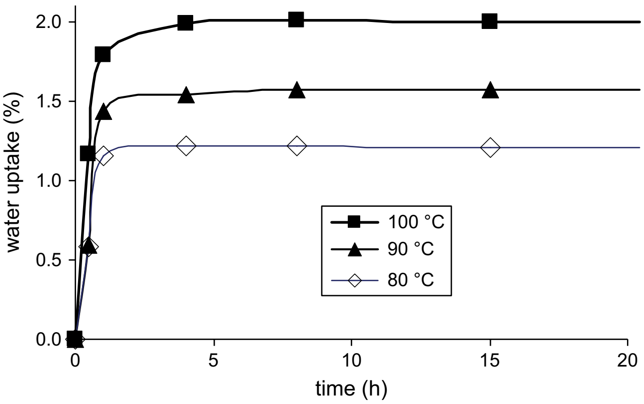


Fig. 10. Evolution of water mass uptake for crystalline PET films of 150 μm thickness versus time and temperature of diffusion (80, 90 and 100 °C).

Table 4 summarizes the results obtained with IPTESI alone according to different treatments of functionalization and crosslinking. Logically, at the lowest temperatures, the modification with IPTESI is disadvantaged by the limited diffusion and solubility of IPTESI (<1% in 3 weeks) and a lower reactivity with the PET end groups (only reaction with alcohol is total in 15 h at 80 °C). The results on films are poor (IF < 10% in 3 weeks) but we can reach approximately 50% of insoluble fraction with amorphous fibers. This might be due a faster diffusion of the reagents in the fibers. Increasing the diffusion temperature permits to reach between 60 and 70% of insoluble fraction. This is consistent with the results obtained using ^1H NMR spectroscopy on model compounds. Taking into account the relative speeds of reaction and diffusion, a majority of chains are α,ω-alkoxysilane functionalized (Figs. 3(a) and 6(b)). Through the reaction of acid with IPTESI, acyloxysilane are mainly formed that could be hydrolysed [53]. However, the presence of a phenyl group in α-position of the acyloxysilane may hindered water action and so explain the observation of insoluble fraction.

The GOPTMSI + IPTESI mixture should lead to a α,ω-alkoxysilane functionalized PET that can be then crosslinked. For amorphous PET fibers immersed for 48 h in the GOPTMSI + IPTESI mixture (50/50 M) at 80 °C, the maximum of crosslinking (insoluble fraction of 57%) is reached after 24 h of sample immersion in water at 80 °C (Fig. 11). The

Table 4
Evolution of the insoluble fraction (IF) versus conditions of IPTESI diffusion and hydrolysis–condensation reactions for amorphous samples

Sample shape	Temperature and time of diffusion T, t	Temperature (°C) for hydrolysis–condensation reactions[a]	IF (%)
Film	160 °C, 72 h	90	30
Fiber	160 °C, 72 h	90	60
Fiber	90 °C, 72 h	90	68
Film	80 °C, 3 weeks	80	10
Fiber	80 °C, 3 weeks	80	50
Fiber	65 °C, 840 h	65	45

[a] Time is equal to 72 h.

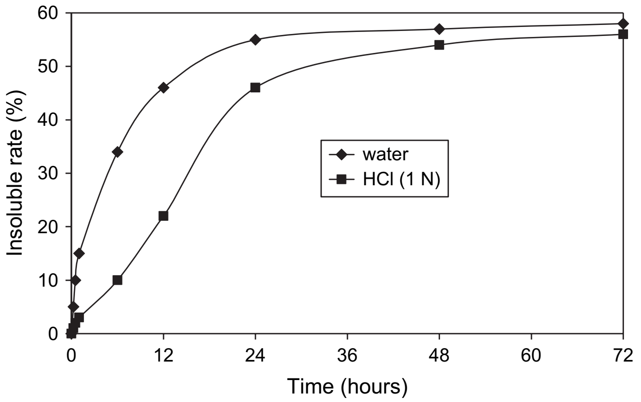


Fig. 11. Evolution of the insoluble fraction versus time of hydrolysis–condensation reactions at 80 °C [samples are first prepared after diffusion of a mixture of GOPTMSI + IPTESI (50/50 M) during 48 h at 80 °C in amorphous PET fibers].

immersion in HCl solution (1 N) at 80 °C does not improve the stage of hydrolysis–condensation reactions. Over 72 h of hydrolysis treatment, we observed a decrease of the insoluble fraction due to degradation of the PET [54].

For crystalline PET films (Fig. 12), we observe the formation of an insoluble fraction ranging between 40 and 70% depending on the time of diffusion of GOPTMSI + IPTESI (50/50 M) at 155 °C, and after water or HCl (1 N) treatment during 72 h at 80 °C. Logically this insoluble fraction increases with the time of diffusion, which enhances the reaction of functionalization.

Finally, we can note that for diffusion of GOPTMSI + IPTESI mixture (50/50 M) at 155 °C (Table 5), the maximum of insoluble fraction (70%) is quickly reached for either amorphous or crystalline fibers and films (1–5 h of diffusion) whereas longer diffusion times are required (up to 72 h) for lower diffusion temperatures such as 60, 80 and 90 °C even with the amorphous PET fibers. These results are consistent with the kinetic of reaction evidenced on model compounds by ^{1}H NMR spectroscopy and also in agreement with the evolution of reagents diffusion as discussed before.

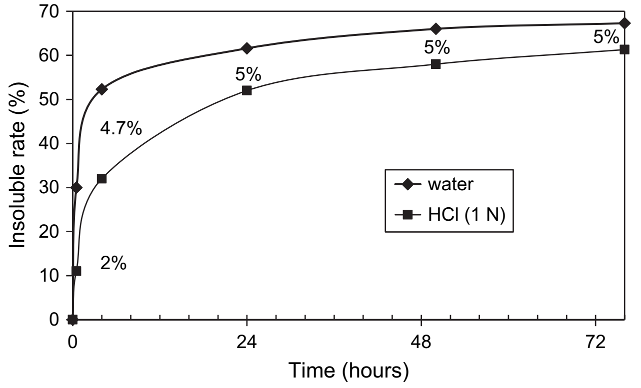


Fig. 12. Evolution of insoluble fraction versus time of diffusion of GOPTMSI + IPTESI mixture (50/50 M) at 155 °C following by hydrolysis–condensation reactions during 72 h at 80 °C for crystalline PET films. Data in percent for each point correspond to the mass uptake.

Table 5
Evolution of the insoluble fraction (IF) versus conditions of GOPTMSI + IPTESI mixture (50/50 M) diffusion and hydrolysis–condensation reactions for different samples of amorphous or crystalline PET

Sample	Temperature and time of diffusion	Temperature (°C) for hydrolysis–condensation reactions[a]	IF (%)
Crystalline film	155 °C, 5 h	80	70
Amorphous film	155 °C, 2 h	80	70
Amorphous fiber	155 °C, 1 h	80	70
Amorphous fiber	90 °C, 72 h	90	66
Amorphous fiber	80 °C, 3 h	80	40
Amorphous film	60 °C, 72 h	60	25
Amorphous fiber	60 °C, 72 h	60	60

[a] Time is equal to 72 h.

3.4. Thermal analysis

DSC thermograms of amorphous PET fibers before and after crosslinking are represented in Fig. 13. Crystallinity is drastically changed between the two samples (the untreated amorphous fibers and the crosslinked ones [IF = 70%, treated with GOPTMSI + IPTESI (50/50 M) at 155 °C for 1 h and hydrolysis–condensation in water at 80 °C for 72 h].

During the first heating ramp, we observe the disappearance of the crystallization exotherm due to the cold crystallization ($T_{cc} = 155$ °C) that happen because of the temperature of treatment higher than the glass temperature ($T_g = 80$ °C). The melting temperature T_m is lowered by 16 °C (from 254 to 238 °C) during the solid state modification because of a plasticizing effect of the reagents upon crystallization and maybe crystallite defects formation because of functionalization/crosslinking.

On the other hand, no crystallization occurs during the cooling ramp (after melting the initial crystallites during the first heating ramp) and hence there is no melting during the second heating ramp. As a conclusion, the crosslinked domains prevent further crystallization. Such phenomenon was already reported by Viallat et al. [55]. Indeed the authors observed that the crystallinity of crosslinked copolymers of ethylene vinyl acetate decreases with increasing the crosslinking density.

3.5. Thermomechanical behavior

First, we studied the properties of amorphous fibers modified at 60 °C after various times of diffusion of the mixture IPTESI + GOPTMSI (50/50 M) and reactions of hydrolysis–condensations at 60 °C for 72 h. Under a temperature ramp of 10 °C/min and a force of 0.01 N ($\sigma_0 = 5.5 \times 10^4$ Pa), Fig. 14 shows the variation of deformation of fibers for different insoluble fractions. The most important result is the variation of the deformation at break with the insoluble fraction. It is clear that the fibers of neat PET treated in the same conditions to that of the crosslinked samples break at 260 °C just above the melting temperature of PET. After the diffusion of IPTESI + GOPTMSI, followed by hydrolysis–condensation's reactions, the crosslinked fibers break-up at higher temperatures. Furthermore, this break-up temperature increases with the insoluble fraction to reach finally $T \approx 320$ °C for the

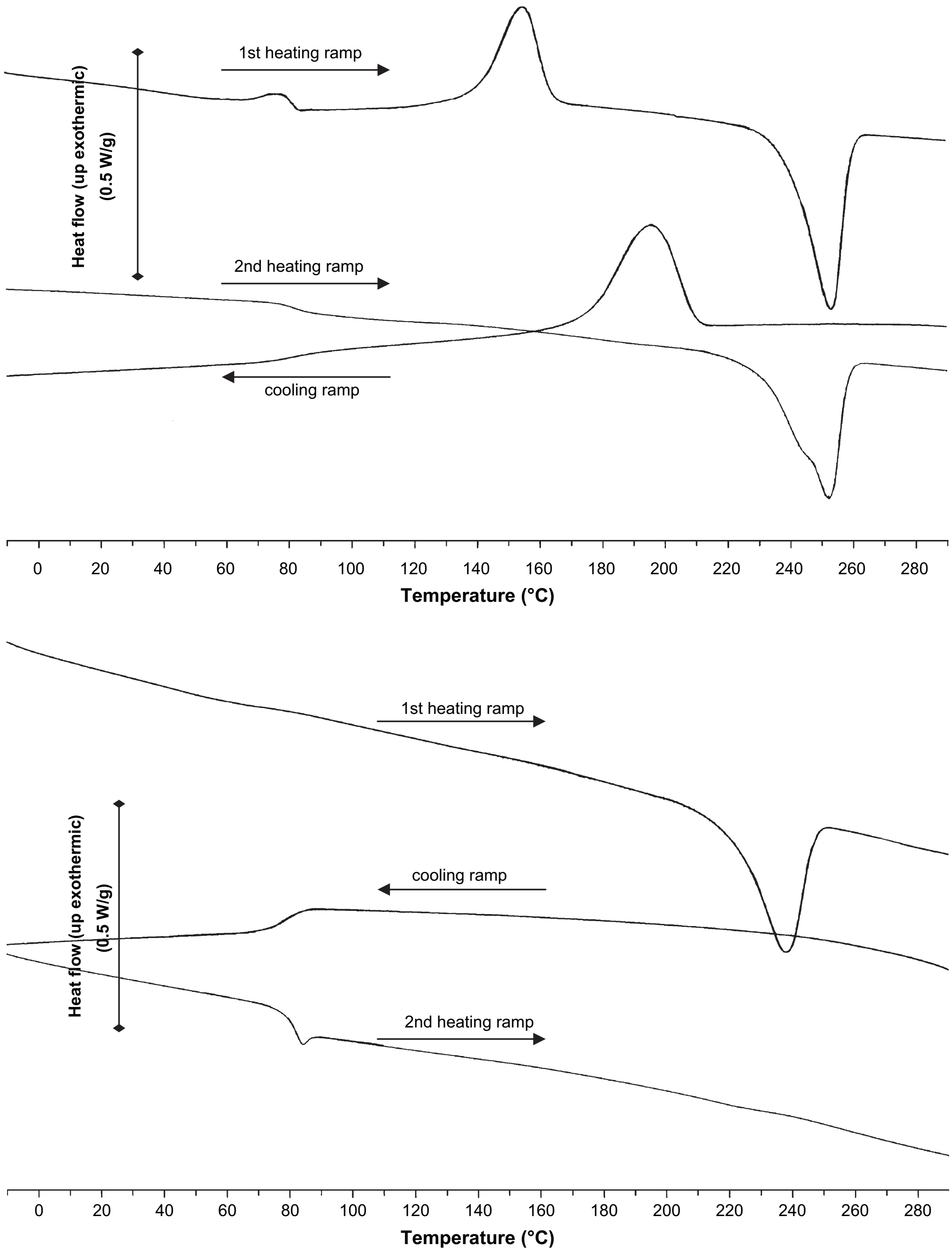


Fig. 13. DSC thermograms of an amorphous PET fiber before (top: IF = 0%) and after modification (bottom: IF = 70%, diffusion of GOPTMSI/IPTESI (50/50 M) at 155 °C for 1 h and hydrolysis–condensation in water at 80 °C for 72 h).

maximal insoluble fraction close to 70%. Consequently these types of crosslinked fibers are thermal resistant up to 320 °C.

As expected, PET considerably flows in molten conditions and totally looses its mechanical properties. Consequently, the neat PET fibers break-up just above the melting temperature of crystalline phase. The formation of a covalent network increases the resistance of PET fibers by hindering molecular motion in molten conditions. As expected, this resistance to creep behavior increases with increasing the crosslinking density. Such a result was already reported by Commereuc et al. [56] on the influence of crosslinking on thermal shrinkage behavior of poly(vinyl chloride) fibers.

Finally, the thermal viscoelasticity behavior of PET films is showed in Fig. 15. As expected, neat PET break-up and cannot be characterized anymore above the PET melting temperature. This result is consistent for crystalline films only (PET reheated and films modified at 150 °C), otherwise the crystallization during the experiment is observed. On the other hand, crosslinked PET films (insoluble fraction of 70%) break-up at higher temperatures ($T > 300$ °C) due to the thermal

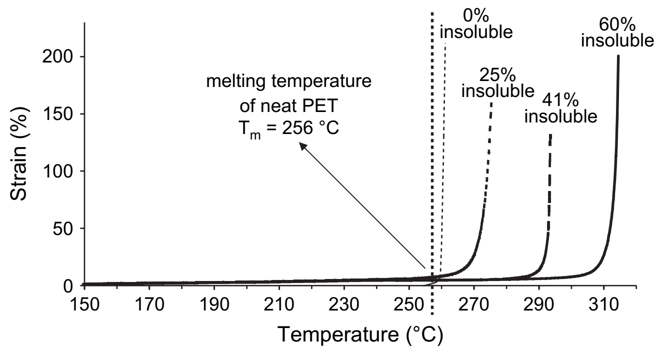


Fig. 14. Deformation of neat and crosslinked PET fibers under constant tension strength of 0.01 N and heating ramp (10 °C/min) from 25 °C. Influence of the crosslinking density on temperature at break.

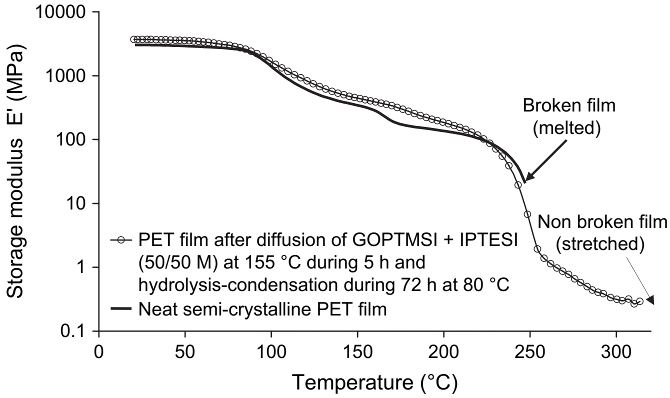


Fig. 15. Thermal viscoelasticity behavior of neat and crosslinked crystalline PET films. Temperature ramp: 3 °C/min, deformation amplitude: 0.05% and frequency $f = 5$ Hz.

degradation of PET. Furthermore, this figure clearly shows the permanent elastic modulus corresponding to the chemical crosslink network. The equilibrium modulus can be determined to be nearly $E_e \approx 4 \times 10^5$ Pa.

From the Flory's theory of the linear viscoelasticity, the molar mass M_c between to chemical crosslinks can be expressed as following:

$$M_c = \frac{3\rho RT(1-\phi)^{1/3}}{E_e} \tag{5}$$

where R is the gas constant, T the absolute temperature ($T \approx 573$ K), ρ is the density at the temperature T and ϕ the chain soluble fraction. According to Rodgers [57] $\rho = 1.14$ g/cm^3 at $T = 573$ K so that $M_c \approx 35{,}000$ g/mol. The soluble fraction is close to 30% so that not all the chains are attached to the chemical network and act as a plasticizer. Finally, the molar mass between two chemical crosslinks is slightly higher to the number average molar mass of neat PET chains ($M_n = 30{,}000$ g/mol). Consequently, this simple calculation agrees with the absence of exchange reactions [58] and confirms that the PET chains are crosslinked by their ends (end-linking network). Indeed PET chains (even very short ones) are always crosslinked by end groups.

4. Conclusion

Contrary to the functionalization of the PET in the molten state, which involves chains' scissions, the functionalization in a solid state makes it possible to functionalize the PET chain-ends with trialkoxysilane groups using the 3-isocyanatopropyltriethoxysilane (IPTESI) and a mixture of IPTESI + 3-glycidoxypropyltrimethoxysilane (GOPTMSI). All the reactions were investigated on model compounds: monomethylterephthalate (MMT) and triethylene glycol monomethylether (TGEMME) for PET–OH and –COOH end groups, respectively, by proton NMR spectroscopy. It evidenced the well-known reactions acid–epoxide and alcohol–isocyanate, respectively, leading in the range of temperature 60–160 °C to alkoxysilane PET end groups. It also showed the appearance of numerous other species due to the presence of alkoxysilane groups such as alcohol/alkoxysilane exchange reaction and acyloxysilane formation.

Furthermore, the diffusion of reagents in solid PET, depending on the initial degree of PET crystallinity, was characterized in the same temperature range through the variation of sample mass. On the other hand, this method allowed us to determine the diffusion coefficients and the solubility of the reagents in solid PET at different temperatures and initial crystallinity degrees.

Following the functionalization stage, the crosslinking reprocess was carried out by hydrolysis–condensation reactions of the trialkoxysilane end groups in hot water or HCl solution (1 N) as for the Sioplas process. As for example, the functionalization treatment of amorphous PET film (8% crystallinity) by a mixture of GOPTMSI + IPTESI (50/50 M) at 155 °C for 1 h followed by hydrolysis–condensation reactions at 80 °C for 72 h gave the most successful results regarding the insoluble fraction of PET chains. Under these conditions, the maximum of insoluble fraction of PET chains reaches 70%, which makes possible to improve the thermomechanical behavior of the PET beyond the melting point (256 °C).

Finally, it was clearly evidenced that modified fibers are thermal resistant up to 320 °C. On the other hand, a permanent elastic modulus is observed corresponding to the formation of a crosslinked network through end-groups' condensation.

Acknowledgements

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