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ORIGINAL PAPER

Effect of a formulation named "Giral" on mechanical properties of a composite based on silica and unsaturated polyester resin

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Abstract To improve the performances of a composite based on silica and unsaturated polyester resin, modification of silica surface and addition of a dispersing agent are required. The surface of raw silica was modified with vinyltrimethoxysilane in acidic conditions, adding methacrylic acid. Moreover, to enhance the compatibility between silica and polyester resin, a block copolymer which reacts as a dispersing agent was added. The mixture of these components is named "Giral." The mechanism of interaction of the different components of the "Giral" with the raw silica is described. Adding this formulation to a mixture of polyester resin and silica leads to a decrease of the viscosity of the polyester resin/silica system and the mechanical properties of the composite thus formed are improved.

Keywords Composites · Mechanical properties · Silica · Unsaturated polyester · Viscosity

Introduction

Study and design of composite materials have been of great interest in many fields such as aviation, construction, optical adhesives, etc. [1, 2]. Composite materials are made by combining an organic matrix which ensures the cohesion of the structure, and fillers for the final properties of the material formed. Thus, variety of organic matrices (thermoplastic or thermosetting resins) combined with different types of

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mineral (silica, clays, various metal oxides, etc.) has produced a large range of composite materials [3, 4]. Performances of these composite materials are often much higher than those of the corresponding material (chemical, mechanical, optical, thermal properties, etc.) that offer promising prospects for use. To access the description of a composite material, it will be necessary to specify the nature of components and their properties, the geometry of the reinforcement, its distribution, and the nature of the reinforcement–matrix interface. A large number of composite materials, generally classified according to the form of reinforcements (fibrous or particulate reinforcement), or by the nature of the matrix (organic, ceramic, and metal) exists and is divided in three categories: the organic matrix composites, which constitute by far the largest volumes today on an industrial scale, the ceramic matrix composites reserved to high-tech applications with high temperature such as space, nuclear, military, and braking (brakes ceramics) and the metal matrix composites for light and ultra-light alloy [5, 6].

Among the different structures of composites, this study has been focused on polyester resin reinforced with fillers and particularly with silica particles. These composite materials are made of a polymer matrix in which particles are well dispersed; they are thus flexible and easy to use even for complex geometries. The inclusion of fillers in a polymer matrix is a common industry practice. However, most of them are not chemically compatible with polymers. Addition of inorganic compounds in organic matrices generally requires implementation costly in energy and sometimes affects the final properties of the material. That's why for many years, studies have been conducted on particles functionalization to modulate the physical and/or chemical properties and to improve the compatibility between the filler and the matrix [7]. The most common way to modify the surface of particles is to attach suitable organic groups. The main compounds used are coupling agents like silanes ($RSiX_3$ with $X = Cl$, RO) [8–11] or organophosphorous compounds ($R_xP(O)(OX)_{3-x}$ with $x = 1$ or 2, $X = H$, Na, alkyl, etc.) [11–13]. Surfactants, as ionic surfactants [14], amphiphilic copolymers [15] or polymer directly grafted onto the inorganic surface [7, 16], can also be used to stabilize particles. The mechanical properties of composite thus formed are influenced by the quality of filler's dispersion.

Developed several years ago, a formulation named "Giral" allows one hand to obtain a good dispersion of fillers (silica, calcium carbonate, etc.) in a polymer matrix (polyester and polyepoxide resins) and, in the other hand, to increase the mechanical properties of the final composite [17, 18]. The "Giral" is composed of a silane, methacrylic acid (MAA), and a block copolymer used as a dispersant. The mechanism of "Giral" (named "Giralyse") has to be clearly identified using silica, which is a mineral filler broadly used in many industrial fields. Silica is used in a wide range of products including tires, scratch-resistant coatings, toothpaste, medicine, microelectronics components or in the building [19–22]. The main objective of this work was to understand the interactions between the surface of silica, taken as a model, and the different components of "Giral" Thermogravimetric analyses, infrared spectroscopy analyses, ^{13}C and ^{29}Si solid state NMR analyses have been performed on samples synthesized from silica and one or more components of "Giral" to determine and to quantify the interactions between the different species which composed the “Giral” and the silica surface. Viscosity measurements on unsaturated polyester resin/silica mixtures containing the components of the “Giral” were realized and test specimens based on polyester resin/silica were prepared to observe the influence of the “Giral’s” components on the mechanical properties. Fracture surface of test specimens were observed by scanning electron microscopy (SEM).

Experimental

Materials

Benzoyl peroxide (BPO, AkzoNobel), diethylamine (DEA, Arkema), methacrylic acid (MAA, Arkema), vinyltrimethoxysilane (VTMO, Wacker), block copolymer named PEO-b-PCL ($Mn_{(SEC)} = 830$, Pdi = 1.4) functionalized at the end of the PCL block with a phosphoric acid function, unsaturated polyester resin (UPE, Distitron Iso lonza 183 RV2 from Polynt and Norsodyne G703 from Cray Valley) were used as received. Two industrial raw silicas were used in this work: silica ACEMATT TS100 (Evonick-Degussa) and silica Millisil C6 (Sifraco, Sibelco group). Toluene (99.3%, Carlo Erba Reagent) was analytical reagent and directly used without any purification.

Interaction of the different components of the “Giral” with the silica surface

For example, modification of raw silica with VTMO (sample Si-VTMO-1) was realized as following: in a 250 mL round bottom flask, 1.9 g of silica Acematt TS100 were introduced in 50 mL of toluene with 0.35 g of VTMO. The solution was heated at 80 °C during 45 min. Every 5 min, 0.06 g of benzoyl peroxide were added. Silica was then recovered by centrifugation (8,000 RPM–20 min), and washed four times with 60 mL of toluene to remove the excess of reagent. Silica particles were finally dried at 80 °C in an oven during the night. The different experiments are shown in Table 1.

Test specimens preparation

Test specimens were prepared by the following method from a mixture composed with 40 wt% UPE, 60 wt% silica Millisil C6 and components of “Giral.” The “Giral” formulation is composed with 0.3 wt% VTMO, 1 wt% MAA, and 0.3 wt% block copolymer named PEO-b-PCL. The sizes of the test specimens are shown in Fig. 1. The catalytic system used to polymerize the mixture was composed of 0.1 wt% DEA, as promoter, and 1.5 wt% BPO, as initiator. This mixture was then flowed in the test specimens frame mold and placed in a steam room at 30 °C under 600 mbars during 1 h. Care was taken to evenly distribute the mixture in the mold to ensure a uniform sample. Test specimens were then recovered and finally cured in an oven at 80 °C during 15 h.

Table 1 Samples preparation in 50 mL toluene with 1.9 g silica ACEMATT TS100 and 0.3 g benzoyl peroxide dissolved in 10 mL of toluene

Samples	Reagents		
	VTMO (g)	MAA (g)	PEO-b-PCL (g)
Si-VTMO-1	0.35		
Si-VTMO-2	0.75		
Si-VTMO-3	1.5		
Si-VTMO-4	3		
Si-MAA-1		0.35	
Si-MAA-2		0.75	
Si-MAA-3		1.5	
Si-MAA-4		3	
Si-PEObPCL-1			0.38
Si-PEObPCL-2			0.75
Si-PEObPCL-3			1.5
Si-PEObPCL-4			3
Si-G1	0.75	0.75	
Si-G2	0.75		0.38
Si-G3		0.75	0.38
Si-G4	0.75	0.75	0.38

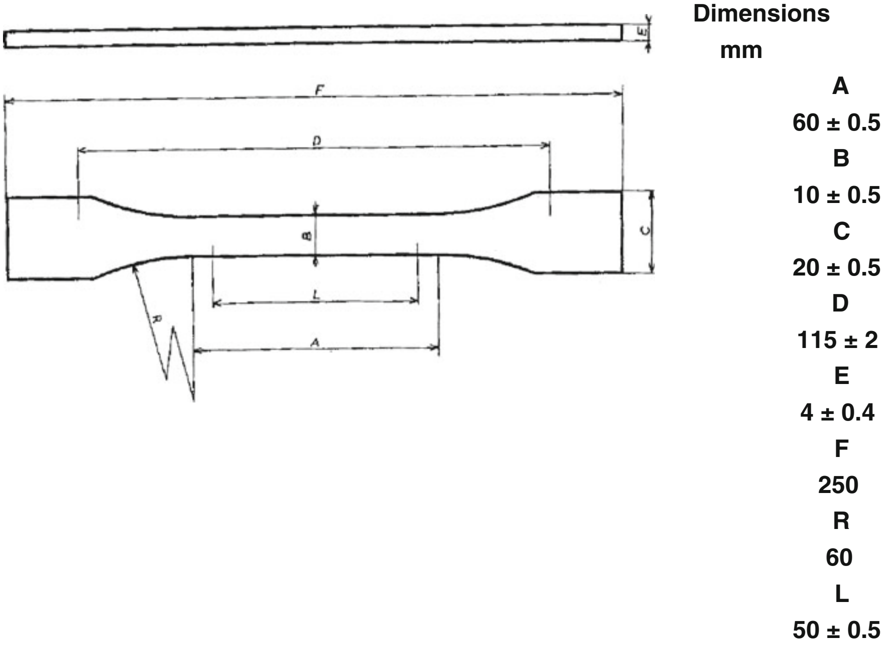


Fig. 1 Sizes of the test specimens for tensile test

Characterizations

FT-IR spectra were monitored with a Bruker IFS66S spectrometer. 100 scans and 4 cm^{-1} resolution were used. Grafted or adsorbed component amounts on modified silica samples were assessed by thermogravimetric analysis (TGA) using a TGA METTLER-TOLEDO 851e thermal system. For the analysis, about 10–20 mg of samples were taken and heated at a constant rate of 10 °C/min under air (purge rate 50 mL/min) from 30 to 1,100 °C. The surface areas of the raw silica were obtained from nitrogen adsorption experiments by the BET analysis at 77 K with a Micromeritics ASAP 2010 analyzer. ^{29}Si and ^{13}C solid state NMR spectra were recorded on a Brüker Avance II 400 spectrometer, using magic angle spinning (MAS) and high power proton decoupling with a Bruker double channel 7 mm probe. For this, zirconium rotors were employed at 79.48 and 100.6 MHz using a pulse angle of $\pi/2$, a recycling delay of 4 s, a spinning frequency of 4 kHz and a contact time of 2 and 4 ms for ^{29}Si and ^{13}C, respectively. Viscosity measurements of silica/UPE resin mixtures were carried out using a Brookfield DV-II + Pro viscosimeter at 50 rounds per min (RPM) under air. Tensile tests of composites test specimens were performed with an INSTRON 4505 machine at a rate of 0.2 mm/min at room temperature. Morphology of the fractured surface of the samples was studied with a FEI Quanta 400 SEM. Transmission electron micrographs (TEM) were taken with a Philips CM200 TEM at an accelerating voltage of 200 kV.

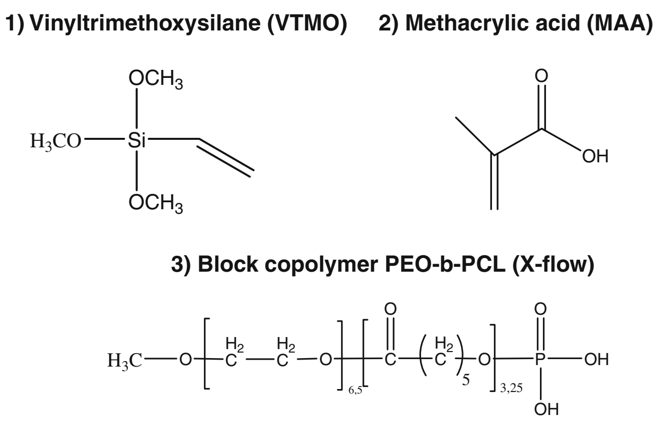
Results and discussion

“Giral” formulation

The “Giral” is a stable formulation made of three components shown in Fig. 2 [18]. Added to a mixture of fillers and resin, this formulation enabled a good dispersion of fillers in resin (implying a decrease of the viscosity). Thus, composite with a high rate of fillers can be obtained (approximately 60–80 wt%). Moreover the reinforcement of the link between filler and polymeric matrix is observed through the mechanical properties which are improved [17, 18].

“Giralyse” mechanism

The mechanism of “Giralyse” implying interactions between the different components of the “Giral” and a filler, is not well known. That’s why during this study we have examined the interactions that can take place between one or more component of the “Giral” and a model filler, silica. During the experiments, BPO, used for the crosslinking of the UPE resin to elaborate the final composite, was added to be close to the application. As it was impossible to realize the study in styrene (solvent of the UPE resin), because of the presence of BPO which could enable its polymerization, we decided to work in toluene (which possess a chemical structure close to that of styrene).



1) Vinyltrimethoxysilane (VTMO) 2) Methacrylic acid (MAA)

3) Block copolymer PEO-b-PCL (X-flow)

Fig. 2 Molecular structures of "Giral's" components

Silica characterizations

To understand the "Giralyse" mechanism, we have worked using a silica having well-known surface properties [23–28]. In this case, ACEMATT TS 100 silica was used because of its high specific surface ($S_{\mathrm{BET}} = 248$ m^2/g). To characterize the raw silica, IR-DRIFT and ^{29}Si solid state NMR analyses were investigated. The IR spectrum highlights the different types of silanols groups present at the surface of silica particles: v (isolated and geminal silanols): 3740 cm^{-1}, v (vicinal silanol): 3650 cm^{-1}, v (siloxane groups): 1860 cm^{-1} and 1350–1000 cm^{-1}. On NMR spectrum, geminal silanols can be distinguished from the isolated ones (Fig. 3). In the NMR Qn terminology, n is the number of bridging oxygens bonded to the central silicon: Q4 peak corresponds to the siloxane bridges (−110 ppm), Q3 to isolated and vicinal silanols (−100 ppm) and Q2 to geminal silanols (−90 ppm) [29–31].

TEM was used to observe the morphology of silica particles (Fig. 4). It was observed that silica particles were aggregated. The mean size of an elemental particle is approximately 11 nm. According to the specific surface area calculated by BET analyses and taking the density of silica ($d = 2$, Table 2), the average diameter of particles can be calculated and is about 10 nm, close to the size measured by TEM. The characteristics of the ACEMATT TS100 silica are summarized in Table 2.

Interactions between silica particles and one component of "Giral"

Vinyltrimethoxysilane: Grafting reaction of VTMO on silica surface was carried out using toluene as a solvent; water adsorbed on silica allows hydrolysis of the VTMO methoxy functions [10, 32–36]. An infrared analysis was performed on Si-VTMO-2 sample to confirm the presence of VTMO on silica. The VTMO features bands (double bond at 2900 and 1550 cm^{-1} and methoxy groups at 2850 cm^{-1}) are noticeable on the spectrum. To determine the nature of links established between the hydroxyl groups of silica and VTMO, solid state NMR was used. On ^{13}C solid state

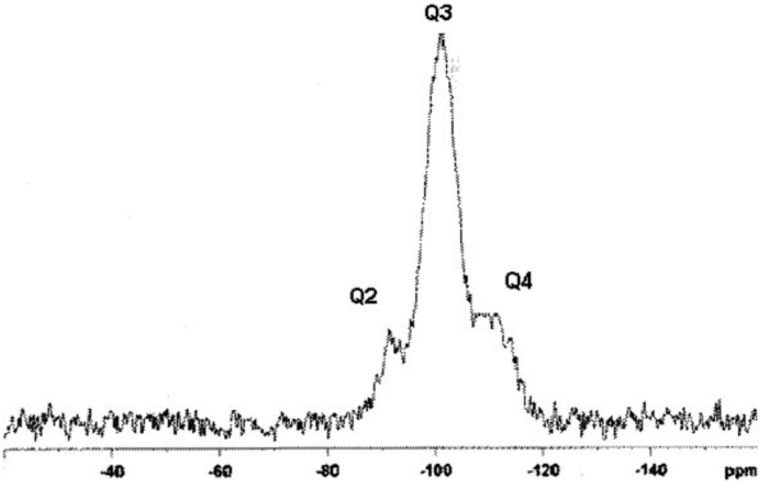


Fig. 3 ^{29}Si NMR spectrum of raw silica

Fig. 4 TEM micrograph of raw silica

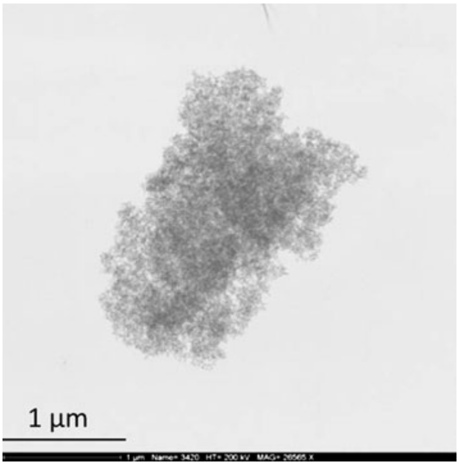


Table 2 Acematt TS100 silica characteristics

Hydrophily[a]	4–4.5 SiOH/nm^2
	7 µmol/m^2
Particle size	MET: 11 ± 3 nm
	BET: 12.5 ± 0.2 nm and 10 µm (D50 laser scattering)[a]
Density[a]	2 g/cm^3
Specific surface (BET)	238 ± 2 m^2/g

[a] Supplier data

NMR spectrum (Fig. 5a), VTMO double bonds were present as well as residual methoxy groups, which suggested that they were not all hydrolyzed or condensed among themselves.

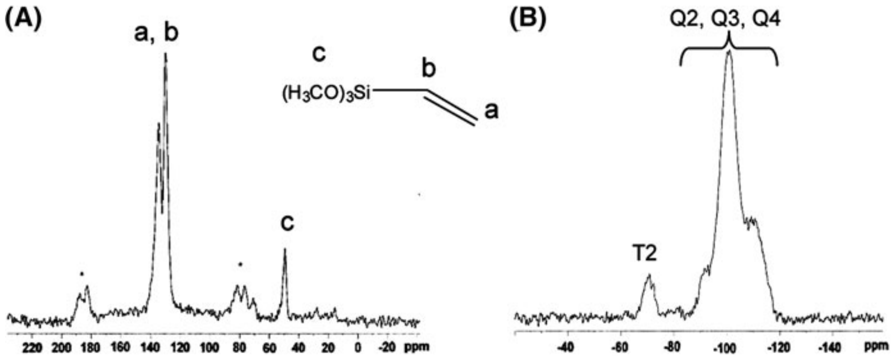


Fig. 5 Si-VTMO-2 NMR spectra: **a** ^{13}C solid state NMR and **b** ^{29}Si solid state NMR

Table 3 Amount of VTMO grafted on silica surface versus amount of VTMO introduced

Samples	Si-VTMO-1	Si-VTMO-2	Si-VTMO-3	Si-VTMO-4
mg VTMO/g of silica introduced	186	400	800	1,600
mg VTMO/g of silica grafted (TGA)	11	11	11	10
μmoles VTMO/m^2 of silica (TGA)	0.8	0.8	0.8	0.7

Figure 5b shows that the ^{29}Si NMR spectrum of the solid sample. The appearance of a T2 peak corresponding to a Si–OR bond as well as the slight decline in Q2 and Q3 peaks showed that two of the three methoxy groups have reacted with silica surface or have condensed on themselves. All silica hydroxyl sites were not grafted because of the steric hindrance of VTMO and the difficult accessibility of some hydroxyl sites. These analyses on silica modified with VTMO confirmed the presence and the grafting of VTMO on silica surface. VTMO was grafted to the surface via a reaction of hydrolysis/condensation and only two methoxy groups condensed.

VTMO grafting density on silica, determined by TGA analysis, as a function of amount introduced, was plotted. Table 3 shows the amounts of VTMO introduced and quantities grafted on the surface of silica, determined by TGA. Only a small amount of VTMO interacts with the surface.

The maximum amount of VTMO that could be grafted to silica surface was 0.8 mol/m^2 or 0.5 molecules per nm^2. If we compare the amount of silanols groups on silica surface (7 μmol/m^2) and the amount of VTMO grafted, the rate of surface hydroxyl groups recovered corresponded to 15%. This value could be explained by steric hindrance of VTMO. These results were compared to silica modification with trivinylmethoxysilane (TVMO), which is a small molecule that has only one methoxy group which can condense on the surface of silica. The recovery rate of TVMO on silica was 45% which means that the hydroxyl groups of silica were not all accessible.

Table 4 Amount of MAA at silica surface

Samples	Si-MAA-1	Si-MAA-2	Si-MAA-3	Si-MAA-4
mg MAA/g of silica introduced	186	400	800	1,600
mg MAA/g of silica adsorbed or grafted (TGA)	9	19	39	78
μmoles MAA/m^2 of silica (TGA)	0.12	0.25	0.37	1.15

The quantities present on silica surface were far less than what might be expected during the condensation of a silane on silica particles [37]. A small amount of VTMO was enough to cover the surface of silica as shown by Si-VTMO-2 sample. This amount corresponds to 0.2 wt% VTMO (in "Giralyse", 0.4 wt% VTMO is introduced).

Methacrylic acid: Silica was modified with MAA in toluene. In a first step, an infrared analysis was performed on Si-MAA-2 sample to confirm the presence of MAA on silica surface. MAA features bands (double bond at 2900 and 1550 cm^{-1} and carbonyl group at 1700 cm^{-1}) are visible on the spectrum. In a second step, the variation of the grafting density of MAA on silica depending on the amount of MAA introduced was plotted. Table 4 shows the amounts of MAA introduced at the beginning of the reaction and those remaining after four washings with toluene, determined by TGA.

At the end of the reaction, toluene washings have eliminated a large excess of MAA meaning that MAA was not strongly anchored to the silica surface. Toluene washings did not eliminate all the MAA. However, further washings with ethanol, which is a polar solvent, helped to eliminate the majority of MAA at the silica surface. This characteristic confirms that MAA was only weakly bond to hydroxyl groups of silica surface (hydrogen bonding or esterification of silica surface creating a Si–OC=O bond easily hydrolysable). To determine the nature of bonds established between the hydroxyl groups of silica and MAA, solid state NMR was used. ^{13}C solid state NMR analysis has been conducted on Si-MAA-2 sample. However, the amount of MAA was not sufficient on silica to be visible on the spectrum. The ^{29}Si solid state NMR analysis showed that the surface of silica was not changed: the intensities of the Q sites were identical to those observed for the raw silica spectrum. Furthermore, no T peaks, which might highlight a possible grafting between MAA and silica surface, were observed. MAA was adsorbed on the surface of silica via hydrogen bonds and was easily desorbed by washing with toluene and ethanol. Because of the sensitivity of NMR, the change of the surface of silica by MAA was not observed.

PEO-b-PCL copolymer: Silica was reacted with PEO-b-PCL in toluene. In a first step, an infrared analysis was performed on Si-PEObPCL-1 sample to verify the presence of PEO-b-PCL on silica surface. The PEO-b-PCL features bands were visible on the spectrum (phosphoric bond at 1350 cm^{-1} and the carboxylic bond at 1700 cm^{-1}). In a second step, variation of grafting density of PEO-b-PCL on silica

Table 5 Amount of X-flow at silica surface

Samples	Si-PEObPCL-1	Si-PEObPCL-2	Si-PEObPCL-3	Si-PEObPCL-4
mg PEO-b-PCL/g of silica introduced	200	400	800	1,600
mg PEO-b-PCL/g of silica adsorbed or grafted (TGA)	100	120	160	190
μmoles PEO-b-PCL/m^2 of silica (TGA)	0.7	0.9	1	1.6

surface versus the amount of PEO-b-PCL introduced was plotted. Table 5 shows the amounts of PEO-b-PCL introduced at the beginning of the reaction and the amounts remaining after four washings with toluene.

When modifying silica surface with PEO-b-PCL, toluene washings eliminate only a small amount of PEO-b-PCL. The curves corresponding to the grafting density of the sample on silica modified by the PEO-b-PCL after four washings in toluene and after a fifth washing with ethanol were plotted. The aim was to observe the influence of solvent on polar interactions developed between PEO-b-PCL and silica. After the fifth washing, ethanol desorbed a large part of PEO-b-PCL, which means that the PEO-b-PCL was not chemically anchored to silica but simply adsorbed. The curve corresponding to a fifth washing with ethanol has a plateau; the maximum amount of PEO-b-PCL observed was 0.2 molecules per nm^2. The rate of surface hydroxyl group's recovery corresponded to 3% after washing with ethanol. The quantity of PEO-b-PCL introduced in the "Giralyse" (sample Si- PEObPCL-1) was sufficient to cover the surface of silica after washing with ethanol. PEO-b-PCL features peaks were observed by ^{13}C solid state NMR. PEO-b-PCL could be grafted to the hydroxyl groups of silica via its phosphoric acid function but the chemical bond so formed is weak due to the Si–O–P bond instability face hydrolysis [11–13, 38]. ^{29}Si solid state NMR confirmed that silica surface was not modified by PEO-b-PCL; no chemical bond were formed since T peaks were not visible. Hence, we can conclude that PEO-b-PCL was simply adsorbed on silica. This copolymer acts as a dispersant in the formulation of "Giral" and is adsorbed to silica through its phosphoric acid function.

Interactions between silica particles and two components of "Giral"

Binary VTMO/MAA: IR-DRIFT analysis was performed on the sample of silica modified with MAA and VTMO, named Si-G1, corresponding to 0.4 wt% MAA and 0.4 wt% VTMO. IR analysis of Si-G1 sample confirmed the presence of the two components on silica. To determine the nature of links established between hydroxyl groups of silica and MAA and VTMO, solid state NMR analyses were performed. In the ^{13}C solid state NMR spectrum (sample Si-G1), only VTMO features peaks were visible. As mentioned previously, the presence of MAA on the silica surface cannot be identified by ^{13}C solid state NMR. Figure 6, corresponding to ^{29}Si solid state NMR spectrum of the sample, allows observing the appearance of peaks T1, T2, and T3, while only T2 peak was observed on Si-VTMO-2 sample

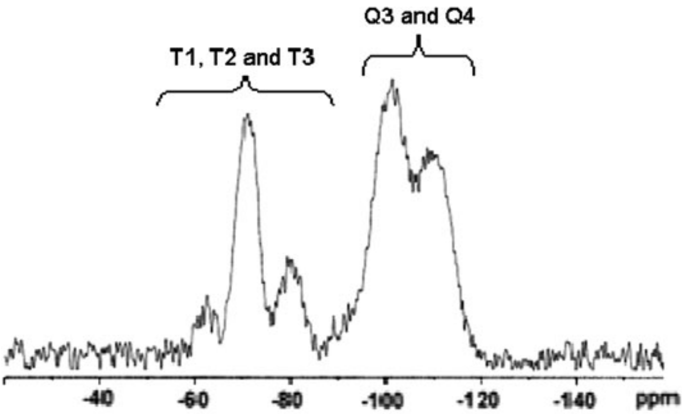


Fig. 6 Si-G1 ^{29}Si CPMAS solid state NMR spectrum

spectrum containing VTMO only. T peaks prove the polycondensation and chemical grafting of VTMO on silica. One, two, or three of the methoxy groups were hydrolyzed and then polycondensed and/or grafted onto silica surface.

Hydroxyl groups number on silica surface has intensively decreased in view of the reduction of Q2 and Q3 peaks compared to the spectrum of silica modified by VTMO sample (Si-VTMO-2) and containing the same amount of VTMO (0.4 wt%). MAA seemed to catalyze the silane condensation on silica (acid catalysis) [33, 39]. Indeed, the presence of MAA was not detected on ^{13}C solid state NMR spectrum, MAA plays an important role in catalyzing VTMO hydrolysis/condensation on silica surface.

Binary VTMO/PEO-b-PCL copolymer: IR-DRIFT analysis was performed on sample of silica modified with VTMO and PEO-b-PCL, named Si-G2, corresponding to 0.4 wt% VTMO and 0.2 wt% PEO-b-PCL and confirmed the presence of these two components. Figure 7a corresponding to the ^{13}C solid state NMR spectrum of Si-G2 sample, showed the features peaks of PEO-b-PCL copolymer and the double bond of VTMO. However, feature peaks of the methoxy groups were no longer visible indicating they had reacted with silica hydroxyl groups and/or had polycondensed.

This result was confirmed by ^{29}Si solid state NMR analysis (Fig. 7b) in which additional T3 peak, corresponding to the total hydrolysis of methoxy groups, appeared compared to silica modified only by VTMO (Si-VTMO-2). Q3 peak reduction and loss of Q2 peak indicate that hydroxyl group's number on silica surface has decreased. PEO-b-PCL phosphoric acid function thus catalyzed silane condensation on silica. To conclude, PEO-b-PCL was adsorbed onto silica via its phosphoric acid groups and catalyzed VTMO methoxy functions hydrolysis which condensed on silica surface or polycondensed.

Binary MAA/PEO-b-PCL copolymer: IR-DRIFT analysis was performed on the sample of silica modified with MAA and PEO-b-PCL, named Si-G3, corresponding

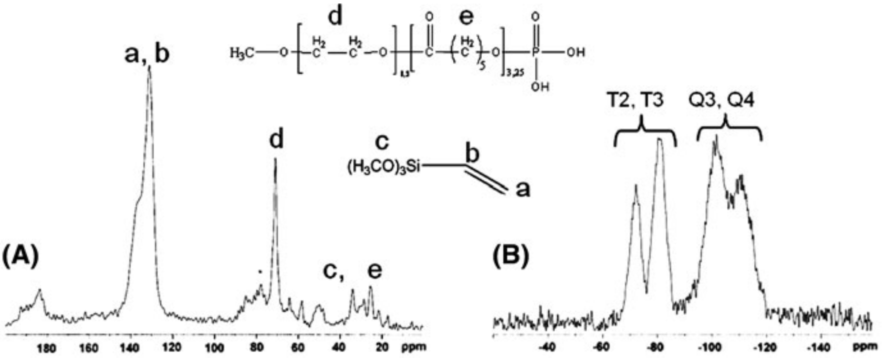


Fig. 7 Si-G2 NMR spectra: **a** ^{13}C solid state NMR and **b** ^{29}Si solid state NMR

to 0.4 wt% MAA and 0.2 wt% PEO-b-PCL and confirmed the presence of these two components. PEO-b-PCL characteristic peaks were present on ^{13}C solid state NMR spectrum, however, as before, the characteristic peaks of MAA were not observed. ^{29}Si solid state NMR analysis of Si-G3 shows that neither MAA nor PEO-b-PCL were chemically grafted to silica. Peaks corresponding to silanols and siloxane Q groups of silica were unchanged. These two components were simply adsorbed (via hydrogen bonds) on silica.

Interactions between silica particles and the "Giral" formulation

After studying the interactions between one or two components of "Giral" and silica, Si-G4 sample, containing the "Giral" formulation, was analyzed. In this case, the percentages of each component in the mixture of silica were: 0.4 wt% of MAA, 0.4 wt% VTMO, and 0.2 wt% PEO-b-PCL. The analyses performed on silica modified by one or two components of "Giral" helped to define the behavior of each component. MAA and PEO-b-PCL were adsorbed on silica, VTMO was grafted onto silica and its grafting was catalyzed in the presence of MAA or PEO-b-PCL. ^{13}C solid state NMR spectrum (Fig. 8a) shows PEO-b-PCL and VTMO feature peaks. As in the case of the Si-G2 sample (containing silica, VTMO, and PEO-b-PCL), VTMO alkoxy groups were not observed. MAA characteristics peaks, as previously, were not observed. Spectra of solid state NMR (^{13}C and ^{29}Si) are identical to those obtained for Si-G2 sample, containing the VTMO/PEO-b-PCL binary. MAA did not appear to have any influence on the grafting of VTMO in the presence of PEO-b-PCL.

VTMO methoxy functions reacted with the surface hydroxyl groups. This hypothesis was confirmed by ^{29}Si solid state NMR analysis (Fig. 8b), with appearance of T2 and T3 additional peaks compared to the spectrum of raw silica and to the clear hydroxyl groups number decrease on silica as shown by the Q2 peak disappearance and the sharp Q3 peak decrease. The presence of PEO-b-PCL improved VTMO condensation on silica while the MAA seemed to have no influence on VTMO grafting in the presence of PEO-b-PCL.

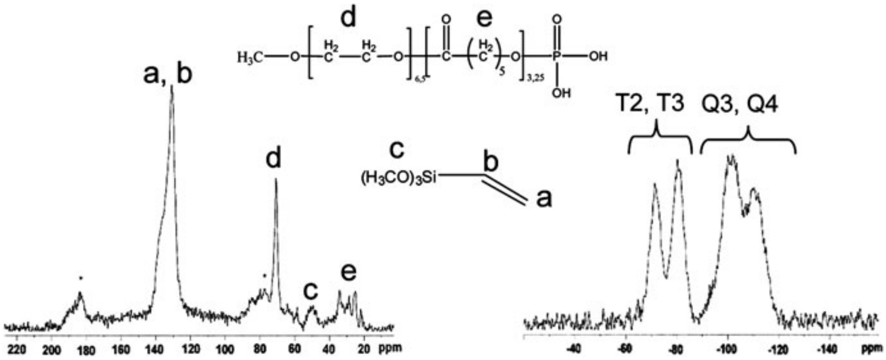


Fig. 8 Si-G4 NMR spectra: **a** ^{13}C solid state NMR and **b** ^{29}Si solid state NMR

Description of the mechanism

The study has highlighted the role of each of the three components of "Giral" (VTMO, MAA, and PEO-b-PCL). The VTMO is grafted on the surface of silica (on average two methoxy groups are hydrolyzed). PEO-b-PCL copolymer is adsorbed at the silica surface. The addition of MAA or PEO-b-PCL improved the VTMO grafting efficiency because of their acidic functions which catalyze silane condensation. According to these analyses, MAA in the formulation of "Giral" did not seem to be necessary. ^{13}C and ^{29}Si solid state NMR analyses cannot highlight the role played by MAA. It should also be noted that we choose to carry out washings to remove non-grafted or strongly adsorbed "Giral's" component, in this case, we were not fully representative of what happens during the "Giralyse" mechanism.

Preparation and mechanical properties of composites based on silica and unsaturated polyester resin

The effect of addition of VTMO, MAA, and/or PEO-b-PCL in the formulation of the composite on the viscosity of the reaction medium and on the mechanical properties of the final composite has been investigated.

UPE resin/silica mixture viscosity

Incorporating a high loading rate of filler in a resin is an important parameter to achieve some properties (opacity, fire retardant, etc.) [40] as to get a good flow for easy implementation. To highlight the role of each "Giral" component, viscosity measurements on UPE resin/silica mixture were done to determine their influence on the dispersion of silica in the polymer matrix. Figure 9 shows the different results.

The presence of VTMO, in a mixture of silica Millisil C6 (60 wt%)/Norsodyne G703 resin (40 wt%), decreased the viscosity. This effect was amplified when MAA

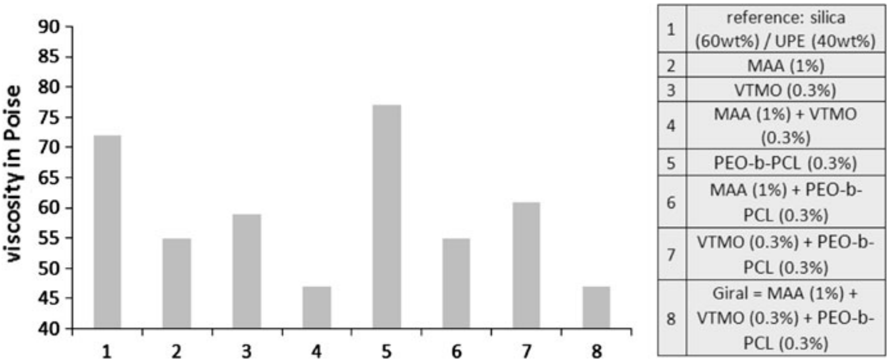


Fig. 9 Viscosity at 50 RPM of a mixture Millisil C6 silica (60 wt%)/Norsodyne G703 UPE resin (40 wt%) with “Giral’s” components

was added. The role of the MAA had not been clearly highlighted in the mechanism of “Giralyse” (“Description of the mechanism” section) but here, MAA played an important role. MAA acid functions catalyzed the silane condensation on silica surface, thus promoting silica dispersion in the polyester resin. According to the histogram above, PEO-b-PCL was not sufficient to disperse silica alone in the resin. At this stage, the role of PEO-b-PCL was not highlighted.

Tensile tests

Test samples were made to observe the influence of each “Giral” component on break stress. Polymerization was conducted using a catalytic system composed of 0.1 wt% DEA and 1.5 wt% BPO. The results are shown in Fig. 10. Each tensile test was conducted on four test specimens. Because of good reproducibility of results, the error margins are not presented. Results from tensile test are relative to composite based on 60 wt% silica/40 wt% UPE resin.

MAA and VTMO alone or used together provided a slight contribution to mechanical properties. In counterpart, addition of PEO-b-PCL is useless. The largest increase (38%) came from the test specimen containing “Giral”. This characteristic highlighted the existence of a synergy between the “Giral” components and showed the importance of each of them in the “Giralyse” mechanism. Influence of components addition conditions to the mixture [silica Millisil C6 (60 wt%)/UPE 183 resin Iso Lonza ARV2 (40 wt%)] was investigated as shown in Table 6.

Separate addition of “Giral” components to the mixture decreased the impact of this formulation. MAA recovered silica surface and prevented VTMO from condensing. However, the effect was optimized if the components were added together. This behavior revealed the existence of a competition between the components to bind to silica surface.

To highlight the influence of VTMO double bond on mechanical properties of the composite formed, VTMO was replaced by an amino silane (APTS, aminopropyltriethoxysilane), which could not chemically anchored to the resin during polymerization.

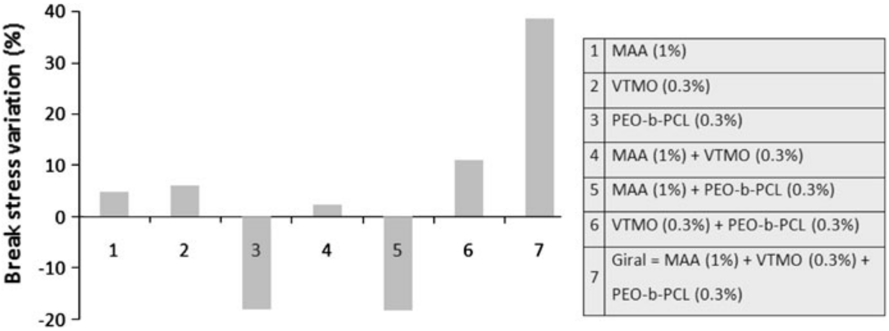


Fig. 10 Break stress variations compared to the reference of composite based on Millisil C6 silica (60 wt%)/UPE Iso Lonza 183 ARV2 resin (40 wt%)—wt% are given compared to the silica/UPE resin mixture

Table 6 Break stress on test specimens based on Millisil C6 silica (60 wt%)/UPE Iso Lonza 183 ARV2 resin (40 wt%) depending on "Giral" addition conditions

"Giral" addition condition	Break stress variation (%)
Each component added separately (MAA then VTMO then PEO-b-PCL)	30
Giral's components added together	38

1% MAA—0.3% VTMO—0.3% PEO-b-PCL

Table 7 Influence of the nature of silane on break stress

"Giral" with 0.3 wt% of	Break stress variation (%)
VTMO	38
APTS	−5

Table 7 shows the variations in the stress at break as the silane was carrying a double bond or not.

The presence of the double bond on the silane was required to improve break stress of test specimens. VTMO double bond permits to create a covalent bond between the organic matrix and silica, enhancing the mechanical properties of the final composite.

Fracture surface observation

SEM was used to observe the features of tensile fracture surfaces and interfacial silica-matrix. This approach enables us to evaluate the performances of composites. Three different types of failure mechanisms could be identified: the matrix failure, the filler fracture, and the filler–matrix interfacial failure [41]. A weak interface or incompatibility between filler and matrix may lead to filler pull out instead of fracture and may reduce the resulting mechanical properties. In this study, combinations of these failures were observed depending on the composition of the

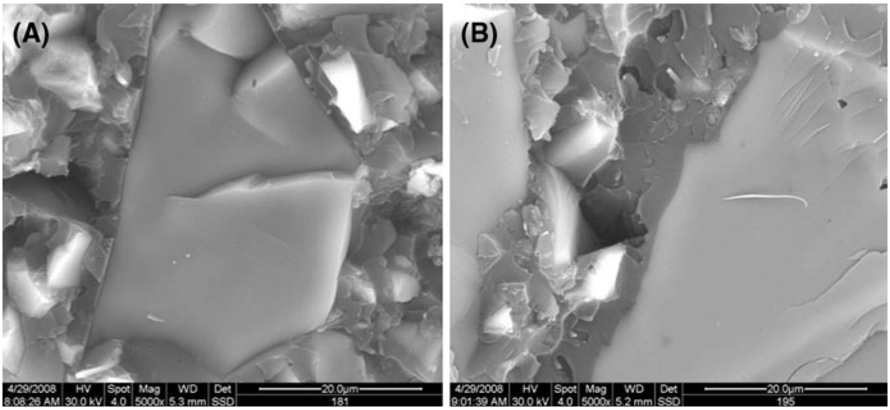


Fig. 11 SEM micrographs of fracture surface of composites based on Millisil C6 silica (60 wt%)/UPE Norsodyne G703 resin (40 wt%), **a** without "Giral" and **b** with "Giral"

composite. Figure 11a shows a representative SEM micrograph corresponding to the crude composite (60 wt% silica/40 wt%UPE) and highlights the gap between silica and matrix and the lack of bonding between them without "Giral."

The interfacial gaps around silica particles decreased when adding VTMO and "Giral's" formulation. Adding "Giral" in the composite improved the cohesion between the filler and the matrix (Fig. 11b). Tensile test results supported the hypothesis that weaker interface leads to a more pronounced pull-out phenomenon, as reduction in break stress was observed.

Analyzes have revealed the influence of MAA on reducing the viscosity of silica (60 wt%)/resin (40 wt%) mixture and the fracture surface of test specimens. It was clear that the sum of the three components of "Giral" provided the best mechanical performances and the best viscosity falls. These behaviors highlighted the existence of a synergy between the three components.

Conclusion

During this work, silica was dispersed in an unsaturated polyester resin to produce a composite material with a high load and to achieve some characteristics such as high mechanical properties. In order to give to our final composite material such properties, "Giral" formulation, composed of a silane (VTMO), MAA, a block copolymer (PEO-b-PCL), was incorporated. "Giral" allowed dispersing high rate of silica in UPE and improving the mechanical properties of the final composite. Although this formulation was effective, its mechanism had to be identified. In a first step, the interaction of each component of "Giral" formulation with the silica surface was highlighted. The study was focused on silica, which had the advantage of being well known and had a high specific surface. TGA, DRIFT, ^{13}C, and ^{29}Si solid state NMR analyses had been made to determine the influence of "Giral's" components. Through these analyses, we determined the role of VTMO that grafted and condensed on silica surface. VTMO anchoring to silica was catalyzed in the presence of MAA or PEO-b-PCL, because of their acidic groups. However, in view of ^{13}C and ^{29}Si solid state NMR analyses, MAA did not seem to be necessary. Instead, at the level of mechanical properties of the composite formed, MAA was an essential component, and its presence conferred higher mechanical properties. In this study, interactions of the "Giral" with the surface of silica have been described and the synergy between them has been highlighted but not explained.

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