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Organic/inorganic hybrid composites prepared by polymerization compounding and controlled free radical polymerization

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Abstract

A new method to produce highly filled and well dispersed polymer solid composites using controlled free radical polymerization has been developed. Grafting of polymers onto ultrafine silica was done in bulk polymerization at 120 °C in presence of *N*-*tert*-butyl-1-diethylphosphono2,2-dimethyl propyl nitroxide (DEPN) as a nitroxide stable free radical. Optimum conditions for *tert*-butyl hydroperoxide grafting onto fumed silica were first determined. The percentage of grafting, the architecture of grafted polymers, the length of chains, and the polydispersity index can be controlled at will using this approach. The effect of the number of grafted polymer chains combined with its molecular weight on the processing of these materials was investigated. The syntheses performed in this work gave grafting percentages of polymers and copolymers ranging from 12 to 88 wt%. All 'synthesized' composites gave stable suspensions in toluene and tetrahydrofuran.

Keywords: Controlled free radical polymerization; Polymerization compounding; Hybrid composites

1. Introduction

Organic/inorganic hybrid composites are relatively new class of materials with improved properties. Development of hybrid composites with desired properties requires a good control of polymer/solid interactions, wetting by the polymeric matrix and good solid dispersion in the matrix. The optimum solution remains however a covalent bond between the solid substrate and the polymeric matrix and encapsulation of the solid by the polymeric matrix. Several methods to graft a polymer onto solid surfaces have been reported in the literature [1–4]. Some focus on the introduction of various initiators onto the surface of a solid substrate followed by an interfacial dispersion polymerization of vinyl monomers [5–7].

The aim of the present work is to report on an approach, called *polymerization compounding* [8–13], in contrast with mechanical compounding, to develop polymer composites with enhanced overall properties. The approach consists in involving the surface of a solid substrate in the polymerization process. For the approach to be used in an efficient way, competition between polymerization at the surface of the solid and in the bulk, i.e. homopolymerization, must be avoided.

In this paper we present the results obtained using the polymerization compounding approach in combination with stable free radical polymerization. The advent of nitroxide stable free radicals, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), to reversibly control the growing polymer chains in free radical polymerization represents a breakthrough in this synthesis route [14–22]. Polymers with narrow molecular weight distribution as well as block copolymers in which several parameters can be controlled (e.g. size and polydispersity of each block, architecture of the polymer such as star comb and other complex architectures) can now be obtained using the pseudoliving stable free radical (SFR) polymerization. This process is based on the simultaneous termination of the polymer radicals with the SFR. Classical free radical polymerization, which has been around for many years, has undergone something of a renaissance with new atom transfer radical polymerization (ATRP) [23]. Such a method of polymerization, of styrene for instance, can lead to polydispersities as

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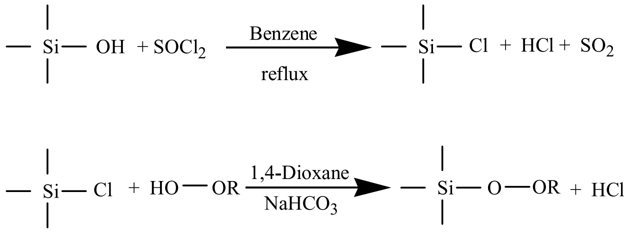

Fig. 1. Surface activation by *tert*-butyl hydroperoxide.

low as 1.04 [24–26]. Because of the ease of performing such polymerizations, it is only natural than there has been further developments of extending its use into grafting onto substrates and nano substrates [27–31]. Such grafting has been done in the past through condensation polymerization, Ziegler–Natta or conventional free radical polymerization [8–13]. With ATRP, polymers or copolymers can be successfully grafted on surface, with a more controlled morphology, such as tethered chains, polymer 'brushes' or patterned films, the latter made with a combination of Langmuir–Blodgett and ATRP techniques [32].

A wider domain of practices and organic grafting reactions [33,34] will then be accessible. Free radical polymerization is also easy to perform, less sensitive to impurities and, more importantly, can be applied to most vinyl monomers in contrast with living anionic [35] or cationic [36,37] polymerization techniques which require rigorous synthesis conditions.

Combination of living free radical polymerization with the polymerization compounding approach to design new composite materials is illustrated here using ultrafine inorganic particles as a solid substrate (fumed silica). Hydroperoxide was used as initiator for the polymerization process. The surface of the solid substrate must first be activated in order to covalently graft the initiator on the solid. Fig. 1 describes the activation and the grafting of the hydroperoxide on the surface of the solid. Dispersion stable free radical polymerization of styrene, butyl acrylate and

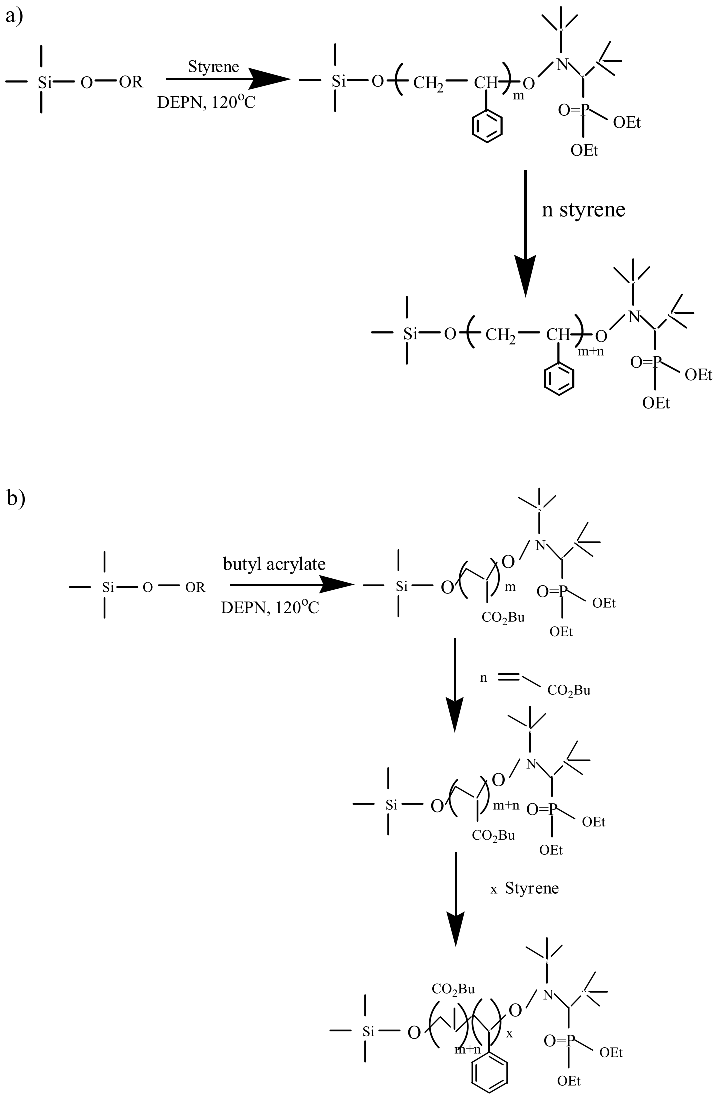

Fig. 2. Mechanism of controlled free radical polymerization grafting: (a) homopolymer composite and (b) copolymer composite.

their copolymers was carried out in presence of modified silica particles and a stable free radical, *N-tert*-butyl-1-diethylphosphono2,2-dimethyl propyl nitroxide (DEPN). Stable free radical polymerization mechanisms for homopolymer and copolymer grafted onto fumed silica are illustrated in Fig. 2(a) and (b) for polystyrene composites and polybutylacrylate-*b*-polystyrene composites respectively. Details of the reactions in Figs. 1 and 2 are given in the following sections.

2. Experimental

2.1. Materials

The solid substrate used in this study is ultrafine fumed silica (Sigma, 99.8%). The specific surface area (BET), particle size, and density are 390 ± 40 m^2/g, 7 nm, and 2.3 g/cm^3, respectively. The ultrafine silica was dried at 120 °C under vacuum before use in any subsequent step of the process.

Anhydrous benzene (99.8%, Aldrich), thionyl chloride low iron (98%, Aldrich), 1,4-dioxane (99.9%, Aldrich), methyl alcohol (99 + %, Aldrich), toluene (99.5%, ACP chemicals), tetrahydrofuran (99.9%, Baker analyzed), *tert*-butyl hydroperoxide (THP) purified by fractional distillation, sodium bicarbonate (99.7%, Fisher Scientific), silver nitrate (99 + %, Aldrich), potassium iodide (A.C.S, Anachemia) were used without further purification.

Styrene (99 + %, Aldrich) and *n*-butyl acrylate (99 + %, Aldrich) were purified using disposable columns to remove *tert*-butylcatechol and hydroquinone monomethyl ether in styrene and *n*-butyl acrylate, respectively. *N-tert*-butyl-1-diethylphosphono2,2-dimethyl propylnitroxide (DEPN, Elf-Atochem) was used as received.

2.2. Methods

Thermogravimetric analyses were performed on a Mettler TG 50 equipped with Star^e software, thermal analyzer under nitrogen flow. The heating rate was set at 10 or 20 °C min^{-1} and temperatures ranged from 25 to 600 °C.

Fourier-transform infrared spectroscopy (FTIR) was performed on a Nicolet Magna 550 spectrometer. The specimens were compressed KBr pellets in which samples were dispersed by grinding using an agate mortar.

Gel permeation chromatography (GPC) experiments were performed with, at the end, a 903 Refractomer (Wyatt Optilab) associated with absorbance detector (Water associates Model 441). A combination of two styrene divinyl benzene copolymer columns (KF802 and KF804) from Shodex was used with THF as the eluent at ambient temperature. The column system was calibrated with Standard monodisperse polystyrenes. Sample detection and quantification were made with a differential refractometer.

The rheological behavior in steady shear flow was studied using a strain controlled rotational rheometer (ARES, Rheometric scientific) with strain control and parallel plate geometry (25 mm diameter plates). Test temperatures were varied from 180 to 220 °C. Time sweep experiments were carried out to ensure that no thermo-oxidative degradation occurred during test measurements. Time–temperature superposition was performed to obtain master curves at a reference temperature of 200 °C.

2.3. Estimation of molecular characteristics of grafted chains

Molecular weights of polymers and copolymers grafted onto silica surface were calculated assuming uniform chains growing from all bonded initiators to the silica surface. For a composite having a volume fraction of grafted polymer with a molecular weight (M) and a density (ρ_p), the volume of polymer matrix is given by:

$$v_p = \frac{f\pi D^3}{6(1-f)} \tag{1}$$

and

$$v_p = \frac{nM}{10^3\rho_p N} \tag{2}$$

where n is the total number of grafted chains per spherical particle (with a diameter D) and $N = 6.023 \times 10^{23}$ molecule/g mol is the Avogadro number.

The parameter n can be determined from the Eqs. (1) and (2):

$$n = \frac{10^3\rho_p fN\pi D^3}{6(1-f)M} \tag{3}$$

The molecular weight corresponding to a grafting percentage α of a particle with a diameter D is:

$$M = \frac{10^3\rho_p fND}{6\alpha(1-f)n_a} \tag{4}$$

where n_a represents the number of hydroxyl groups per nm^2 present on the surface of the solid particle.

2.4. Introduction of tert-butyl hydroperoxide onto fumed silica surface

Grafting of the initiator was carried out in two steps. The first step consists in the chlorination of silanol groups by thionyl chloride [38]. Introduction of *tert*-butyl peroxide (THP) was then achieved by the reaction of chlorosilyl groups on the surface with THP in the presence of sodium bicarbonate as a dehydrogenation catalyst [6]. The chlorination of the silanol groups followed by the introduction of the initiator on the surface of fumed silica is shown in Fig. 1.

Table 1
Polymerization of styrene at 120 °C, [DEPN] = 2.5[THP]

[Styrene] (mol/l)	[THP] (mmol/l)	Time (min)	Conversion (%)	$M_{n,\,exp}$[a] (g/mol)	$M_{n,\,exp}/M_{n,\,th}$[b]	M_w/M_n[c]
8.7	3.56	30	8	10,464	1.07	1.1
8.7	3.56	75	20	27,130	1.11	1.3
8.7	3.56	210	50	58,134	0.95	1.3
8.7	3.56	420	70	86,447	1.01	1.2

[a] Experimental number of average molecular weight determined by SEC using polystyrene standards.

[b] Theoretical number of average molecular weight calculated as: $M_{n,\,th} = ([\text{Monomer}]/2[\text{Initiator}])M_{w\ monomer} \times \text{conversion}$.

[c] Polydispersity index determined by SEC.

Chlorination of silanol groups with thionyl chloride. 6 g of silica, 50 ml of thionyl chloride and 50 ml of benzene were charged into a flask equipped with a reflux condenser. The reaction mixture was refluxed under continuous magnetic stirring. Unreacted thionyl chloride and benzene were removed by distillation and the remaining solid was dried under vacuum at 90 °C. The treated silica was stored in anhydrous atmosphere under vacuum.

tert-Butyl hydroperoxide grafting onto silica surface. 6 g of fumed silica having chlorosilyl groups, 90 ml of dioxane, 12 ml of THP and 0.3 g of sodium bicarbonate were introduced into a flask and the reaction mixture was stirred under dry nitrogen at 20 °C in the dark. The reaction was stopped after 12 h and the modified silica was washed with methanol repeatedly and dried under vacuum at room temperature. The treated ultrafine silica was stored under vacuum in a refrigerator.

Titration of chlorosilyl groups on silica surface. 0.2 g of silica, 0.01 g of sodium bicarbonate and 25 cm^3 of desionized water were introduced in an Erlenmeyer. Then hydrogen chloride formed by the hydrolysis of chlorosilyl groups was titrated with 0.1 mole/l of silver nitrate solution using potassium chromate solution as indicator [39].

Determination of peroxide groups on silica surface. Into an Erlenmeyer flask charged with 0.2 g of ultrafine silica grafted with peroxide groups and 10.0 cm^3 of acetic anhydride, 0.5 g of potassium iodide was added and the mixture was stirred for 20 min. Then isolated iodide was titrated with 0.1 mole/l of sodium hyposulfite using starch as an indicator [40].

Table 2
Polymerization of *n*-butyl acrylate at 120 °C, [DEPN] = 2.5[THP]

[BuA] (mol/l)	[THP] (mmol/l)	Time (h)	Conversion (%)	$M_{n,\,exp}$[a] (g/mol)	$M_{n,\,exp}/M_{n,\,th}$[b]	M_w/M_n[c]
6.9	2.86	3	14	25,900	1.20	1.14
6.9	2.86	8	31	58,200	1.21	1.20
6.9	2.86	14	50	85,800	1.11	1.23
6.9	2.86	24	70	11,3700	1.05	1.22
6.9	2.86	43.5	98.9	155,800	1.02	1.23

[a] Experimental number of average molecular weight determined by SEC using polystyrene standards.

[b] Theoretical number of average molecular weight calculated as: $M_{n,\,th} = ([\text{Monomer}]/2[\text{Initiator}])M_{w,\ monomer} \times \text{conversion}$.

[c] Polydispersity index determined by SEC.

2.5. Polymerization procedures

Bulk polymerization of styrene. In a typical reaction, a 2 l glass tube reactor with screw-type agitator was cleaned and dried and then charged with styrene (8.7 mol/l), THP (3.56 mmol/l) and DEPN (8.9 mmol/l). The mixture was purged by nitrogen for 1 h before heating. The polymerization reaction was carried out at 120 °C under N_2 (see Table 1).

Bulk polymerization of butyl acrylate. Butyl acrylate (6.9 mol/l), THP (2.86 mmol) and DEPN (7.15 mmol/l) were introduced into a glass tube reactor and the mixture was purged by nitrogen for 1 h. The polymerization was performed in a way similar to that described for styrene (see Table 2).

Fumed silica-polystyrene composites syntheses (SiPS). The preparation of SiPS composites was carried out as follows: ultrafine silica containing THP initiators, DEPN, and styrene were degassed under a continuous nitrogen flux for 1 h. The polymerization was carried out in two steps. The first step consists in the preparation of a composite ultrafine silica polystyrene macro-initiators (SiPS-DEPN). The SiPS-DEPN composite was redispersed in toluene. This stable suspension was washed by successive centrifugation–redispersion cycles (15,000 rpm, 30 min) in order to remove non grafted PS-DEPN polymer produced by the decomposition of THP. Then, the composite was redispersed in styrene and the polymerization was conducted for 7 h at 120 °C. The SiPS composite was redispersed in toluene, washed by centrifugation–redispesion cycles as described previously, and dried under vacuum at 90 °C. The reaction conditions for all SiPS composites syntheses are given in Table 3. The first step is performed in order to avoid

Table 3
Syntheses conditions of homopolymer composites

Sample	First step					Second step	
	$n_{styrene}$ (mole)	n_{THP} (mmole)	n_{DEPN} (mmole)	t_{r1} (h)	m_{silica} (g)	$n_{styrene}$ (mole)	t_{r2} (h)
$SiPS_{20}$	0.2	0.08	0.2	2.5	12	0.3	7
$SiPS_{30}$	0.2	0.08	0.2	2.5	12	0.17	7
$SiPS_{44}$	0.17	0.34	0.85	2	53	0.53	7
$SiPS_{52}$	0.18	7.2	18	3	12	–	–

Table 4
Syntheses conditions of copolymer composites

Sample	First step					Second step		Third Step	
	n_{BuA} (mole)	n_{THP} (mmole)	n_{DEPN} (mmole)	t_{r1} (h)	$m_{(silica)}$ (g)	n_{BuA} (mole)	t_{r2} (h)	$n_{styrene}$ (mole)	t_{r3} (h)
SiPuA-*b*-PS$_{14}$	0.21	0.39	0.97	3	60	0.24	24	0.75	8
SiPuA-*b*-PS$_{20}$	0.21	0.39	0.97	3	60	0.14	24	1.05	7

competition between polymerization on the surface of the solid substrate and polymerization in the bulk.

SiPS$_{78}$ sample. 98 g of fumed silica containing 0.32 mmole of THP, DEPN (0.79 mmole), styrene (0.35 mole) and 40 ml of toluene were introduced into a reactor. The mixture was degassed for 1 h under nitrogen atmosphere, after that the polymerization was carried out at 120 °C for 15 h. The composite was washed with a large volume of toluene and dried at 90 °C under vacuum.

Fumed silica-poly(n-butyl acrylate)—polystyrene composites syntheses (SiPBuA-b-PS). SiPBuA-*b*-PS composites were prepared as follows: ultrafine silica containing THP initiator, DEPN, and butyl acrylate were degassed under nitrogen atmosphere for 1 h. The mixture was polymerized for 3 h at 120 °C. Then the obtained composite (SiPBuA) was redispersed in THF (stable suspension), washed by successive centrifugation–redispersion cycles, and dried in vacuum at ambient temperature. This composite was then redispersed in butyl acrylate and degassed in nitrogen atmosphere for 1 h. This mixture was heated for 7 h at 120 °C. The SiPBuA composite was washed in toluene, and then redispersed in styrene. The polymerization in styrene was conducted under nitrogen atmosphere for 7 h. This hybrid composite was then dried under vacuum at 90 °C. The experimental conditions for SiPBuA-*b*-PS composites syntheses are described in Table 4.

Table 5
Introduction of THP groups onto silica surface

Functional group	Composition of silica surface			
	50 h[a]		96 h[a]	
	mmole/g	molecule/nm^2	mmole/g	molecule/nm^2
Silanol	1.37	4	1.37	4
Chlorosilyl[a]	0.55	0.84	0.79	1.22
THP[b]	0.40	0.62	0.6	0.92

[a] The time reaction (50 and 96 h) corresponds only to chlorosilylation.
[b] The THP introduction onto the surface was carried out for 12 h.

Table 6
Elemental analysis of peroxide grafting onto silica surface using various initial concentrations of THP

Samples[a]	[THP]$_0$ (mole/l)	C (%)	Grafted THP (molecule/nm^2)
1	1.14	3.3	0.95
2	0.3	3.7	1.0
3	0.06	4.0	1.1

[a] THP grafting onto fumed silica surface was carried out with modified silica containing 1 chlorosilyl group per nm^2.

SiPBuA-b-PS$_{7.4}$. 6 g of ultrafine silica containing 0.4 mmole of THP, DEPN (1 mmole), and butyl acrylate (0.89 mole) were degassed under nitrogen atmosphere for 1 h. The mixture was polymerized for 4 h at 114 °C. Then the obtained composite SiPBuA was redispersed in THF (stable suspension), washed by successive centrifugation–redispersion cycles, and dried in vacuum at ambient temperature. Then, this composite was redispersed in 20 ml of styrene (0.17 mole) degassed in nitrogen atmosphere for 1 h, and the mixture was heated for 7 h at 114 °C. The composite SiPBuA-*b*-PS was redispersed in toluene, precipitated from a large excess of methanol, and dried under vacuum at 80 °C. Conditions for preparation, in similar conditions, of samples of SiPBuA-*b*-PS$_{14}$ and SiPBuA-*b*-PS$_{20}$ are given in Table 4.

Composites were also extracted with THF using a Soxhlet apparatus for 48 h and no loss of free polymer was observed after washing by successive centrifugation/redispersion cycles in the first step of polymerization.

3. Results and discussion

3.1. Effect of reaction time on the chlorination of silanol groups

Treatment of fumed silica with thionyl chloride for 50

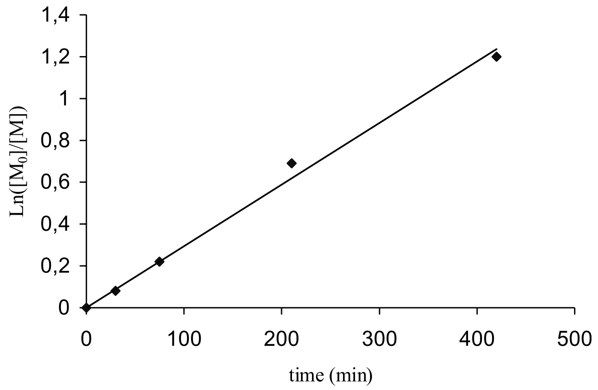

Fig. 3. Plot of Ln([M$_0$]/[M]) vs polymerization time for styrene polymerization at 120 °C with [THP] = 3.56×10^{-3} mol L^{-1} and [DEPN]/[THP] = 2.5.

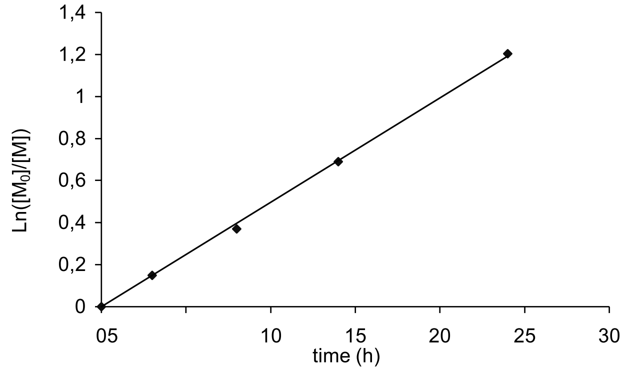

Fig. 4. Plot of Ln($[M_0]/[M]$) vs polymerization time for *n*-butyl acrylate polymerization at 120 °C with [THP] $= 2.86 \times 10^{-3}$ mol L^{-1} and [DEPN]/[THP] = 2.5.

and 96 h resulted in the introduction of 0.84 and 1.22 molecule/nm^2 of chlorosilyl groups, respectively (see Table 5). These values indicate that under these conditions, only 20 and 30%, respectively, of silanol groups were chlorinated on the basis of 4 OH/nm^2 for bare fumed silica. Table 5 also shows the effect of reaction time on the conversion of silanol to chlorosilyl groups. Increasing the reaction time from 50 to 96 h resulted in a 50% increase of the chlorination of silanol groups and the grafted initiator. The content of peroxide groups introduced onto the surface by the reaction of *tert*-butyl hydroperoxide with chlorosilyl groups, after 12 h, was 0.62 molecule/nm^2 and 0.92 molecule/nm^2. This indicates that in both cases about 75% of chlorosilyl groups reacted with *tert*-butyl hydroperoxide. This may be due to steric hindrance between functional groups on the silica surface [40].

The optimum conditions concerning the introduction of peroxide groups were also studied. Three experiments with different concentrations of THP in the presence of fumed silica containing one chlorosilyl group per nm^2 were performed (see Table 6). The reaction is stoichiometric and complete after 24 h regardless of THP concentration. These results indicate that the controlling step in the surface modification process is the chlorination of the hydroxyl groups present on the surface of fumed silica.

3.2. *Living free radical polymerization of styrene and butyl acrylate*

The kinetic parameters (polymerization rate and conversion) of grafted polymers are very important in the preparation of composites. Indeed the bulk polymerization of styrene and butyl acrylate with THP as initiator and DEPN as a stable free radical at 120 °C have been studied. Molecular weight, polydispersity index (PI) and monomer conversion are summarized in Tables 1 and 2 (see also Figs. 3 and 4), respectively. It was found that the polymerization proceeds in accordance with a living mechanism in all cases. Molecular weight of the resulting polymers was indeed found to be proportional to conversion. The same kinetic parameters were used in presence of silica on the kinetic. Several studies on polymerization of styrene and methyl methacrylate indeed showed that the presence of silica does not affect the rate of polymerization [41,42]. It was also observed during the syntheses of composites that the conversion times of monomers are similar to those obtained in the bulk polymerization of the homopolymers.

Table 7
Thermogravimetric analysis of SiPS composites

Sample	Loss weight (%)	Solid volume fraction (%)
$SiPS_{78}$	12.4	77.9
$SiPS_{52}$	29.6	51.8
$SiPS_{44}$	39.1	43.8
$SiPS_{29}$	55.0	29.0
$SiPS_{20}$	66.2	20.3
$SiPS_{5.9}$	87.8	5.9

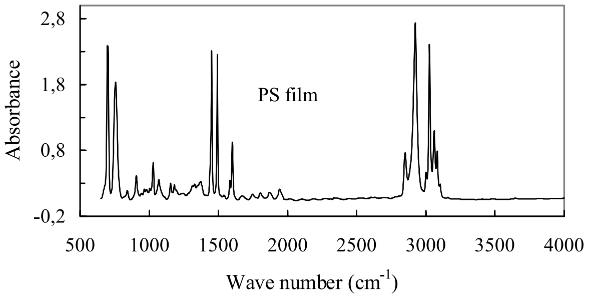

Fig. 5. FTIR spectra of PS film.

3.3. *Composition and structure of hybrid composites*

Fig. 5 shows FTIR spectra for a polystyrene film. Skeletal vibration involving carbon–carbon stretching within the ring absorb in the 600–1585 and 1500–1400 cm^{-1} regions. Aromatic C–H bands occur between 3100 and 3000 cm^{-1}. Weak combination and overtone bands appear in the 2000–1650 cm^{-1} region. The pattern of the overtone bands is characteristic of the substitution pattern of the ring. Because they are weak, the overtone and combination bands are most readily observed in spectra obtained from thick samples. Stretching vibration for C–H alkane are obtained in the 2840–3000 cm^{-1} range.

The static absorption at room temperature (23 °C) of a

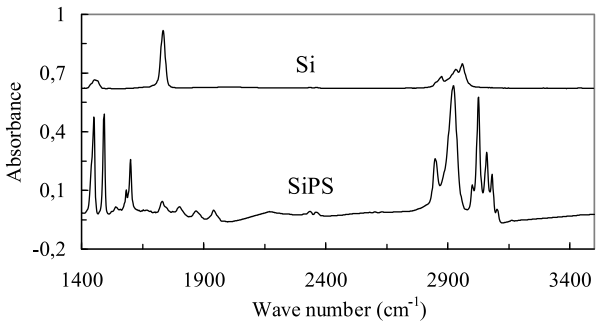

Fig. 6. FTIR spectra of bare silica (Si) and SiPS composite.

Table 8
Thermogravimetric analysis of SiPBuAPS composites

Sample	Weight loss (%)	Silica volume fraction (%)
SiPBuA	20.3	66.3
SiPBuA-*b*-PS_{20}	66.4	20.2
SiPBuA	24.2	61.1
SiPBuA-*b*-PS_{14}	75.2	14.2
SiPBuA	60	28.2
SiPBuA-*b*-$PS_{7.4}$	86.2	7.4

SiPS composite film (Fig. 6) shows similar bands as those observed in the preceding spectra of pure polystyrene. Some bands in the region between 1400 and 600 cm^{-1} are screened by the strong silica absorption.

The amount of grafted polymers, for each synthesis of SiPS composites was determined by thermogravimetric analysis (see Table 7). The results shown in this table indicate that the polymerization compounding approach can be used to prepare both highly loaded composites (77.9 vol%) and low silica content composites (5.9 vol%). Some of the highly loaded composites could not be prepared by conventional techniques (mechanical mixing and solvent dispersion and precipitation). The results for composites with PBuA and PbuA-*g*-PS matrices are shown in Table 8. These results were also obtained by thermogravimetry. They indicate that the structure of grafted polymer on the surface of fumed silica can also be controlled using the polymerization compounding approach in combination with living free radical polymerization. All these materials gave stable suspensions in the solvents of the grafted polymers (toluene and tetrahydrofyran).

There are essentially two ways to produce composites using the polymerization compounding approach. For a given volume fraction and particle diameter, composites can be obtained either with a relatively high molecular weight but small number of grafted macromolecules per particle, or vice versa. In the case of $SiPS_{78}$, the solid volume fraction is very high (78%) and the molecular weight of the grafted polymer chains is 4.15×10^4 g/mole. The number of polymer chains per particle is however very small (0.77 chain/particle, see Table 9). This particular composite was not easy to process (compression moulding). Particle/particle contacts due to the small number of grafted chains per particle made this composite friable. It is worth mentioning however that it would not be possible to prepare the equivalent one using conventional methods. On the other hand for the $SiPS_{52}$, the volume fraction of silica is still relatively high (52%). However, the number of grafts per particle (142 chains/particle) is much higher than that of the $SiPS_{78}$ and the molecular weight of the grafted chains is comparatively very small (703 g/mole, see Table 9). This composite was also found to be friable. Table 9 indicates that for the other composites, the number of grafts per particle is still small ($SiPS_{44,30,20}$) but these composites were mouldable. The $SiPS_{5.9}$ has a molecular weight comparable to that of the $SiPS_{78}$ but the number of grafts is much higher. This particular composite ($SiPS_{5.9)}$ was, as expected, easy to process.

The results of Table 9 clearly indicate that particle diameter is an important parameter in the design of composites using polymerization compounding approach. For very small particle diameters, it will be very difficult to design highly loaded composites with high molecular weight grafted chains and high number of grafted chains per particle. Calculations using Eqs. (3) and (4) indicate that for the same molecular weight of grafted chains (4×10^4 g/mole) and the same solid volume fraction (78%), increasing the particle diameter from 7 to 70 nm will result in an increase of the number of chains per particle from 0.77 to 770. Highly loaded composites with high molecular weights and appropriate rheological characteristics can probably be obtained with solid substrates having relatively large dimensions.

Table 10 shows the results obtained for composites with PBuA and PBuA-*b*-PS grafted copolymer. Similar conclusions regarding the number of grafts per particle and molecular weight of grafted chains can be drawn. The SiPBuA-*b*-$PS_{7.4}$ composite for which the number of grafted chains per particle is 15.4 and the overall molecular weight of 9.6×10^5 g/mole was found to have a zero-shear viscosity $\eta_0 = 2 \times 10^5$ Pa s at 200 °C. The zero-shear viscosity of a monodisperse polystyrene of a similar molecular is about $\eta_0 = 10^4$ Pa s at 200 °C. Using the Maron–Pierce [43] equation:

$$\eta_r = \frac{\eta}{\eta_m} = \frac{1}{[1 - (\phi/A)]^2}, \tag{5}$$

where η_r, η and η_m are the relative viscosity, the viscosity of the composite and the viscosity of the matrix, respectively, ϕ the filler volume fraction and A a constant equal to 0.68

Table 9
Theoretical molecular weight of grafted polystyrene chains in SiPS composites

Sample	$SiPS_{78}$	$SiPS_{52}$	$SiPS_{44}$	$SiPS_{30}$	$SiPS_{20}$	$SiPS_{5.9}$
ρ (kg/m^3)	1014	1014	1014	1014	1014	1014
f	0.221	48.2	0.562	0.710	0.797	94.1
D (nm)	7	7	7	7	7	7
α (10^{-3})	1.25	230.7	2.50	2.50	2.50	57.9
M (10^3 g/mole)	42	0.7	94	180	287	48
n	0.77	142	1.54	1.54	1.54	35.67

Table 10
Theoretical molecular weight of grafted copolymer chains in SiBuAPS composites

Sample	SiPBuA$_{66}$	SiPBuAPS$_{20}$	SiPBuA$_{61}$	SiPBuAPS$_{14}$	SiPBuA$_{28}$	SiPBuAPS$_{7.4}$
ρ(kg/m^3)	1014	1014	1014	1014	1014	1014
f	0.34	0.80	0.39	0.86	0.72	0.926
D (nm)	7	7	7	7	7	7
α (10^{-3})	2.5	2.5	2.5	2.5	25.7	25.7
M (10^3 g/mole)	39_{PBuA}	266_{PS}	49_{PBuA}	419_{PS}	23_{PBuA}	73_{PS}
n	1.54	1.54	1.54	1.54	15.4	15.4

for glass spheres in molten polymers [44], we obtain a relative viscosity $\eta_r = 1.26$ or a zero-shear viscosity $\eta_0 = 1.26 \times \eta_{0,m} = 1.26 \times 10^4$ Pa s, largely below that measured for our composite. This can be attributed to the strong interactions between the grafted polymer chains and the solid substrate. The zero-shear viscosity is indeed very sensitive to such interactions. At high shear rates (equivalent to those encountered in extrusion or injection moulding processes), the viscosity of suspensions tends towards that of the matrix [45]. Processing of these materials can thus be performed while the enhanced solid/matrix interactions can be maintained for improved service properties. A detailed study of the rheology of such composites will be presented in a forthcoming paper.

The results of Tables 9 and 10 indicate that the combination of the polymerization compounding technique and the living free radical polymerization can effectively lead to composite materials with controlled architecture. Again, with appropriate particle diameter, composites having controlled molecular weight and composition of grafted chains together with appropriate flow properties can be designed. Materials that can meet the requirement of not only the application but also of the process to be used can thus be designed using this approach.

4. Conclusions

Organic/inorganic hybrid composites can be prepared using the polymerization compounding approach in combination with living free radical polymerization. This new route allows an easy control of molecular weight, polydispersity index and architecture of grafted polymers and copolymers onto solid surfaces. All synthesized composites gave stable suspensions in polymer solvents. The graft density of the polymer can be adjusted in a wide range by simply controlling the introduction and the conversion of initiators onto the solid substrate surface. Composites with a small number of grafted chains per particle were found to be difficult to process while those with relatively high number of grafted chains show acceptable rheological characteristics. The number of grafted chains per solid particle is found to be an important parameter. It depends on the particle diameter for a given molecular weight of the grafted polymer chains. Highly loaded composites with appropriate polymer molecular weight and flow properties can be designed provided a suitable choice of particle diameter is made. Work is still needed to optimize all these parameters and obtain composites with tailored processing and final properties.

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