

Composites prepared from silica gel and furfuryl alcohol with p-toluenesulphonic acid as the catalyst

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Summary

Composites of furfuryl alcohol and silica gel or Aerosil were prepared using p-toluenesulphonic acid as catalyst at room temperature. The molar ratio furfuryl alcohol/p-toluenesulphonic acid was varied between 64.7 and 10. The surface of silica gel was partially coated when composite was prepared with the lower quantity of acid while the use of the higher proportion of acid produces the start of particle agglutination. The thickness of the polymer layer completely coating the surface of the composites ranged between around 10 to 39 Å. Preliminary results suggest that composites could be used as adsorbent of organic pollutants from water.

Introduction

Furfuryl alcohol (FA) polymerizes readily in presence of acids [1]. The mechanism of resinification in solution has been extensively studied. It starts with the condensation of the 2-hydroxymethyl group with the hydrogen of C5, and linear chains are predominantly formed in the early stage of the polymerization. A sequence of parallel reaction produce polyconjugated chains that are responsible for the colour of the resin and the most probable intermediates for the occurrence of branching and final crosslinking of the products [2,3].

Studies of the FA–trifluoroacetic acid (TFA)–silica gel (SG) system [4,5] showed that the polycondensation occurs both homogeneously in the solvent and heterogeneously on the solid surface. The relative extent of each process depends on the ratio of the concentrations of furfuryl alcohol/trifluoroacetic acid. When this ratio is 3.9 a polymer of M_n (SEC) between 1500 and 3000 g mol⁻¹ is isolated from the homogeneous phase. The polymer is similar to that obtained in the furfuryl alcohol–dichloromethane (DCM)–trifluoroacetic acid system [6]. On the surface of the silica, a crosslinked polymer is formed, which is joined to the solid by Si—O—C bonds according to FTIR spectra [4].

Several aspects remain still unexplored and some of them take our interest.

In previous work the percentage of grafting (PG) has been reported as a criterion of the composite polymer content and to compare composites prepared under different conditions. However, PG gives only partial information because the specific surface of the solid is not taken into account and the same PG value are related with wider polymer layer for silica with less specific surface. Consequently, PG value is inappropriate to compare the occurrence of composite agglutination in different systems. More valuable information is obtained from the report of the polymer mass per specific surface and the thickness of the polymer layer.

Moreover, no test of the possible use and solvent resistance of these composites have been reported.

The present study concerns the preparation of composite from silica gel and furfuryl alcohol with p-toluensulphonic acid (PTS), the influence that it may exert on the polymer grafting and the formation of polymer layers with different thickness and the possibility to use composite as adsorbent.

Experimental

Composites preparation

All experiments were carried out with pure reagents. The composites were obtained from activated silica K-60 (SG, MERCK) or Aerosil 300 (DEGUSSA, BET surface area 300 m²/g) and FA in DCM following the procedure previously described [4]. The crude composite was washed several times with DCM and it was extracted with THF in a Soxhlet.

The percentage of grafting (PG) was calculated by thermo gravimetric analysis according to $PG = 100(\text{mass of polymer grafted})/\text{mass of silica}$.

The surface concentration of the polymer (C_s), defined as the polymer mass per specific surface of silica, was calculated according to $C_s = 10PG/\text{BET specific surface of silica (mg/m}^2\text{)}$.

Preparation of polyFA-coated silica

Solutions of polyFA in DCM, as well as solutions of polyFA and TFA were used to coat the silica-gel.

PolyFA physically adsorbed in silica-gel (polyFA-SG) was obtained immersing 2 g of activated silica-gel K-60 in 10 ml of DCM solution of polyFA (422 g/L) under occasional stirring during 8 to 72 hours. PolyFA-SG were filtered, washed with DCM and dried.

Coating of silica particles with acidic solution of polyFA was carried out mixing the solution of 170 mg polyFA in 5 ml of DCM with a mixture of 851 mg of activated SG, 0.096 ml of TFA and 5 ml of DCM. After 72 hours the coated silica was isolated, washed successively with chloroform and THF and extracted with THF during 8 hours. The material was dried off in an oven at 125°C.

Average thickness

The average thickness of the polyFA layer coating the SG particles (T_{ave}) was determined by measurements of the density (ρ) of the polyFA obtained in solution, the

BET specific surface of silica (S) and the mass of the polymer layer (m , by thermogravimetric analysis) according to: $T_{ave} = m/(\rho S) = 10 \text{ PG}/(\rho S)$.

Preparation of polyFA

The preparation of polyFA has been described elsewhere [6]. The soluble polymer was isolated and its density was determined with a picnometer using ethanol as non-solvent. Crosslinked polyFA was isolated too. It was successively extracted with 1,2-dichloroethane and THF in a Soxhlet during 8 hours. PolyFA was dried off in an oven at 125°C, ground and sieved.

Preparation of polydivinylbenzene

Divinylbenzene (DVB, BDH, techn., 80% mixture of isomers) was polymerized in suspension at 80 °C using dibenzoyl peroxide as initiator. The density of the polymer was determined by means of a picnometer.

Instruments

Thermal analysis. TG and DTA were registered in a DERIVATOGRAPH Q-1500 (MOM, Budapest). The heat rate was 10 °C/min.

BET area. Composites were degassed under vacuum at 150 °C and the BET isotherm was measured in a sortometer Carlo Erba 1800.

Results and discussion

The main focus of this work was the preparation of a composite which could be used as adsorbent. The design of the material considered a high crosslinking of the polyFA by using PTS as catalyst and the achievement of a polymer layer as thin as possible to avoid the retention, after soxhlet extraction, of oligomers that could be adsorbed on the surface of composites, or trapped into the polymer network, and released during any evaluation of composite for analytical chemistry uses.

Composite preparation

The preparation of composites shown in Table 1 followed the same pattern as that described by Spange et al [5] for the formation of composites from silica gel and FA in presence of TFA. PTS is insoluble in DCM but in presence of FA the system becomes homogeneous. Both the FA polymerization and its further reticulation are faster with PTS than with TFA. Hence, composites are produced with a concentration of PTS around tenfold lower than those required when TFA is used. In most of the experiments we employed a furfuryl alcohol to silica gel (FA/SG) ratio of 0.37 (g/g) taking into account that grafting percentage in TFA-FA-silica gel system pass through a maximum for this FA/SG ratio [5].

Composites prepared from FA and Aerosil or silica gel are dark brown while the color of supernatant solutions depends on the PTS concentration. The yield of polymer in solutions and the color intensity increase with PTS concentration and they are maximal in experiments like A-5.

Values of PG increase with growing PTS quantities. The SEM of composites agree with the results reported earlier for composites prepared with TFA as catalyst [7]

which predict particle agglutination only for composites with PG > 60%, such as K5 with PG = 72.6 %; while for composite K1 to K4 no aggregation of particles are expected and the polymer layer coating the surface of the composite is likely to be very thin. SEM was used to get evidence of this prediction. Bare silica and composites K2 and K5 were examined. Figure 1 and 2 are representative examples of the results. The first one corresponds to a sample portion of K5 in which the particles are not agglutinated. This micrograph is similar to those of composite K2 and the bare silica. However, Figure 2 shows the SEM of another sample portion of K5 that reveals the particle agglutination. The micrographs in Figure 1 and 2 indicate that the agglutination process was developing, but not completed, during the preparation of K5.

Table 1. Mass, surface concentration and thickness of the polyFA layer formed on the SG and Aerosil surfaces using different proportions of FA and PTS.

Experiment	Silica (g)	PTS (g)	FA (ml)	FA/PTS mol/mol	DCM (ml)	PG (%) ^{a)}	C _S ^{b)} mg/m ²	Polymer thickness (Å)
^{c)} K-1	2	0.020	0.65	64.7	50	5.7	0.35	2.83
K-2	2	0.025	0.65	51.8	50	22.0	1.36	10.9
K-3	2	0.027	0.65	48	50	25.0	1.54	12.4
K-4	2	0.032	0.65	40.5	50	56.3	3.47	27.9
^{d)} K-5	6	0.300	1.50	10	135	77.6	4.79	38.5
^{e)} A-1	2	0.020	0.65	64.7	50	16.3	0.54	4.36
A-2	2	0.025	0.65	51.8	50	32.6	1.09	8.74
A-3	2	0.027	0.65	48	50	63.9	2.13	17.1
A-4	2	0.032	0.65	40.5	50	117.9	3.93	31.6
^{d)} A-5	4	0.200	1.00	10	180	133.6	4.46	35.8

^{a)} Calculated by TG according to $PG = 100(\text{polyFA mass})/\text{SG mass} = m(\text{EXO}_1 + \text{EXO}_2)/m_{\text{SG}}$. Values of EXO₁ and EXO₂ are reported in table 2.

^{b)} $C_S = 10PG/(\text{BET specific surface of silica})$.

^{c)} Silica-gel KG-60 was used in K-set experiments.

^{d)} Experiments were carried out with a AF/Silica (g/g) ratio = 0.28. In the others this ratio was 0.37.

^{e)} Aerosil 300 was used in A-set experiments.

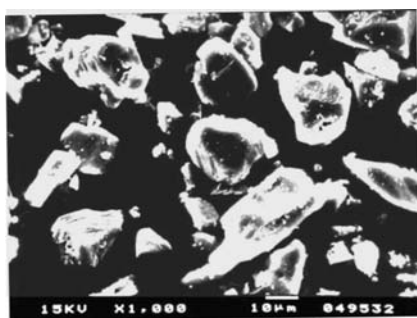


Figure 1. SEM of a sample of composite K5 in which particles are independent.

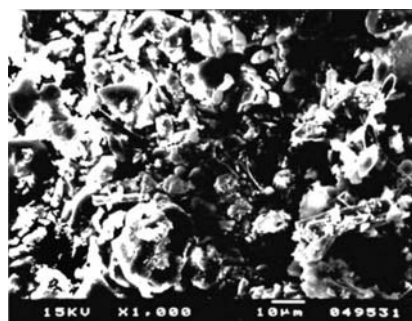


Figure 2. SEM of a sample of composite K5 in which particles are agglutinated.

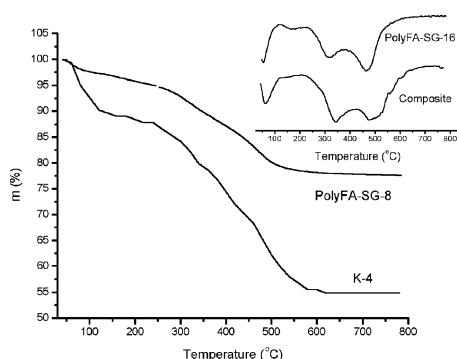


Figure 3. TG and DTG (onset) curves of composite (K-4) and polymer adsorbed on silica (PolyFA-SG-8).

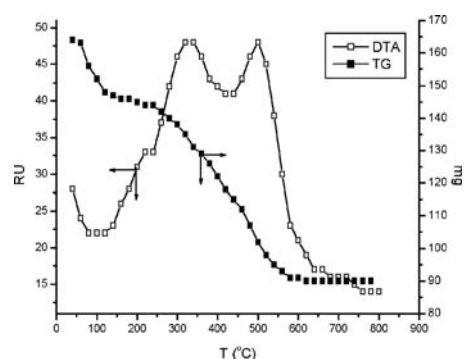


Figure 4. DTA and TG curves of silica gel-polyFA composite (K-4).

The average thickness of the polymer layer

The average thickness of the polyFA layer coating the SG particles (T_{ave}) can be estimated from the polymer mass per surface area of the silica, i.e. the surface concentration of the polymer ($C_s = 10PG/BET$ surface of silica), divided by the density of polyFA (1.2446 g/cm^3).

PG was determined by thermal analysis. Figure 3 shows typical DTA and TG analysis of a composite and Table 2 summarizes all the results. DTA shows three different peaks one endothermic due to water elimination and two exothermic peaks with maxima around 343 and 510 °C (see Table 2) involving the polymer decomposition.

Values of PG as well as C_s and T_{ave} are reported in Table 1. The measured value of $162 \text{ m}^2/\text{g}$ for silica KG-60 was used to calculate C_s of composites of series K while the nominal value of $300 \text{ m}^2/\text{g}$ for Aerosil was employed for the calculation of C_s of series A. Due to the bigger area of Aerosil the PG values of their composites are greater using the same experimental conditions than those of series A. Hence, C_s values are likely to be used to compare the magnitude of the polymer layer coating the silica surface.

The validity of the method described above to estimate the T_{ave} of the polyFA layer on composites was checked combining the ρ value achieved by us for polyDVB and the values reported by Fisher et al. [8] for the specific surface of the solid and the polymer mass when spherical nonporous silica with BET area of $2.9 \text{ m}^2/\text{g}$ was coated with DVB-base polymer and a sample with $PG = 16\%$ (corresponding to 14% mass loss in TGA measurement) was examined by TEM. They mapped by elemental spectroscopic image (ESI) the elemental distribution of carbon across the silica sphere and reported an estimate of the coating thickness of 3.0 \AA . Considering that the density of the polymer layer is the same as the density of the polyDVB prepared in suspension (1.048 g/cm^3 , see experimental part), the T_{ave} (C_s/ρ) is 5.2 \AA . This value is in agreement with that obtained by ESI, which is not an average value.

The minimum thickness of the polymer layer that completely coated the silica surface (MTL) of polyFA-SG composites is likely to be consistent with a layer formed by chains which could be equivalent to those obtained in the first stage of FA polymerization in solution. It is known that this kind of polymerization produces

Table 2. Results of DTA and TG measurements of composites from silica gel or Aerosil with FA and PTS.

Sample	FA/PTS (g/g)	Thermal effect { Ti -Tm - Tf (°C) }			Mass loss (mg)		
		Endo	Exo1	Exo2	Endo	Exo1	Exo2
K-1	36.71	59-149-234	230-320-450	450-500-660	12.70	4.80	5.50
K-2	29.37	25-74-117	176-357-435	435-509-648	11.33	13.10	15.70
K-3	27.19	53-89-116	210-366-455	455-526-680	8.64	13.00	19.90
K-4	22.94	52-97-169	223-343-440	440-510-740	13.73	17.17	31.76
K-5 ^{a)}	5.65	31-116-138	250-356-450	450-536-660	6.63	21.58	34.02
A-1	36.71	47-96-167	167-293-376	376-462-551	12.17	3.95	4.60
A-2	29.37	46-74-120	190-340-436	436-538-649	8.87	16.13	21.80
A-3	27.19	66-121-146	224-389-480	480-579-708	11.60	22.00	30.50
A-4	22.94	45-110-140	200-360-450	450-560-700	13.20	23.91	41.23
A-5 ^{a)}	5.65	31-91-171	249-358-436	436-549-645	18.20	26.45	39.67

^{a)} Experiments were carried out with a FA/S (g/g) ratio = 0.28. In the others this ratio was 0.37. Ti, Tm and Tf are respectively the temperatures at initial, maximum and end of the peak.

colored and branched chains from the beginning of the reaction. The higher molecular weight of polyFA before crosslinking starts is around 2500 g mol^{-1} [2]. Despite its peculiarities, the polymerization on the silica surface occurs in a similar way to that in solution [4,5] and the increasing T_{ave} can be related with the increase of branches or crosslink before particle agglutination takes place. If we use the polyFA prepared in solution as a model of chains which can coat the silica particles by physical adsorption it is possible to calculate the MTL.

The results of the adsorption of polyFA on SG (polyFA-SG) are shown in Table 3. Samples of polyFA-SG obtained after 8 to 72 hours of contact of SG with neutral or acid solution of polyFA in DCM present practically the same polymer adsorption, which is presented in table 3 as PG to make the comparison with the results shown in table 1 easier.

The adsorbed polymer from neutral solution is strongly retained by silica but not chemical bound to the surface like in composite since the extraction of the samples with THF reduces the PG to values between 1 to 3 % (Table 3). A difference between both kinds of material is observed by comparing the thermal analysis of their samples. That of polyFA-SG shows a mass lost between 120 and 230 °C in their TG and DTG thermograms due to compounds of low M_n adsorbed on silica (Figure 1). However, the presence of TFA in polymer solution produces polyFA grafting or crosslinking on the SG surface since the material resist the soxhlet extraction with THF without polymer release.

Obtaining a unique value for the adsorption of polyFA on SG (PG average of $18 \pm 1\%$) indicates that the surface of silica was saturated with this polymer quantity and that MTL is likely to be formed. The T_{ave} was calculated as described above and compare with the molecular size of two of the possible pentamers produced during the FA polymerization, whose geometry was optimized by the semi empirical method PM3. Figure 5 shows that the distance between the targets atoms (11.96 and 8.93 Å) are in agreement with the estimated value of 9.1 Å for T_{ave} and suggest that the branches directed from the solid surface to the solution could be equivalent to pentamer chains.

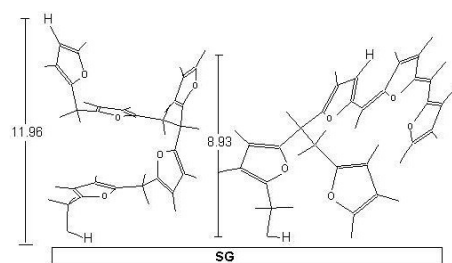
Table 3. Results of the experiments of polyFA adsorption on silica gel after washing with DCM and subsequent extraction with THF.

Sample ^{a)}	PG (%)	C _S ^{c)} g/m ² (10 ³)	Polymer thickness (Å)	PG after THF extraction (%)
PolyFA-SG-8	18	1.11	8.9	1.1
PolyFA-SG-16	18	1.11	8.9	3.0
PolyFA-SG-24	19	1.17	9.4	3.1
PolyFA-SG-72	17	1.05	8.4	-
Average	18 ± 1	1.14 ± 0.04	8.7 ± 0.6	
PolyFA-SG-72- TFA ^{b)}	16	0.99	7.9	

^{a)} Numbers indicate the corresponding contact time (h) of silica-gel with polyFA solution.

^{b)} Polymer solution contained TFA.

^{c)} C_S = PG/(100) x BET surface of silica).

**Figure 5.** Representation of two branched pentamers adsorbed on the surface of silica gel: one with saturated backbone and the other with conjugated double bond in it.

According to these results it is expected that the silica surface of composite with C_S < 9.8 x 10⁻⁴ g/m² was not completely coated. This condition is fulfilled by composites K-1, A-1 and A-2 (Table 1). This prediction was confirmed using fluoride acid as a sensor of the bare silica-gel surface in composites of series K considering that composites with silica surface not completely coated can react readily with the acid. It was observed that after immersion of K samples in HF solution (40%) during two minutes only K1 was strongly attacked and lost 92.5% of its mass.

Composite as adsorbent

Composites were tested unsuccessfully as adsorbent for HPLC. Small quantities of oligomers are released under pressure although no soluble products were obtained by previous Soxhlet extraction of composites.

The possibility that the oligomers liberated were trapped in the polymer network and diffused to the solvent during the column elution is contradictory with the results discussed above because the T_{ave} is too thin to retain oligomers after the Soxhlet extraction of composites. An alternative explanation could be related with the possibility that polyFA undergoes mechanolysis. It is well documented that whenever materials that consist of macromolecules are submitted to mechanical effort the scission of covalent bonds takes place [9]. The start of solvent flow through the column produces friction between particles that could induce the cleavage of polyFA branches.

Composite were also tested as adsorbent of water pollutants (pyrethroids). The stability of the materials extracted with DCM and THF was checked since any release

of FA oligomers during the analysis is undesirable and it has been reported the presence of soluble oligomers ($M_n < 580 \text{ g mol}^{-1}$) in composites of FA-acetaldehyde-SG [10].

Retention of pyrethroids ranging between 85 to 100 % and recoveries around 60 % were found in preliminary results suggesting that composite can be used as solid phase for solid-phase extraction. With this aim, the quantitative evaluation of composite is in progress.

Conclusions

Silica-gel can be completely coated with polyFA using mol ratios of FA/PTS ranging from 10 to 52. The thickness of the polymer layer increases as this ratio decreases and the beginning of the agglutination process of particles is observed when the average thickness of the polymer layer reaches a value around 38 Å.

PolyFA undergo probably mechanolysis under solvent flow at high pressure. The lack of robustness of polyFA layer makes the composites unsuitable as HPLC adsorbent. However, composites from polyFA and silica gel can be used as adsorbents to remove residues of pyrethroids and PCB insecticides from polluted water.

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