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ORIGINAL CONTRIBUTION

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Synthesis of acrylic-modified sol–gel silica

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Abstract Silica was obtained by sol–gel process through hydrolysis and condensation of tetraethyl orthosilicate (TEOS) using molar fraction of H_2O/TEOS=9 under alkaline catalysis, at different reaction times (5 min to 24 h). At the end of each time, the reaction medium appeared as a suspended microparticle system. After solvent evaporation, the yield was calculated to be around 100% and practically independent of the time of reaction. The silica had its surface modified through the condensation reaction with acryloyl chloride forming organically modified silica. The unmodified and modified silica were characterized by thermogravimetry and derivative thermogravimetry (TG/DTG), infrared spectrometry (FT-IR), size particle and optical microscopy (OM). The acrylic content was independent of the reaction time. The methodology represents an alternative route to obtain silica with an unsaturated organic group, able to polymerize and stabilize up to 300–400°C. The modified material has a potential application as compatibilizing filler in dental composite.

Keywords Sol–gel process · Hybrid acrylic–silica · Acryloyl chloride · FT-IR · TG/DTG

Introduction

The sol–gel process is a method that permits to prepare hybrid organic–inorganic structures under light reaction conditions such as low temperature and pressure, besides high-purity products. This process is based on hydrolysis and condensation reactions of metal alkoxides. The mechanism involves a nucleophilic attack of the water molecule to the alkoxide molecule [Si–$(OR)_4$], generating $(RO)_3$–Si–OH species. Successively, that group can react by itself or with an alkoxide group to create siloxane structures. Through this process, amorphous silica can be produced, and its high surface area makes it attractive to modification by chemical reactions [1].

There are two types of hybrid material. The first is considered as being inorganic particles dispersed in an organic matrix. In this material, normally polymers or non-polymerized monomers, the phases interact physically through hydrogen bonds or other type of intermolecular interaction. This route generates homogeneous materials when the inorganic phase particles are of nanometric size. In the second one, the organic–inorganic segments are chemically linked through covalent bond. Thus, there is higher interfacial phase adhesion than found in a blend [2–9].

The synthesis of hybrid material is too relevant since a unique material will have properties of both organic–inorganic constituents. The silica surface can be modified through sol–gel in situ chemical reactions such as silanization, nitration, etc. Often, the silanization reaction can be carried out by condensation between a trialkoxide silane or polymer and hydroxyl group present in the silica surface,

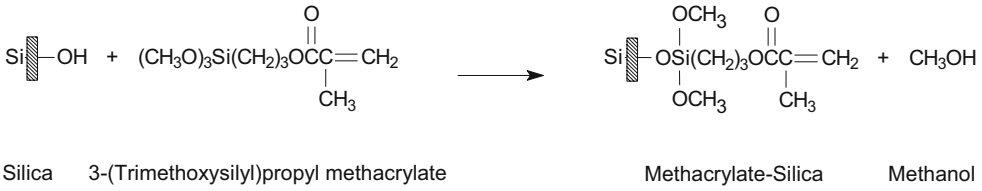

Fig. 1 Schematic representation of a silanization reaction

even considering that alkoxysilyl group is unstable in the presence of water. For instance, a schematic representation of reaction between 3(trimethoxysilyl)propyl methacrylate and silica particle producing methacrylate–silica is shown in Fig. 1 [10–13].

In this work, silica was obtained by sol–gel process at different reaction times, catalyzed by nucleophilic species at 50°C. The silica surface was modified by condensation reaction with acryloyl chloride, generating an organic/inorganic structure. The surface modification was evaluated by techniques such as thermogravimetry (TG), derivative thermogravimetry (DTG), infrared spectrometry (FT-IR) and optical microscopy (OM). The methodology represents an alternative route of modification of silica surface and has a promising use as filler of dental restoration composite.

Experimental

Materials

Hydrochloric acid, benzoyl chloride, dry ethanol, ammonium hydroxide, potassium hydroxide and hydroquinone were purchased from Vetec Química Fina and Reagen Quimibrás. Tetraethyl orthosilicate (TEOS) was manufactured by Wako Pure Chemical. All of them were used as received. Acrylic acid was received from Petroflex S/A and was distilled under normal pressure, using hydroquinone as inhibitor. Methylene chloride from Vetec Química was distilled using phosphorus pentoxide as drying agent.

Silica preparation

In a 250-mL round-bottomed flask were poured 100 mL of dry ethanol and 14 mL (0.06 mol) of TEOS. The system was maintained in silicon bath oil until stabilization of the temperature at 50°C under stirring. Thereafter, it was poured 9.7 mL (0.54 mol) of distilled water and 1.3 mL (0.01 mol) of 28% aqueous solution of ammonium hydroxide (molar ratio $NH_4OH/H_2O/TEOS$=0.1:5.4:0.6), under dry nitrogen atmosphere. The reaction was carried out at seven different times (5 min, 30 min, 1 h, 2 h, 3 h, 6 h, 24 h). At the end of each reaction, it was poured 2.3 mL of 37% aqueous solution of hydrochloric acid to adjust the pH to around 2. The solvent was evaporated using a Rotavapor, at 70°C, under vacuum, and the resultant solid was dried in an oven at 130°C for 24 h. Finally, the excess of the unreacted precursors was rinsed with distilled water and then filtered and dried in an oven at 100°C, until constant weight was attained.

Table 1 Actual yield vs reaction time of condensation of TEOS to silica

Reaction time (h)	0.08[a]	0.5[b]	1	2	3	6	24
Actual yield (%)	97	96	97	99	98	99	99

TEOS Tetraethyl orthosilicate
[a]0.08 h=5 min
[b]0.5 h=30 min

Disassociation treatment of silica particles

Silica (3 g) and 30 mL of methylene chloride were introduced in a small round-bottomed flask (50 mL) and were maintained in contact for 24 h as a closed system. Thereafter, the system was stirred under magnetic stirring for 1 h. Then, the flask content was poured in a Petri plate to permit the natural evaporation of the solvent. Finally, the powder was dried in an oven at 100°C until constant weight was achieved.

Synthesis of acryloyl chloride

In a 500-mL round-bottomed flask were poured 68.5 mL (1 mol) of acrylic acid, 173 mL (1.4 mol) of benzoyl

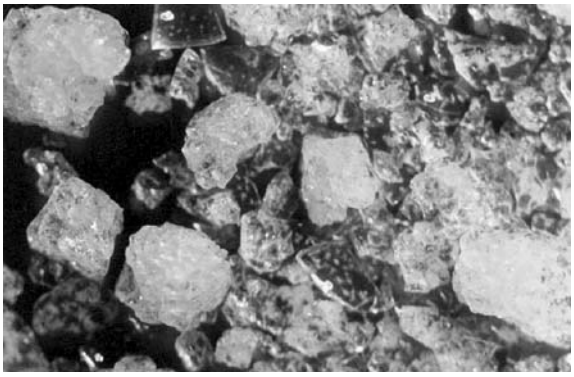

Fig. 2 Optical photomicrograph of silica (2 h) before disassociation (×18)

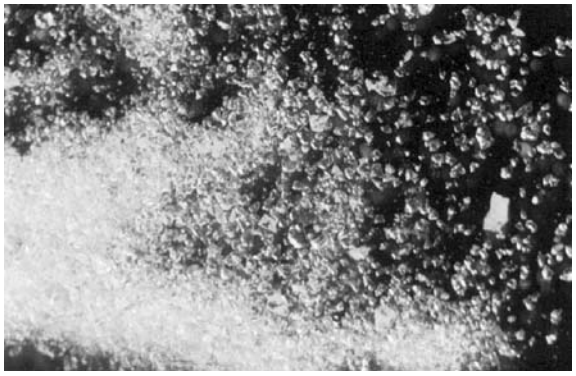

Fig. 3 Optical photomicrograph of silica (2 h) after disassociation (×18)

chloride (molar ratio $CH_2CHCOOH/C_6H5COCl$=1:1.4) and 0.16 g (0.001 mol) of hydroquinone as inhibitor. A distillation system was joined to the flask to permit diffusion of dry nitrogen (inlet) and hydrochloric acid (outlet) vapors that were neutralized in aqueous solution of potassium hydroxide. The reacting mixture was heated under stirring, and a distilled fraction (70–80°C) was received in another flask containing hydroquinone, at 5°C. The distilled fraction was redistilled to obtain a new fraction (72–74°C), which was maintained hermetically closed under refrigeration [14].

Silica modification

In a 200-mL round-bottomed flask were poured 70 mL of dry methylene chloride, 1.5 g of silica (dried at 130°C for 3 h) and acryloyl chloride (molar ratio $SiO_2/CH_2CHCOCl$=0.025:0.005). The system was stirred at room temperature for 24 h in the absence of light. Thereafter, the solvent was evaporated, and the remaining solid was dried under vacuum, in the absence of light, until constant weight was obtained.

Characterization of unmodified and modified silica

The unmodified silica was analyzed by TG using a Rigaku model TAS100 equipped with assembly TG8110. Approximately 20 mg of sample was tested at temperature range of 30–1200°C and heating rate of 10°C/min using a mixture of nitrogen (50 mL/min) and oxygen (8 mL/min) gases. The TG/DTG curves were obtained.

The analysis of modified silica was performed in a thermoanalyser Perkin-Elmer model TGA7 using 10 mg of sample, temperature range of 30–800°C and heating rate of 10°C/min under nitrogen atmosphere (50 mL/min). The TG/DTG curves were achieved.

Both materials were characterized by FT-IR using Perkin-Elmer equipment model 1720X. The spectra before and after modification were performed from KBr disk, considering 20 scans, from 4000 to 400 cm^{-1}.

The OM analysis was carried out in an Olympus microscope model SZH10 equipped with photographic system. The photos were taken using magnification of ×10 and zoom 2 or 7.

The size particle of unmodified silica before and after disassociation was analyzed in a mechanical sieve assembly model Retsch As200 basic, in the range of 18, 30, 70, 80, 100, 140, 325 and >325 mesh, for 30 min.

Results and discussion

Synthesis and size particle of silica

The yield was high and practically independent of the reaction time, attaining values around 100%. It was calculated considering the following reaction being the actual yield (Table 1) determined by subtracting the content of adsorbed water from TG/DTG curves [15].

$$n\,Si(OR)_4 + 2n\,H_2O \rightarrow n\,SiO_2 + 4n\,ROH$$

During the drying process, the coalescence of silica microparticles took place, generating structures with dimension up to 900 μm (30–18 mesh). Our interest was to

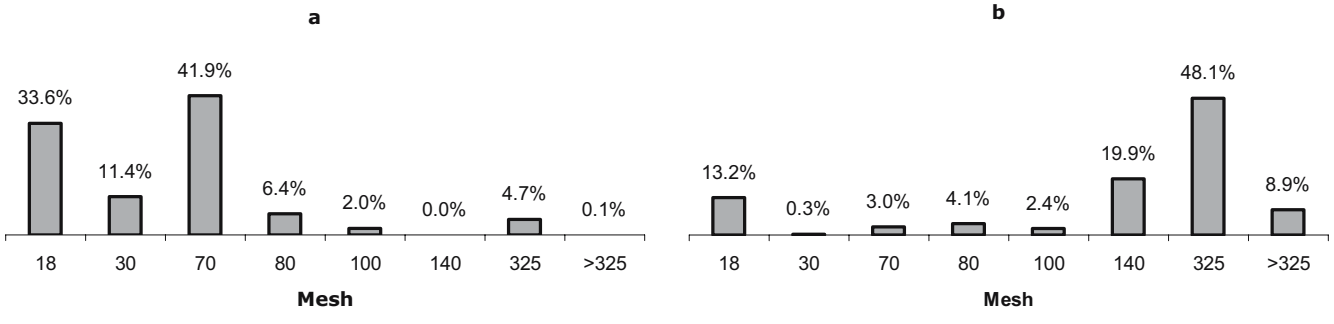

Fig. 4 Size particle of silica (2 h) before (**a**) and after (**b**) disassociation

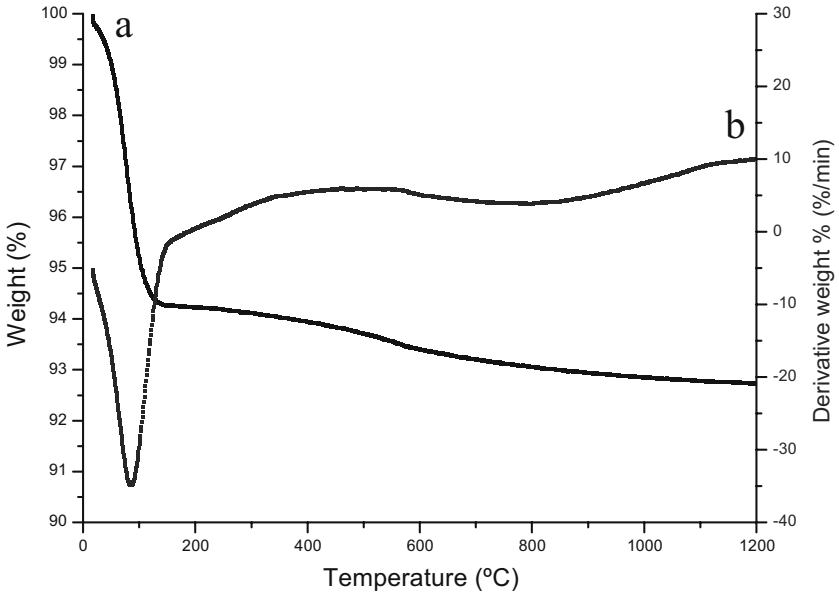

Fig. 5 Thermogravimetric (TG; **a**) and derivative thermogravimetric (DTG; **b**) curves of silica (1 h)

obtain small particles; thus, we have performed the disassociation of silica samples, as described in the experimental section.

As illustrated, the optical photomicrographs (Figs. 2 and 3) show the effect of the disassociation treatment on the size of silica particles (2 h). It is clear that the particles were fragmented as small transparent broken glass particles. Figure 4 shows the size particle distribution of silica (2 h) before and after disassociation. Before handling, the size particle was higher than 210 μm (80 mesh, 87.1% of the total), and thereafter, the size attained was lower than 110 μm (140 mesh, 76.1% of the total). The size particle has decreased but the methodology did not provide a unique size.

Table 2 Physisorbed water and hydroxyl contents of the silica samples by TG/DTG

Reaction time (h)	Initial temperature of second mass loss (°C)	First mass loss (%)	Second mass loss (%)	Physisorbed water (mg/g SiO_2)	OH group content (mg/g SiO_2)
0.08[a]	145	4.5	1.0	45	187
0.5[b]	142	4.6	1.0	46	187
1	142	4.9	1.1	49	204
2	137	4.0	1.2	40	187
3	139	3.5	1.0	35	187
6	120	2.0	0.6	20	102
24	130	0.7	0.5	7	102

TG Thermogravimetry, *DTG* derivative thermogravimetry
[a]0.08 h=5 min
[b]0.5 h=30 min

Adsorbed water and hydroxyl content

Thermogravimetric curves of the silica samples showed similar profiles as found in the literature [13]. Figure 5 presents the TG/DTG curves of silica sample (1 h). Two decays of loss of weight were observed.

At the beginning (120–150°C), there was an abrupt drop related to the loss of adsorbed water on the silica surface by volatilization (Table 2). Up to 1 h of reaction, the content of adsorbed water was practically constant and thereafter decreased continuously due to the increase of siloxane linkage and the reduction of peripheric surface hydroxyl groups (Fig. 6). By comparison, the content of adsorbed water of

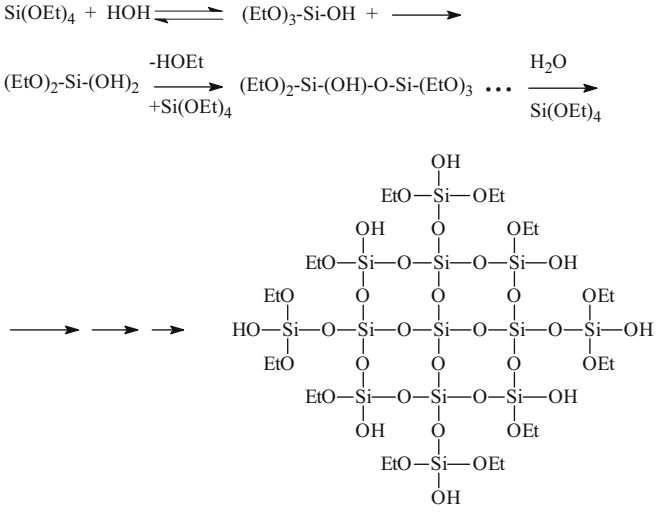

Fig. 6 Condensation reaction of silane alkoxide forming –Si–O– structure

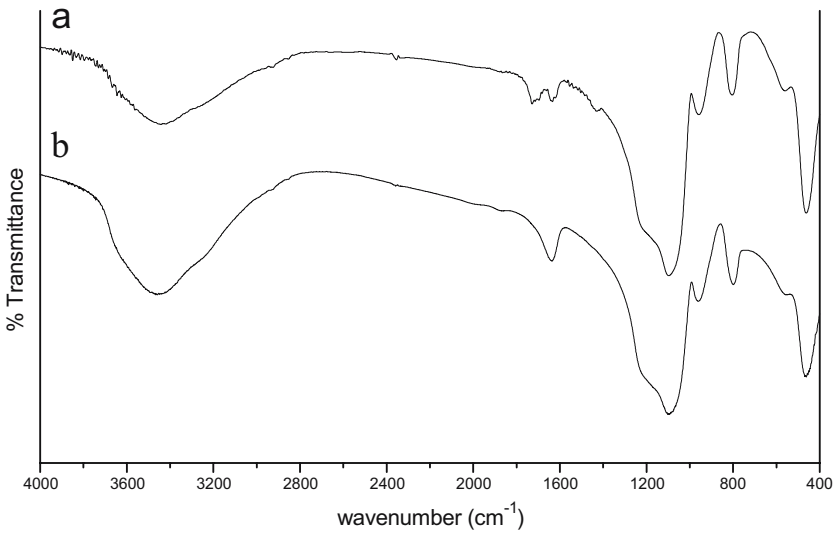

Fig. 7 IR spectra of modified (**a**) and unmodified (**b**) silica (6 h)

silica sample (5 min) was almost seven times higher than that of silica (24 h).

The second decay (400–1200°C) is related to dehydroxylation step with subsequent releasing of water molecules due to condensation of silanol groups and formation of siloxane linkage. The hydroxyl content was calculated taking into account the procedure described in the literature [16]:

$$N_{OH}(SiO) = 2n_{H_2O} = 2\frac{[\%\text{weight}(t_i) - \%\text{weight}(t_f)]}{100M_{H2O}}$$

where $N_{OH}(SiO_2) = 2n_{H_2O}$ = number of hydroxyl groups per gram of silica , $[\%\ \text{weight}(t_i) - \%\ \text{weight}(t_f)]$ = loss of weight in the temperature interval, t_i=initial temperature, t_f=final temperature and M_{H_2O}= molar mass of water .

The hydroxyl content is also listed in Table 2. Up to 3 h of reaction, the hydroxyl content was practically constant, decreasing after that time and attaining a constant value. The hydroxyl content of silica (30 min) was twice higher than that of silica (24 h). There is a direct relationship between the number of hydroxyl groups and adsorbed water content. When the hydroxyl content decreased, the adsorption of water is also reduced.

Effect of modification on thermal curves, IR spectra and morphology of silica surface

The unmodified and acrylic-modified silica samples were evaluated by IR, and the IR spectra of the two silica (6 h) are illustrated in Fig. 7. The spectra of unmodified silica evidenced the absorptions at 3450 cm^{-1} (symmetric stretching –OH–), 1640 cm^{-1} (bending of HOH), 1100 cm^{-1} (asymmetric stretching of –Si–O–Si–), 950 cm^{-1} (stretching of –Si–O–CH_2–CH_3) and 800 cm^{-1} (symmetric stretching of –Si–O–Si–). For the acrylic-modified silica, besides the characteristic absorptions of silica, new IR bands could be detected in the spectra such as 1720 cm^{-1} (symmetric stretching, –C=O–) and 1410 cm^{-1} (bending, –CH_2–), attributed to the condensed acrylic portion [15, 17, 18]. The result indicates that the proposed modification was effective, generating an acrylic–silica modified structure as shown in Fig. 8.

The thermal curves of modified silica showed two additional decays when compared to the unmodified one. A representative TG/DTG curve of modified silica (30 min) is shown in Fig. 9. There are four decays. At the beginning (35–200°C), there are two peaks: one at lower temperature (loss of residual monomer and solvent) and another at higher temperature (loss of adsorbed water). The third decay (200–400°C) was attributed to loss of acrylic portion

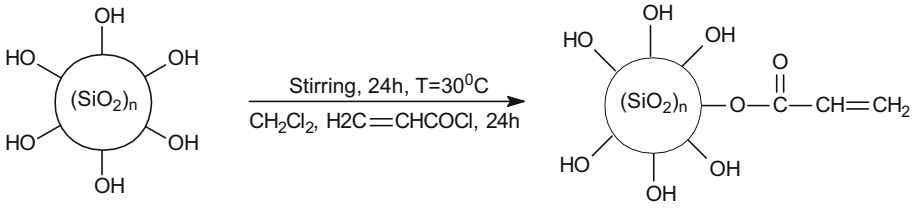

Fig. 8 Acrylic–silica modified structure

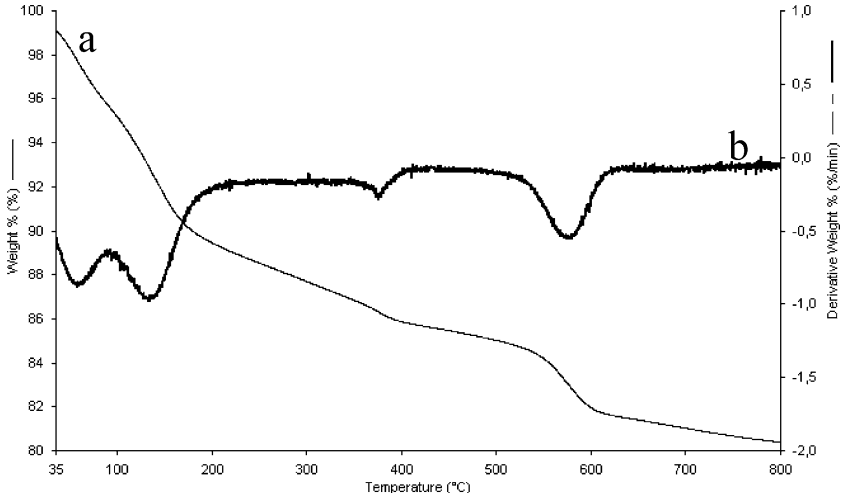

Fig. 9 TG (**a**) and DTG (**b**) curves of modified silica (30 min)

Table 3 Acrylic content incorporated on silica samples

Reaction time (h)	0.08[a]	0.5[b]	1	3	6	24
Incorporated acrylic (%)	0.094	0.444	0.656	0.223	0.065	0.035

[a]0.08 h=5 min
[b]0.5 h=30 min

incorporated on silica surface, which was not observed in the TG/DTG curve of unmodified silica. The last one (450–650°C) corresponded to silica's dehydroxylation step. The acrylic content (Table 3) on silica surface was measured by TG/DTG considering the peak area of the first derivative curve. It was expected that incorporated acrylic had a direct relationship with hydroxyl content but it did not occur probably due to many factors: variable size and morphology of silica, besides lower accessibility between reactive groups during the modification reaction.

The optical photomicrographs (Figs. 10 and 11) show the external surface of the silica particle (30 min) before and after the modification reaction, respectively. The unmodified silica particle (Fig. 10) is an amorphous, transparent material and is similar to fragmented glass. The surface of modified silica particle is opaque (Fig. 11), indicating that the acrylic monomer was incorporated, resulting in an acrylic–silica modified structure. It was not possible to distinguish in the photo if there is only one or an agglomeration of silica particle.

Fig. 10 Optical photomicrograph of silica particle (30 min) before modification (×18)

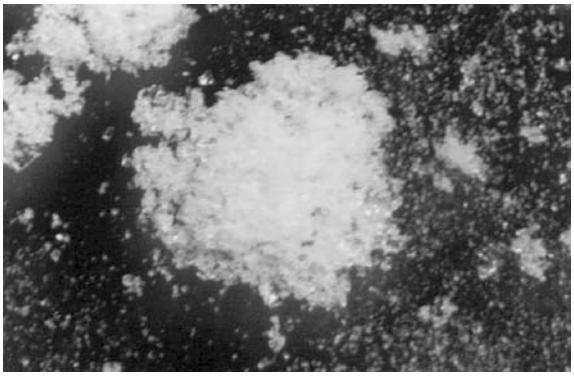

Fig. 11 Optical photomicrograph of silica particle (30 min) after modification (×62)

Conclusions

Silica was obtained by sol–gel process through hydrolysis and condensation of TEOS at 50°C, at different reaction times and in alkaline conditions. The produced silica was modified by direct condensation reaction with acryloyl chloride. The results confirmed that an acrylic–silica modified structure was formed. The methodology represents an alternative route to obtain silica with an unsaturated organic group, able to polymerize and stabilize up to 300–400°C. The material can be employed as compatibilizing filler in dental composite.

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