

The effect of different cross-linking agents on the properties of hybrid films

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Organic-inorganic hybrid films were prepared by sol-gel method, using different alkoxysilanes. All formulations were enriched with tetraisopropyl orthotitanate (TIP) or aluminium sec-butoxide (ASB), used as cross-linking agent. Thermal stabilities of the final hybrid films were evaluated and it was observed that the films with ASB, present a temperatures at which the maximum degradation rate (T_{vmax}) is much lower than films with TIP. This effect is probably due to the presence of ALOH groups, which can play a role of catalyst over organic chains degradation.

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1. Introduction

Organic-inorganic hybrid materials prepared by the so-called sol-gel process have been a subject of intense research in the past decade. This process makes possible a relatively easy incorporation of a pure inorganic phase into a matrix organic. A low-temperature procedure, high purity of reactants, and possibility of mixing of precursors of organic and inorganic phases on molecular level are the main advantages of this technique. The alkoxysilane compounds $R_{4-n}-Si(OR)_n$ are usually used as precursors of an inorganic phase formulation. The „sol-gel process“ consists of hydrolysis of alkoxysilanes and subsequent condensation to form linear polysiloxane (R_2SiO)_n or branched and cross-linked silsesquioxane ($RSiO_{3/2}$)_n from trialkoxysilanes as well as silica (SiO_2)_n structures from tetraalkoxysilanes [1]. The reaction is accelerated when acid or base catalysts are employed. Because of the capability of polymer networks to trap small molecules, sol-gel-derived materials open a route of applications for catalyst support, molecular sieves, proton conducting membranes, and so on [2].

Alumina, silica or titania are considered as the main ceramic materials for the formation of the asymmetric structures [3, 4].

Our main issue in the present paper was the investigation of influence of Ti and Al ions over the matrix structure, using different cross-linking agents, like tetraisopropyl orthotitanate (TIP) or aluminium sec-butoxide (ASB). As starting precursors, different alkoxysilanes (RTES) were chosen: methyltriethoxysilane (MeTES), phenyltriethoxysilane (PTES), octyltriethoxysilane (OTES), vinyltriethoxysilane (VTES) and (3-glycidyloxypropyl)trimethoxysilane (GMPS). Due to the high reactivity of cross-linking agent (TIP or ASB)

in sol-gel reactions, maleic anhydride (MA) was added as complexing agent.

Electron microscopy study was supplemented with thermal stability and spectral analyses to observe the internal structure of the films and explain the measured properties.

2. Experimental

2.1 Materials

Methyltriethoxysilane (MeTES, Merck-Suchardt), vinyltriethoxysilane (VTES, Merck-Suchardt), phenyltriethoxysilane (PTES, Fluka), (3-glycidyloxypropyl)trimethoxysilane (GMPS, Fluka) were used as a silica source, while tetraisopropyl orthotitanate (TIP, Fluka AG) and aluminium sec-butoxide (ASB, Fluka) were used as a cross-linking agents. Maleic anhydride (MA, Fluka AG) was used as a complexing reagent in sol-gel reaction. Benzoinedimethylacetal (FIN) (ICPAO) was added to the base sol-gel formulation, with VTES, as UV photo initiator.

2.2 Procedure

Hybrid films were prepared by the sol-gel process, in two-steps, because cross-linking agents (TIP (0.8 ml) or ASB (0.7 ml)) hydrolyzes at a much higher rate than the RTES. First, RTES was prehydrolyzed in acidic conditions with ethanol (5 ml) and water (0.56 ml) for 1h, under continuous stirring. As a second step, maleic anhydride (MA) and the cross-linking agent (TIP or ASB) were added to the solution, together with the second portion of

water (1.2 ml) and mixed for another hour. Because ASB was very viscous, it was necessary to prepare a solution for its dissolving. Thus, ASB (0.7 ml) was dissolving in carbon tetrachloride (CCl_4 (3 ml)) resulting a clear solution. A small amount from this solution (0.7 ml) was

added in the second step of sol-gel process. The amounts of materials used are summarized in table 1. Hybrids films were deposited on glass slides by dip-coating and then the slides were dried at room temperature (25°C).

Table 1. The amounts of materials used for preparation of hybrids films.

MeTES (ml)	MeTES/PTES (ml)	MeTES/VTES (ml)	MeTES/GMPS (ml)	EtOH (ml)	H ₂ O (ml)	TIP (ml)	ASB (ml)	MA (g)
9	4.4/5.4	4.4/4.8	4.4/5.2	5	1.76	0.8	0.7	0.152

3.1 Techniques

The thermal analyses (TGA) were realized with a Du Pont 2000 instrument with heat rate of $20^\circ\text{C}/\text{min}$.

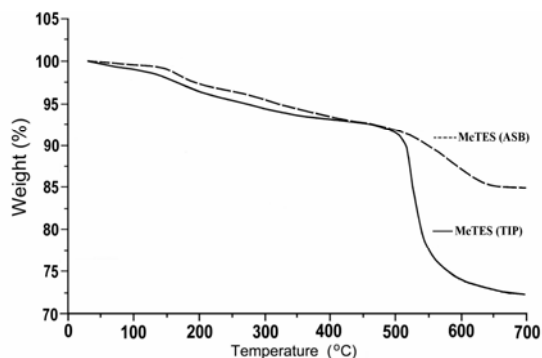
Micro-Raman measurements have been performed on the samples, using a Renishaw Invia spectrometer equipped with RenCam CCD detector and Leica DMLM microscope. A wavenumber calibration using the silicon peak ($519.5 \pm 1 \text{ cm}^{-1}$) before measurements has been performed. Raman spectra were collected with the following operational conditions: high power 785 nm laser ($\geq 300 \text{ mW}$ output in the near-infrared), the laser power at the source was above 19 mW.

FT-IR spectra, in the range $400\text{--}4000 \text{ cm}^{-1}$ using a Fourier transforms infrared spectrometer (Tensor 37 from Bruker) were measured in ATR mode using Golden Gate unite.

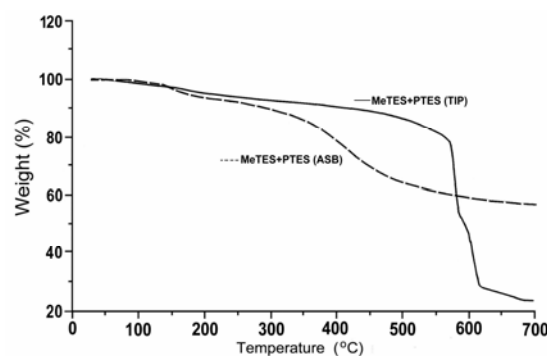
The surface of the hybrid films was visualized by scanning electron microscopy (SEM) (FEI QUANTA 200).

3. Results and discussion

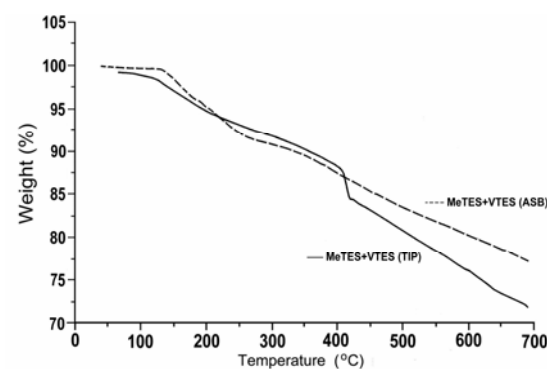
The thermal stability of hybrid systems was determined by TGA as weight loss during a programmed heating (Fig. 1). The temperatures were compared, at which the degradation rates are maxima (Fig. 2).



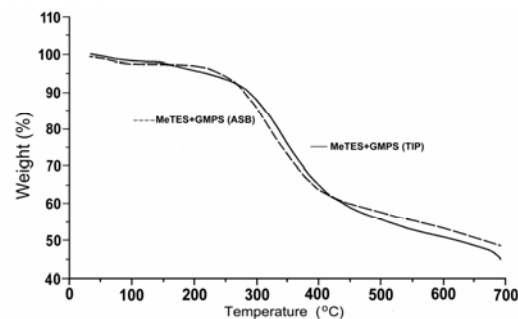
(a)



(b)



(c)



(d)

Fig. 1. Thermogravimetric curves for hybrids: a) MeTES, b) MeTES+PTES, c) MeTES+VTES, d) MeTES+GMPS, in the presence of different cross-linking agents.

Decomposition temperature depends on the precursors type, the preparation conditions, dimensions and local structure inside the network. The chemical nature of the organic group coupled to the Si atom, is extremely important in the structure building and temperature-resistance of the end products. Hybrid systems loose bounded water, solvent and probable other organic groups generated during the condensation reaction in the temperature range between 200-350°C, all bounded in the pores of composite.

For the MeTES (TIP)-based system, it was observed a weight loss at 530°C. The individual small particles with a high titania content can aggregate into bigger structures, preceding the transformation to anatase [5]. The $\text{CH}_3\text{-SiO}_2$ and/or TiO_2 networks, protected through titanium external spheres, will start to be decomposed.

The structure of MeTES+PTES (TIP)-based system is the most complex because present the higher decomposition temperature as against the other systems (Fig. 2). The composite degradation involves structure collapse, with burning of former protected organics.

For the MeTES+VTES (TIP)-based system, the decomposition temperature for main vinyl chain is 413°C. The vinyl-terminated alkoxyde (VTES) has a very high reactivity and its organic group can be more easily accommodated in a growing inorganic network.

The MeTES+GMPS (TIP)-based system present a decomposition temperature above 340°C. The polar structure of this system maintain inside the volatile compounds which are release or decomposed at a low temperature than 440°C.

Comparing the systems prepared with TIP with systems prepared with ASB, it was observed that the Ti and O atoms arrangement take place in the initial amorphous structure of systems enriched with TIP. For the network with TIP, the films surface presents a high superficial polarity and a higher affinity for interactions. The TIP presence in the systems leads at an advanced thermal degradation above 400°C. The $\text{CH}_3\text{CH}_2\text{-SiO}_2$ and/or TiO_2 superficial bonds probably will decompose slowly.

The replacement of TIP with ASB leads to a shift of the maximum degradation rate towards lower temperatures. This behavior is probably generated by the catalyzing effect of AlOH groups over the organic chains degradation. Also, it was observed that the ASB decomposed the hybrid films step by step and the degradation of organic parts take place faster because of this phenomenon. The weight loss at temperatures rises up to 200°C can be suitable for organic residues combustion. The higher temperature was observed for MeTES (ASB)-based system (584°C) which can be attributed for combustion of residual alkoxy groups. In case of MeTES+GMPS (ASB) was observed a weight loss at 321°C which can be due to the oxidation of OR groups

connected at the end of organic-inorganic chains. The temperature range between 150°C-250°C indicate the formation of partially soluble compound in acidic medium. It can be formed an oligomer or polymeric material composed from Al-O blocks with alkoxydes [6].

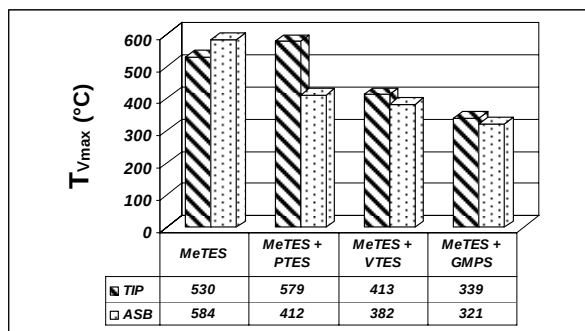


Fig. 2. Variation of the temperature at which the degradation rate is maximum (T_{vmax}) for hybrids as function of alkoxy silane nature and of cross-linking agents. Also, Raman spectra for hybrid films, obtained both in the presence of TIP or ASB, were recorded (Fig. 3).

After evaluation of Raman spectra of hybrid films, for all samples, the Si-O-Si group was observed in the spectral region between 450-550 cm^{-1} (stretching vibration).

In these spectra, the deformation mode of $\delta(\text{CH}_2)$ group was observed in the spectral region between 1400-1470 cm^{-1} . The $\delta(\text{CH}_3)$ group was present at $\sim 1380 \text{ cm}^{-1}$.

The Raman spectra (Fig. 3 b and d) shows the present of a line at 1600 cm^{-1} that can be assigned to $-\text{CH}=\text{CH}_2$ group (C-H vibration, CH_2 rocking vibration).

The line at 650 cm^{-1} (symmetric vibration) assigned to Si-OCH₃ group, shows that some species are partially hydrolyzed. Furthermore, a line also appears at 1033 cm^{-1} . It is assigned to CH₃-OH (symmetric vibration). Thus, the hydrolysis reaction in an acidic medium is almost complete. The line that appear at $\sim 490 \text{ cm}^{-1}$ can be assigned to $-\text{Si}(\text{OSi})_3$ group. This is characteristic of a three-dimensional inorganic "network" in which the silicon atoms are also bound to organic group [7].

The presence of line at 930 cm^{-1} , with multiple lines at 560 cm^{-1} and at 1100 cm^{-1} respectively, can indicate the presence of amorphous oxohydroxide (Fig. 3 c). A line at 750 cm^{-1} was observed in some species and in other not. This observation shows the disappearance of solvent.

Two types of silicon groups probably form the walls of the silica glass cage: silanols (Si-OH) and siloxanes (Si-O-Si). Both groups are indeed of lower polarity and higher hydrophobicity than water. Silica surfaces can be hydrophobic, as occurs when the surface chemical groups are mainly siloxane (Si-O-Si) groups, or hydrophilic, when contain the surfaces exposed silanol (Si-OH) groups [8].

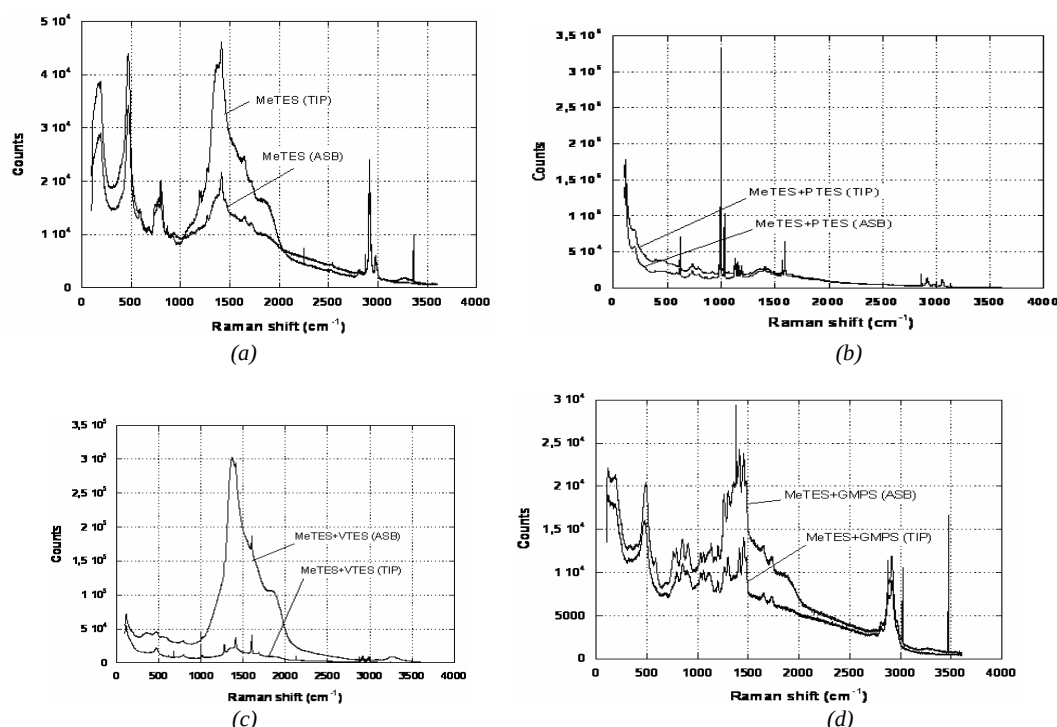


Fig. 3. Raman spectra for hybrid films: a) MeTES, b) MeTES+PTES, c) MeTES+VTES, d) MeTES+GMPS, in the presence of different cross-linking agents.

After evaluation of FT-IR spectra of MeTES (TIP)-based hybrid films, the Si-O-Si bond was founded in the spectral region between 1000-1200 cm^{-1} (stretching asymmetric vibration), more exactly at 1006 cm^{-1} (Fig. 4). The presence of Si-O group was observed at 905 cm^{-1} (bending vibration of Si-O-Si group). The characteristic bands of Si-CH₃ group were founded at 760 cm^{-1} (strong band, swinging vibration of CH₂), at 855 cm^{-1} (swinging vibration of CH₂) and at 1270 cm^{-1} , respectively (medium band, symmetrical deformation vibration of C-H bond).

In the FT-IR spectra were observed a shift toward low wavenumbers, when in the reaction is used the ASB as a cross-linking agent. First shift was observed at 900 cm^{-1} , which is characteristic to Si-O bond. In case of added TIP, this bond appears at 905 cm^{-1} . Second shift was observed at $\sim 1000 \text{ cm}^{-1}$, corresponding to Si-O-Si bond (network formation). In case of added TIP, this bond appears at 1006 cm^{-1} . These shifts toward lower wavenumbers can be due to the interactions between silica matrix and aluminium ions.

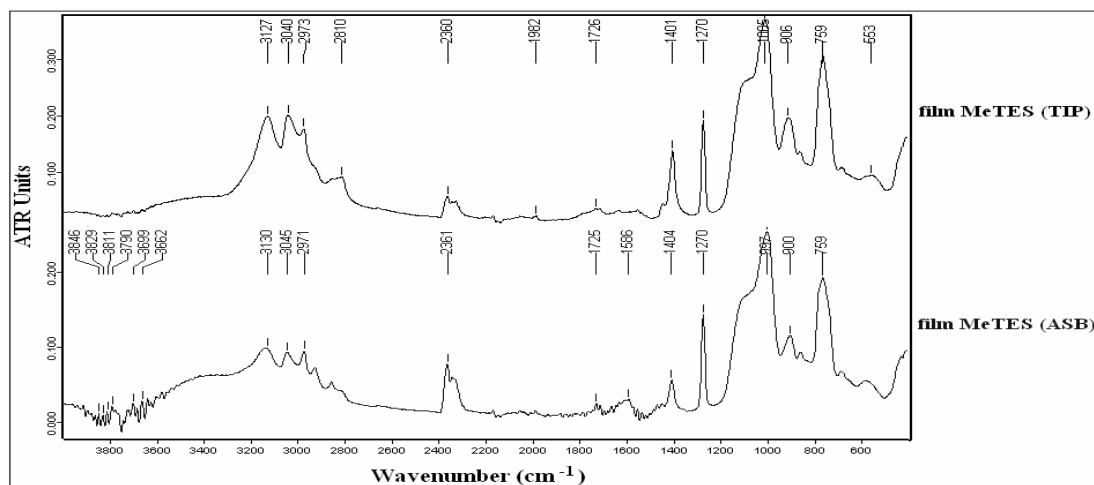


Fig. 4. FT-IR spectra of hybrid films with MeTES, in the presence of different cross-linking (TIP or ASB).

After evaluation of FT-IR spectra of MeTES+PTES-based hybrid films were founded different modifications,

(Fig. 5). The Si-O-Si bond was founded at 1014 cm^{-1} when is added TIP (stretching asymmetric vibration), and at

1008 cm^{-1} when is added ASB, respectively. The characteristic bond for Si-O appears at 905 cm^{-1} in case of TIP, and at 900 cm^{-1} in case of ASB. These shifts toward lower wavenumbers can be due to the cross-linking agent,

which produces different interactions with silica matrix in sol-gel process. The presence of phenyl group from PTES was observed at 696 cm^{-1} and at 477 cm^{-1} respectively.

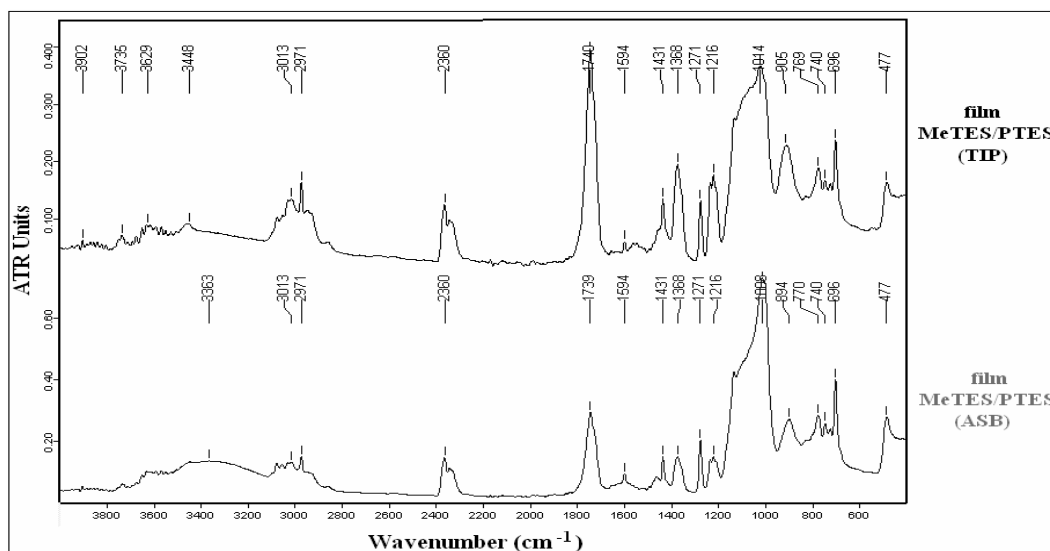


Fig. 5. FT-IR spectra of hybrid films with MeTES/PTES, in the presence of different cross-linking agents (TIP or ASB).

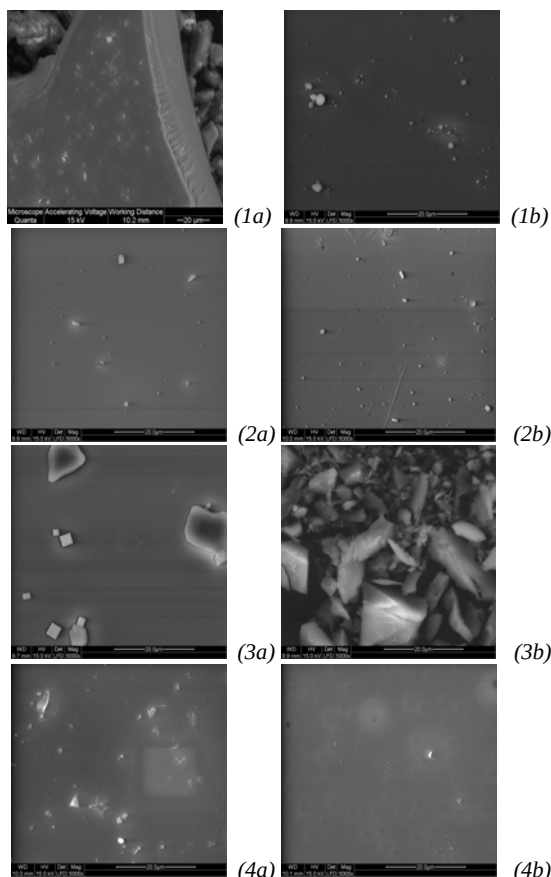


Fig. 6. Surface morphology of hybrid films with: 1) MeTES, 2) MeTES+PTES, 3) MeTES+VTES, 4) MeTES+GMPS, using different cross-linking: a) TIP, b) ASB.

The multiple bands with low intensity indicate the presence of C-C bond in the spectral region between 1400-1600 cm^{-1} . The presence of bands at 2970 cm^{-1} , in all samples with MeTES as well as with MeTES+PTES, is due to the stretching vibration mode of C-H bond which belong to methyl and methylene groups. The Si-O-H free group was detected at 3630 cm^{-1} . The bond at 1740 cm^{-1} indicates that some silica species are partially hydrolyzed during the sol-gel reaction. The OH group, which result from silica and adsorbed water, appear in a low ratio. This observation is confirmed by the presence of low intensity bands at ~3400 cm^{-1} and at 2360 cm^{-1} , respectively. The C-C bonds (stretching vibration) appear at 1594 cm^{-1} , and the presence of C-H bonds was observed at 740 cm^{-1} (out-of-plane vibration) [9].

Fig. 6 show that the hybrid films are homogeneous without any phase separation both in the presence of TIP or ASB. SEM images of organic-inorganic hybrid films confirm the existence of grains with relatively small surfaces.

The chemical modification of precursor produces a change in the films structure with ASB. The large pore is considerate as a pore between particles, forms the aggregation of colloidal particles during the sol-gel process.

4. Conclusions

In this study, the hybrid films were obtained using different precursors and cross-linking agents. All films were homogeneous and transparent. The resulting materials have more capacity retention of solvent (i.e., water, ethanol) and suffer reorganization at heating above 400°C. The titanium derivatives contribute to structure building of R-TIP particles (R=methyl, phenyl, vinyl).

Thermal stabilities of the final hybrid films were evaluated. Using ASB caused a shift of maximum degradation rate of alkyl chain toward lower temperatures. This effect is probably due to the presence of AlOH groups, which can play a role of catalyst over organic chains degradation. FT-IR spectra present also the shifts of wavenumbers as function of cross-linking agent due to the interactions between silica matrix and agent. SEM images show that the hybrid films are homogeneous without any phase separation both in the presence of TIP or ASB. For following-up studies and possible applications of these hybrid films, it is worthwhile to look further into the relationships: internal structure-macroscopic properties.

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