U.P.B. Sci. Bull., Series B, Vol. 75, Iss. 4, 2013 ISSN 1454 – 2331

PREPARATION OF HYDROPHOBIC SURFACE BASED ON HYBRID SILICA FILMS BY SOL-GEL PROCESS

Cătălin Ilie SPĂTARU[1], Violeta PURCĂR[2], Dan DONESCU[3], Marius GHIUREA[4], Otilia CINTEZĂ[5], Teodora MICLĂUŞ[6]

The most important and generally accepted way to characterize highly hydrophobic surfaces is by their wettability. This property involves a contact angle (CA) measurement between a surface and a liquid droplet. There were obtained nanostructured silica thin films from organo-modified silane precursors; a systematic study on the modification of film-forming hybrids surfaces obtained by co-hydrolysis and polycondensation of tetramethoxysilane with different alkyltrialkoxysilanes was performed. The analysis of the surface energy by contact angle method allows the determination of surface energy components and their correlation with wetting properties. The properties of the final hybrids obtained by the sol–gel process were significantly affected by the precursor alkyl chain lengths.

Keywords: sol-gel process, silica films, hydrophobicity, surface energies, organic-inorganic hybrids

1. Introduction

The synthesis of a new class of materials, inorganic-organic hybrid composites, has attracted growing interests because of the possibility of combining the properties of both inorganic and organic components. Organically-modified ceramics, in which organic groups are covalently attached to siloxane networks, is a convenient method to produce silica-based hybrids by sol-gel process using organoalkoxysilanes ($R_nSi(OR')_{4-n}$) [1].

The elaboration of organic-inorganic composites and their usage as structural and biomedical materials was very important due to their potential applications in catalysis, photonics and electronics. The multilayered organic-

---

[1] PhD student, National R&D Institute for Chemistry and Petrochemistry, Polymer Department, Bucharest, Romania, e-mail: catalin_spataru2004@yahoo.com

[2] PhD chem., National R&D Institute for Chemistry and Petrochemistry, Polymer Department, Bucharest, Romania

[3] Prof., National R&D Institute for Chemistry and Petrochemistry, Polymer Department Bucharest, Romania

[4] PhD. Phys., National R&D Institute for Chemistry and Petrochemistry, Polymer Department Bucharest, Romania

[5] Prof., Physical Chemistry Department, University POLITEHNICA of Bucharest, Romania

[6] Student, Physical Chemistry Department, University POLITEHNICA of Bucharest, Romania

inorganic thin films are one of the most important systems because they are expected to exhibit unique properties arising from structural anisotropy and compositional varieties [2].

Nanoscience and nanotechnology give a great interest to the self-assembly process of molecules into nanoscale structures. Recently, the self-assembly of amphiphilic molecules has been widely exploited to create nanostructured organic-inorganic composites due to fundamental interest and a wide range of potential applications.

Two general approaches have been proposed: 1-solution synthesis of inorganics in the presence of molecular assembly, which usually relies on non-covalent interactions such as hydrogen or ionic bonds between inorganic and organic components and 2-design of molecular building blocks capable of self-assembly and subsequent inorganic cross-linking [4].

It is well-known that silica-based hybrids in which organic groups are covalently attached to siloxane networks can be produced by hydrolysis and polycondensation of organosilanes containing Si-C and Si-OR (or Si-Cl) bonds. The chemical design or organosilanes at the molecular scale leads to modifications of the structures and properties of hybrids.

However, the products are generally amorphous solids, and control of their nanostructure is one of the most important subjects with respect to the creation of advanced materials [5-7].

In order to induce strong hydrophobic separations there was highlighted the possibility to obtain ordered organic-inorganic hybrids through sol-gel process only in the case when the alkyltrialkoxysilane chain length is long enough ($C_{14} – C_{18}$) [1, 8-10].

The real challenge is represented by the development of new strategies to control the organization of hybrid materials without the use of surfactants.

The surface obtained by sol-gel processes of alkyltrialkoxysilanes in the presence of tetraalkoxysilanes can become hydrophobic depending on the trifunctionalised derivates concentration and chain length [7, 11-13].

The hydrophobicity of homogeneous hybrids surfaces obtained by copolymerization of alkyltrialkoxysilanes is also affected by the alkyl radical length from co-monomers, a phenomenon proved in previous studies [14, 15].

Therefore, this paper presents a systematic study on the modification of film-forming hybrids surfaces obtained by copolymerization of tetramethoxysilane with different alkyltrialkoxysilanes. The chain length of the alkyl derivate varies between C_1 and C_{18}, some of them (methyl, vinyl, propyl) contains short chains, and others C_{16}, C_{18} very long chains. According to Kuroda, the ratio between TMOS and organo-modified derivatives was 1:4 [1]. This paper also studies the influence of unsaturated hydrocarbon part/chain was studied.

2. Experimental

2.1. Materials

Precursors: methyltrimethoxysilane (MTMS, 98%, Fluka), vinyltriethoxysilane (VTES, 98%, Fluka), propyltrimethoxysilane (PTMS, 97%, Fluka), hexadecyltrimethoxysilane ($C_{16}H_{33}TMS$, 85%, Fluka), octadecyltrimethoxysilane ($C_{18}H_{37}TMS$, 90%, Aldrich) and tetramethylorthosilicate (TMOS, 99%, Aldrich) were used as silica sources. Water, glycerine and α-bromonaphthalene (ABN) (all from Sigma-Aldrich) were used as liquids for contact angle measurements.

2.2. Film preparation

Synthetic method [2]: Cohydrolysis and polycondensation have been performed in a water-ethanol mixture of molar ratio 50:19, according to a procedure from reference [1]. Briefly, 4.487 g TMOS and the required amount of organo-modified silica compound were dissolved in 16.682 g EtOH under continuous stirring and heating from room temperature up to 40 ºC. When temperature was reached, 2.19 ml HCl 0.1 N solution was added, accompanied by 90 min stirring.

Organic-inorganic hybrids were obtained in 2 steps:

- obtaining the organic modified silica material by sol-gel process at a temperature that ensures the homogeneity of the mixture
- preparation of the film by deposition onto glass slide at 40 ºC and drying at room temperature.

Molar ratio used for reaction mixtures was:

$C_nTMS : TMOS : EtOH : H_2O : HCl = 1 : 4 : 50 : 19 : 0.03$

3. Methods

FT-IR spectra were performed from the hybrid films with Tensor 37 (Bruker), equipped with ATR Golden Gate unit. Absorption interval was between 400 and 4000 cm^{-1}. Thermal and caloric analyses were performed in air (20 ºC/min) using a TA TGA Q5000 IR instrument, respectively in He (10 °C/min) using a TA DSC Q2000 instrument. The surface of the hybrid films was visualized by environmental scanning electron microscopy (ESEM) (FEI QUANTA 200). The ESEM images were obtained in low vacuum mode. The samples were deposited on a conductive stub and dried at the room temperature. Contact angles for the hybrid films (towards three liquids with different polarities: H_2O, glycerine and α-bromonaphthalene (ABN)) were determined using a DataPhysics OCA 15^+ Contact Angle Tensiometer instrument, equipped with a digital camera connected to PC. Obtained data was used to calculate the surface energies and their components.

4. Results and discussion

In the present work there were prepared various silica materials through sol-gel process acid catalysis. The material was deposited on glass substrates as a thin film and submitted to various analyses.

Hybrid silica materials were investigated by using FT-IR spectrophotometry, thermogravimetric analysis and differential calorimetry by TGA, respectively DSC. The films deposited on glass substrates were investigated by scanning electron microscopy SEM and were submitted to the determination of the contact angles towards several liquids with different polarities in order to calculate the surface energy and their components.

Using the silane precursors from this present work, the hydrophobic moiety could eventually retard the hydrolysis/condensation reaction involved in the silica network formation. Long or bulky organic functionalities cannot be easy accommodated in the growing inorganic matrix [1].

FT-IR spectra are devoted to evidence the formation of organic-inorganic matrix (Fig. 1).

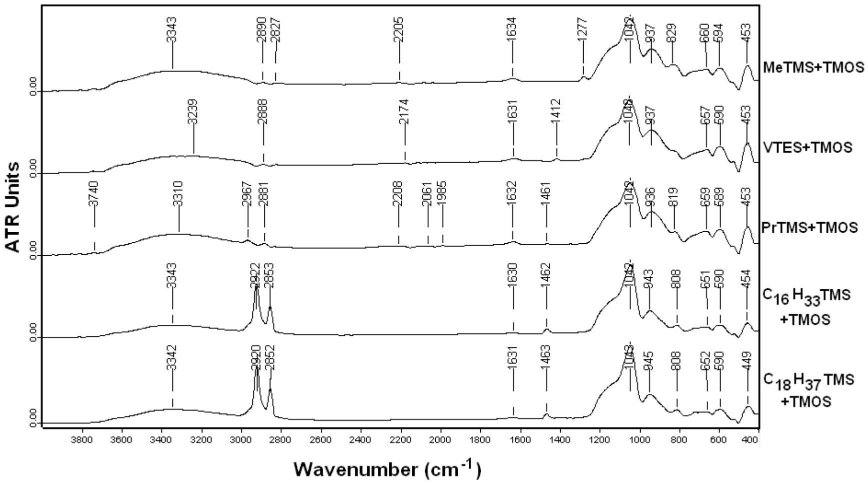

Fig. 1 - FT-IR spectra for hybrid films

It can also exhibit signals characteristic to Si-O-Si group (asymmetric stretching vibration and bending vibration) and signals characteristic to Si-CH_3 or Si-alkyl groups. The FTIR spectra of the obtained hybrid samples using different silane precursors are shown in Fig. 1, which gives a clear evidence for surface modification. In the low frequency region, 700–1400 cm^{-1}, fundamental Si–O bands can be observed for all studied samples (bending vibrations at ~900 cm^{-1} and assymmetric stretching vibrations at ~1000 cm^{-1}, respectively) - this is invariant with surface modification, but confirms the formation of silica network.

As it ca be seen, there are also signals corresponding to OH groups, from silica and absorbed water, at ~3370, ~2350 and ~1630 cm^{-1} for all the obtained hybrids.

The bands at ~2850 and ~2900 cm^{-1} of $–CH_2$ due to C–H symmetric and antisymmetric stretching respectively indicate the presence in the peak positions is perhaps attributed to the entanglements of hydrocarbon chains. The intensity of the C-H stretching bands is higher for the silica modified with longest alkyl chains ($C_{16}H_{33}$TMS-TMOS and $C_{18}H_{37}$TMS-TMOS hybrids). This fact confirms the existence of alkyl groups on the silica surface, which which is in agreement with previously published data [20-22].

TGA and DSC characterization

In the present work, TGA analysis was employed in the evaluation of the thermal stability of hybrid films obtained by sol–gel process (20 ºC/min in air atmosphere). The different weight losses can be appreciated in Fig. 2. In order to follow some significant effects, the weight loss was studied in three temperature intervals: 0-120 ºC (I), 120-400 ºC (II), 400-600 ºC (III) (see Table 1).

Table 1

Thermal decomposition for the five hybrid systems

Hybrid system	Weight loss (%)		
	0-120 ºC	120-400 ºC	400-600 ºC
MTMS-TMOS	11.20	4.45	1.85
VTES-TMOS	9.49	3.95	1.35
PTMS-TMOS	8.17	5.26	1.25
$C_{16}H_{33}$TMS-TMOS	4.03	35.65	6.54
$C_{18}H_{37}$TMS-TMOS	4.12	37.17	6.89

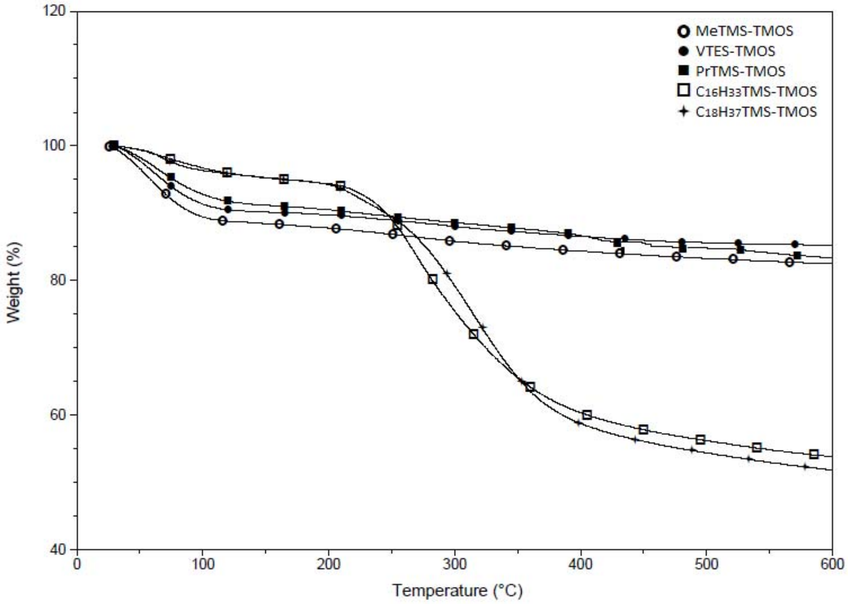

Fig. 2 Thermal decomposition for the five hybrid systems

The most important differences were observed:

- **in the first temperature interval** which corresponds to the release of water content; quantity of water that sample is losing, decreases with the increasing of hydrocarbon chain. This proves that the $C_{16}H_{33}$TMS-TMOS and $C_{18}H_{37}$TMS-TMOS hybrid systems are hydrophobic.

- **the 2nd temperature interval** corresponds to the decomposition of hydrocarbon chain. This explains the significant weight loss in case of $C_{16}H_{33}$TMS-TMOS and $C_{18}H_{37}$TMS-TMOS hybrid systems observed in the range of 120 – 400 ºC, which is due to the $C_{16}H_{33}$TMS and $C_{18}H_{37}$TMS decomposition.

- **in the third temperature interval**, dehydroxylation of the Si–OH groups occurred, which resulted in the formation o Si–O–Si groups. We note that the thermal degradation behavior suggested is in some agreement with previous literature works [17].

From the thermogravimetric analysis there can be establish that systems with long hydrocarbon chain precursors have not absorbed too much water (quantity of water decreases with the increasing of hydrocarbon chain), strengthening the hydrophobic idea. The results are in agreement with some previous published data [18, 19].

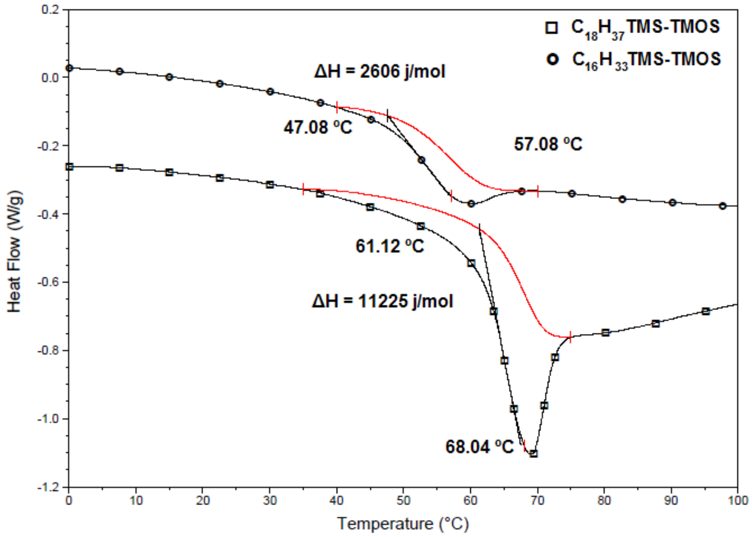

Fig. 3 Melting enthalpy for $C_{16}H_{33}$TMS-TMOS and $C_{18}H_{37}$TMS-TMOS hybrid systems

In Fig. 3 it can be seen that the melting enthalpy for $C_{18}H_{37}$TMS-TMOS hybrid system is much higher than the one for $C_{16}H_{33}$TMS-TMOS hybrid systems. This means a higher packing degree and a better structuring, induced by a higher hydrocarbon chain.

SEM characterization

The surface of hybrid films was examined through environmental scanning electron microscopy (ESEM). As can be seen from Fig. 4a, many cracks are clearly observed on film of sample obtained with MTMS precursor because of too much TMOS content used in comparison with short alkyl chain precursor. The film-forming property of sol–gel derived organic–inorganic hybrids and CA of hybrid film are improved gradually (Fig. 5) with the increase of the length of the hydrocarbon chain of the precursor.

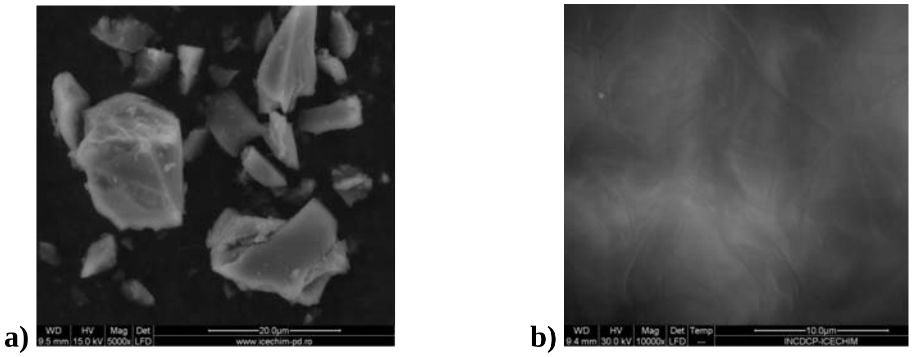

Fig. 4 a) MTMS-TMOS hybrid b) $C_{18}H_{37}$TMS-TMOS hybrid

From the recorded ESEM images in Fig. 4b it can be observed that hybrid systems using precursors with long hydrocarbon chain are much uniform than the other hybrid systems. A high ratio MTMS/TMOS implies no film forming.

Contact angle measurements

The hybrid films have been subjected to the determination of contact angles necessary to calculate the surface energy and its components, using three liquids with different polarities. The contact angle was calculated from drop image, after shape accentuation and radius and string reading. The results are presented in the following tables.

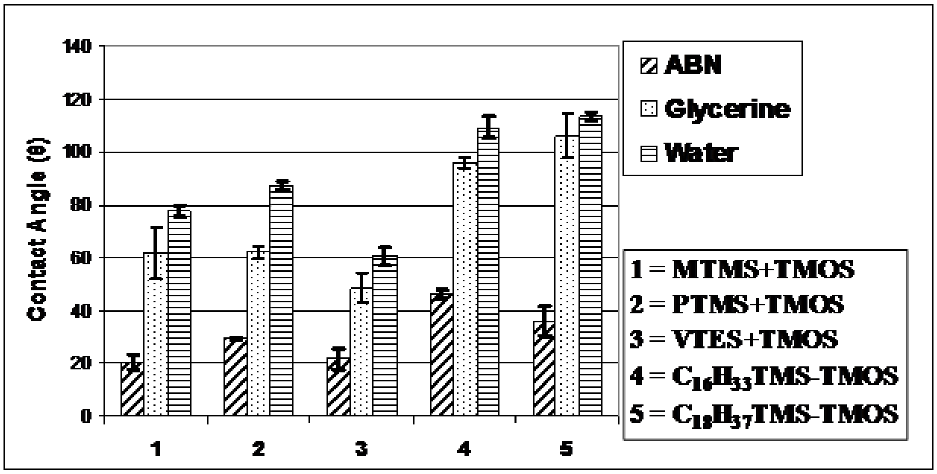

Fig. 5 - Values for the contact angles (θ) of different liquids at the surface of films prepared with different precursors

A representation of the contact angles measured for the hybrid samples it can be seen in Fig. 5. Three different liquids were used:

- α, bromonaphtalene (non-polar solvent);
- glycerine (polar solvent);
- water (polar solvent).

In the case of the non-polar solvent, rather small and invariable values of the contact angle were obtained (starting from ≈20º for MTMS-TMOS hybrid up to ≈40º for the $C_{16}H_{33}$TMS-TMOS).

Table 2

OWRK Method (dispersion component + polar component)

Hybrid System	**Surface Energy (mN/m)**	Dispersion component + Polar component
MTMS-TMOS	42.49	33.38 + 9.11
VTES-TMOS	53.43	38.02 + 15.41

PTMS-TMOS	38.72	38.46 + 0.26
$C_{16}H_{33}$TMS-TMOS	26.24	25.98 + 0.27
$C_{18}H_{37}$TMS-TMOS	26.10	25.57 + 0.53

Table 3

ACID-BASE THEORY Method (LW* component + acid component + alkaline component)

Hybrid System	**Surface Energy (mN/m)**	**Components (LW, acid and alkaline) (mN/m)**	
MTMS-TMOS	39.99	LW comp.	36.81 ± 0.41
		acid comp.	0.56 ± 0.38
		alkaline comp.	4.46 ± 0.14
VTES-TMOS	45.46	LW comp.	39.25 ± 0.41
		acid comp.	0.38 ± 0.38
		alkaline comp.	25.47 ± 0.14
PTMS-TMOS	38.01	LW comp.	38.00 ± 0.41
		acid comp.	0.00 ± 0.38
		alkaline comp.	0.96 ± 0.14
$C_{16}H_{33}$TMS-TMOS	25.95	LW comp.	25.95 ± 0.41
		acid comp.	0.00 ± 0.38
		alkaline comp.	0.31 ± 0.14
$C_{18}H_{37}$TMS-TMOS	23.83	LW comp.	23.83 ± 0.41
		acid comp.	0.00 ± 0.38
		alkaline comp.	0.52 ± 0.14

*LW = Lifshitz - Van der Waals interaction energy

When glycerin or water (polar solvents) was used, the contact angles determined were much higher than in the previous case and the increasing tendency was rather natural : 79º (MTMS), 62º (VTES) - probably due to the unsaturated double bond, 87º (PTMS) < 110º ($C_{16}H_{33}$TMS) < 113º ($C_{18}H_{37}$TMS).

Using the contact angles for the hybrid systems measured towards several liquids, were calculated the surface energies, through various methods.

As it can be seen in the tables above (Table 2 and 3), the surface energy calculated by both OWRK and ACID-BASE THEORY methods, are in a good accordance with the contact angles measured for the hybrid systems deposited over glass substrate.

As it was expected lower values of the surface energy was noticed in the case of $C_{16}H_{33}$TMS-TMOS and $C_{18}H_{37}$TMS-TMOS systems comparatively with the systems with small alkyl chains. This proves the hydrophobicity for the samples containing long hydrocarbon chain.

The contact angle for water demonstrates that we have no superhydrophobic surfaces (CA >150º) [16].

In Fig. 6 (below) there is presented a representation of the surface energies calculated by OWRK and ACID-BASE THEORY function of hydrocarbon chain length of the silane precursors, for a better understanding of how the variation of the silane precursors influence the wetting properties (wettability) of the obtained hybrids.

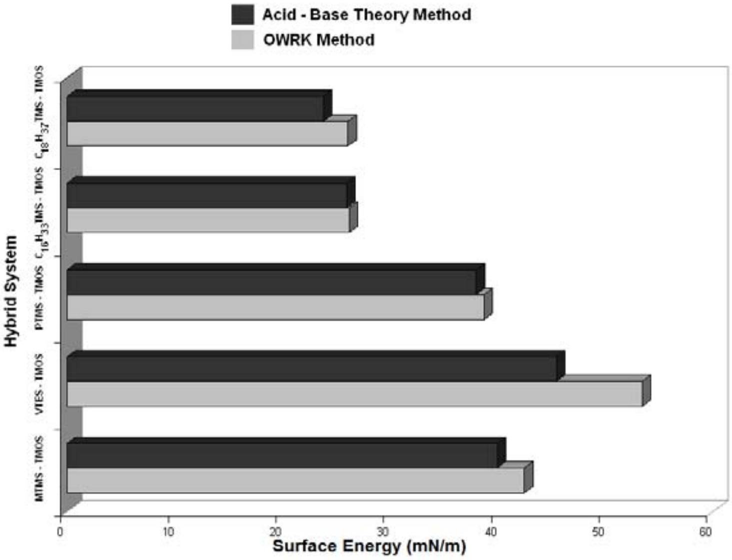

Fig. 6 Surface energy (mN / m) for each hybrid system

5. Conclusions

By analyzing the FT-IR spectra for the obtained samples can be observed signals characteristic to Si-O-Si groups (asymmetric stretching vibration and bending vibration) and signals characteristic to Si-CH_3 group and particularly for Si-alkyl groups in the case of $C_{16}H_{33}$TMS-TMOS and $C_{18}H_{37}$TMS-TMOS systems.

From the thermogravimetric analyses there can be established that systems with long hydrocarbon chain precursors have not absorbed too much water (quantity of water decreases with the increasing of hydrocarbon chain), which strengthens the hydrophobic behavior.

The DSC and environmental scanning electron microscopy (ESEM) measurements have proven that systems using precursors with long hydrocarbon chain are much uniform. This means a higher packing degree and a better structuring, induced by a higher hydrocarbon chain.

The contact angle measurements and the surface energy calculated are in a good agreement with the other performed analyses and prove that the samples containing long hydrocarbon chain are highly hydrophobic.

The obtained film-forming hybrid materials with high hydrophobic behavior can be used for various coverings (eg. buildings treatment against moisture and graffiti, heritage objects protection). Active recent research on hydrophobic materials might eventually lead to industrial applications. Patterned hydrophobic surfaces have the promises for the microfluidic devices and can drastically improve the surface based bioanalysis.

Aknowledgement

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/107/1.5/S/76909.

Violeta Purcar acknowledges the financial support of strategic grant POSDRU/ 89 / 1.5 / S / 58852, Project „Postdoctoral programme for training scientific researchers” cofinanced by the European Social Found within the „Sectorial Operational Program Human Resources Development 2007-2013”.

REFERENCES

[1] *Shimojima, K. Kuroda*, Designed synthesis of nanostructured siloxane-organic hybrids from amphiphilic silicon-based precursors, Chem Rec., 2006, **6**(2), 53-63

[2] *M. Sakurai, A. Shimojima, M. Heishi, K. Kuroda*, Preparation of mesotructured siloxane-organic hybrid films with ordered macropores by templated self-assembly, Langmuir 2007, **23**, 10788-10792

[3] *A. Shimojima, K. Kuroda*, Direct formation of mesostructured silica-based hybrids from novel siloxane oligomers with long alkyl chains, Angew. Chem. Int. Ed., 2003, **42**, 4057-4060

[4] *L. Nicole, C. Boissiere, D. Grosso, A. Quach, C. Sanchez*, Mesostructured hybrid organic-inorganic thin films, J. Mater. Chem. 2005, **15**, 3598-3627

[5] *Y-J. Eo, D-J. Kim, B-S. Bae, K-C. Song, T-Y. Lee, S-W. Song*, Coating of tetraethylortosilicate (TEOS) / Vinyltriethoxysilane (VTES) hybrid solution on polymer films, Journal of sol-gel science and technology, 1998, **13**, 409-413

[6] *D. L. Ou, A. B. Seddon*, Near- and mid-infrared spectroscopy of sol-gel derived ormosils: vinyl and phenyl silicates, Journal of non-crystalline solids, 1997, **210**, 187-203

[7] *K. Tadanaga, K. Azuta, T.Minami*, Preparation of organic-inorganic hybrid coating films from

vinyltriethoxysilane-tetraethoxysilane by the sol-gel method, Journal of the Ceramic Society of Japan, **105**, 555-558 (1997)

[8] *A. Shimojima, N. Umeda, K. Kuroda*, Synthesis of layered inorganic-organic nanocomposite films from mono-, di-, and trimethoxy(alkyl)silane – tetramethoxysilane systems, Chem. Mater., 2001, **13**, 3610-3616

[9] *A. Shimojima, K. Kuroda*, Structural control of multilayered inorganic-organic hybrids derived from mixtures of alkyltriethoxysilane and tetraethoxysilane, Langmuir, 2002, **18**, 1144-1149

[10] *A. Shimojima, C-W. Wu, K. Kuroda*, Structure and properties of multilayered siloxane-organic hybrid films prepared using long-chain organotrialkoxysilanes containing C=C double bonds, J. Mater. Chem., 2007, **17**, 658-663

[11] M.*B. Smith, K. Efimenko, D. A. Fischer, S.E. Lappi, P.K. Kilpatrick, J. Genzer*, Study of the packing density and molecular orientation of bimolecular self-assembled monolayers of aromatic and aliphatic organosilanes on silica, Langmuir 2007, **23**, 673-683

[12] *W. Wang, B. Gu*,Self-assembly of two and three dimensional particl arrays by manipulating the hydrophobicity of silica nanospheres, J. Phys. Chem. B, 2005, **109**, 22175-22180

[13] *R.S. Underhill, A.V. Jovanovic, S.R. Carino, M. Varshney, D. O. Shah, D. M. Dennis, T. E. Morey, R. S. Duran*, Oil-filled silica nanocapsules for lipophilic drug uptake: Implications for drug detoxification therapy, Chem. Mater., 2002, **14**, 4919-4925

[14] *V. Uricanu, D. Donescu, A.G. Banu, S. Serban, M. Olteanu, M. Dudau*, Organic-inorganic hybrids made from polymerizable precursor, Materials Chemistry and Physics, **85** (2004), 120-130

[15] *V. Uricanu, D. Donescu, A.G. Banu, S. Serban, M. Vasilescu, M. Olteanu, M. Dudau*, Influence of film structure and precursor composition on rhodamine B retention in dye-dopped ormosils, Journal of sol-gel science and technology, **32**, 23-39, 2005

[16] *X. Feng, L. Jiang*, Design and creation of superwetting / antiwetting surfaces, Adv. Mater, 2006, **18**, 3063-3078

[17] *R. Brambilla, J. H.Z. dos Santos, M. S.L. Miranda, R. L. Frost*, Thermal stability of octadecylsilane hybrid silicas prepared by grafting and sol–gel methods, Thermochimica Acta, **469** (2008) 91–97

[18] *T. Shigeno, M. Nagao, T.Kimura, K. Kuroda*, Direct Silylation of a Mesostructured Precursor for Novel Mesoporous Silica KSW-2, Langmuir, 2002, **18** (21), 8102–8107

[19] *J. B. Brzoska, I. B. Azouz, F. Rondelez, A. N. Parikh, D. L. Allara*, Transition temperatures for n-Alkyltrichlorosilane Monolayers, Langmuir 1997, **13**, 2588-2590

[20] *S. A. Kulkarni, S. B. Ogale, K. P. Vijayamohanan,* J. Colloid Interface Sci. 2008, **318**, 372–379

[21] *R. Ianchis, M. C. Corobea, D. Donescu, I. D. Rosca, L. O. Cinteza, L. C. Nistor, E. Vasile, A. Marin, S. Preda*, Advanced functionalization of organoclay nanoparticles by silylation and their polystyrene nanocomposites obtained by miniemulsion polymerization, J Nanopart Res 2012, **14**, 1233

[22] *D. Donescu, R. Somoghi, C. Nistor, R. Ianchis, M. Ghiurea, G. Prodan, C. Radovici*, Copolymerization in dispersion of divinyl benzene–maleic anhydride in the presence of silylated montmorillonite clays, Polymer Bulletin 2012, **68**, 993–1007