EFECTUL SILANIZĂRII ASUPRA COMPOZITELOR PE BAZĂ DE ALUMINĂ ȘI ACID POLIMETACRILIC CU APLICAȚII CA MATERIALE PENTRU PROTEZE DENTARE THE EFFECT OF SILANIZATION ON ALUMINA - POLY(METHACRYLIC ACID) COMPOSITES WITH APPLICATIONS AS DENTURE BASE MATERIALS

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The aim of this work was to prepare via in situ radical polymerization polymethacrylic acid/Al₂O₃ composite materials and to modify the structure of alumina with two silane coupling agents, 3-aminopropyl-trimethoxysilane (APTMS) and dichlorodimethylsilane (DMDCS). Also, the influence of silanization on the physico-mechanical properties of the resulting composite materials was studied. The surface modification of inorganic particles appears as an efficient technique to improve interactions between polymer matrix and nanoparticles.

The modification of alumina was investigated using transmission Fourier transform infrared spectroscopy that confirmed the success of the silanization procedure. The crystalline phase was identified using XRD analysis and the presence of alumina in the composite materials is demonstrated according to ASTM. Scanning electron microscopy revealed in all the analyzed samples alumina particles with spherical morphology that are embedded homogeneously in the organic polymer matrix. Also, the mechanical properties of composites were investigated based on xylene porosimetry and compression testing.

The composite materials synthesized in this study demonstrated a good potential for application in dentistry as dental resins or denture base materials.

Scopul acestei lucrări a fost de a obține prin polimerizare radicalică in situ materiale compozite de tipul acid polimetacrilic/Al₂O₃ și de a modifica structura aluminei cu doi agenți de cuplare silanici, 3-aminopropiltrimetoxisilan (APTMS) și diclorodimetilsilan (DMDCS). De asemenea, s-a dorit studierea influenței silanizării asupra proprietăților fizico-mecanice ale materialelor compozite rezultate. Modificarea suprafeței particulelor anorganice este utilizată ca o tehnică eficientă pentru a îmbunătăți interacțiunile dintre matricea polimerică și nanoparticule.

Alumina modificată a fost investigată utilizând spectroscopia în infraroșu cu transformată Fourier (FTIR) care a confirmat succesul procedurii de silanizare. Faza cristalină a fost identificată utilizând analiza de difracție de raze X (XRD) și prezența aluminei în materialele compozite este demonstrată conform fișelor ASTM. Microscopia electronică de scanare a relevat în toate probele analizate particule de alumină cu morfologie sferică care sunt încorporate omogen în matricea polimerică organică. De asemenea, proprietățile specifice ale compozitelor au fost investigate pe baza porozimetriei cu xilen și a rezistențelor mecanice la compresiune.

Materialele compozite sintetizate în acest studiu au demonstrat un bun potențial pentru aplicații în stomatologie ca rășini dentare sau materiale pentru protezele dentare.

Keywords: Alumina, Polymethacrylic acid, Composite materials, Denture base materials

1. Introduction

In modern dentistry, the application of resinbased composites continues to increase, and in the majority of countries has completely replaced mercury amalgams [1].This trend is generated by government legislation regarding the application of products that contain mercury and by their esthetic quality, fast and on-demand setting process, excellent physic-mechanical properties and for the chemical bonding potential with tooth tissue [2].

However, because of the differences related to chemical bonding of these materials, the interaction is very weak at the interface leading to no significant values in practical situations. For these reasons, the surface modification of inorganic particles appears as an efficient technique to overcome the incompatibility and improve interactions between polymer matrix and nanoparticles. Such approach is expected to lead to a homogenous distribution of the filler as well as better properties for polymer composites [3].

Alumina (Al_2O_3) is a representative bioinert ceramic with a variety of applications in industry as well as in medicine [4]. Alumina has the potential to improve electrical resistivity and thermal conductivity of polymers [5, 6]. The application of poly(methacrylic acid) (PMAA) in medicine was poorly investigated in the past but can lead to good results by incorporating alumina particles that can bring bioinertness to the composite. In order to enhance the homogeneity of alumina in the

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4 A.T. Cucuruz, E. Andronescu, A. Cucuruz, G. Pelin / The effect of silanization on alumina - poly(methacrylic acid) composites with applications as denture base materials

polymer matrix and prevent aggregation, it is desirable to treat alumina with coupling agents, such as silane and titanate [7]. Modifying alumina structure with silanes is quite a new trend and not as widely used before as silanization of silica that has been extensively employed in the past [8]. Silane coupling agent acts as a chemical bridge between the organic matrix and the reinforcement filler. This bond improves the interfacial adhesion between the two phases and leads to a significant effect on the overall performance of final composites [9]. By conditioning the surface of the materials, surface roughness is increased and new micropore scan be created for a good embedment of silanes [10].

On the other hand, the use of silanes in order to modify inorganic surfaces has been taken into consideration lately. Specifically, nanoporous alumina membranes have been silanized with alkylated trimethoxysilanes in order to obtain notably better properties than the unmodified membrane [11]. Silanes were also applied for composites with inorganic fillers such as glass fibers or other mineral fillers. Also, they are used for enhancing adhesion in many adhesive formulations and as substrate primers [12].

All these improvements in dental adhesive systems made for bonding resin composites to tooth structure have enhanced the clinical application of polymeric restorative materials to the position that they are now considered the material of choice for esthetic restoration [13, 14].

In this work, two silane coupling agents were used as surface modifying agents for alumina. Also, polymethacrylic acid/Al₂O₃ composites were prepared via *in situ* radical polymerization method exploiting the better compatibility between the two phases of the composite materials.

2. Experimental

2.1. Reagents

Methacrylic acid (MAA) purrum monomer ≥98% and alumina (Al₂O₃ - 99.997% trace metals basis) were supplied by Sigma-Aldrich. Benzoyl peroxide (initiator) purrum \geq 97% was supplied by APTMS 97% Fluka. (3-aminopropyl-DMDCS ≥99.5% trimethoxysilane) and (dichlorodimethylsilane) were both supplied by Sigma-Aldrich. Acetone puriss≥ 99.5% was supplied by Sigma-Aldrich. Acetic acid puriss was supplied by Riedel-de Haën. All reagents were used without any further purification. The chemical structures of the employed coupling agents are presented in Figure 1:



Fig. 1 - Chemical structures of the two silane coupling agents used in this study / Structurile chimice ale celor doi agenți de cuplare silanici utilizați în acest studiu.

2.2. Silanization procedure

The silanization process consisted in the immersion of aluminium oxide in a solution based on acetone, acetic acid and distilled water in a mass ratio of 10:2:1. The silane agent was added in a percentage of 1% reported to the oxide. The reaction was allowed to occur under magnetic stirring for 24 hours at room temperature. Samples were then filtered and dried.

2.3. Synthesis of the composite materials

Composite materials based on PMAA/Al₂O₃-APTMS PMAA/Al₂O₃, and PMAA/Al₂O₃-DMDCS were obtained by free radical polymerization process. First, the oxide was dispersed into the monomer, in a mass ratio of 1:2 under magnetic stirring. The initiator was added at a ratio of 1% with respect to the monomer; homogenization was maintained for 30 minutes at 80°C. Then, the resulting dispersions were transferred in glass molds and the final stage of polymerization was conducted at 90°C for 2 hours. The schematic representation of the work procedure is presented in Figure 2.

2.4. Methods

The microstructures, composition and thermal behavior of the synthesized composite materials were determined by FT-IR, XRD, SEM and ATD-TG. Also, the mechanical properties of the composites were determined in order to observe the influence of the silanes coupling agents.

FT-IR spectroscopic measurements were performed using a Thermo Scientific Nicolet 6700 spectrometer. The spectra were recorded on a wavenumber range of 400–4000cm⁻¹ for transmission and 675-4000cm⁻¹ for ATR at room temperature with a resolution of 4 cm⁻¹.

X-ray diffraction analysis was performed on a Shimadzu XRD 6000 diffractometer at room temperature. It was used the Cu K α radiation from a Cu X-ray tube. The samples were scanned in the Bragg angle, 2θ range of $10 - 87^{\circ}$ at a scan rate of 2° min⁻¹. All samples were ground to fine powders



Fig. 2 - Schematic representation of the work procedure for obtaining PMAA/Al₂O₃, PMAA/Al₂O₃-APTMS, PMAA/Al₂O₃-DMDCS composite materials / *Reprezentarea schematică a modului de lucru pentru obținerea materialelor compozite* PMAA/Al₂O₃, PMAA/Al₂O₃-APTMS, PMAA/Al₂O₃-DMDCS.

before analysis. XRD analysis is useful to identify crystalline phases and to determine their concentrations.

Scanning Electron Microscopy (SEM) was used to determine the morphology and was also useful to show the compatibility between phases. SEM images were taken with a HITACHI S2600N with an EDAX probe. All samples were covered with a silver layer prior to imaging.

Differential thermal analysis (DTA) coupled with thermogravimetric analysis (TGA) were performed in air atmosphere with a Shimadzu DTG-TA-50H equipment at a heating rate of 10°C. Thermal analysis was used to determine the behavior of the composites and to observe quantitative changes by increasing temperature.

Compressive strength and Young's modulus were determined using an INSTRON 5982 equipmentat a speed of 1mm/min. Compressive mechanical stress and elastic modulus tests were determined on 9 cylindrical specimens, 3 specimens for each composite material according to ISO 604: 2002 "Plastics—Determination of compressive properties" and ASTM C39 "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens".

The porosity and density of the composite materials were determined using Arthur's method. This assumed the initial weighting of the samples in air then samples were placed in a vacuum desiccator for 30 minutes in order to eliminate the air from the pores. After this step, the samples were immersed in xylene for 30 minutes. At the end, the samples were weighted both in air and in solvent [15].

3. Characterization

3.1. Fourier transform infrared spectroscopy

Transmission FT-IR spectra confirmed the success of the silanization of Al_2O_3 following the surface treatment. Figure 3 is representative for this aspect. The frequencies and assignments of each vibrational band are listed in Table 1.

For the unmodified alumina the broad peaks between 4000-3000cm⁻¹can be assigned to the stretching bands of the various types of surface hydroxyl groups (M-OH) of alumina. A broad peak corresponding to -COOH of methacrylic acid is observed in the 3400–3900 cm⁻¹range.

When compared to the spectrum of control Al_2O_3 , the spectra of Al_2O_3 -APTMS and Al_2O_3 -DMDCS present three new distinct peaks at about 2920, 2848 and 1384cm⁻¹ that can be attributed to the stretching vibrations of $-CH_2$ and $-CH_3$ groups.

Because the silanization process took place in a strong hydrophilic environment, the spectra of treated alumina show an enhancement of –OH stretching at about 3454, 3446cm⁻¹ typically assigned to the hydrolysis of alumina [16].

FT-IR spectra of PMAA/Al₂O₃, The PMAA/Al₂O₃-APTMS and PMAA/Al₂O₃-DMDCS composites were recorded in attenuated total reflectance (ATR) mode on the 675-4000cm⁻¹ range (Figure 4). The absence of the peak characteristic to the C=C double bond, at around 1640cm⁻¹ and attributed to the monomer proves the success of the polymerization. On the other hand, all three spectra are characterized by two specific peaks, at about 1695 and 1163cm⁻¹. The first is characteristic to the carbonyl (C=O) vibrational frequency while the second can be attributed to the formation of ether bridges (CH₃-O-CH₃) between polymer and the two silanes.

3.2.X-Ray diffraction

The crystalline phase was emphasized using XRD analysis and diffractograms were useful in order to identify the oxide based on the diffraction peaks (Fig. 5). The presence of alumina in the composite materials is demonstrated according to ASTM sheets [00-083-2080] for all the samples, which correspond to the rhombohedral structure (a = 4.7607 Å and c = 12.995 Å) and the polymer do not negatively influences the intensity of alumina diffraction peaks in all three cases.

The XRD spectrum of Al₂O₃ shows the 20 peaks at 25.49°, 35.09°, 37.71°, 43.29°, 52.50° and 57.56° with orientation along (012), (104), (110), (113), (024) and (116) plane, respectively, confirming the existence of α -Al₂O₃. Fig. 5 shows the characteristic features of PMAA by highlighting a very wide peak at 20=14.54°.

Table 1

FTIR wavenumbers (cm⁻¹) assignments of the main bands for Al₂O₃, Al₂O₃-APTMS, Al₂O₃-DMDCS / Valorile FTIR (cm⁻¹) ale principalelor benzi de absorbție a Al₂O₃, Al₂O₃-APTMS, Al₂O₃-DMDCS

Al ₂ O ₃	Al ₂ O ₃ -APTMS	Al ₂ O ₃ -DMDCS	Assignment	Ref.
-	489	489	Si-O in-plane stretching (υ Si-O-Si)	-
451 – 595 – 648	-	-	Al-O	-
-	727	-	CH ₂ rock-twist (τ CH2)	17
-	1097	-	Si-O in-plane stretching (u Si-O-Si)	18,19
-	1384	1384	CH_3 (ethoxy) symmetric deformation (δ CH_3)	18,19
-	1637	-	Al-OHNH₂ bending (δ NH₂ hydrogen bonded)	20,21
1696	-	-	C=0	-
-	2848	2848	CH_2 symmetric stretching (vs CH_2)	18,19,22
-	2920	2920	CH_2 asymmetric stretching (vas CH_2)	18,19,22
3856 - 3744 - 3615	3454	3446	ОН	23



Fig. 3 - Transmission FT-IR spectra of Al₂O₃, Al₂O₃-APTMS and Al₂O₃-DMDCS / *Spectrele de transmisie FT-IR ale Al₂O₃, Al₂O₃-APTMS <i>şi Al₂O₃-DMDCS*



Wavenumber (cm-1)

Fig. 4 - ATR FT-IR spectra of PMAA/Al₂O₃, PMAA/Al₂O₃-APTMS, PMAA/Al₂O₃-DMDCS composite materials / Spectrele ATR FT-IR ale PMAA/Al₂O₃, PMAA/Al₂O₃-APTMS și PMAA/Al₂O₃-DMDCS



Fig. 5 - XRD spectra of PMAA/Al₂O₃, PMAA/Al₂O₃-APTMS, PMAA/Al₂O₃-DMDCS composite materials / Interferențele de difracție ale PMAA/Al₂O₃, PMAA/Al₂O₃-APTMS și PMAA/Al₂O₃-DMDCS

3.3. Differential Thermal Analysis

DTA-TG analyzes were performed for both PMAA/untreated Al₂O₃ and PMAA/silanized Al₂O₃ composites in order to observe their thermal stability.

As can be noticed from Figure 6, TG analysis indicated a relative similarity regarding the thermal behavior for all three composites with a minor difference in terms of mass loss. There by, the loss in the range of 40–1000°C was 55.815% in

case of PMAA/Al_2O_3 composite, 57.34% for PMAA/Al_2O_3-APTMS and 64.26% for PMAA/Al_2O_3-DMDCS.

The phenomena that occur in the material and are accompanied by a mass loss are centralized in Table 2.

This slightly higher mass loss of the silanized samples can be attributed to the breaking of CH₃-O-CH₃ether bonds established between polymer and silanes.

3.4. Scanning electron microscopy

The microstructural characteristics of the synthesized composites were determined by scanning electron microscopy on surfaces resulted from mechanical testing, so inside the samples. Figure 6 presents the SEM images recorded at different magnifications for all the obtained composites. As can be noticed from Figure 7, in all the analyzed samples, alumina particles with morphology spherical are embedded homogeneously in the organic polymer matrix. For PMAA/ Al₂O₃ composite materials, the particle size ranges from 2.17 to 1.08 µm and for PMAA/ Al₂O₃_APTMS, from 0.72-1.44 µm. However, the composite PMAA/Al₂O₃ DMDCS exhibits the highest degree of homogeneity, indicating a good compatibility between the polymer matrix and the functionalized oxide. As can be seen from the C3 microscopy image, the functionalized aluminum oxide powder is almost entirely embedded in the polymer matrix. The results obtained in this case can be correlated with the ones from the mechanical strengths (see Table 3).

Assignment of fragment loss / Pierderea de masă și efectele înregistrate							
Composite materials	T range [°C]	Mass loss Estim. [%]	Assignment of fragment lost				
PMAA/Al ₂ O ₃ -APTMS	40-152	2.246	Loss of residual water				
	152-303	10.503	Dehydration reaction that forms poly(methacryl acid) anhydride				
	303-428	37.656	Decomposition of poly(methacrylic acid)network				
	428-545	6.232	Loss of the remaining organic moieties				
	545-1000	0.649					
PMAA/AI ₂ O ₃ -DMDCS	40-176	7.243	Loss of residual water				
	176-306	11.526	Dehydration reaction that forms poly(methacr acid) anhydride				
	306-436	38.084	Decomposition of poly(methacrylic acid) netwo				
	436-543	6.476	Loss of the remaining organic moieties				
	543-1000	0.760	-				
PMAA/Al ₂ O ₃	40-165	4.160	Loss of residual water				
	165-303	9.080	Dehydration reaction that forms poly(methacrylicacid) anhydride				
	303-422	36.590	Decomposition of poly(methacrylic acid) netwo				
	422-541	5.558	Loss of the remaining organic moieties				
	541-1000	0.426	-				



A.T. Cucuruz, E. Andronescu, A. Cucuruz, G. Pelin / The effect of silanization on alumina - poly(methacrylic acid) composites with applications as denture base materials



Fig. 6 - TG and DTG curves for: a. PMAA/Al₂O₃-APTMS; b. PMAA/Al₂O₃-DMDCS; c. PMAA/Al₂O₃/ *Curbele TG și DTG pentru:* a. PMAA/Al₂O₃-APTMS; b. PMAA/Al₂O₃-DMDCS; c. PMAA/Al₂O₃.



Fig. 7 - SEM images of PMAA/Al₂O₃, PMAA/Al₂O₃-APTMS and PMAA/Al₂O₃-DMDCS composite materials / *Imaginile SEM ale* PMAA/Al₂O₃, PMAA/Al₂O₃-APTMS și PMAA/Al₂O₃-DMDCS.

Table 3

Composite material	Apparent density (g/cm³)	Open porosity (%)	Absorption (%)	Compressive strength [MPa]	Modulus (Automatic Young's) [MPa]
PMAA/Al ₂ O ₃	1.17	27.79	20.82	8.57	339
PMAA/Al ₂ O ₃ _APTMS	1.21	21.59	15.71	12.29	577
PMAA/AI ₂ O ₃ _DMDCS	1.25	19.83	13.94	12.47	833

Physico-mechanical properties of synthesized composites / Proprietățile fizico-mecanice ale materialelor compozite sintetizate

3.5. Physico-mechanical properties of synthesized composites

In the present study, mechanical strength and compressive elasticity modulus were determined on on 9 cylindrical specimens, 3 specimens for each composite material, cylindrical shape with the height and diameter approximately equal, as well as the apparent density, open porosity and the absorption degree by Arthur's method, as described above.

The oxide silanization leads to a reduction of porosity according to the values presented in Table 3, while improving strength that increases in both cases with about 45%. The values obtained for the compressive strengths of the composite materials with the two silanizing agents recorded close values, with a measurement error of 5%.

Silanization was associated with а modification of the Young's modulus. When compared to the control composite based on unmodified oxide, a sharp increase of the Young's modulus, by 70% in case of silanization with APTMS and 146% for DMDCS was recorded as visible in Figure 8. This suggests that between alumina silanized with DMDCS and PMAA there is a stronger binding than with APTMS and this fact complies with the electronic microscopy images noticing a much better embedding of the Al₂O₃ particles as very compact aggregates in case of PMAA/Al₂O₃-DMDCS composite (by comparison, figures C3 and B3).

4.Conclusions

In this work, composite materials based on poly(methacrylic acid) and alumina were synthesized by free radical polymerization in the presence of oxide particles. Also, aluminium oxide was functionalized with two silane coupling agents whose influence on the physico-mechanical properties of the composites was investigated. Both silanes proved to have a significant effect on the overall performance of composites by establishing bonds with the polymer matrix and the filler.

SEM images showed a uniform distribution of the spherical particles of alumina inside the organic matrix for all three composites. However,





Fig. 1 - Mechanical tests performed on PMAA/Al₂O₃, PMAA/Al₂O₃-APTMS and PMAA/Al₂O₃-DMDCS composite materials/*Testele mecanice înregistrate pe materialele compozite PMAA/Al*₂O₃, *PMAA/Al*₂O₃-*APTMS și PMAA/Al*₂O₃-DMDCS

the silanized oxides proved to lead to a more efficient bonding with the polymer, the best compatibility with PMAA being achieved with DCDMS functionalized Al₂O₃. These data are in good correlation with mechanical properties and porosimetry determinations.

The composite materials synthesized in this study confer the premises for application in dentistry as dental resins or denture base materials, further biological assessments being necessary.

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REFERENCES

- J. G. Leprince, W.M.P., M. A. Hadis, J. Devaux, G. Leloup, Progress in dimethacrylate-based dental composite technology and curing efficiency. Dental Materials Journal, 2013. 29(2), 139-156.
- J.L. Ferracane, Resin composite—State of the art. Dental Materials, 2011. 27, 29-38.
- W. Viratyaporn, R.L.L., Spectroscopic analysis of poly(methyl methacrylate)/alumina polymer nanocomposites prepared by in situ (bulk) polymerization. Journal of Materials Science 2010. 45, 5967-5972.
- Y.M. Kong, C.-J.B., S.H. Lee, H.W. Kim, H.E. Kim, Improvement in biocompatibility of ZrO₂–Al₂O₃ nanocomposite by addition of HA. Biomaterials, 2005. 26, 509-517.
- C. Ghitulică, et al., Alumina porous ceramic materials prepared by slip casting. Silicates Industriels, 2002. 67(3-4), 33-36.
- S. Stoleriu, et al., Influence of Preparation Conditions on Nanometric Characteristics of Zirconia and Alumina Powders. Revista Romana de Materiale-Romanian Journal of Materials, 2011. 41(3), 255-261.
- Y.C. Yang, S.B.J., B.G. Kim, P.R. Yoon, Examination of dispersive properties of alumina treated with silane coupling agents, by using inverse gas chromatography. Powder Technology, 2009. **191**, 117-121.
- V. Szczepanski, S. Smirnov, Stability of silane modifiers on alumina nanoporous membranes. Journal of Membrane Science, 2006. 281: p. 587-591.
- M.M. Karabela, I.D.S., Effect of the structure of silane coupling agent on sorption characteristics of solvents by dental resin-nanocomposites. Dental materials, 2008. 24, 1631-1639.
- C.Y.K. Lung, J.P.M., Aspects of silane coupling agents and surface conditioning in dentistry: An overview. Dental Materials Journal, 2012. 28, 467-477.
- J.L. Hardin, N.A.O., E.D. Steinle, G.A. Meints, Spectroscopic analysis of interactions between alkylated silanes and alumina nanoporous membranes. Journal of Colloid and Interface Science, 2010. 342, 614-619.
- Y.Xie, C.A.S.H., Z. Xiao, H. Militz, C. Mai, Silane coupling agents used for natural fiber/polymer composites: A review. Composites: Part A 2010, 41, 806-819.

- M. Ficai, E.A., A. Ficai, G. Voicu, B.S. Vasile, Poly bis-GMA/HA based hybrid composite materials. UPB Scientific Bulletin Series B, 2011. **73**, 75-84.
- J.M. Antonucci, D.N.Z., K. Tang, S. Lin-Gibson, B.O. Fowler, N.J. Lin, Synthesis and characterization of dimethacrylates containing quaternary ammonium functionalities for dental applications. Dental Materials Journal, 2012, 28, 219-228.
- E. Andronescu, C. Ghiţulică, G. Voicu, S. Stoleriu, Nanopulberi si Materiale ceramice. Obtinere si caracterizare. Politehnica Press, 2008.
- Y.Bao, J.-Z.M., Polymethacrylic acid/Namontmorillonite/SiO2 nanoparticle composites structures and thermal properties. Polymer Bulletin, 2011. 66, 541-549.
- H. Murata, et al., Vibrational-Spectra, Normal Vibrations And Rotational-Isomerism Of Alkylsilanes .1. Propylsilane, Butylsilane And Their Si-Perdeuterium Compounds, Journal of Molecular Structure, 1979. 52(1), 1-11.
- D.G. Kurth, and T. Bein, Thin-Films Of (3-Aminopropyl)Triethoxysilane On Aluminum-Oxide And Gold Substrates, Langmuir, 1995. 11(8), 3061-3067.
- C.H. Chiang, H. Ishida, and J.L. Koenig, The Structure Of Gamma-Aminopropyl triethoxysilane On Glass Surfaces, Journal of Colloid and Interface Science, 1980. 74(2), 396-404.
- S.R. Culler, H. Ishida, and J.L. Koenig, Structure Of Silane Coupling Agents Adsorbed On Silicon Powder, Journal of Colloid and Interface Science, 1985. 106(2), 334-346.
- S.R. Culler, H. Ishida, and J.L. Koenig, Ft-Ir Characterization Of The Reaction At The Silane Matrix Resin Interphase Of Composite-Materials, Journal of Colloid and Interface Science, 1986. **109**(1), 1-10.
- Ek S., E.I. liskola, and L. Niinisto, Gas-phase deposition of aminopropylalkoxysilanes on porous silica, Langmuir, 2003. 19(8), 3461-3471.
- O.B. Belskaya, I.G. Danilova, M.O. Kazakov, R.M. Mironenko, A.V. Lavrenov and V.A. Likholobov, FTIR Spectroscopy of Adsorbed Probe Molecules for Analyzing the Surface Properties of Supported Pt (Pd) Catalysts, Infrared Spectroscopy – Materials Science, Engineering and Technology, InTech, 2012.