




Synthesis of polycalciumphenylsiloxane and composites based on the skeleton of a sea urchin with the resulting polymer

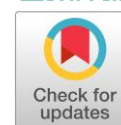
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This paper belongs to the MOSM2021 Special Issue.

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Abstract

In this work, we obtained polycalciumphenylsiloxane (PCPS) by the interaction of calcium bis (acetylacetonate) with polyphenylsiloxane. The first method consisted in boiling the starting reagents in toluene for several hours; the second was as follows: the mixture of the starting reagents was preliminarily treated mechanically in a ball mill, followed by boiling in toluene for several hours. Two fractions, soluble and insoluble, were isolated in both syntheses. They were investigated using IR, NMR spectroscopy, thermogravimetric analysis, and gel permeation chromatography. It was shown that the insoluble fraction is a mixture of calcium acetylacetonate and polyphenylsiloxane with a small calcium ion content. The soluble fraction is polycalciumphenylsiloxane. The yield of the soluble fraction is higher in the second synthesis method. The polymers obtained in the first and second synthesis methods are similar in composition and structure, which was confirmed by physicochemical methods. Next, the skeleton of the sea urchin *Strongylocentrotus intermedius* was treated with a soluble fraction in toluene. In this case, a composite was obtained, which was treated with 2–3% hydrochloric acid and then calcined at a temperature of 600 °C. At each stage, the composition of the composites was investigated using elemental analysis and IR spectroscopy. The morphology was investigated using scanning electron microscopy.

Keywords

polyphenylsiloxane
calcium acetylacetonate
sea urchin skeleton
mechanochemical activation

Received: 18.02.22

Revised: 13.05.22

Accepted: 01.06.22

Available online: 14.06.22

1. Introduction

Biomimetic systems, such as shells of mollusks, sea urchins, and sponges, are potentially attractive as templates containing calcium and magnesium for the production of nanobioceramics [1, 2]. Significant interest has been drawn towards the combination of calcium-containing templates with polyorganosiloxanes based on trifunctional organosilicon fragments with high thermal and hydrolytic stability and a uniformly organized structure [3, 4]. At the same time, as was shown recently, biological objects containing calcium and magnesium are most promising for obtaining bioceramics based on the resulting wollastonite, forsterite [5]. Organosiloxane oligomers upon high-temperature condensation gradually transform into inorganic silicates, retaining the original structure [6].

It is known [7, 8] that natural biominerals are organo-inorganic composites with a well-developed calcium-containing skeleton.

The interpenetrating mineral composites of *Strongylocentrotus intermedius* form the skeleton of structured calcium nanocrystals. Taking into account the possibility of biomimetic application of the sea urchin skeleton for obtaining nanomaterials of a certain structure, the aim of this work was to synthesize polycalciumphenylsiloxane based on calcium acetylacetonate and to obtain composites by the interaction of a soluble polymer with the skeleton of the sea urchin *Strongylocentrotus intermedius*.

2. Experimental

Toluene was distilled before synthesis. Calcium chloride used was of reagent grade. Acetylacetone was distilled in vacuum before synthesis. Calcium bis-acetylacetonate was obtained by the method described elsewhere [9].

2.1. Synthesis of polyphenylsiloxane (PPS)

A solution of 100.75 g (0.5 mol) of phenyltrichlorosilane in 150 ml of sulfuric ether was added dropwise to a mixture of 150 ml of sulfuric ether and 250 ml of distilled water placed in a 1 L flask equipped with a mechanical stirrer and a reflux condenser. The synthesis was carried out with constant cooling of the flask to $-20\text{ }^{\circ}\text{C}$ and vigorous stirring for one hour. The organic ether layer was separated on a separating funnel, washed with distilled water until neutral, and dried over anhydrous sodium sulfate (20 g Na_2SO_4) for a day. Ether was distilled off while heating the mixture in a water bath, and at the final stage, a rotary evaporator was used. The product was dried in a vacuum oven at $80\text{ }^{\circ}\text{C}$. A substance of the composition $[\text{C}_6\text{H}_5\text{SiO}_{1.5}\cdot 0.17\text{H}_2\text{O}]_n$ was obtained with a yield of 93.7%. Found: Si – 21.2%, C – 54.5%.

2.2. Synthesis of polycalciumphenylsiloxane (method 1)

A mixture of 2.58 g (0.1 mol) $(\text{C}_6\text{H}_5\text{SiO}_{1.5})_n$, calcium bisacetylacetonate and 100 ml of toluene was placed in a one-neck flask equipped with a reflux condenser and boiled for 12 h. A soluble fraction was isolated by filtration.

2.3. Synthesis of polycalciumphenylsiloxane (method 2)

The mechanochemical activation of the reagents was carried out in a planetary ball mill "Pulverisette 6" at a frequency of 600 rpm for three minutes. The ratio of the packing weight to the payload weight was 1.8. PPS weighing 2.58 g (0.01 mol) and $(\text{acac})_2\text{Ca}$ with a weight of 1.0 g (0.01 mol) were added to the activator. After mechanochemical activation, the entire reaction mixture was dissolved in dry toluene (100 ml) and boiled for 12 hours. The soluble fraction was precipitated with hexane (100 ml) from a solution in toluene. Received a soluble fraction – $\text{PCa}(\text{acac})\text{PS}$ (relative mass fraction 65.4%). Elemental analysis data are presented in Table 1.

2.4. Synthesis of composites No. 1–3

Composites 1–3 were obtained using the skeleton of the sea urchin *Strongylocentrotus intermedius*. The composite No. 1 was obtained by interaction of the sea urchin skeleton with a soluble fraction of polymer 1.1 (method 1) by boiling for an hour in a toluene solution with the mass of the sea urchin skeleton to the mass of the polymer ratio of 1.0:0.1, followed by distilling off the solvent to 1/5 of the initial volume of the solution. Solution was dried on a rotary evaporator at $80\text{ }^{\circ}\text{C}$ and 100 torr. The solid fraction was filtered off and dried in air. The composite No. 2 was obtained by processing composite No. 1 in 2–3% hydrochloric acid until the emission of

carbon dioxide stopped. The resulting product was washed with distilled water and dried in air to a constant weight. The composite No. 3 was obtained by calcining the composite No. 2 at a temperature of $600\text{ }^{\circ}\text{C}$ for 30 min.

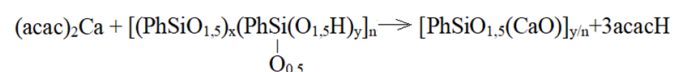
Infrared spectra of polymer samples were recorded on a Spectrum-1000 spectrometer (Perkin Elmer) in KBr tablets. Diffraction patterns were recorded on an Advance-D8 device (Bruker) using $\text{Cu K}\alpha$ radiation in the angle range $20 < 2\theta < 90$ in the point-by-point scanning mode. The maximum deviation of the reflection position, determined according to NIST SRM 1976, is less than 0.0102θ . Gel chromatography was performed on a column with a diameter of $D = 12\text{ mm}$ and a length of $L = 1200\text{ mm}$; gel carrier: cross-linked polystyrene 4% divinylbenzene, grain diameter $0.10\text{--}0.08\text{ nm}$, free volume (V_0) equal to 30 ml, fractions of the toluene solution were taken in 3 ml, determination of the polymer content was carried out by the gravimetric method with an accuracy of 0.1 mg. The column was calibrated using the following organosilicon compounds: octaphenylcyclsilsesquioxane, trimethyltriphenylcyclsiloxane, calcium acetylacetonate.

Nuclear magnetic resonance (NMR) spectra were recorded on an Advance II-400MHz high-resolution spectrometer (Bruker, Germany). Solvents: deuteriochloroform, dimethylsulfoxide. NMR spectra of solid samples were recorded on Advance AV-300 (MAS · NMR) "Bruker" Germany. Scanning electron microscopy was performed using a TM3000 Hitachi electron microscope (Japan). SEM images of the samples were obtained using a S-3400N Hitachi scanning electron microscope (Japan) and a Carl Zeiss Crossbeam 1540xb with an Oxford Instruments X-Max 80 energy dispersive detector (Carl Zeiss, Germany). Thermogravimetric analysis was performed on a DTG-60 H differential thermogravimetric analyzer.

3. Results and discussion

The interaction of calcium bis (acetylacetonate) with polyphenylsiloxane was carried out in two different ways. Method 2 differed from method 1 by the use, in addition to boiling in toluene, of the preliminary mechanochemical treatment [10].

The interaction proceeded according to the equation:



In both syntheses (1 and 2), two fractions were isolated – soluble (1.1 and 2.1) and insoluble (1.2 and 2.2). The elemental analysis of the fractions is shown in Table 1.

Table 1 Elemental analysis of soluble and insoluble fractions of syntheses 1 and 2.

No. fraction	Found, %			Calculated for gross formula, %			
	C	Si	Ca	C	Si	Ca	Gross formula
1.1	36.7	22.8	13.8	34.0	22.6	13.5	$[(\text{PhSiO}_{1.5})_{1.4}(\text{SiO}_2)_{1.0}(\text{CaO})_{1.0}]_n$
1.2	48.0	0.4	19.9	47.0	0.4	19.2	$\{[\text{Ca}(\text{O})_{0.5}(\text{acac})_{1.6}]_{3.3}(\text{PhSiO}_{1.5})\}_n$
2.1	37.5	21.8	16.2	34.2	21.0	15.8	$[(\text{PhSiO}_{1.5})_{1.2}(\text{SiO}_2)_{0.7}(\text{CaO})_{1.0}]_n$
2.2	47.4	1.5	19.1	46.9	1.5	19.1	$\{[\text{Ca}(\text{O})_{0.5}(\text{acac})_{1.5}]_9(\text{PhSiO}_{1.5})\}_n$

Gel chromatography of soluble fractions 1.1 and 2.1 was carried out; the results were identical. It was shown that both fractions are high molecular weight compounds (Figure 1).

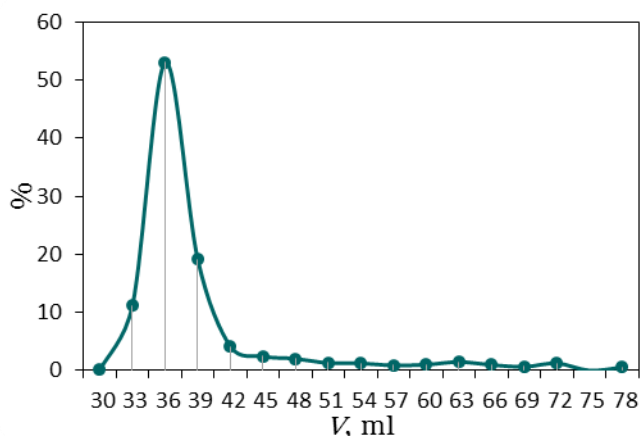


Figure 1 Gel permeation chromatography data for fraction 1.1.

IR spectra were recorded for all fractions (Figure 2).

In the IR spectra of soluble fractions of syntheses 1 and 2, absorption bands of medium intensity are observed at 3627 cm^{-1} , corresponding to stretching vibrations of the O-H bond at the silicon atom; a weak band at 3402 cm^{-1} corresponds to the vibrations of the O-H bond in coordinated molecules water. Several bands at 3095 , 3074 , 3030 , 3016 , and 3006 cm^{-1} correspond to the vibrations of C-H bonds in aromatic radicals as well as the C-H bonds at the γ -carbon of chelate groups. The absorption bands at 1570 and 1631 cm^{-1} correspond to the stretching vibrations

of the C=C and C=O bonds in the acetylacetonate ring; the absorption bands at 1431 and 1384 cm^{-1} correspond to the stretching vibrations of the C-C bond in the aromatic radical and in the chelate ring. Intense bands were also observed at 1134 , 1029 , 999 cm^{-1} , corresponding to stretching vibrations of $\equiv\text{Si-Ph}$, $\equiv\text{Si-O-Si}\equiv$ bonds, respectively; absorption bands at 495 , 455 and 447 cm^{-1} correspond to deformation vibrations of bonds Si-O and Ca-O, respectively. Such a set of absorption bands corresponds to the vibrations of bond groups found in typical polymetalorganylsiloxanes [10].

IR spectra of insoluble fractions of syntheses 1 and 2 are similar and contain the following absorption bands: at 3467 , 3371 , 3230 cm^{-1} – correspond to stretching vibrations of O-H bonds in coordinated water molecules; at 3074 and 2989 , 2920 cm^{-1} – correspond to stretching vibrations of C-H bonds in the phenyl and chelate rings, respectively; at 1637 , 1608 and 1519 cm^{-1} – correspond to stretching vibrations of C=O, C=C bonds in the acetylacetonate ring; at 1460 cm^{-1} and 1398 cm^{-1} – correspond to stretching vibrations of the C-C bond, respectively, in the phenyl and chelate rings; at 1016.918 cm^{-1} – correspond to vibrations of Si-O bonds; at 445 and 424 cm^{-1} – correspond to vibrations of Ca-O bonds in metallsiloxane [5] and in the chelate ring [11]. To establish the main structural fragments constituting the empirical formula of the polymers, ^1H , ^{13}C , ^{29}Si NMR spectra were recorded for all fractions and calcium bis(acetylacetonate) as a control sample.

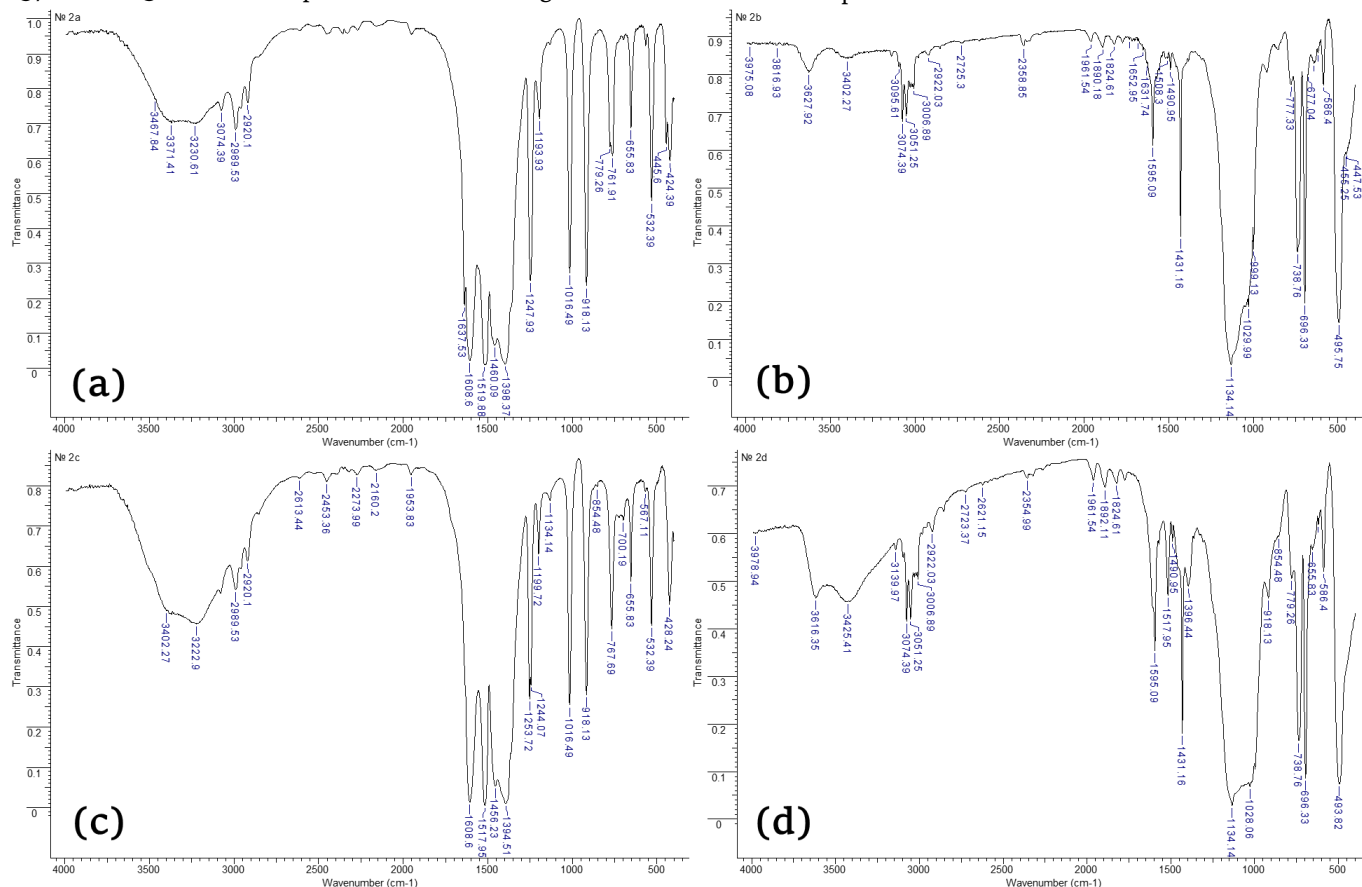


Figure 2 IR spectra of fractions: 1.1(a), 1.2(b), 2.1(c), 2.2(d).

The ^1H NMR spectrum of calcium bis (acetylacetonate) (Figure 3a) contains a signal at 1.66 ppm, which corresponds to the chemical shift of the proton in the CH_3 group, and a signal at 5.05 ppm, which corresponds to the chemical shift of the methine proton. The ^{13}C NMR spectrum (Figure 3b) contains signals at 28.38 ppm, 99.40 ppm, and 188.33 ppm, corresponding to carbon in the CH_3 and $\gamma\text{-CH}$ group, respectively.

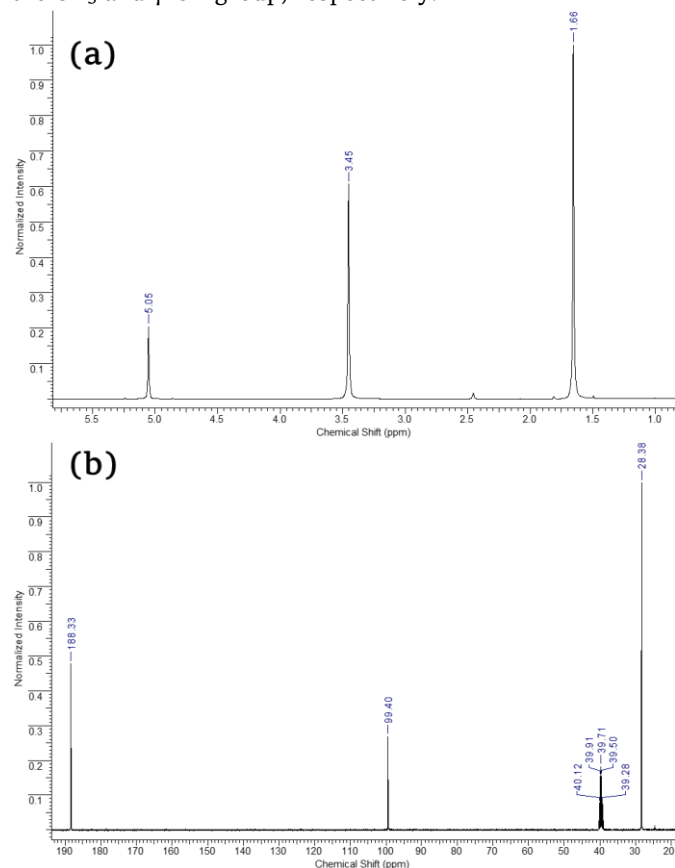


Figure 3 NMR spectra of ^1H (a), ^{13}C (b) calcium bis-(acetylacetonate), solvent – dimethylsulfoxide.

In the ^1H NMR spectra of soluble fractions of syntheses 1 and 2 (Figures 4a, 5a), there are signals in the region from 6 to 8 ppm, corresponding to the proton shift of the phenyl group located at the silicon atom, and signals of low intensity at 1.79 ppm and 5.1 ppm, corresponding to the protons of CH_3 and CH groups. The region 2.29–2.5 ppm corresponds to protons of associated water and DMSO.

The ^{13}C NMR spectrum of soluble fractions (Figures 3b, 4b) of syntheses 1 and 2 contains signals in the range of 125.6–134 ppm, corresponding to the resonance of the carbon atoms of the phenyl group. The difference in the ^{13}C spectra is observed for the soluble fraction of synthesis 2, where there are low-intensity signals of the carbon atoms of the acetylacetonate groups, which is associated with the high calcium content in this fraction (Table 1), and, accordingly, a small part of the calcium atoms has chelating groups. To confirm the composition and structure of the soluble and insoluble fractions of the first synthesis, thermal destruction was investigated. The nature of the thermal destruction of ladder polyorga-

nosiloxanes [2, 3] can determine the yield and composition of the products of the interaction of siloxanes with metal complexes.

Earlier in [12] it was shown that heating the products of the interaction of vanadium bis (acetylacetonate) with polyphenylsiloxane to 300 °C sharply increased the yield of the target product due to the removal of acetylacetonate groups and the formation of the $\text{-M-O-Si}\equiv$ bond. The TG-DTA curve of insoluble fraction 1.2 (Figure 6) shows three exothermic effects at 290, 380, and 460 °C, the weight loss at which is 43%, while the mass of acetylacetonate groups in the gross formula (Table 1) corresponds to 40%. The exo effect and loss of mass of the sample at a temperature of ~ 600 °C corresponds to the oxidation of phenyl groups. In this case, the sum of oxides by TGA is 28%, which is close to the calculated sum of oxides according to the gross formula, 27.6%.

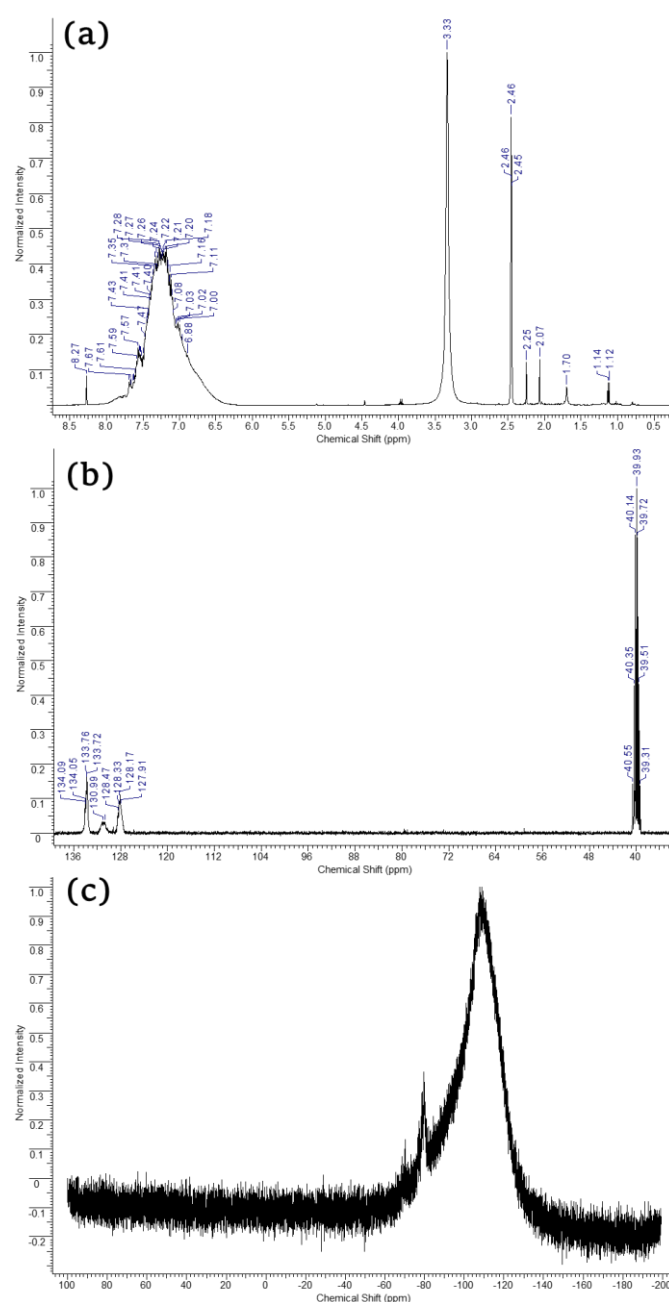


Figure 4 NMR spectra of ^1H (a), ^{13}C (b), ^{29}Si (c) fractions 1.1.

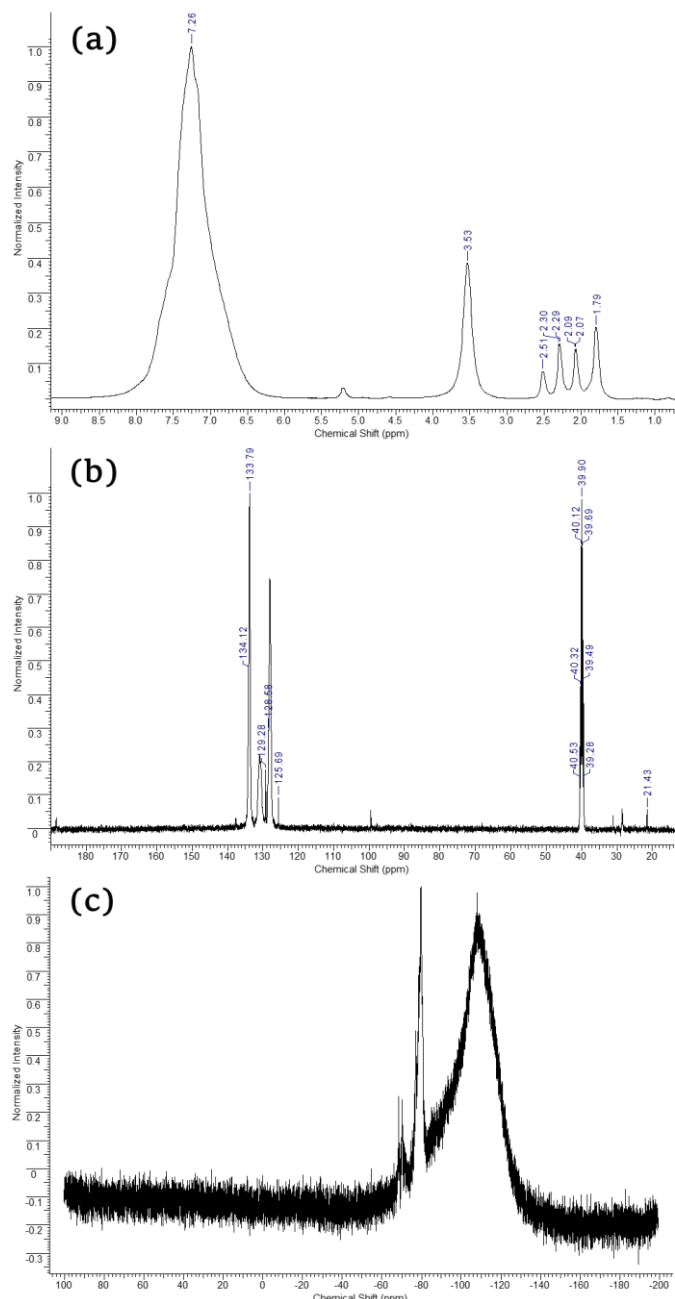


Figure 5 NMR spectra of ¹H (a), ¹³C (b), ²⁹Si (c) fractions 2.1.

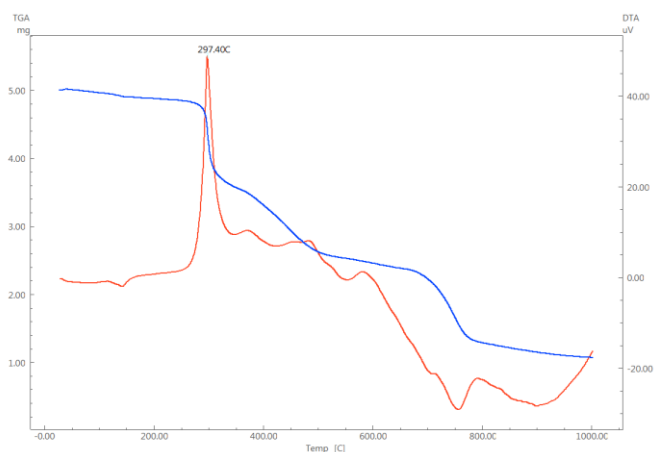


Figure 6 TG and DTA curves for the fraction 1.2.

The DTA plot of the soluble fraction (1.1) (Figure 7) shows an exothermic effect at 625 °C, which corresponds

to the abstraction and oxidation of phenyl groups in polycalcium-phenylsiloxane. It is known [13] that the silicon-phenyl bond is destroyed at a temperature of 550–600 °C. The sum of oxides after 800 ° according to TGA data for the soluble fraction 1.1 is 66.9%. According to the proposed empirical formula (Table 1) the amount of oxides is 68.2%.

The soluble fractions of both syntheses have an amorphous structure (Figure 8a, b). The difference lies in the presence of an admixture of calcium acetylacetonate in the soluble fraction 1.1 of the first synthesis (Figure 8a).

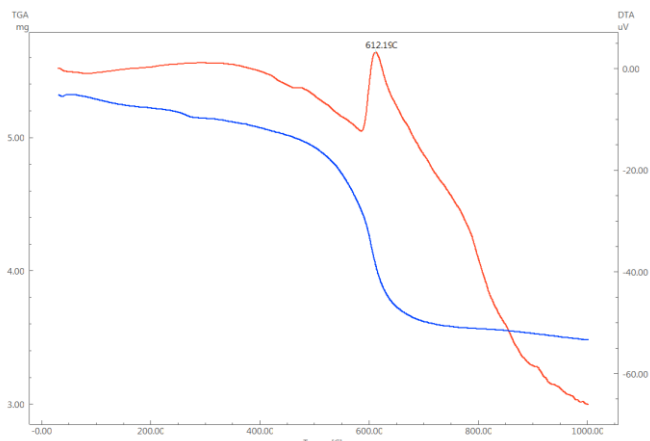


Figure 7 TG and DTA curves for the fraction 1.1.

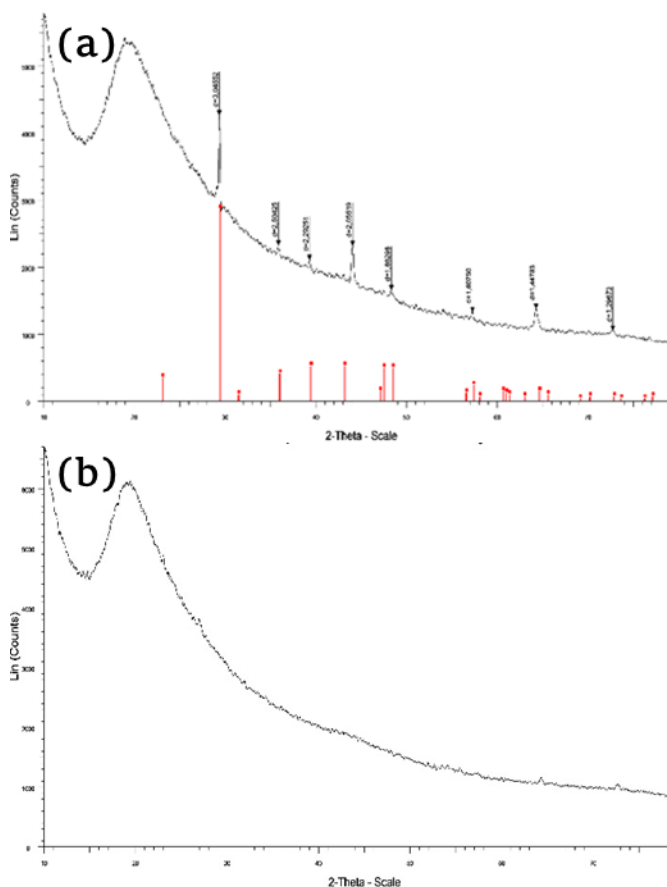


Figure 8 Diffraction patterns of soluble fractions: 1.1 (a), 2.1 (b).

The composites 1–3 were obtained using the skeleton of the sea gray urchin *Strongylocentrotus intermedius* and the soluble fractions 1.1 and 2.1. The IR spectrum of the composite No. 1 (Figure 9a) shows absorption bands at 1410–1460 cm^{-1} , which belong to the vibrations of the C=O bond in carbonate. These bands are absent in the starting polymer. The rest of the absorption bands are similar to the bands in the IR spectrum of the soluble fraction 2.1 (Figure 2c).

The composite No. 2 was obtained by treating composite No. 1 with 2–3% hydrochloric acid until the emission of carbon dioxide ceased. The IR spectrum of the composite No. 2 is similar to the IR spectrum of the soluble fraction 2.1 (Figure 2c).

The composite No. 3 was obtained by calcining the composite No. 2 at a temperature of 600 °C for 30 min. In the IR spectrum of the composite No. 3, absorption bands corresponding to the vibrations of C–H, C–C, C=O bonds disappear, and absorption bands remain at 1100–900 cm^{-1} , 590 cm^{-1} , 495 cm^{-1} (Figure 9c).

Using scanning electron microscopy, the surface of the composites No. 1–3 was examined (Figure 10).

For the composite No. 1, a continuous polymer-coated surface is observed (Figure 10a). After treatment with hydrochloric acid (Figure 10b), the manifestation of an inverted structure is observed, which completely repeats the internal structure of the gray hedgehog [15].

After heating the composite No. 2 at 500–600 °C, the morphology changed dramatically and the structure of the skeleton, which was not completely dissolved by acid, appeared (Figure 10c).

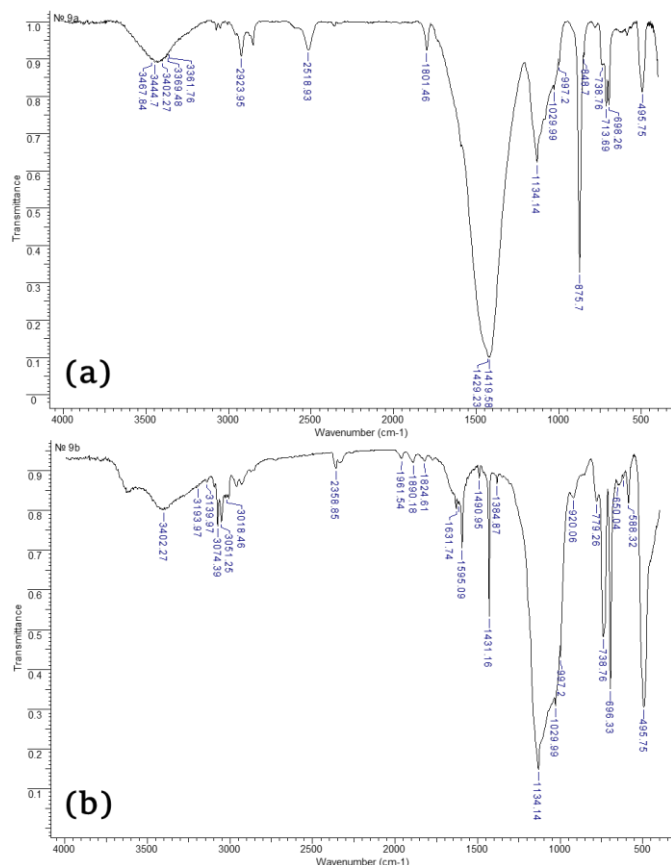


Figure 9 IR spectra of composites: No. 1 (a); No. 3 (b).

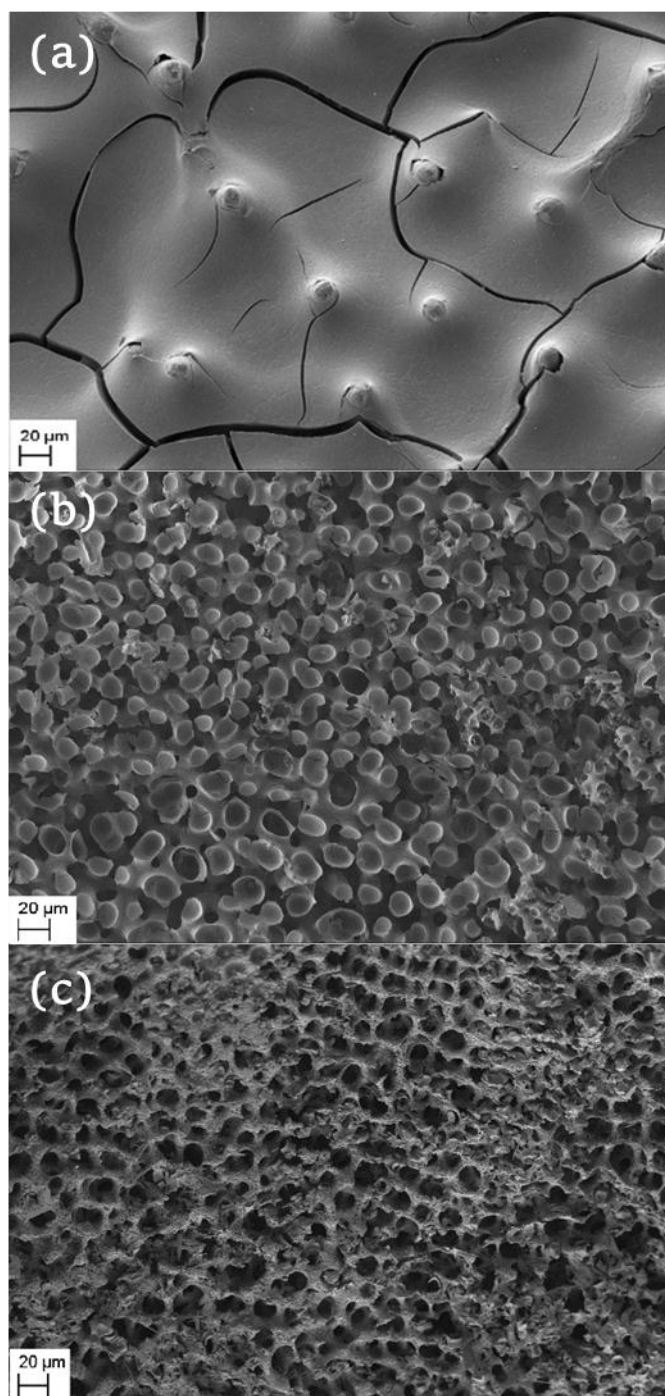


Figure 10 Surface morphology of composites: No. 1 (a), No. 2 (b), No. 3 (c).

The chemical composition of the surface film of the composites No. 1–3 was investigated using EDX spectroscopy (Table 2).

In the composite No. 1, polycalciumphenylsiloxane formed a film on the surface of the hedgehog's skeleton, as evidenced by the disturbed ratio of silicon to calcium. Thus, the skeleton “shines” through the film on the surface. After treatment with acid, an internal structure formed by polycalciumphenylsiloxane was opened (Figure 10b), while calcium was also extracted from polycalciumphenylsiloxane; that is, this structure consists mainly of polyphenylsiloxane with a small calcium content. After heating, the degradation of the organosilicon component

on the surface took place, and the remaining calcite skeleton of the hedgehog appeared, since the calcium content on the surface increased sharply. In this case, a calcium silicate film was formed.

Table 2 The chemical composition of the surface film of composites No. 1–3.

No. composite	The chemical composition of the surface film, %			
	C	Si	Ca	Si/Ca
1	55.20	5.68	6.12	1.33
2	59.10	14.10	0.65	31.0
3	14.96	4.01	22.98	0.25

4. Conclusion

The reaction of calcium bis (acetylacetonate) with polyphenylsiloxane yielded soluble polycalciumphenylsiloxane, the composition and structure of which was confirmed by IR, NMR, GPC data, which does not differ from those for the known metallocsiloxanes obtained under similar conditions. The skeleton of the sea urchin was treated with a soluble fraction of polycalciumphenylsiloxane and the composite No. 1 was obtained, which had a filled skeleton space on the surface and inside. After the treatment with hydrochloric acid of the composite No. 1, a three-dimensional polymer structure was obtained, which is an inverted internal structure of a hedgehog stereome. After calcination, the three-dimensional polymer structure is destroyed, forming calcium silicate on the surface.

Supplementary materials

No supplementary materials are available.

Funding

This research had no external funding.

Acknowledgments

None.

Author contributions

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Conflict of interest

The authors declare no conflict of interest.

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References

- Coradin T, Lopes PJ. Biogenic Silica Patterning: Simple Chemistry or Subtle Biology? *ChemBioChem*. 2003;3:1–9. doi:[10.1002/cbic.200390044](#)
- Sanchez C, Arribart H, Madeleine GG. Biomimetic and bioinspiration as tools for the design of innovative materials and systems. *Nature Mater*. 2005;4:277–288. doi:[10.1038/nmat1339](#)
- Michalczyk MJ, Farneth WE, Vega AJ. High temperature stabilization of crosslinked siloxanes glasses. *Chem Mater*. 1993;5(12):1687–1689. doi:[10.1021/cm00036a001](#)
- Eguchi K, Zank GA. Silicon Oxycarbide Glasses Derived from Polymer Precursors. *J Sol-Gel Sci Technol*. 1998;13:945–949. doi:[10.1023/A:1008639727164](#)
- Choudhary R, Kumar Venkatraman S, Bulygina I, Senatov F, Kaloshkin S, Anisimova N, Kisilevskiy M, Knyazeva M, Kukui D, Walther F, Swamiappan S. Biomineralization, dissolution and cellular studies of silicate bioceramics prepared from egg-shell and rice husk. *Mater Sci Eng C*. 2021;118:111456. doi:[10.1016/j.msec.2020.111456](#)
- Levitsky MM, Zavin BG, Bilyachenko AN. Chemistry of metallocsiloxanes. Current trends and new concepts. *Russ Chem Rev*. 2007;76(9):907–926. doi:[10.1070/RC2007v07n09ABEH003691](#)
- Prockop DJ, Fertala A. The collagen fibril: the almost crystalline structure. *J Struct Biol*. 1998;122:111–118. doi:[10.1006/jsbi.1998.3976](#)
- Erlich H, Brunner E, Simon P et al. Calcite reinforced silica-silica joints in the biocomposite skeleton of deep-sea glass sponges. *Adv Funct Mater*. 2011;21:3473–3481. doi:[10.1002/adfm.201100749](#)
- Kuzmina NP, Chechernikova MV, Martynenko LI. Calcium acetylacetonates. *J Inorg Chem*. 1990;35(11):2776–2780.
- Shapkin NP, Kapustina AA, Dombai NV, Libanov VV, Khalchenko IG, Gardionov SV, Gribova VV. Synthesis and physico-chemical characteristics of polymolybdenum(VI) phenylsiloxanes by means of different methods. *Polym Bull*. 2020;77(3):1177–1190. doi:[10.1007/s00289-019-02790-3](#)
- Morozova NB, Zharkova GI et al. Synthesis and physico-chemical study of β -diketonates of alkaline earth metals. *Novosibirsk*; 1989. 28 p.
- Shapkin NP, Kapustina AA, Gardionov SV, Khalchenko IG, Libanov VV, Tokar EA. Studies of Interaction of Polyphenylsiloxane with Vanadyl Bis-Acetylacetonate. *Silicon*. 2019;11(5):2261–2266. doi:[10.1007/s12633-017-9551-z](#)
- Berman A, Addadi L, Kvick Å, Leiserowitz L, Nelson M, Weiner S. Intercalation of sea urchin proteins in calcite: study of a crystalline composite material. *Sci*. 1990;250:664–667. doi:[10.1126/science.250.4981.664](#)
- Seto J, Ma Y, Davis S et al. Structure-property relationships of a biological mesocrystal in the adult sea urchin spine. *Proc Nat Acad Sci*. 2012;109:3699–3704. doi:[10.1073/pnas.1109243109](#)
- Shapkin NP, Papynov EK, Panasenko AE, Khalchenko IG, Mayorov VYu, Drozdov AL, Maslova NV, Buravlev IYu. Synthesis of porous biomimetic composites: A sea urchin skeleton used as a template. *Appl Sci*. 2021;11;19:8897. doi:[10.3390/app11198897](#)