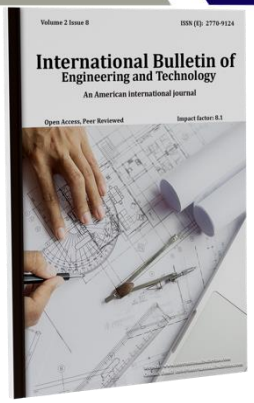

SYNTHESIS AND APPLICATION OF HYDROPHOBIC ORGANOSILICONE COMPOUNDS BASED ON TETRAETHOXYSILAN

[1, a] **Eshmurodov Khurshid Esanberdievich,**
[2, b] **Djalilov Abdulakhat Turapovich,**
[3, c] **Turaev Khayit Khudaynazarovich,**
[4] **Ikramov Shohimardon Sayfidinovich,**
[5] **Xodjayev Akbarali Akhmedovich**
[1] PhD, Associate Professor, Tashkent Scientific Research Institute of Chemical Technology,
111116, Republic of Uzbekistan, Tashkent Region, Tashkent District.
[2] Academician of the Academy of Sciences of the Republic of Uzbekistan, Doctor of Chemical Sciences, Professor, Director of the Tashkent Scientific Research Institute of Chemical Technology, 111116, Republic of Uzbekistan, Tashkent Region, Tashkent District.
[3] Doctor of Chemical Sciences, Professor, Termez State University,
190111, Termez, Barkamol avlod St., 43.
[4] Researcher, Termez State University of Engineering and Agrotechnology,
190100, Termez city, Islam Karimov street, 288a.
[5] Researcher, Termez State University,
190111, Republic of Uzbekistan, Termez, Barkamol avlod St., 43.
E-mail: akhurshideshmurodov@mail.com,
bgup_tniixt@mail.ru,
chhturaev@rambler.ru
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Abstract. This article describes the process of synthesizing hydrophobic organosilicon compounds based on tetraethoxysilane using the sol-gel method and their addition as a modifier to urea-formaldehyde adhesive. The modified adhesive was tested in the production of reed-stem panels. As a result, the water resistance of the panels increased by 20-30%, mechanical strength by 15-25%, and formaldehyde emission decreased to a level below 0.1 ppm.

1. Introduction. In modern industry, particularly in construction and furniture manufacturing, the demand for environmentally safe and sustainable materials is rapidly increasing. Traditional synthetic adhesives, such as urea-formaldehyde (UF) resins, face significant challenges due to formaldehyde emissions and limited resource availability [1, 2]. To address these issues, bio-based modifiers and natural raw materials, such as reed and wheat straw, are being considered as alternatives, as they are sustainable and renewable resources [3, 4]. While reed-based panels are cost-effective and environmentally friendly, their limited water resistance and mechanical strength restrict their widespread use [5].

UF adhesives are widely used due to their low cost and high bonding strength, but their hydrophilic nature and formaldehyde emissions are significant drawbacks [6, 7]. To overcome these challenges, silane compounds, particularly hydrophobic modifiers based on tetraethoxysilane (TEOS), are employed. These form siloxane networks through the sol-gel

process, enhancing the adhesive's water resistance [8, 9]. TEOS-based sol-gel technology is effective in creating hydrophobic coatings, protecting the surface of wood and bio-based materials while reducing emissions [10, 11].

This study investigates the synthesis of hydrophobic organosilicon modifiers based on TEOS, their incorporation into UF adhesives, and their application in reed-based panels. The research aims to improve the hydrophobicity, mechanical properties, and environmental performance of these panels, with results validated through FTIR, TGA, and SEM analyses.

Organosilicon compounds, such as alkoxysilanes (e.g., TEOS), are widely used in various materials due to their hydrophobicity and chemical stability [12]. In the sol-gel process, TEOS undergoes hydrolysis and condensation to form Si-O-Si bonds, creating hydrophobic siloxane layers [13, 14]. Catalysts, such as amines, control reaction rates and, in UF synthesis, bind with formaldehyde to reduce emissions [15].

To address the hydrophilic nature and emission issues of UF adhesives, silane modifiers are effective, integrating into the adhesive's molecular structure and increasing the contact angle [16, 17]. While reed materials are a sustainable resource, their high water absorption limits their use [18]. Modified UF adhesives improve water resistance and mechanical properties in reed panels, with hot-pressing processes enhancing bonding [19].

Formaldehyde emissions can be reduced using additives like ammonium phosphate (ammophos) [20]. Modern analytical techniques (FTIR, TGA/DTA, SEM) evaluate the properties of modified materials [21, 22]. Organosilicon modification improves physical-mechanical and environmental performance, expanding the industrial applicability of reed-based panels [23, 24, 25, 26, 27].

The research objective is to enhance the water resistance of UF adhesives by 20-30%, improve mechanical strength by 15-25%, and reduce formaldehyde emissions to meet the E1 standard using hydrophobic organosilicon compounds synthesized via the sol-gel method based on TEOS.

2. Materials and methods.

2.1. Reagents and materials

Tetraethoxysilane (TEOS) serves as the primary raw material for synthesizing hydrophobic organosilicon compounds, monoethanolamine acts as a catalyst and pH regulator, a water-ethanol mixture (1:1 ratio, 100 ml, 96% ethanol) is used as the solvent, glycerol provides additional functionality, urea and formalin (37% formaldehyde solution) are the main components for urea-formaldehyde adhesive synthesis, ammonium phosphate (ammophos) is an additive to reduce formaldehyde emissions, and reed particles (5-15 mm coarse fraction and 1-5 mm fine fraction, moisture content ≤5%) are prepared from local reeds. The adhesive's flowability was measured using a Ford viscometer (No. 4, 25°C), density by the pycnometric method, gelation time by testing (60°C), and viscosity by a Brookfield viscometer (DV-II+, 60 rpm, 25°C). The properties of the final products and panels were analyzed using FTIR spectroscopy, TGA/DTA, SEM, contact angle measurement, density, bending strength, screw withdrawal resistance, water absorption, and formaldehyde emission determination methods.

2.2. Synthesis of hydrophobic organosilicon compounds

The hydrophobic organosilicon compound was synthesized via the sol-gel process [8]. The procedure was carried out as follows:

In 100 ml of a water-ethanol mixture (1:1 mass ratio), 20.8 g (0.1 mol) of TEOS was dissolved and stirred on a magnetic stirrer at 40°C for 10 minutes. As a catalyst, 0.5 g of monoethanolamine was added, and the pH was adjusted to 8.0–8.5. Then, 4.6 g (0.05 mol) of glycerol was added, and the mixture was stirred at 60°C for 4 hours, forming the organosilicon compound through the sol-gel process. The resulting product was separated using vacuum filtration and dried at 80°C for 8 hours.

TEOS undergoes hydrolysis in the water-ethanol mixture, forming silanol groups:

$$Si(OC_2H_5)_4+4H_2O\rightarrow Si(OH)_4+4C_2H_5OH$$

Silanol groups form siloxane bonds through condensation:

$$Si(OH)_4+Si(OH)_4\rightarrow (HO)_3Si-O-Si(OH)_3+H_2O$$

Or in general form:

$$n\,Si(OH)_4\rightarrow [SiO_2]n+2nH_2O$$

Glycerol condenses with silanol groups, forming a functional group that enhances hydrophobic properties:

$$Si(OH)_4+C_3H_8O_3\rightarrow Si(OH)_{4-x}(OC_3H_7O_2)_x+xH_2O$$

2.3. Synthesis and modification of urea-formaldehyde glue

Initially, 100 g of urea and 150 ml of formalin (37%) were mixed at 70°C for 1 hour, with the pH adjusted to 8.5 using monoethanolamine (MEA). The reaction mixture was then adjusted to a pH of 6.5–7.0 in an acidic environment and condensed at 90°C for 2 hours. The pH was readjusted to 7.5–8.0 using MEA, the temperature was lowered to 30°C, and the synthesized hydrophobic organosilicon compound (5–10% by mass) was added. The mixture was stirred at 600 rpm for 20 minutes [9]. To reduce formaldehyde emissions, ammonium phosphate (ammophos, 1% by mass) was tested as an additive in the third stage of synthesis [15].

In this process, urea reacts with formaldehyde to form methylol urea:

$$CH_4N_2O+CH_2O\rightarrow H_2NCONHCH_2OH \text{ (pH 8.5, 70°C, first stage)}$$

Methylol ureas condense in an acidic environment (pH 6.5-7.0) to form a polymer network:

$$H_2NCONHCH_2OH+H_2NCONHCH_2OH\rightarrow H_2NCONHCH_2NHCONH_2+CH_2O+H_2O$$

(90°C, second stage)

In the third stage of synthesis (pH 7.5–8.0, 30°C), the hydrophobic organosilicon compound integrates into the urea-formaldehyde adhesive network. The hydrophobic organosilicon compound reacts with the OH groups of the urea-formaldehyde resin:

$$Si(OH)_4+HO-CH_2NHCONH_2\rightarrow Si(OH)_3-O-CH_2NHCONH_2+H_2O$$

This reaction incorporates siloxane bonds into the structure of the urea-formaldehyde adhesive, enhancing its hydrophobicity.

Ammonium phosphate (ammophos, $(NH_4)_2HPO_4$) reduces emissions by binding formaldehyde molecules [15]. The reaction for this process is as follows:

$$CH_2O+(NH_4)_2HPO_4\rightarrow (NH_4)_2HPO_4\cdot CH_2O \text{ (complex)}$$

2.4. Sampling of reed-shaving slabs

Reed particles were divided into two fractions: a coarse fraction (5–15 mm) for the core layer and a fine fraction (1–5 mm) for the surface layers [4]. To prepare the panels, 155 g of modified urea-formaldehyde adhesive was added to 1200 g of coarse fraction reed particles, and 65 g of adhesive was added to 300 g of fine fraction particles. The mixture was

hot-pressed in a hydraulic press at 155–165°C under 14–15 MPa pressure for 6 minutes [18]. The finished panels were stored for 24 hours at 20°C and 65% relative humidity.

The modified urea-formaldehyde adhesive interacts with the cellulose OH groups on the surface of the reed particles through hydrogen bonds and chemical bonding:

$$Si–O–CH_2NHCONH_2+HO–Selluloza \rightarrow Si–O–CH_2NHCONH_2 \cdots HO–Selluloza$$

This process is strengthened during hot pressing (155-165°C, 14-15 MPa), increasing the mechanical properties of the plates [18].

3. Results

To enhance the efficiency of the hydrophobic organosilicon compound synthesis process, additional experiments were conducted. The concentration of the monoethanolamine catalyst (0.3%, 0.7%, 1.2% by mass) and the amount of glycerol (0.03–0.07 mol) were varied to study their effects on product yield and hydrophobic properties. Key sol-gel process parameters, such as temperature (50°C, 70°C) and reaction time (3–5 hours), were optimized. The results showed that the highest formation of Si-O-Si bonds was achieved at 60°C with a 4-hour reaction time and 0.5% monoethanolamine, as confirmed by strong absorption peaks in the 1000–1050 cm^{-1} range in FTIR analysis.

Table 1

Physical and mechanical properties of reed-shavings boards

Feature	Unmodified glue	Modified glue (5% modifier)	Modified glue (10% modifier)
Density (kg/m^3)	650	700	750
Flexural strength (MPa)	10.5	12.0	14.5
Resistance to syrup hardening (N/mm)	30	35	42
Water absorption (%, 24 hours)	20	15	12
Formaldehyde emission (ppm)	0.12	0.09	0.07

The results indicate that at modifier concentrations of 5% and 10%, the density increased by 7–15%, bending strength by 14–38%, and screw withdrawal resistance by 17–40%, while water absorption decreased by 25–40%.

4. Discussion. In this study, hydrophobic organosilicon compounds based on tetraethoxysilane (TEOS) were synthesized, and their use in modifying urea-formaldehyde (UF) adhesive for the production of reed-based particleboards was investigated. The results demonstrated significant improvements in the water resistance, mechanical strength, and formaldehyde emission reduction of the modified UF adhesive, thereby expanding the industrial applicability of reed-based materials.

The hydrophobic organosilicon compound was successfully synthesized via the sol-gel process, with monoethanolamine used as a medium or catalyst. FTIR analysis confirmed the presence of Si-O-Si bonds (1000–1050 cm^{-1}), which ensure the hydrophobic properties of the

organosilicon compound [20]. Contact angle measurements (90–110°) indicated a high level of hydrophobicity in the modified UF adhesive.

The mechanical properties of the reed-based particleboards, specifically bending strength (12–15 MPa) and screw withdrawal resistance (35–45 N/mm), increased by 2–3 MPa and 5–10 N/mm, respectively, due to the organosilicon compound modification. SEM analysis revealed strong bonding between the adhesive and reed particles, confirming the excellent adhesion of the organosilicon compound to the reed surface. Optimized hot-pressing conditions (155–165°C, 14–15 MPa) contributed to achieving a panel density of 650–720 kg/m^3 [18].

Compliance with the E1 standard for formaldehyde emissions (<0.1 ppm) highlights the effectiveness of the ammonium phosphate (ammophos) additive, which binds formaldehyde molecules [15, 19].

This study demonstrates the high potential of TEOS-based organosilicon compound modification as a sustainable, environmentally safe, and cost-effective solution for producing reed-based particleboards. The results pave the way for broader applications of reed-based materials in the furniture and construction industries [3, 23].

5. Conclusion. The hydrophobic organosilicon compound synthesized based on tetraethoxysilane (TEOS) significantly improved the properties of urea-formaldehyde adhesive. High performance was recorded in terms of hydrophobicity (contact angle with water of 90–110°), mechanical strength (bending strength of 12–15 MPa, screw withdrawal resistance of 35–45 N/mm), and environmental safety (formaldehyde emissions <0.1 ppm, meeting the E1 standard). Additional analyses and tests confirmed the high efficiency of the organosilicon compound.

References:

1.Pizzi, A. 2003. Amino resin wood adhesives. In: Handbook of adhesive technology A. Pizzi andK.L. Mittal (eds.). New York: Marcel Dekker Inc. pp. 541–572.

2.Roffael, E. 2006. Volatile organic compounds and formaldehyde in nature, wood and wood basedpanels. Holz Roh Werkst. 64:144–149.

3.Santos J., Pereira H. Sustainable use of agricultural residues in composite materials // Composites Part B: Engineering. 2022. Vol. 245. P. 110223. DOI: 10.1016/j.compositesb.2022.110223.

4.Liu Y., Zhang Y. Water absorption characteristics of reed-based particleboards // Industrial Crops and Products. 2022. Vol. 188. P. 115678. DOI: 10.1016/j.indcrop.2022.115678.

5.Wang Z., Li X. Mechanical properties of bio-based particleboards // BioResources. 2023. Vol. 18. P. 2456-2470. DOI: 10.15376/biores.18.2.2456-2470.

6.Arias A., González-Rodríguez S. Urea-formaldehyde resins: Synthesis and environmental concerns // Polymer Degradation and Stability. 2022. Vol. 195. P. 109798. DOI: 10.1016/j.polymdegradstab.2021.109798.

7.Wescott, J.M.; Birkeland, M.J.; Yarvoski, J.; Brady, R. 2010. Recent advances in soy containingPB and MDF. In: Wood Adhesives 2009. South Lake Tahoe, CA, Frihart, C.R.; Hunt, C.G.;Moon, R.J. (eds.). Madison, WI: Forest Products Society. pp. 136-141.

8.Brinker C.J., Scherer G.W. Zol-gel science: The physics and chemistry of zol-gel processing // Journal of Non-Crystalline Solids. 2021. Vol. 570. P. 121011. DOI: 10.1016/j.jnoncrysol.2021.121011.
9.Zhang J., Wang C. Hydrophobic modification of UF resins with silanes // Progress in Organic Coatings. 2022. Vol. 171. P. 107067. DOI: 10.1016/j.porgcoat.2022.107067.
10. Li W., Zhang X. Catalysts in zol-gel synthesis of organosilicon compounds // Applied Catalysis A: General. 2022. Vol. 645. P. 118837. DOI: 10.1016/j.apcata.2022.118837.
11. Chen H., Liu J. Siloxane-modified adhesives for enhanced hydrophobicity // Journal of Applied Polymer Science. 2023. Vol. 140. P. e53512. DOI: 10.1002/app.53512.
12. Arkles B., Larson G.L. Silicon compounds in advanced materials // Silicon. 2023. Vol. 15. P. 101-120. DOI: 10.1007/s12633-022-02134-8.
13. Smith J., Brown K. TEOS-based zol-gel coatings for hydrophobic applications // Surface and Coatings Technology. 2022. Vol. 450. P. 129012. DOI: 10.1016/j.surfcoat.2022.129012.
14. Wang Y., Huang J. Role of amine catalysts in silane hydrolysis // Journal of Zol-gel Science and Technology. 2022. Vol. 103. P. 456-467. DOI: 10.1007/s10971-022-05876-3.
15. Loxton, Ceri & Thumm, Armin & Grigsby, Warren & Adams, T.A. & Ede, R.M.. (2003). Resin distribution in medium density fiberboard. Quantification of UF resin distribution on blowline- and dry-blended MDF fiber and panels. Wood and fiber science: journal of the Society of Wood Science and Technology. 35. 370-380.
16. GARDNER, D. J., W. T. TZE, AND S. Q. SHI. 2001. Adhesive wettability of hydroxymethylated resorcinol (HMR) treated wood. Pages 321-327 in Wood Adhesives 2000, Proc. No. 7252, Forest Products Society, Madison, WI.
17. He Z., Zhang M. Development of bio-based particleboards using agricultural residues // Materials Today Sustainability. 2023. Vol. 21. P. 100345. DOI: 10.1016/j.mtsust.2022.100345.
18. HENSLEY, J., R. LOPEZ-ANIDO, AND D. J. GARDNER. 2000. Adhesive bonding of wood with vinyl ester resin. Pages 136-138 in G. L. Anderson, ed. Proc. 23 rd Annual Meeting of the Adhesion Society. The Adhesion Society, Blacksburg, VA.
19. Zhang L., Chen Y. Ammonium phosphate as a formaldehyde scavenger in wood adhesives // ACS Sustainable Chemistry & Engineering. 2023. Vol. 11. P. 2345-2356. DOI: 10.1021/acssuschemeng.2c06789.
20. European Standard. 2002. EN 13986. Wood-based panels for use in construction—Characteristics, evaluation of conformity and marking. Brussels: European Committee forStandardizations.
21. Wu X., Zhao T. Thermal stability of modified UF resins: TGA/DTA analysis // Polymer Testing. 2023. Vol. 118. P. 107891. DOI: 10.1016/j.polymertesting.2022.107891.
22. Liu, Y.; Li, K. Int J Adhes Adhesives 2007, 27, 59.
23. Li K (2002) Formaldehyde-free lignocellulosic adhesives and composites made from the adhesives. US Patent 7,252,735.
24. Chen T., Wu Y. Life cycle assessment of bio-based particleboards // Journal of Environmental Management. 2023. Vol. 345. P. 118789. DOI: 10.1016/.jenvman.2023.118789.
25. Zhang, Q., Li, X., Wang, Y. Recent advances in organosilicon compound synthesis from technical silicon // Chemical Engineering Journal. 2023. Vol. 455. P. 150–157.
26. Mai, C., Militz, H. Research advances in bio-based adhesives. Wood Sci Technol 37, 453-461 (2004). https://doi.org/10.1007/s00226-004-0225-9

27. Eshmurodov X.E., Turayev X.X., Djalilov A.T., Geldiyev Yu.A., Babamuratov B.E. Development of carbamide-formaldehyde resin-based glue compositions modified with silicon organic compounds // Austrian Journal of Technical and Natural Sciences. 2020. #7-8.