

FRIEDEL-CRAFTS REACTION OF VINYLTRIMETHOXYSILANE  
WITH STYRENE AND COMPOSITE MATERIALS ON THEIR BASEOmar Mukbaniani<sup>1,2</sup>, Tamara Tatrishvili<sup>1,2, ✉</sup>, Nikoloz Kvinikadze<sup>1,2</sup>, Tinatin Bukia<sup>3</sup>,  
Zurab Pachulia<sup>4</sup>, Nana Pirtskheliani<sup>2,4</sup>, Gia Petriashvili<sup>3</sup><https://doi.org/10.23939/chcht17.02.325>

**Abstract.** Friedel-Crafts alkylation reaction of vinyltrimethoxysilane with styrene was performed in the presence of anhydrous AlCl<sub>3</sub>. Alkoxy(4-vinylphenethyl)silane has been obtained. The synthesized products were identified by <sup>1</sup>H, <sup>13</sup>C, COSY NMR, and FTIR spectroscopy. Calculations using the quantum-chemical non-empirical density functional theory (DFT) method for the reaction between vinyltrimethoxysilane and styrene performed for ortho-, meta- and para-positions were discussed. For the theoretical modeling an online prediction program “Priroda-04: A quantum-chemical program suite” was used. Composite materials based on wood sawdust with various dispersion qualities and synthesized trimethoxysilylated styrene as a binding and reinforcing agent with degrees of silylation (5 %), in the presence of various organic/inorganic additives, fire retardants, and antioxidants, have been developed at different temperatures and pressures *via* hot press method or extrusion. The physico-mechanical properties of composites have been investigated.

**Keywords:** trimethoxy(4-vinylphenethyl)silane, alkylation reaction, FTIR and NMR spectroscopy, DFT.

## 1. Introduction

Polymeric binders are one of the most vital components of organic coatings because they serve as a material that integrates with the other components. In this context, the molecular structure of polymeric binders should be designed to benefit the specific purposes of the coatings (*i.e.*, protection against corrosion, abrasion, and microbial

fouling).<sup>1-4</sup> A broad range of polymers, including polyesters, epoxides, polyurethanes, polyureas, acrylics, vinyl acetates, silicones, silicates, polyvinyl chlorides, phenolics, and vinylidene fluorides, are used as binders for organic coating materials.<sup>5</sup> These polymers are primarily produced from petrochemical raw materials. Due to environmental and economic problems caused by the detrimental influence of fossil fuel resources, renewable resources have recently gained considerable importance for their benefits, such as low cost, availability, and biodegradability.<sup>6-12</sup>

Vinyltrimethoxysilane is a kind of vinyl-based silane, which is widely used in crosslinked polyethylene production, glass fiber processing, and inorganic filler surface modification as a coupling and linking agent simultaneously.<sup>13</sup>

Natural fibers have been found to be excellent reinforcing materials for preparing polymer matrix-based composites. In the present study, both raw and surface modified Agave fiber reinforced polystyrene matrix-based composites were prepared in order to explore the effect of reinforcement on the mechanical properties of the matrix.<sup>14</sup>

Due to increased environmental concerns natural fibers have recently attracted great attention for the synthesis of fiber-reinforced polymer matrix-based composites.<sup>15-17</sup> These composites have additional advantages such as low cost<sup>5</sup>, availability, high specific strength,<sup>18</sup> and biodegradability;<sup>19</sup> they are nonabrasive and easy to be processed. Among various polymer matrices, thermoplastics are mostly used in the manufacture of plastic/wood composites.<sup>20</sup> Styrene is one of the most important thermoplastics which is in great demand due to its transparency, fluidity, and good electrical insulation properties.<sup>21,22</sup>

Composite materials obtained from natural fibers are intensively studied due to their ecological nature and specific properties. The advantages of natural fibers are their continuous supply, easy and safe processing, and biodegradable nature.

<sup>1</sup> Ivane Javakhishvili Tbilisi State University, Department of Macromolecular Chemistry, I. Tbilisi, IO Chavchavadze Ave., 1, 0179, Georgia

<sup>2</sup> Institute of Macromolecular Chemistry and Polymeric Materials, Ivane Javakhishvili Tbilisi State University, I. Tbilisi, Chavchavadze Ave., 13, 0186, Georgia

<sup>3</sup> Vladimir Chavchanidze Institute of Cybernetics of the Georgian Technical University, Z. Tbilisi, Andzaparidze St. 5, 0186, Georgia

<sup>4</sup> Sokhumi State University, Faculty of Natural Sciences, Mathematics, Technologies and Pharmacy, Tbilisi, Politkovskaya St., 61, 0186, Georgia

✉ [tamar.tatrishvili@tsu.ge](mailto:tamar.tatrishvili@tsu.ge)

© Mukbaniani O., Tatrishvili T., Kvinikadze N., Bukia T., Pachulia Z., Pirtskheliani N., Petriashvili G., 2023

Great interest has been directed to the development of new composites obtained from thermoplastic polymer matrices, which are based on renewable plant materials. This interest is caused not only by their environmental and economic benefits, but also by such interesting properties as renewability, biodegradability, low density, high strength, and relatively low price.<sup>23-28</sup>

Trimethoxysilylated styrene was synthesized to be used as a binder and reinforcement material in a wood polymer composite, which is safe for the human organism. Investigation of the Friedel-Crafts alkylation reaction of vinyltrimethoxysilane with styrene in the mixture of ortho-, meta-, and para-styrene and predicting the direction of this reaction using the non-empirical density functional theory (DFT) have been carried out.<sup>29-31</sup> Density functional theory is widely applied to both molecules and materials, but well-known energetic delocalization and static correlation errors in practical exchange-correlation approximations limit quantitative accuracy.<sup>32-36</sup>

This study aims at using the non-empirical density functional theory regarding the Friedel-Crafts alkylation reaction of vinyltrimethoxysilane with styrene to produce trimethoxy(4-vinylphenethyl)silane as well as forming and characterizing composite materials based on dry sawdust of pine and trimethoxy(4-vinylphenethyl)silane and styrene as a binder and reinforcement agent.

## 2. Experimental

### 2.1. Materials

Synthetic manipulations were carried out under an atmosphere of dry nitrogen gas. All solvents were degassed and purified before using according to standard literature methods: toluene, hexane, and tetrahydrofuran were distilled from sodium/benzophenone ketyl. Styrene, vinyltrimethoxysilane and  $\text{AlCl}_3$  were purchased from Aldrich and used as received or distilled prior to use.

Composites based on dry sawdust of pine used trimethoxy(4-vinylphenethyl)silane and styrene as a binder and reinforcement agent, which was obtained *via* an alkylation reaction of vinyltrimethoxysilane with styrene according to the literature data.<sup>37</sup>

### 2.2. Characterization

Fourier transform infrared spectroscopy (FTIR) studies were conducted on a NicoletTM iS50 FTIR Spectrometer-Thermo Fisher Scientific in the infrared region of  $4000\text{--}400\text{ cm}^{-1}$  (scan 32, resolution  $4\text{ cm}^{-1}$ ); band intensities were denominated in transmittance. Analytical sample was finely dispersed powder (1-2 mg).  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and COSY NMR spectra were recorded on a Bruker ARX400 NMR spectrometer at a 400 MHz operating

frequency with  $\text{C}_6\text{D}_6$  as the solvent and an internal standard.

Thermogravimetric investigations were carried out on a "Paulic-Paulic-Erday" derivatograph (model MOM-102). The rate of temperature increase during tests was  $\approx 10\text{ deg/min}$  in an open area.

### 2.3. Alkylation Reaction of Vinyltrimethoxysilane with Styrene

74.0 g (0.5 mol) of styrene and 2.0 g (0.0150 mol) of aluminum chloride were placed in a three-necked flask connected with a backflow condenser and dropping funnel. 74.12 g (0.5 mol) of vinyltrimethoxysilane was added from the dropping funnel under constant stirring. The mixture was heated for 3 hours and then 5.130 mL of triethylamine (3.724 g, 0.0368 mol) were added dropwise, cooled in an ice bath and stirred for 30 minutes. After that, the reaction mixture was heated for 2 hours under stirring.<sup>38</sup> During cooling, a precipitate appeared on the walls, which was filtered and vacuumed. After distillation of 92 g the viscous product in vacuum, 51 g (55 %) of a transparent viscous product was obtained.

### 2.4. Processing

The composites were prepared by hot pressing of highly dispersed (20-30  $\mu\text{m}$ ) dry pine sawdust with trimethoxysilylated styrene (with 1 % dicumyl peroxide) as a binder and reinforcement agent. The samples were created under pressures up to 15 MPa at the temperatures of 433, 453, and 463 K for 5 min. Two types of samples have been created: cylindrical (for investigation of water absorption) and rectangular (for mechanical testing).

After cooling, the samples were weighed, and the density of the composites was calculated. After that, the samples were placed in water for 3 hours to determine the water absorption index. The same manipulation was carried out after 24 hours.

### 2.5. Testing Methods

**Water absorption  $X$**  (in percent) was calculated by the formula:

$$x = \frac{m_2 - m_1}{m_1} 100,$$

where  $m_1$  and  $m_2$  are the weights of the sample before and after water absorption.

**Bending testing.** Bending testing (also known as flexural testing) was performed on parallelepipeds with a length of 10 cm and a vertical square cross-section of  $1\text{ cm}^2$ . Each specimen was placed on two prisms, with a distance of 8.0 cm between the prisms. The indenter was a metal cylinder with a diameter of 10 mm applied from

above to the midpoint of the specimen. Bending strength (or flexural strength) is defined as the stress needed to create a breaking point (a crack) on the outer surface of the test specimen.<sup>39</sup>

**Impact viscosity** determination, also called shock viscosity determination, is a technique applied to soft solids<sup>40,41</sup> and is essentially a drop impact test. The drop height ( $h$ ) is the vertical distance between the upper surface of the tested material ( $h_1$ ) and the bottom surface of the drop hammer at the end of the impact event ( $h_2$ ). With the sample mass  $m$  and the acceleration  $g$ , the work performed by the falling hammer is  $mg(h_1 - h_2)$ , normalized with respect to the horizontal cross-section of the specimen  $FF$ .<sup>41</sup>

**Vicat softening depth**, also known as Vicat hardness, is the determination of the depth of the indentation with respect to the top surface caused by a flat-ended indenter with a cross-section of  $1 \text{ mm}^2$ . Several loads defined below were applied; the cross-section of the indenter end was circular.

### 3. Results and Discussion

The first information about the functionalization of styrene with vinyl-containing silicon-organic compounds

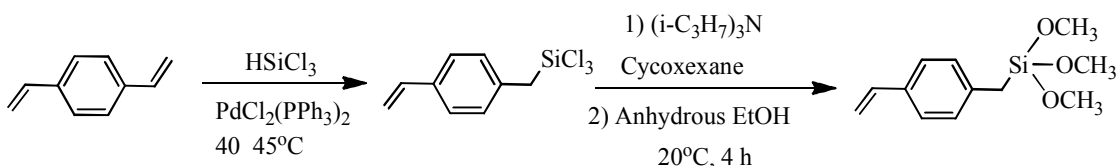
in the presence of Lewis acid ( $\text{FeCl}_3$  and  $\text{AlCl}_3$ ) in solution was reported by Titvinidze *et al.*<sup>42</sup> It was shown that the yields of the alkylation reaction of vinyltriethoxysilane with styrene in the presence of  $\text{AlCl}_3$  are higher than in the presence of  $\text{FeCl}_3$ .

Trialkoxy(4-vinylphenethyl)silane ( $\text{StSi}(\text{OR})_3$ ) type monomers were synthesized *via* two-step reactions: hydrosilylation reaction of 1,4-divinylbenzene with trichlorosilane, followed by esterification reactions with primary alcohols.<sup>43,44</sup> The yield of the trialkoxy group-containing compounds is about 50 %.

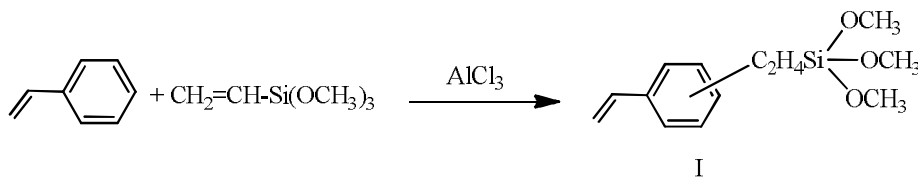
The alkylation reaction of vinyltrimethoxysilane with styrene (1:1, w/v) in the presence of anhydrous  $\text{AlCl}_3$  as the catalyst was carried out. The reaction proceeds according to the following scheme 2.<sup>38</sup>

The synthesized trimethoxy(vinylphenethyl) silane is a viscous liquid. The structure of trimethoxy(vinylphenethyl) silane was confirmed by FTIR-,  $^1\text{H}$ ,  $^{13}\text{C}$ , hetero COSY, and  $^{29}\text{Si}$  NMR spectra. Moreover, experimentally determined values of the molecular mass and molecular refraction were in good agreement with the calculated values. This confirms the structure of trimethoxy(vinylphenethyl) silane as shown in Scheme 2.

Some physicochemical characteristics of trimethoxy(vinylphenethyl)silane are presented in Table 1.



**Scheme 1.** The reaction scheme of the trimethoxy(4-vinylphenethyl)silane synthesis



**Scheme 2.** Alkylation reaction of vinyltrimethoxysilane with styrene

**Table 1.** Some physicochemical properties of trimethoxy(vinylphenethyl)silane

#	Compound	$T_{\text{Boiling}} \text{ (K)}$ $P=10\text{mmHg}$	Yield, %	$n_D^{20}$	$d_4^{20}$	$M^*$	$MR^{**}$
I	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{C}_2\text{H}_4-\text{Si}(\text{OCH}_3)_3$	354–358	55	1.4650	0.9433	$\frac{252}{-}$	$\frac{73.85}{72.80}$

\* Molecular masses were determined *via* ebullioscopy method.

\*\* Molecular refraction: calculated values are in the numerator, found values – in the denominator

In the IR spectra of trimethoxy(vinylphenethyl) silane (Fig. 1), the absorption bands at 3081-3059, 1630, 1598, 1494 and 698  $\text{cm}^{-1}$  are characteristic of stretching and deformation vibrations of asymmetric and symmetric C-H stretching of the aromatic ring. The stretching and deformation vibrations of aliphatic C-H bonds (-CH<sub>2</sub>-) are observed at 2942 and 2840  $\text{cm}^{-1}$ , respectively. The absorption bands observed at 1275  $\text{cm}^{-1}$  corresponds to the C-O (-C-O-CH<sub>3</sub>) stretching vibration. At 1190, 1076, 1009 and 968  $\text{cm}^{-1}$  the absorption bands are characteristic for the Si-O-CH<sub>3</sub>, and also Si-C stretching are observed at 809  $\text{cm}^{-1}$ . The absorption bands at 767  $\text{cm}^{-1}$  are characteristic of methylene =CH<sub>2</sub> group.<sup>45</sup>

In the <sup>1</sup>H NMR spectra of the synthesized compound, we can see the aliphatic group signals (2H, m, CH<sub>2</sub>) as multiple signals with chemical shifts at  $\delta=1.1$  ppm; also CH<sub>2</sub> group signals appear at 3.2 ppm (2H, m, C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>) as a multiple signal. The signals of CH<sub>3</sub> group protons appears as a singlet signal at 3.3–3.5 ppm (9H, m, Si-O-C H<sub>3</sub>). The signals of aromatic group can be seen as multiple signals at the region of 5.59–6.0 and 7.2, 7.3–7.6 ppm (4H, m, CH) (Fig. 2).

The chemical shifts of these signals are close to the values, determined by Swanson.<sup>43</sup> Supposedly, alkylation occurs with the formation of isomeric compounds of ortho- and para-addition and chemical overlap takes place.

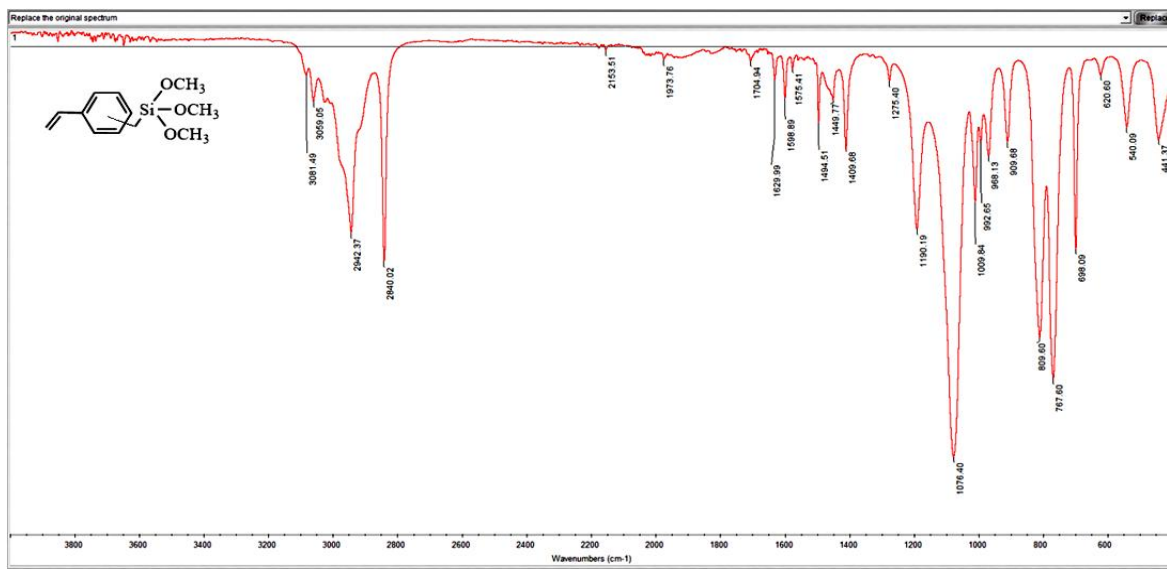


Fig. 1. IR spectra of trimethoxy(vinylphenethyl)silane

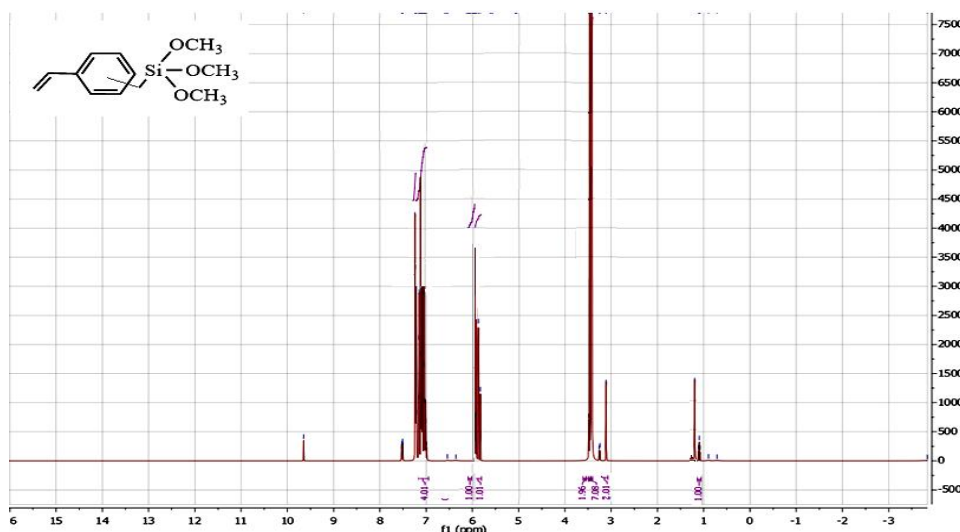


Fig. 2. <sup>1</sup>H NMR spectra of trimethoxy(vinylphenethyl)silane

In  $^{13}\text{C}$  NMR spectra of the synthesized compound, the carbon atom signals of the aliphatic  $\text{CH}_2$  group appear in the 14.60 ppm and 30.2 ppm upfield region.  $\text{CH}_3$  group signals appear at the region of 51.9 ppm, which corresponds to three carbon atom signals, and  $\text{C}=\text{C}$  vinyl group signals and aromatic group signals of phenyl ring appear in the region of 112.4–139.8 ppm.  $^{13}\text{C}$  NMR spectrum (Fig. 3) is in accordance with  $^1\text{H}$  NMR spectrum.

Fig. 4 presented the hetero COSY NMR spectra of trimethoxy(vinylphenethyl)silane, where the  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectra correlate with each other.

According to the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, it is evident that the alkylation reaction was performed. However, it is difficult to detect the direction (para- or ortho-position) in which alkylation proceeds, since the signals overlap, which is confirmed by studying the simulated NMR<sup>46,47</sup> spectra by the online prediction program (ChemBioDraw Ultra 14.0<sup>48</sup> and MestreNova<sup>49</sup>). However, based on quantum-chemical modeling of the alkylation reaction of vinyltrimethoxysilane with styrene we assume that the alkylation reaction probably proceeds mainly in the ortho-position.

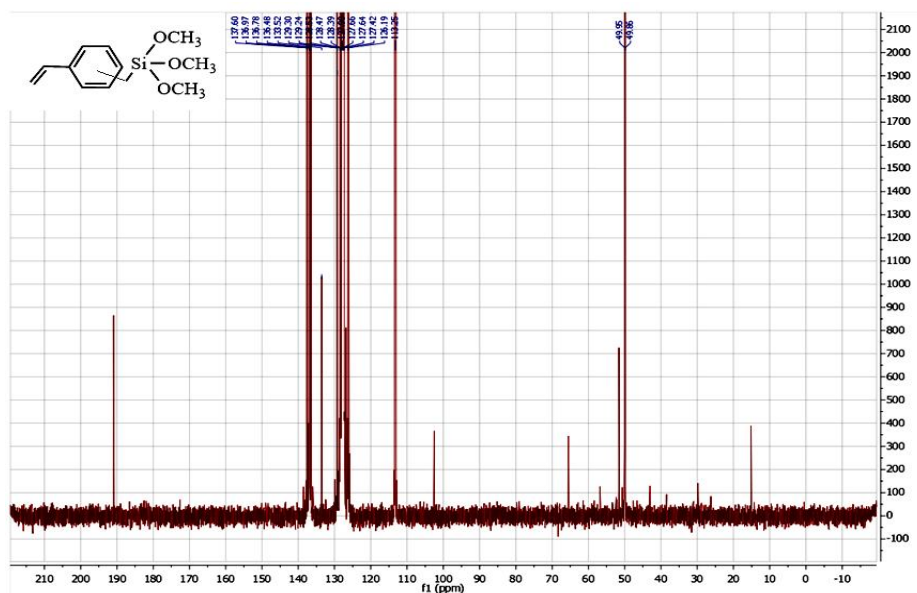


Fig. 3.  $^{13}\text{C}$  NMR spectra of trimethoxy(vinylphenethyl)silane

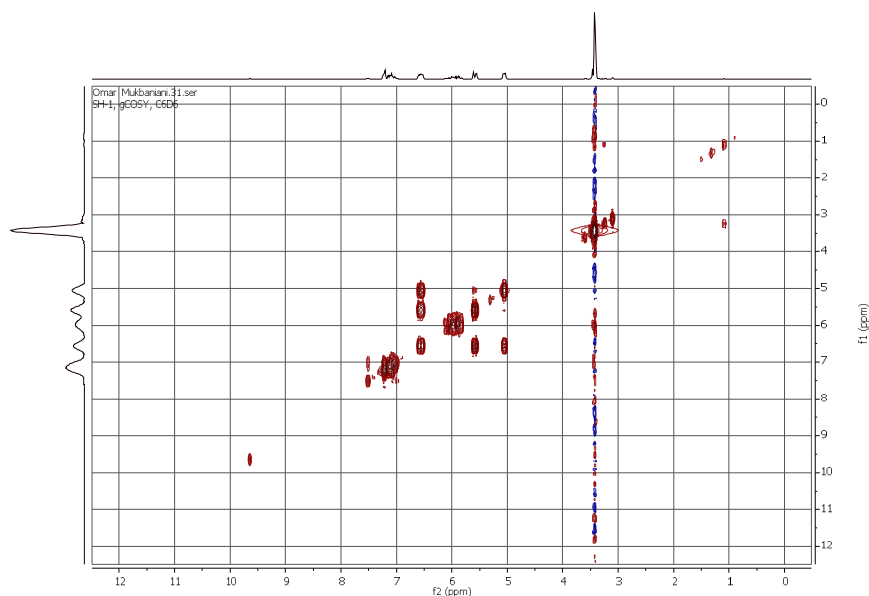
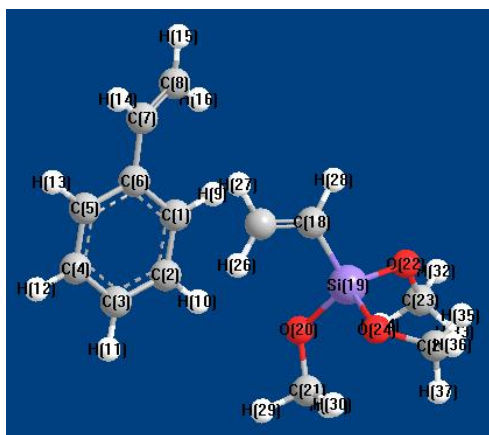


Fig. 4. COSY NMR spectra of trimethoxy(vinylphenethyl)silane

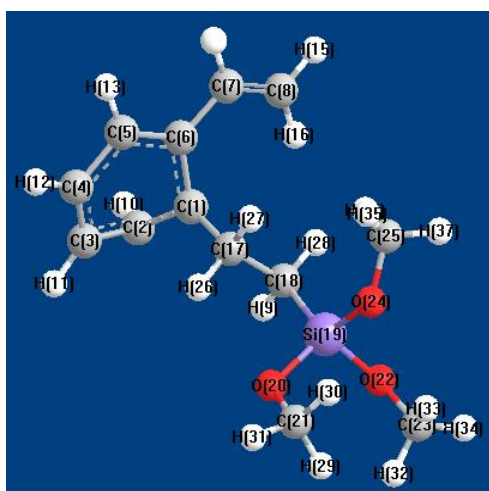
For a detailed study of alkylation reaction direction, quantum-chemical calculations were carried out using the non-empirical density functional theory (DFT).<sup>50</sup> For the theoretical calculation online prediction program “Priroda-04: A quantum-chemical program suite” was used. Addition reactions in *ortho*-, *meta*- and *para*-states were discussed.

The distances between the carbon atoms ( $C_1$ - $C_{17}$ ,  $C_2$ - $C_{17}$ ,  $C_3$ - $C_{17}$ ) and between the carbon and hydrogen atoms ( $H_9$ - $C_{18}$ ,  $H_{10}$ - $C_{18}$ ,  $H_{11}$ - $C_{18}$ ) were taken to be 1.0 Å longer than the bond distance in the final product. The distances between the atoms varied at intervals of 0.05 Å.

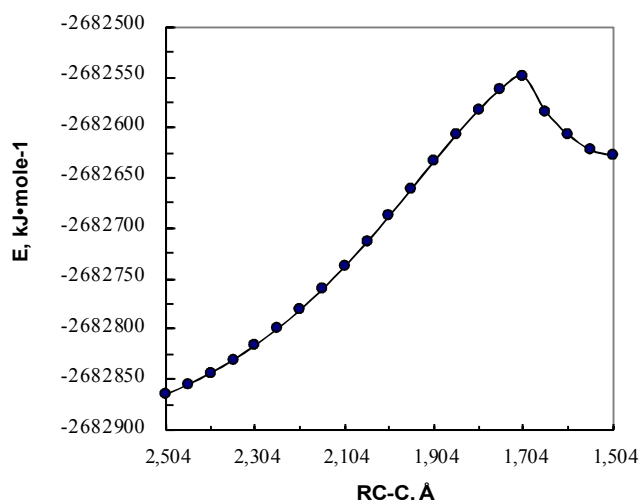
The initial states of the systems are given in Figs. 5, 8 and 11, and the final states – in Figs. 6, 9 and 12. The dependence of the energy change ( $\Delta E$ ) of the systems on the distances between the atoms is given in Figs. 7, 10 and 13.



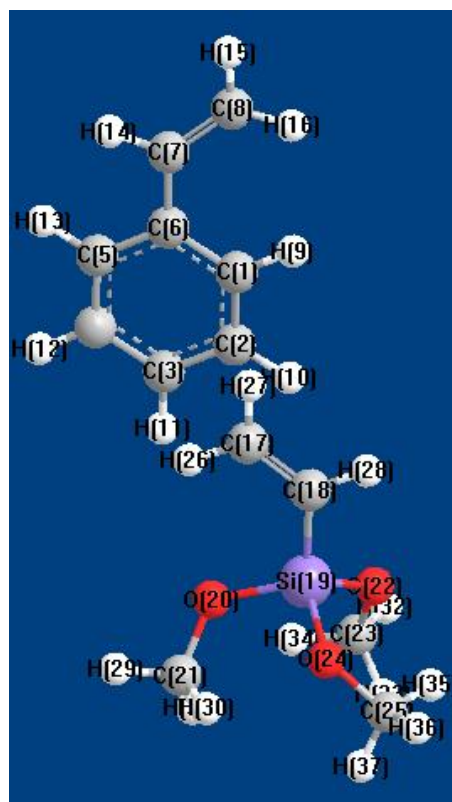
**Fig. 5.** Initial state of monomers involved in the Friedel-Crafts alkylation reaction of vinyltrimethoxysilane with styrene (*ortho*-addition)



**Fig. 6.** Final state of monomers involved in the Friedel-Crafts alkylation reaction of vinyltrimethoxysilane with styrene (*ortho* addition)



**Fig. 7.** Dependence of energy change ( $\Delta E$ ) between carbon atoms  $C_1$ - $C_{17}$  on distance ( $R_{C-C}$ ) in model Friedel-Crafts alkylation reaction of vinyltrimethoxysilane with styrene (*ortho*-addition)



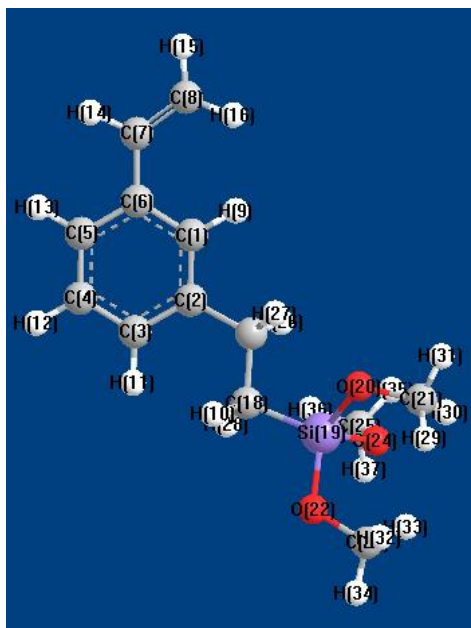
**Fig. 8.** Initial state of monomers involved in the Friedel-Crafts alkylation reaction of vinyltrimethoxysilane with styrene (*meta*-addition)

One can see from Fig. 7, during approaches of the  $C_1$  carbon atom to the  $C_{17}$  carbon atom at the distance of  $R_{C_1-C_{17}} = 1.704$  Å the system energy increases. Simulta-



neously the bond order between  $C_1$  and  $C_2$  atoms in the styrene molecule decreases from 1.36 up to 1.00, and between  $C_1$  and  $C_6$  atoms – from 1.47 up to 1.23. The bond order between  $C_1$  carbon atom and  $H_9$  hydrogen atom also decreases (0.92–0.52) and new bonds are observed ( $P_{C_1-C_{17}} = 0.72$  and  $P_{C_{18}-H_9} = 0.41$ ). The double bond moves to a single C-C bond. The hydrogen atom is completely turn off from the  $C_1$  carbon atom ( $P_{C_1-H_9} = 0.00$ ) and joined to the carbon  $C_{18}$  atom ( $P_{C_{18}-H_9} = 0.93$ ).

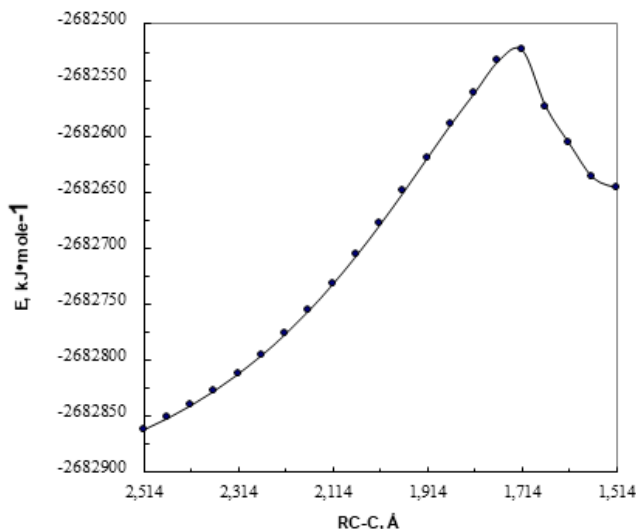
The activation energy  $\Delta E^*$  is 315.61 kJ/mol, and heat effect of the reaction  $\Delta E$  is 237.02 kJ/mol. As we can see, the reaction is endothermic. Given that there are four reaction centers in the system [broken bonds (2):  $C_1-H_9$ ,  $C_{17} = C_{18}$ ; generated bonds (2):  $C_1-C_{17}$ ,  $C_{18}-H_9$ ], the mentioned activation energy must be divided by four. In this case, the activation energy calculated for one reaction center is  $\Delta E^* = 315.61 \text{ kJ/mol}/4 = 78.90 \text{ kJ/mol}$ , which means that the obtained value corresponds to the energy characteristic of the chemical reactions.



**Fig. 9.** Final state of monomers involved in the Friedel-Crafts reaction of vinyltrimethoxysilane with styrene (*meta-addition*)

It is obvious from Fig. 10, that during approaches of the  $C_2$  carbon atom to the  $C_{17}$  carbon atom at the distance of  $R_{C_2-C_{17}} = 1.714 \text{ \AA}$  the system energy increases. Simultaneously the bond order between  $C_2$  and  $C_3$  atoms in the styrene molecule decreases from 1.36 up to 1.13, and between  $C_2$  and  $C_1$  atoms – from 1.38 up to 1.14. The bond order between  $C_2$  carbon atom and  $H_{10}$  hydrogen

atom also decreases (0.93–0.50) and new bonds are observed ( $P_{C_2-C_{17}} = 0.73$  and  $P_{C_{18}-H_{10}} = 0.43$ ). The double bond moves to a single C-C bond. The hydrogen atom is completely turn off from the  $C_2$  carbon atom ( $P_{C_2-H_{10}} = 0.00$ ) and joined to the carbon  $C_{18}$  atom ( $P_{C_{18}-H_{10}} = 0.94$ ).



**Fig. 10.** Dependence of energy change ( $\Delta E$ ) between carbon atoms  $C_2$ - $C_{17}$  on distance ( $R_{C-C}$ ) in model Friedel-Crafts alkylation reaction of vinyltriethoxysilane with styrene (*meta-addition*)

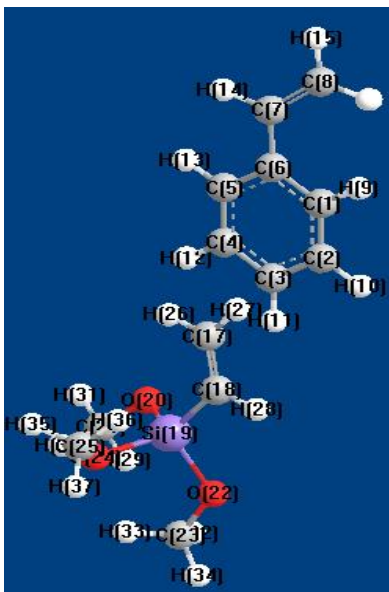
The activation energy  $\Delta E^*$  is 338.90 kJ/mol, and heat effect of reaction  $\Delta E$  is 215.91 kJ/mol. As we can see, the reaction is endothermic.

Given that there are 4 reaction centers in the system [broken bonds (2):  $C_2-H_{10}$ ,  $C_{17} = C_{18}$ ; generated bonds (2):  $C_2-C_{17}$ ,  $C_{18}-H_{10}$ ], the mentioned activation energy must be divided by 4. In this case, the activation energy calculated for one reaction center is  $\Delta E^* = 338.90 \text{ kJ/mol}/4 = 84.73 \text{ kJ/mol}$ , which means that the value obtained corresponds to the energy characteristic of the chemical reactions.

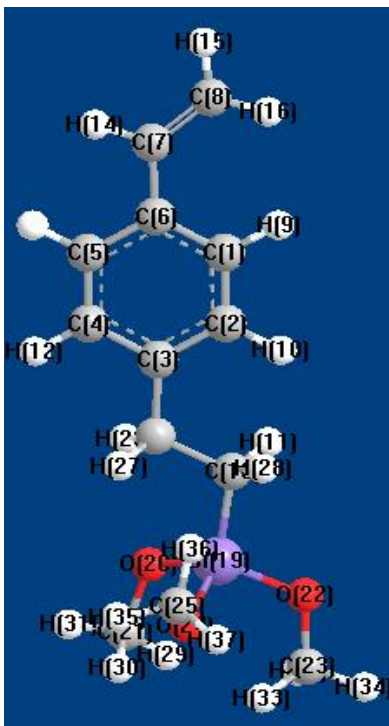
One can see from Fig. 13, that during approaches of the  $C_3$  carbon atom to the  $C_{17}$  carbon atom at the distance of  $R_{C_3-C_{17}} = 1.719 \text{ \AA}$  the system energy increases.

Simultaneously the bond order between  $C_3$  and  $C_4$  atoms in the styrene molecule decreases from 1.39 up to 1.12, and between  $C_3$  and  $C_2$  atoms – from 1.38 up to 1.10. The bond order between  $C_3$  carbon atom and  $H_{11}$  hydrogen atom also decreases (0.94–0.53) and new bonds are observed ( $P_{C_3-C_{17}} = 0.72$  and  $P_{C_{18}-H_{11}} = 0.40$ ). The double bond moves to a single C-C bond. The hydrogen atom is

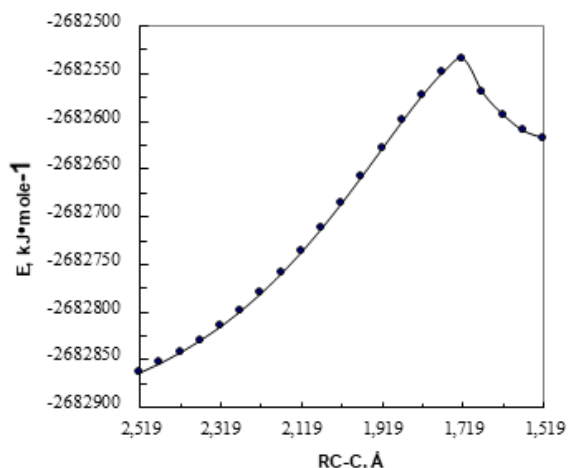
completely turned off from the  $C_3$  carbon atom ( $P_{C_3-H_{11}} = 0.00$ ) and joined to the carbon  $C_{18}$  atom ( $P_{C_{18}-H_{11}} = 0.93$ ).



**Fig. 11.** Initial state of monomers involved in the Friedel-Crafts alkylation reaction of vinyltrimethoxysilane with styrene (*para*-addition)



**Fig. 12.** Final state of monomers involved in the Friedel-Crafts reaction of vinyltrimethoxysilane with styrene (*para*-addition)



**Fig. 13.** Dependence of energy change ( $\Delta E$ ) between carbon atoms  $C_3$ - $C_{17}$  on distance ( $R_{C-C}$ ) in modal Friedel-Crafts alkylation reaction of vinyltrimethoxysilane with styrene (*para*-addition)

The activation energy  $\Delta E^*$  is 329.18 kJ/mol, and heat effect of reaction  $\Delta E$  is 246.11 kJ/mol. As we can see, the reaction is endothermic.

Given that there are 4 reaction centers in the system [broken bonds (2):  $C_3$ - $H_{11}$ ,  $C_{17} = C_{18}$ ; generated bonds (2):  $C_3$ - $C_{17}$ ,  $C_{18}$ - $H_{11}$ ], the mentioned activation energy must be divided by 4. In this case, the activation energy calculated for one reaction center is  $\Delta E^* = 329.18 \text{ kJ/mol} / 4 = 82.30 \text{ kJ/mol}$ , which means that the value obtained corresponds to the energy characteristic of the chemical reactions.

According to the values of the activation energy, it is energetically most convenient to join in the ortho-state.

However, the quantum-chemical approach uses the three-dimensional molecular structure, while the prediction method does not take stereochemistry into account. Also, the latter method works satisfactorily only if a similar structure is found in the database.<sup>51</sup> So, during this alkylation reaction, the mixture of ortho- and para-addition isomers is obtained.

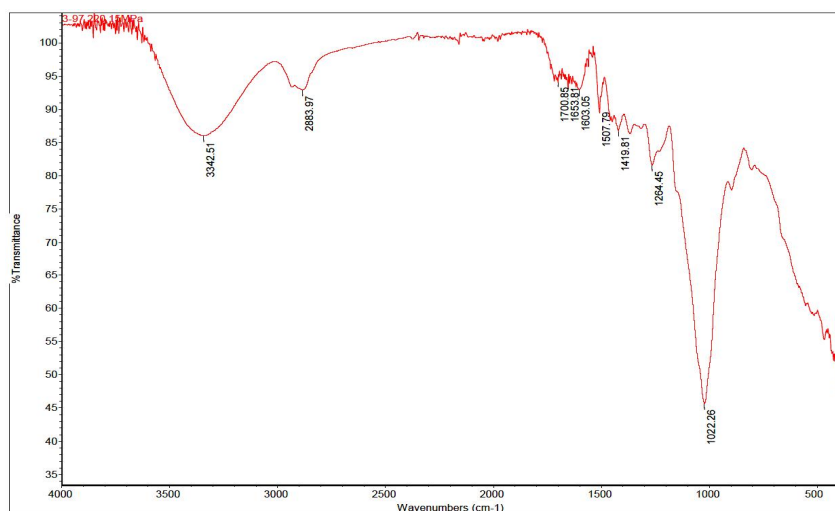
There composites on the base of dry sawdust of pine with trimethoxysilylated styrene as a binder and reinforcement agent were prepared according to the technique described in Subsection 2.4. The weight ratio of trimethoxysilylated styrene and sawdust was 5:95.

During hot pressing at 473 K, the binder in the composites burned and small particles of filler throw out from the press mould. Therefore, the composites were obtained at a temperature of 433–463 K.

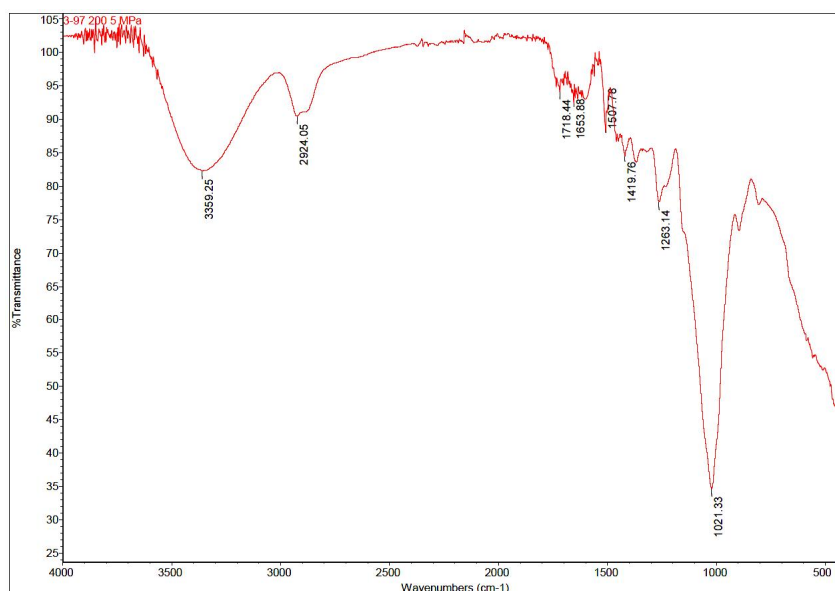
As for the obtaining of composites under a pressure of 15 MPa, this condition was established on the basis of studies conducted by our group.

FTIR investigations for composites have been carried out (Fig. 14).





a



b

**Fig. 14.** FTIR spectra of composites II (a) and IV (b) based on the trimethoxy(vinylphenethyl)silane and sawdust

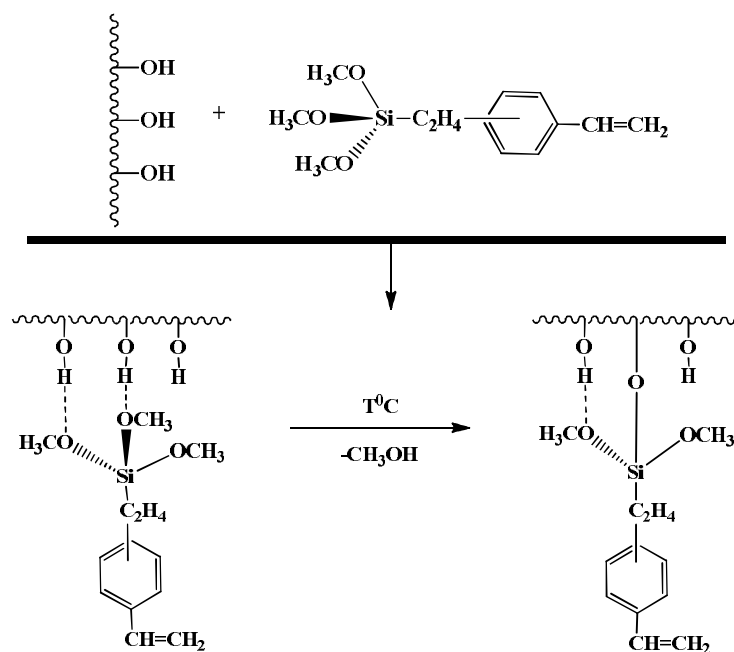
In the FTIR spectra, one can observe the characteristic asymmetric stretching vibrations of the siloxane Si–O–C up to a maximum at 1021 and 1022  $\text{cm}^{-1}$ . Absorption bands at 1263 and 1264  $\text{cm}^{-1}$  correspond to the asymmetric absorption bands characteristic of O–C bonds. Absorption bands at 1419  $\text{cm}^{-1}$  are characteristic of C–H bend.

At 1507, 1603 and 1653  $\text{cm}^{-1}$  we can see the C=C–C aromatic ring vibrations. Absorption bands at 2883 and 2924  $\text{cm}^{-1}$  are characteristic of aliphatic C–H bonds and bands at 3343 and 3363  $\text{cm}^{-1}$  correspond to the OH bond.

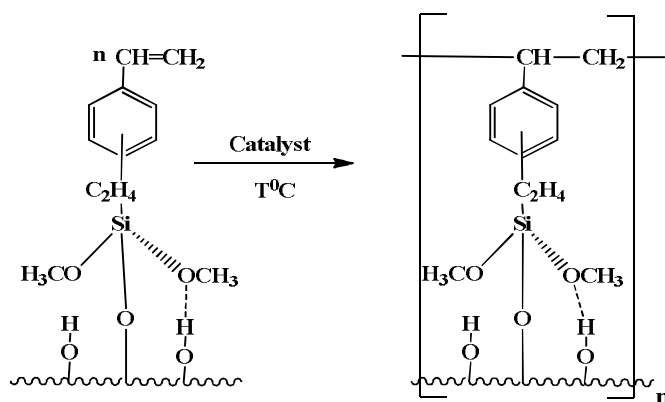
Water absorption was studied for the composites. The experimental results are presented in Table 2, from

which one can see, that by increasing obtaining temperature of composites from 433 to 463 K, the water absorption value decreases from 18.6 % to 3.97 %. The depth of the etherification reaction was found to be increased with increasing temperature. The reaction results in the creation of new covalent bonds between the filler and the binder – the reaction proceeds according to Scheme 3.

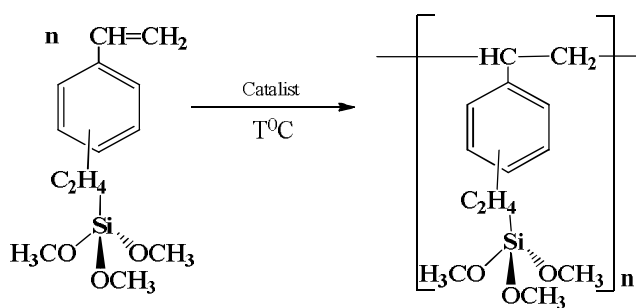
It is possible, that the filler crosslinking and reinforcement processes take place. It is not excluded, that in this case, the binder is associated with the filler matrix and will undergo polymerization relative to the vinyl group according to Scheme 4.



**Scheme 3.** Interaction and etherification reactions of trimethoxysilylated styrene and cellulose



**Scheme 4.** *In situ* polymerization reaction of trimethoxysilylated styrene with fillers



**Scheme 5.** *In situ* polymerization of trimethoxysilylated styrene in a matrix

Further, perhaps, a polymer formed on the surface during *in-situ* polymerization, interacts with the cellulose surface according to Scheme 5.

This polymer chain reacts with the cellulose hydroxyl group in the filler in the same way as monomeric trimethoxysilylated styrene, which forms donor-acceptor bonds and initiates the esterification reaction, which forms a Si-O-C covalent bond between the filler and the binder.

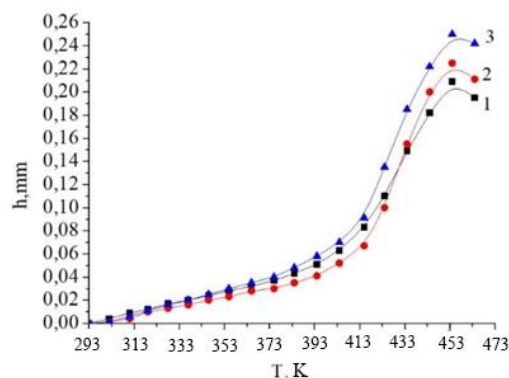
Thermal stability of wood polymer composites was studied by the Vicat method. The temperature reflects the point of softening to be expected when a material is used in an elevated temperature application. These results are shown in Fig. 15, according to which the softening temperature of composites increases with increasing temperature.

An increase in the softening temperature in composites is due to an increase in the degree of esterification reactions, which also increases the frequency of crosslinking, *i.e.*, the filler and the crosslinking agent form a unified system. Moreover, during *in-situ* polymerization a composite reinforcement takes place. This increases the softening temperature of the composite.

Physical-mechanical investigations were performed for the composites.<sup>52,53</sup> As can be seen from the data of Table 3, the increase in temperature increase the values of the bending strength. The value of impact viscosity also increases, which is caused by the intermolecular chemical interaction between the binder and the filler. Thus, the role of trimethoxy(vinylphenethyl) silane as a binder and the stabilizing agent is well demonstrated.

**Table 2.** Water absorption of the composites (obtained) based on sawdust (pine) and trimethoxisilylated styrene

#	Composite (wt%)	P, MPa	T, K	Weight, (g)	Volume, (cm <sup>3</sup> )	Density, g/cm <sup>3</sup>	Weight after 3 h exposure in water (g)	Weight after 24 h exposure in water (g)	Water absorption after 24 h exposition in water in wt.%
II	5 % Silyl. Styrene+95 % sawdust	15	433	3.728	2.58	1.44	3.824	4.424	18.6
III	5 % Silyl. Styrene+95 % sawdust	15	453	3.630	2.54	1.43	3.699	3.921	8
IV	5 % Silyl. Styrene+95 % sawdust	15	463	3.600	2.53	1.42	3.677	3.743	3.97



**Fig. 15.** Dependence of the depth of the sample on the composites temperature (Vicat method). Curve 1 corresponds to composite II (5 % Silyl. Styrene, 433 K), curve 2 – composite III (5 % Silyl Styrene., 453 K), curve 3 – composite IV (5 % Silyl. Styrene, 463 K)

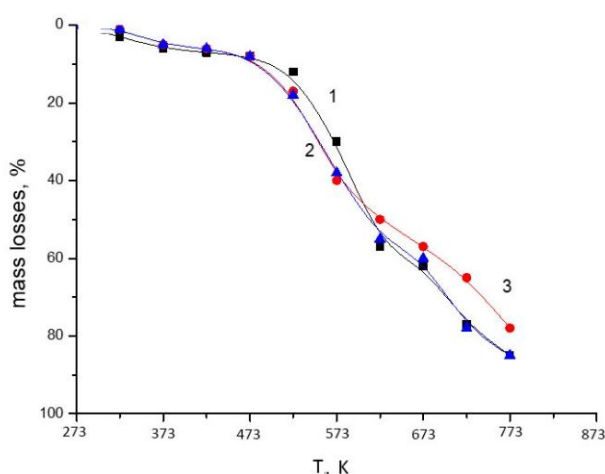
**Table 3.** Physical-mechanical properties of composites based on sawdust and trimethoxy(vinylphenethyl) silane (Dependence of bending strength and impact viscosity values of composites on the preparation conditions)

#	Composite	T, K	Pressure, MPa	S (cm <sup>2</sup> )	R Bending strength (kg/cm <sup>2</sup> )	D Impact viscosity (kJ/m <sup>2</sup> )
II	5 % Silyl. Styrene+95 % sawdust	433	15	1.089	45,08	16,07
III	5 % Silyl. Styrene+95 % sawdust	453	15	1.074	53,19	16,29
IV	5 % Silyl. Styrene+95 % sawdust	463	15	1.0584	56,94	17,47

Note: rate of temperature increase ≈10 deg/min in an open area

TG curves of the investigated composites are presented in Fig. 16. It is evident, that with an increase in temperature the mass losses of composites are increased. Presented figure shows mass losses at 373 K temperature, which are connected with chemical reactions of functional groups of sawdust with functional groups of binders.

About 10 % of mass losses can be observed in the temperature range of 493–503 K. Obviously, this mass loss is due to moisture in the composites or the release of methyl alcohol. In this temperature interval condensation processes may proceed with unreacted hydroxyl groups as well as with hydroxyl and methoxyl groups. The main destruction process runs intensively from 503–623 K and up to 773 K till the full destruction of composites.



**Fig. 16.** TGA curves of composites, in the open area, rate of temperature increase is 10 °C/min. Curve 1 –composite II (5 % Silyl. Styrene, 433 K), curve 2 –composite III (5 %Silyl. Styrene., 453 K), curve 3 –composite IV (5 %Silyl. Styrene, 463 K)

Differential scanning calorimetry (DSC) investigations were also performed for composites. The figure with the results is not included for brevity. In some composites the so-called glass transition temperature  $T_g \approx 190$  K. As discussed by I. Kalogeras and H. Lobland,<sup>54</sup> representing a glass transition region, for instance, 30 K wide, by a single number is not only an uphill battle. Still, it provides a confusing image of the situation. The softening temperatures are in the range of 243 to 313 K.

## 4. Conclusions

Based on the results and analysis of this study, it is concluded that the alkylation product trimethoxy (vinylphenethyl)silane has been obtained by the Friedel-Crafts alkylation reaction of vinyltrimethoxysilane with

styrene. The structure and composition of the product was proved by FTIR,  $^1\text{H}$ ,  $^{13}\text{C}$  and Cozy NMR spectroscopy. For a more detailed study of the direction of the alkylation reaction, quantum-chemical calculations were performed using the non-empirical density functional theory (DFT). According to the values of the activation energy, it is energetically most convenient to join in the ortho-state.

However, it's known that this method does not consider the steric factors of the molecule caused by the ortho-addition of vinyltrimethoxysilane to styrene. So, referring to the NMR spectra data, it was concluded, that the alkylation reaction proceeds with the formation of a mixture of ortho- and para-addition.

For polymer composites, thermal properties have been studied, in particular, the dependence of the softening temperature on the temperature of obtained composites. It was concluded that the softening temperature increases with the increase in pressing temperature. It was determined that when the pressing temperature increases, the water absorption decreases, and it is 4 times lower than the water absorption of the conventional wood bubble board produced today, which is within 20–30 %.

Physical-mechanical properties of composites were studied. It was established that with the increase in the pressing temperature of the composite, the flexural strength and the value of the impact viscosity increase.

## Acknowledgments

The financial support of the Shota Rustaveli national scientific foundation of Georgia (Project #FR-21-4630) is gratefully acknowledged.

## References

- [1] *The Chemistry and Physics of Coatings*; Marrion, A., Ed.; The Royal Society of Chemistry: Cambridge, 2004.
- [2] *Organic Coatings: Science and Technology*; Wicks, Z.W., Jones, F.N.; Pappas, S.P.; Wicks, D.A., Eds.; John Wiley & Sons: New Jersey, 2007.
- [3] *High-performance organic coatings*; Khanna, A.S., Ed.; CRC Press: Florida, 2008.
- [4] Talbert, R. *Paint Technology Handbook*; CRC Press: Florida, 2008.
- [5] *Hybrid Materials: Synthesis, Characterization and Applications*; Kickenbick, G., Ed.; WILEY-VCH: Weinheim, 2007.
- [6] Tsujimoto, T.; Uyama, H.; Kobayashi, S. Synthesis of High-Performance Green Nanocomposites from Renewable Natural Oils. *Polym. Degrad. Stab.* **2010**, *95*, 1399-1405. <https://doi.org/10.1016/j.polymdegradstab.2010.01.016>
- [7] Tsujimoto, T.; Uyama, H.; Kobayashi, S. Green Nanocomposites from Renewable Resources: Biodegradable Plant Oil-Silica Hybrid Coatings. *Macromol. Rapid Commun.* **2003**, *24*, 711-714. <https://doi.org/10.1002/marc.200350015>
- [8] Xia, Y.; Larock, R.C. Vegetable Oil-Based Polymeric Materials: Synthesis, Properties, and Applications. *Green Chem.* **2010**, *12*, 1893-1909. <https://doi.org/10.1039/C0GC00264J>

- [9] Galià, M.; de Espinosa, L.M.; Ronda, J.C.; Lligadas, G.; Cádiz, V. Vegetable Oil-Based Thermosetting Polymers. *Eur. J. Lipid Sci. Technol.* **2010**, *112*, 87-96. <https://doi.org/10.1002/ejlt.200900096>
- [10] Lligadas, G.; Ronda, J.C.; Galià, M.; Cádiz, V. Novel Silicon-Containing Polyurethanes from Vegetable Oils as Renewable Resources. Synthesis and Properties. *Biomacromolecules* **2006**, *7*, 2420-2426. <https://doi.org/10.1021/bm060402k>
- [11] *Bailey's Industrial Oil and Fat Products. Volume 6. Industrial and Nonedible Products from Oils and Fats*; Shahidi, F., Ed.; John Wiley & Sons: New Jersey, 2005.
- [12] Tasdelen-Yucedag, C.; Erciyes, A.T. Modification of Polycaprolactone-Styrene-Vinyl Trimethoxysilane Terpolymer with Sunflower Oil for Coating Purposes. *Prog. Org. Coat.* **2014**, *77*, 1750-1760. <https://doi.org/10.1016/j.porgcoat.2014.05.024>
- [13] Jingzhou Jianghan Fine Chemical Co Ltd. Synthesis Method of Vinyltrimethoxysilane Oligomer. CN103396434A, November 20, 2013.
- [14] Singha, A.S.; Rana, R.K. Natural Fiber Reinforced Polystyrene Composites: Effect of Fiber Loading, Fiber Dimensions and Surface Modification on Mechanical Properties. *Mater. Des.* **2012**, *41*, 289-297. <http://dx.doi.org/10.1016%2Fj.matdes.2012.05.001>
- [15] Sreenivasan, V.S.; Ravindran, D.; Manikandan, V.; Narayanasamy, R. Influence of Fibre Treatments on Mechanical Properties of Short *Sansevieria cylindrica*/Polyester Composites. *Mater. Des.* **2012**, *37*, 111-121. <https://doi.org/10.1016/J.MATDES.2012.01.004>
- [16] Arrakhiz, F.Z.; El Achaby, M.; Kakou, A.C.; Vaudreuil, S.; Benmoussa, K.; Bouhfid, R.; Fassi-Fehri, O.; Qaiss, A. Mechanical Properties of High Density Polyethylene Reinforced with Chemically Modified Coir Fibers: Impact of Chemical Treatments. *Mater. Des.* **2012**, *37*, 379-383. <https://doi.org/10.1016/j.matdes.2012.01.020>
- [17] Massoodi, R.; El Hajjar, R.F.; Pillai, K.M.; Sabo, R. Mechanical Characterization of Cellulose Nanofiber and Biobased Epoxy Composites. *Mater. Des.* **2012**, *36*, 570-576. <http://dx.doi.org/10.1016%2Fj.matdes.2011.11.042>
- [18] Yang, H.S.; Kim, H.J.; Park, H.J.; Lee, B.J.; Hwang, T.S. Effect of Compatibility Agents on Rice Husk Flour Reinforced Polypropylene Composites. *Compos. Struct.* **2007**, *77*, 45-55. <https://doi.org/10.1016/j.compstruct.2005.06.005>
- [19] Kim, H.-S.; Yang, H.-S.; Kim, H.-J. Biodegradability and Mechanical Properties of Agro Flour Filled Polybutylene Succinate Biocomposites. *J. Appl. Polym. Sci.* **2005**, *97*, 1513-1521. <https://doi.org/10.1002/app.21905>
- [20] Torres, F.G.; Cubillas, M.L. Study of the Interfacial Properties of Natural Fibre Reinforced Polyethylene. *Polym. Test.* **2005**, *24*, 694-698. <http://dx.doi.org/10.1016/j.polymertesting.2005.05.004>
- [21] Arrakhiz, F.Z.; Elachaby, M.; Bouhfid, R.; Vaudreuil, S.; Essassi, M.; Qaiss, A. Mechanical and Thermal Properties of Polypropylene Reinforced with Alfa Fiber under Different Chemical Treatment. *Mater. Des.* **2012**, *35*, 318-322. <http://dx.doi.org/10.1016/j.matdes.2011.09.023>
- [22] Amin, S.; Amin, M. Thermoplastic Elastomeric (TPE) Materials and their Use in Outdoor Electrical Insulation. *Rev. Adv. Mater. Sci.* **2011**, *29*, 15-30.
- [23] Biron, M. *Thermoplastics and Thermoplastic Composites. Technical Information for Plastics Users*; Oxford: Butterworth-Heinemann, 2007.
- [24] Ichazo, M.N.; Albano, C.; Gonzalez, J.; Perera, R.; Candal, M.V. Polypropylene/Wood Flour Composites: Treatments and Properties. *Compos. Struct.* **2001**, *54*, 207-214. [https://doi.org/10.1016/S0263-8223\(01\)00089-7](https://doi.org/10.1016/S0263-8223(01)00089-7)
- [25] Lee, S.-H.; Ohkita, T. Mechanical and Thermal Flow Properties of Wood Flour-Biodegradable Polymer Composites. *J. Appl. Polym. Sci.* **2003**, *90*, 1900-1905. <https://doi.org/10.1002/app.12864>
- [26] Katz, H.S.; Milevski, J.V. *Handbook of Fillers for Plastics*; RAPRA: New York, 1987.
- [27] Mareri, P.; Bastide, S.; Binda, N.; Crespi, A. Mechanical Behaviour of Polypropylene Composites Containing Fine Mineral Filler: Effect of Filler Surface Treatment. *Compos. Sci. Technol.* **1998**, *58*, 747-752. [https://doi.org/10.1016/S0266-3538\(97\)00156-5](https://doi.org/10.1016/S0266-3538(97)00156-5)
- [28] Rosa, S.M.L.; Santos, E.F.; Ferreira, C.A.; Nachtigall, S.M.B. Studies on the Properties of Rice-Husk-Filled-PP Composites: Effect of Maleated PP. *Mater. Res.* **2009**, *12*, 333. <https://doi.org/10.1590/S1516-14392009000300014>
- [29] Tatrishvili, T.; Koberidze, Kh.; Mukbaniani, O. Quantum-Chemical AM1 Calculations for Hydride Addition Reaction of Methyltrimethoxysilane to 1,3-Cyclohexadiene. *Proceedings of the Georgian National Academy of Sciences* **2007**, *35*, 297-300.
- [30] Mukbaniani, O.; Tatrishvili, T.; Titvinidze, G. AM1 Calculations for Hydrosilylation Reaction of Methyltrimethoxysilane with Hexane-1. *Proceedings of the Georgian Academy of Science* **2006**, *32*, 109-114.
- [31] Tatrishvili, T.; Titvinidze, G.; Mukbaniani, O. AM1 Calculations for Hydride Addition Reaction of Methyltrimethoxysilane with Styrene. *Georgian Chemical Journal* **2006**, *6*, 58-59.
- [32] Mukbaniani, O.; Pirtskheliani, N.; Tatrishvili, T.; Patstasia, S. Hydrosilylation Reactions of  $\alpha,\omega$ -Bis(trimethylsiloxy) methylhydridesiloxane to Allyloxytriethoxysilane. *Georgia Chemical Journal* **2006**, *6*, 254-255.
- [33] Zhao, Y.; Truhlar, D.G. Density Functional Theory for Reaction Energies: Test of Meta and Hybrid Meta Functionals, Range-Separated Functionals, and Other High-Performance Functionals. *J. Chem. Theory Comput.* **2011**, *7*, 669-676. <https://doi.org/10.1021/ct1006604>
- [34] Wałęsa, R.; Kupka, T.; Broda, M.A. Density Functional Theory (DFT) Prediction of Structural and Spectroscopic Parameters of Cytosine Using Harmonic and Anharmonic Approximations. *Struct. Chem.* **2015**, *26*, 1083-1093. <https://doi.org/10.1007/s11224-015-0573-0>
- [35] Burke, K. Perspective on Density Functional Theory. *J. Chem. Phys.* **2012**, *136*, 150901. <https://doi.org/10.1063/1.4704546>
- [36] Kirste, B. Applications of Density Functional Theory to Theoretical Organic Chemistry. *Chem. Sci.* **2016**, *7*, 1000127. <https://refubium.fu-berlin.de/handle/fub188/15854>
- [37] Aneli, J.; Shamanauri, L.; Markarashvili, E.; Tatrishvili, T.; Mukbaniani, O. Polymer-Silicate Composites with Modified Minerals. *Chem. Chem. Technol.* **2017**, *11*, 201-209. <https://doi.org/10.23939/chcht11.02.201>
- [38] Mukbaniani, O.; Tatrishvili, T.; Markarashvili, E.; Londaridze, L.; Pachulia, Z.; Pirtskheliani, N. Synthesis of Triethoxy(Vinylphenethyl)Silane with Alkylation Reaction of Vinyltriethoxysilane to Styrene. *Oxid. Commun.* **2022**, *45*, 309-320.
- [39] Demchuk, Yu.; Gunka, V.; Pyshyiv, S.; Sidun, Yu.; Hrynychuk, Yu.; Kucinska-Lipka, Ju.; Bratychak, M. Slurry Surfacing Mixed on the Basis of Bitumen Modified with Phenol-Cresol-Formaldehyde Resin. *Chem. Chem. Technol.* **2020**, *14*, 251-256. <https://doi.org/10.23939/chcht14.02.251>
- [40] Bashta, B.; Astakhova, O.; Shyshchak, O.; Bratychak, M. Epoxy Resins Chemical Modification by Dibasic Acids. *Chem. Chem. Technol.* **2014**, *8*, 309-316. <https://doi.org/10.23939/chcht08.03.309>
- [41] Liu, C.; Tanaka, Y.; Fujimoto Y. Viscosity Transient Phenomenon during Drop Impact Testing and Its Simple Dynamics Model. *World Journal of Mechanics* **2015**, *5*, 33-41. <http://dx.doi.org/10.4236/wjm.2015.53004>
- [42] Titvinidze, G.; Tatrishvili, T.; Mukbaniani, O. Chemical Modification of Styrene with Vinyl Containing Organosiloxane via Diels-Alder Reactions. Abstracts of Communications of International

Conference Enikolopov's Readings, Erevan, Armenia, 4-7 October, 2006; p. 74.

[43] Swanson, N. Polybutadiene Graft Copolymers as Coupling Agents in Rubber Compounding. Ph.D. Thesis, Graduate Faculty of the University of Akron, USA, 2016.

[44] Guy, L.; Pevere, V.; Vidal, T. Use of a Specific Functionalised Organosilicon Compound as a Coupling Agent in an Isoprene Elastomer Composition Including a Reinforcing Inorganic Filler. US 0225233A1, 2012.

[45] Smith, B.C. Distinguishing Structural Isomers: Mono- and Disubstituted Benzene Rings. *Spectroscopy* **2016**, *31*, 36-39.

[46] <https://www.nmrdb.org/13c/index.shtml?v=v2.121.0>

[47] <https://docs.chemaxon.com/display/docs/nmr-predictor.md>

[48] ChemBioDraw Ultra 12.

[https://www.perkinelmer.com/Product/chemoffice-plus-cloud-\[31\].](https://www.perkinelmer.com/Product/chemoffice-plus-cloud-[31].)

[30]. chemofficepc?fbclid=IwAR2M\_sx\_7vTofwMAugXMb0M4xbyylk yHa4xt0jcRdrETOC8qDtpmSHjdudA

[49] MestreNova. <https://mestrelab.com/software/mnova/nmr/>

[50] Mukbaniani, O.; Tatrishvili, T.; Pachulia, Z.; Londaridze, L.; Markarashvili, E.; Pirtskheliani, N. Quantum-Chemical Modeling of Hydrosilylation Reaction of Triethoxysilane to Divinylbenzene.

*Chem. Chem. Technol.* **2022**, *16*, 499-506.

<https://doi.org/10.23939/chcht16.04.499>

[51] Febrianto, F.; Yoshioka, M.; Nagai, Y.; Mihara, M.; Shiraiishi, N. Composites of Wood and Trans-1,4-isoprene Rubber II: Processing Conditions for Production of the Composites. *Wood Sci. Technol.* **2001**, *35*, 297-310. <https://doi.org/10.1007/s002260100102>

[52] Mukbaniani, O.; Brostow, W.; Aneli, J.; Londaridze, L.; Markarashvili, E.; Tatrishvili, T.; Gencel, O. Wood Sawdust Plus Silylated Styrene Composites with Low Water Absorption. *Chem. Chem. Technol.* **2022**, *16*, 377-386. <https://doi.org/10.23939/chcht16.03.377>

[53] Mukbaniani, O.; Aneli, J.; Tatrishvili, T.; Markarashvili, E.; Londaridze, L.; Kvinikadze, N.; Kakalashvili, L. Wood Polymer

Composite Based on a Styrene and Triethoxy(Vinylphenethyl)Silane. *Chem. Chem. Technol.* **2023**, *17*, 35-44. <https://doi.org/10.23939/chcht17.01.035>

[54] Kalogeras, I.M.; Hagg Lobland, H.E. The Nature of the Glassy State: Structure and Transitions. *J. Mater. Educ.* **2012**, *34*, 69-94.

*Received: September 06, 2022 / Revised: November 13, 2022 /*

*Accepted: December 20, 2022*

## РЕАКЦІЯ ФРІДЕЛЯ–КРАФТСА ВІНІЛТРИМЕТОКСИСИЛАНУ ЗІ СТИРЕНОМ ТА КОМПОЗИТНІ МАТЕРІАЛИ НА ЇХНІЙ ОСНОВІ

**Анотація.** Здійснено алкілювання стирену вінілтриметоксисиланом за реакцію Фріделя–Крафтса в присутності безводного  $AlCl_3$ . Отримано алкокси(4-вінілфенетил)силан. Синтезовані продукти ідентифікували за допомогою  $^1H$ ,  $^{13}C$ , COSY ЯМР та FTIR спектроскопії. Обговорено розрахунки з використанням методу квантово-хімічної неемпіричної теорії функціоналу густини (DFT) для реакції між вінілтриметоксисиланом і стиреном, здійсненої за орто-, мета- і пара-положеннями. Для теоретичного моделювання використовували програму онлайн-прогнозування "Priroda-04: A quantum-chemical program suite". За різних температур і тисків методом гарячого пресування або екструзії були одержані композиційні матеріали на основі деревної тирси різної дисперсності та синтезованого триметоксисилірованого стирену як в'язучого й армувального агента зі ступенями силілування (5 %) у присутності різноманітних органічних/неорганічних добавок, антипіренів та антиоксидантів. Досліджено фізико-механічні властивості композитів.

**Ключові слова:** триметокси(4-вінілфенетил)силан, реакція алкілювання, FTIR і ЯМР спектроскопія, DFT.