PREPARATION OF ORGANOSILIC RESIN BASED ON PARTIALLY HYDROLYZED VEGETABLE OIL AND STUDY OF ITS PROPERTIES

Eshmurodov Kh.E., Djalilov A.T.
Tashkent research institute of chemical technology
e-mail: khurshideshmurodov@mail.com

Abstract. *In this study, a stepwise synthesis method for obtaining an organosilicon resin based on partially hydrolyzed vegetable oil was developed. In the first stage, monoglyceride was obtained by opening two ester bonds of triglyceride through alkaline hydrolysis. In the second stage, the terminal –OH group of the monoglyceride was selectively chlorinated with HCl in the presence of a* $ZnCl_2$ *catalyst. In the third stage, the chlorinated monoglyceride was subjected to a nucleophilic substitution reaction with sodium metasilicate, resulting in a hybrid siloxane–monoglyceride containing Si–O–C bonds. In the fourth stage, the obtained product underwent polycondensation with phthalic anhydride to form an organosilicon resin. IR and Raman spectroscopy analyses confirmed the presence of aromatic rings, carbonyl groups, siloxane (Si–O–Si), and silyl-ether (Si–O–C) linkages in the structure of the resin.*

Introduction. Organosilicon compounds are widely used in polymer chemistry, coating materials, construction chemistry, and composite manufacturing due to their high thermal stability, hydrophobicity, dielectric durability, and chemical inertness. Polymers containing siloxane structures are particularly distinguished by their exceptional resistance to atmospheric influences and oxidation. Therefore, siloxane–polyesters modified with organic fragments have recently been regarded as one of the most promising directions for producing organo-silicate materials from inexpensive and renewable raw materials.

Monoglycerides derived from vegetable oils represent a natural, environmentally friendly, and renewable resource, and the synthesis of hybrid organosilicon polymers based on them is considered highly relevant in biopolymer technology. The primary and secondary hydroxyl groups in their structure can undergo reactions with silicates, organic anhydrides, and chlorinating agents, enabling the formation of complex polycondensation systems. In particular, the reaction of chlorinated monoglycerides with sodium metasilicate leads to the formation of Si–O–C bonds, allowing the synthesis of organic–inorganic hybrid polyesters.

The aim of this study is to scientifically substantiate the process of obtaining an organosilicon resin by preparing monoglyceride through partial hydrolysis of vegetable oil, performing its selective chlorination, reacting it with sodium metasilicate, and conducting polycondensation with phthalic anhydride. Additionally, the work focuses on determining the structural characteristics of the synthesized materials using IR and Raman spectroscopy and evaluating the physicochemical properties of the resulting resin.

Experimental part. The synthesis of the organosilicon resin based on partially hydrolyzed vegetable oil was carried out in the following stages: in the first stage, monoglyceride was obtained by partially alkaline hydrolyzing the vegetable oil. For this purpose, 0.11 mol of triglyceride was subjected to two-thirds hydrolysis with 0.22 mol of NaOH:

$$\text{(RCOO-CH}_2\text{-CH(OOCR)-CH}_2\text{-OOCR) + 2NaOH} \rightarrow$$
$$\rightarrow \text{CH}_2\text{(OH)-CH(OOCR)-CH}_2\text{-OH + 2RCOONa}$$

R – represents the fatty acid residue. NaOH cleaves the two terminal ester bonds of the triglyceride via nucleophilic attack, while the central ester bond remains intact. The hydrolysis yield was 85–90%. The reaction mixture was washed with water, the sodium salt of the higher fatty acid was removed, and the monoglyceride was obtained.

In the second stage, the obtained monoglyceride was chlorinated with HCl: the monoglyceride was reacted with HCl in the presence of a $ZnCl_2$ catalyst at 120 °C for 3 hours:

$$\text{CH}_2\text{(OH)-CH(OOCR)-CH}_2\text{-OH} \rightarrow \text{CH}_2\text{(OH)-CH(OOCR)-CH}_2\text{-Cl + H}_2\text{O}$$

The process proceeds according to the following mechanism: $ZnCl_2$ acts as a catalyst by activating the hydroxyl group and facilitating the nucleophilic attack of HCl. One of the terminal –OH groups (CH_2–OH) is selectively chlorinated. The chlorination yield was 85–88%. The product was neutralized with a 5% $NaHCO_3$ solution, dried, and purified by vacuum distillation.

In the third stage, the chlorinated monoglyceride was reacted with sodium metasilicate:

$$\text{2CH}_2\text{(OH)-CH(OOCR)-CH}_2\text{-Cl + Na}_2\text{SiO}_3 \rightarrow$$
$$\rightarrow \text{CH}_2\text{(OH)-CH(OOCR)-CH}_2\text{-O-Si(=O)-O-CH}_2\text{-CH(OOCR)-CH}_2\text{(OH) + 2NaCl}$$

The reaction mechanism is a nucleophilic substitution in which the Cl^- group leaves and an O–Si bond is formed. The resulting NaCl by-product was washed out with water, while the organic layer was extracted with diethyl ether and dried.

In the fourth stage, the obtained siloxane–monoglyceride was subjected to polycondensation with phthalic anhydride. For this purpose, 0.07 mol of siloxane–monoglyceride (40 g) was reacted with 0.07 mol of phthalic anhydride (10.3 g) at 180 °C for 4 hours under vacuum (0.25 atm) in the presence of 0.5 g of PTSA catalyst:

$$n[CH_2(OH)\text{-}C(COOR)\text{-}CH_2\text{-}O\text{-}Si(=O)\text{-}O\text{-}CH_2\text{-}C(COOR)\text{-}CH_2(OH)] + nC_8H_4O_3 \rightarrow$$
$$\rightarrow HO\text{-}[CH_2\text{-}C(COOR)\text{-}CH_2\text{-}O\text{-}Si(=O)\text{-}O\text{-}CH_2\text{-}C(COOR)\text{-}CH_2\text{-}O\text{-}$$
$$\text{-}CO\text{-}C_6H_4\text{-}CO\text{-}]_n\text{-}OH + nH_2O$$

In this reaction, the terminal –OH group of the monoglyceride reacts with phthalic anhydride, resulting in an esterification process that leads to chain elongation, with a yield of 82%. The product was purified by vacuum filtration, washed with diethyl ether, and dried at 80 °C for 12 hours. The resulting resin was light yellow, viscous, and soluble in organic solvents such as toluene and DMF.

Physicochemical and mechanical properties of the resulting organosilicon resin.

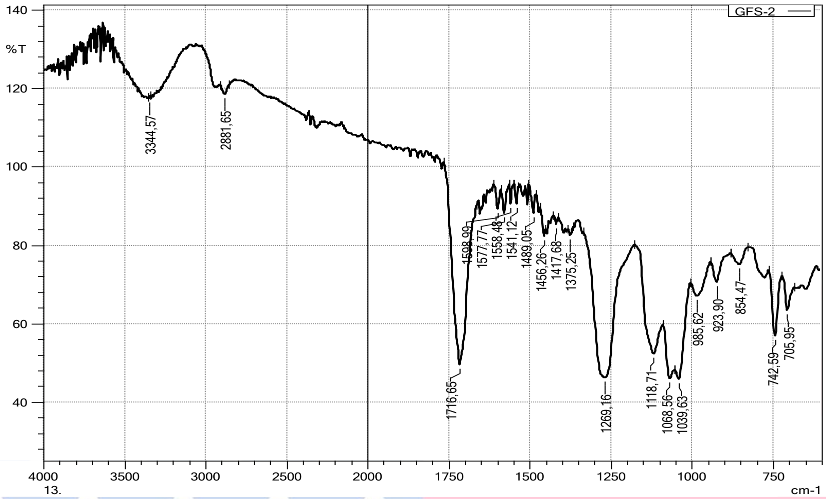

Figure 1. IR spectrum of the resulting organosilicon resin

In the IR spectrum of the obtained organosilicon resin, the broad and medium-intensity absorption band at 3344.57 cm^{-1} corresponds to the valence vibrations of terminal –OH groups in the polymer chain, confirming the presence of unreacted hydroxyl groups remaining after polycondensation with phthalic anhydride, as well as the HO–[…]–OH terminal fragments in the structure. The strong peak at 1716.65 cm^{-1} is attributed to the carbonyl (C=O) stretching vibrations originating from fatty acid esters and phthalate esters, indicating the successful incorporation of the chlorinated monoglyceride into the phthalate structure. The bands at 1598.99 and 1577.77 cm^{-1} correspond to aromatic C=C stretching vibrations, confirming the complete integration of the phthalic anhydride fragment. The strong and wide bands observed at 1118.71 and 1068.56 cm^{-1} (along with 1039.63 cm^{-1}) are fully consistent with the Si–O–Si and Si–O–C stretching vibrations formed as a result of the nucleophilic substitution reaction with sodium metasilicate. These signals reliably demonstrate the selectivity of the chlorination stage and the successful introduction of the siloxane bridge through the metasilicate component.

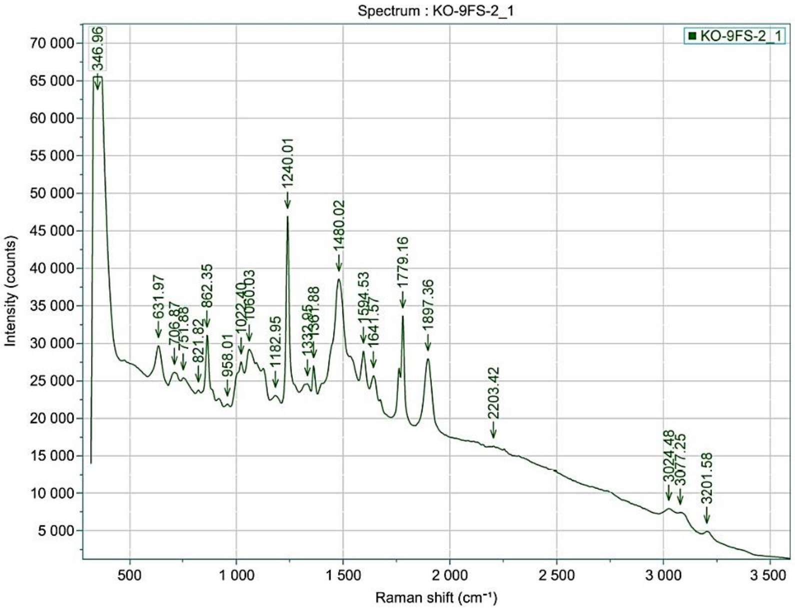

Figure 2. Raman spectrum of the resulting organosilicon resin

The clear peaks in the Raman spectrum of the obtained organosilicon resin fully confirm its chemical structure: the peak at 3086.91 cm^{-1} corresponds to aromatic =C-H vibrations, indicating the presence of a phthalate ring; the strong peak at 1779.16 cm^{-1} corresponds to a high-energy carbonyl (C=O) vibration characteristic of phthalate; the peak at 1643.31 cm^{-1} corresponds to an aromatic C=C resonance vibration; the peak at 1126.08 cm^{-1} corresponds to the Si-O-C bond and the peak at 1060.03 cm^{-1} corresponds to the Si-O-Si stretching vibration characteristic of the siloxane network, which reliably confirms the successful completion of the siloxane bridge formed by the reaction with sodium metasilicate and the chlorination step, as well as the hybrid structure connected by the -O-Si(=O)-O- bridge in the formula.

Conclusion. In this study, an organosilicon resin was successfully obtained through sequential stages of partial hydrolysis, chlorination, silicate substitution, and polycondensation based on vegetable oil. The two ester bonds of the triglyceride were efficiently cleaved through alkaline hydrolysis, resulting in the development of a high-yield monoglyceride production method. The terminal hydroxyl group of the monoglyceride was selectively chlorinated with a yield of 85–88% in the presence of a $ZnCl_2$ catalyst. The reaction of the chlorinated monoglyceride with sodium metasilicate proceeded with high selectivity, forming a hybrid structure containing a siloxane bridge through Si–O–C linkages. The polycondensation process with phthalic anhydride yielded the final organosilicon resin with an 82% efficiency. IR and Raman spectral analyses clearly confirmed the presence of aromatic rings, carbonyl groups, siloxane (Si–O–Si), and silyl-ether (Si–O–C) linkages within the resin structure. Owing to its flexibility, hydrophobicity, and good solubility in organic solvents, the obtained organosilicon resin shows strong potential for applications in coating materials, composites, surface finishes, and specialized polymer binders.

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