Rheological Investigation of Sol-Gel Systems Based on 3-Methacryl-Oxypropyl Trimethoxysilane

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Abstract. The influence of various factors (temperature, concentration of starting substances and catalyst of sol-gel process) on the rheological behavior of sol-gel systems on the basis of the organic-inorganic precursor – 3-methacryloxypropyl trimethoxysilane – was investigated by viscosimetry. The elastic and friction components of viscosity were estimated from the gradient dependence measurements using the optimization method. The integral activation energy of the gelation process in the studied sol-gel systems was calculated.

Keywords – sol-gel system, 3-methacryloxypropyl trimethoxysilane, dynamic viscosity, gradient dependence of viscosity, activation energy
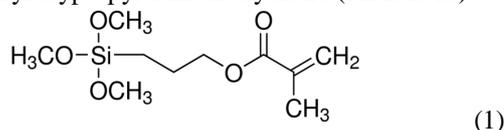
I. Introduction

Membrane science and technology are of great interest for many researchers and are constantly considered as one of the priority scientific and technical directions. Membranes are widely used in alternative energy, electrodialysis, ion-exchange processes, etc.

A lot of membranes are synthesized on the basis of hybrid organic-inorganic materials, what ensures the achievement of desired properties. Sol-gel technology has a number of advantages in comparison with other methods of synthesis: simplicity, eco-friendliness, possibility of modification of material properties by introducing modifying substances at the synthesis stage.

One way of obtaining hybrid organic-inorganic membranes with the use of sol-gel technology is to form them from organic-inorganic precursors that contain organic functional groups and inorganic alkoxysilane groups undergoing sol-gel transformation.

3-methacryloxypropyl trimethoxysilane (MAPTMS)

$$\text{H}_3\text{CO}-\underset{\underset{\text{OCH}_3}{|}}{\overset{\overset{\text{OCH}_3}{|}}{\text{Si}}}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\underset{\underset{\text{CH}_3}{|}}{\text{C}}\overset{\overset{\text{O}}{\parallel}}{}=\text{CH}_2 \tag{1}$$

is one of the promising starting materials for such syntheses because it contains methacrylic fragments capable to form C-C bonds in polymerization process and alkoxysilane groups near Si atom that can form siloxane chains in sol-gel process [1, 2].

MAPTMS is often used together with the other alkoxysilane – tetraethoxysilane (TEOS), which is the most commonly used alcoxysilane in sol-gel synthesis. When added to sol-gel system based on TEOS, MAPTMS acts as a structural modifier. As a result of the modifier influence, the final siloxane network acquires the necessary properties (for example, hydrophobicity, flexibility). Thus, in [3] a mixture of MAPTMS and TEOS was used in a molar ratio of 4: 1. Hydrolysis of a mixture of precursors was carried out in a solution ethanol – water. Investigation of sol-gel process of alkoxysilanes mixture by ^{29}Si NMR and FTIR allowed to optimize the duration of hydrolysis of both components and subsequently to prepare organic-inorganic hybrid materials – sol-gel coatings for metallic surfaces.

For the wider use of precursor MAPTMS in sol-gel processes, it is necessary to study its rheological behavior under different conditions.

II. Experimental

Solutions of sol-gel precursors were prepared by mixing TEOS, MPTMS, ethanol, water and phosphoric acid in appropriate ratios, at constant stirring on a magnetic stirrer (500 rpm) at different temperatures. The rheological behavior of these systems was investigated using the rotary viscosimeter RHEOTEST 2.1 (VEB MLW, GDR).

For sol-gel precursors the dependence between the shear stress τ and the shear rate D_r was established. Dynamic viscosity was determined by the ratio: $\eta = \tau / D_r$, where η is the dynamic viscosity (Pa • s); τ is shear stress (Pa); D_r is the shear rate (s^{-1}).

III. Results and discussion

The percolation point corresponds to such concentration of macromolecules and their conformational size, at which the conformational volumes of macromolecules begin to overlap leading to a sharp increase in viscosity of sol-gel system. Consequently, the state of gelation can be estimated by monitoring the changes in viscosity of the system in time.

Dynamics of viscosity of sol-gel systems was investigated at high angular speeds of rotation of the working cylinder (ω = 4.05 rps). We obtained the dependencies of viscosity:

- on temperature for 5 sol-gel systems of different compositions;
- on MAPTMS content;
- on the content of sol-gel process catalyst – orthophosphoric acid. The exaple of measured dependencies is presented in Fig. 1.
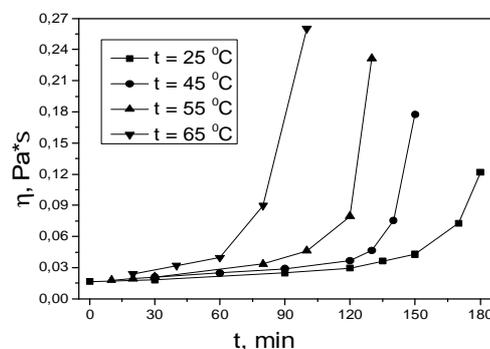

Fig. 1. Viscosity change in time for sol-gel system MAPTMS: TEOS: C_2H_5OH: H_3PO_4: H_2O = = 0.25: 0.75: 4: 1.2: 4 (mol) at different temperatures

From obtained dependencies the time of achievement of percolation point t_g, which corresponds to the beginning of gelation process, was determined. The obtained data are summarized in Table. 1.

TABLE 1

DYNAMICS OF SOL-GEL SYSTEMS STRUCTURING

System composition (mol)	H_3PO_4 (mol)	Temp° C	t_g min
MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O = = 0,4:0,6:4:X:4	1,2	25	300
MAPTMS:TEOS:C_2H_5OH: :H_3PO_4:H_2O = = 0,25:0,75:4:X:4	1,2	25	150
		45	130
		55	100
		65	70
	1,8	45	130
		65	120
TEOS:C_2H_5OH:H_3PO_4: :H_2O = 1:4:X:4	1,2	25	100
		45	30
		55	10
		65	5
	1,8	45	30
		65	7

The temperature dependence of the gelation time can be described by the Arrhenius equation: $\ln (t_g) = A + E / RT$, where E is activation energy of the gelation process.
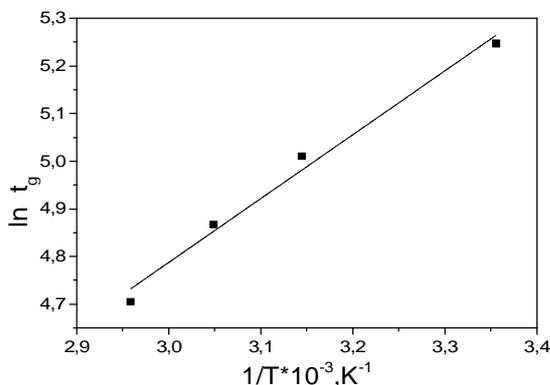
Fig. 2. Temperature dependence of gelation time in sol-gel system MAPTMS: TEOS: C_2H_5OH: H_3PO_4: H_2O = = 0.25: 0.75: 4: 1.2: 4 (mol)

Experimentally determined activation energy of gelation process is 22.5 kJ/mol for the system MAPTMS: TEOS: C_2H_5OH: H_3PO_4: H_2O = 0.5: 0.75: 4: 1.2: 4 (mol) and 44.9 kJ/mol for the system TEOS : C_2H_5OH: H_3PO_4: H_2O = 1: 4: 1.2: 4 (mol).

The gradient dependence of sol-gel system viscosity was measured in the range of speeds of the working cylinder of 0.5 – 243 rpm (Fig. 3). The frictional and elastic components of viscosity and coefficient b, which characterizes the segmental motion of macromolecules, for each sol-gel system at different conditions were calculated using the optimization method in ORIGIN 5.0 program.
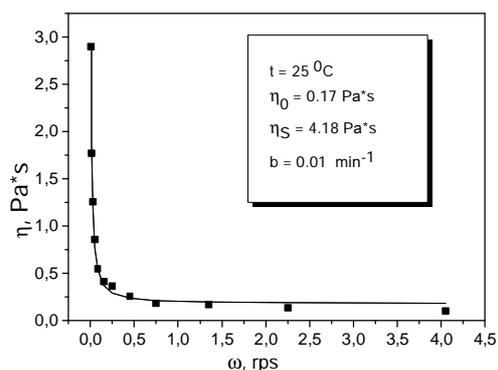
Fig. 3. Gradient dependence of viscosity of the system MAPTMS: TEOS: C_2H_5OH: H_3PO_4: H_2O = = 0.4: 0.6: 4: 1.2: 4 (mol)

Calculated values of viscisity parameters show their dependence on the system composition, temperature and the catalyst content. In all cases, the elastic component of the viscosity is greater than the frictional one, which indicates a significant contribution to viscosity of the segmental motion of macromolecules. With increasing temperature, we observe the growth of viscosity, and the elastic component changes more significantly.

Conclusion

Investigation of sol-gel systems viscosity of various composition based on precursors TEOS and MAPTMS allowed to determine the effect of temperature, composition of the system, the catalyst concentration on the time of achievement of percolation point, when gelation occurs. These results are of practical importance for synthesis of organic-inorganic composites using sol-gel process. It was established that the replacement of TEOS by MAPTMS slows down the gelation process. Studying of the gradient dependence of viscosity of sol-gel systems allowed to determine the frictional η_o and elastic η_s components of viscosity depending on temperature and the initial composition of the system.

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