

Thin Coatings Based on Highly Filled Syntactic Foams with Siloxane Bonds

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Abstract In this article was explore the process of preparation of thin coatings based on syntactic foams with silicone adhesive. Proposed chemist of the curing process. The regularities of changes in the physical and mechanical properties of materials on the mixture composition. Was made the choice of optimal parameters form a coating. Resulting coating may be used in construction, engineering, shipbuilding, aviation and other industries as heat-insulating and sound-proof material.

Keywords: syntactic foams, silicones, hollow glass spheres, coating

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1. Introduction

Syntactic foams are used in various fields of science and technology comparatively for a long time. They are used in such spheres as aviation, aerospace, mechanical engineering, shipbuilding, construction. The advantages of these materials include high physical and mechanical properties in combination with low density. However, the use of the polymer matrix as a binder causes the polymer limits of the material functionality due to the low thermal resistance and susceptibility to decomposition by the influence of UV radiation. In this connection silicone binders stir considerable interest due to their highly resistance to the temperature and adverse weather conditions. However, the silicone binders are characterized by not enough high mechanical strength. The object of this work was to find the optimal process conditions for obtaining thin coatings on the basis of syntactic foam with a binder oligodimetilsiloksan with the end OH-groups and the study of physical and mechanical properties of the resulting materials.

2. Objects and Methods

1. Low molecular weight heat-resistant rubber dimetilsiloksan-linear oligo dimetilsiloksan [ODMS] with the end OH-groups and a molecular weight of 20,000 to 75,000. This material is produced at the plant of synthetic rubber (Kazan) branded SKTN-A (B) (a low molecular weight heat-resistant rubber dimetilsiloksan) in accordance with GOST 13835-73.

2. 50% solution of diethyl dicaprylate tin tetraetoksilane (catalyst 18) is used as a hardening agent, in accordance with TU 6-02-805-78.

3. Hollow glass microspheres made of sodium silicate glass with packed density 18 kg/m³.

2.1. Methods of Investigation

1. Test Method for Tensile ASTM D3039 (GOST 15873-70);

2. Standard Test Method for Youngs' Modulus, Tangent Modulus, and Chord Modulus. ASTM E 111 (Standard Method for determination of modulus of elasticity in accordance with GOST 9550-81).

3. Adhesion of the polymer film (tensile separation) was determined by breaking steel plate in diameter 1.5 cm onto a substrate polymer film. Separation has been carried out by using a digital Adhesion PSO-MG4 in a form of the processor electronic load cell automatically recalculated a force of strength in the separation.

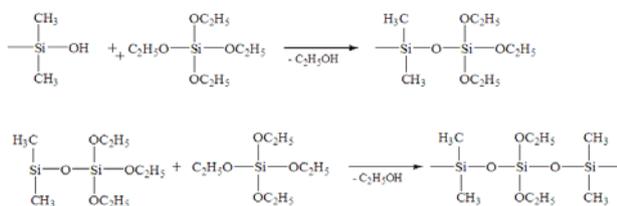
4. Standard Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation. ASTM D2794.

3. Experiment

The transformation of low molecular weight linear organosiloxanes with the end OH groups in the three-dimensional structure is under the influence of tetraethoxysilane, products of it partial hydrolysis (Ethyl silicate 40) and other organosilicon compounds. Catalysts are organostanic compounds, lead stearate, and organic compounds of other transition metals [1,2,3]. The mechanism of action of organostanic catalysts is explained by the formation of the intermediate activated complex with subsequent elimination of alcohol, catalyst regeneration and the formation of a siloxane bond [4,5]. During the three-dimensional polycondensation reaction, the formation of the gel, as stitched chemical relationship

between linear macromolecules cannot be separated from each other under the influence of the solvent. Gel represents one giant macromolecule. The emerging and increasing of the gel is accompanied by a sharp increasing of the system viscosity of. In this connection the reaction of the functional groups is slowing, and the polycondensation at this stage rarely comes through.

Presumably the reaction proceeds with the release of ethyl alcohol by the scheme:



Etc.

For polyfunctional monomer the conversion level in the gel point depends on their functionality.

The completion level of the reaction (p) can be calculated by the formula (1) [6]:

$$P = 2 / f - 2 / x - f \quad (1)$$

where f -the system functionality; x -average degree of polycondensation.

At high values of the equation x , $(2 / x - f)$ tends to zero. Then the system polycondensation containing an equimolar ratio of the components (2 mol with the end dimethylsiloxane OH groups have 1 mol of tetraethoxysilane), the functionality of which is 2.66, the degree of the polycondensation reaction completion is $2 / 2,66 = 0.75$.

Growth chain stage defines all the main characteristics of the polymer: MW, the polymer composition, molecular weight distribution. Both physical (viscosity increase system shielding chain reaction centers solvent molecules) and chemical factors lead to the interruption of the chain growth. The influence of the glass filler on the polycondensation polydimethylsiloxane and tetraethoxysilane may occur due to the presence of OH groups on the surface of the glass. Thus, in [7] that the colloidal particles of Aerosil (size 3-10 nm) can interact with the OH-groups and block the access of the hardener to them.

To determine the effect of the filler on the polycondensation, the control experiment using the composition as unfilled and filled: Aerosil and hollow microspheres, was set up (Table 1).

Table 1. The influence of the filler on the gel time of 17.5% solution of ODMS in toluene ($T_0 = 298 \text{ K}$)

Filler mp \ 100 mp binder	The concentration of OH groups on the surface of the filler, group / nm ² *	Catalyst 18, mp	Gel time, min.
PMS	Aerosil		
-	-	2	164 ± 8
-	-	6	10 ± 1
150	4,2 – 5,7	2	171 ± 7
150	4,2 – 5,7	6	9 ± 2
-	10	2	No gel
-	10	3	
-	3	6	420 ± 12

* - The concentration of hydroxyl groups on the surface of the filler [8]

The experiments showed that the PSM in contrast to Aerosil, due to the larger size, don't significantly effect on the rate of polycondensation reaction. Thus, in description of the polydimethylsiloxane curing kinetics the influence of glass microspheres can be neglected, it can significantly simplify the description of the kinetic process scheme.

3.1. The Selection of Optimal Process Curing Parameters

The method for coating compositions on the protected surface is considered to be promising to obtain thin coatings.

Table 2. SF density dependence on the composition and viscosity of the composition

The binder content in SP, % (v)	Concentration ODMS in toluene, %	The viscosity of the composition at $T = 298 \text{ K}$, mPa*s	Experimental coating density, kg/m ²	calculated density, kg/m ²
10	17,5	650	291 ± 15	297
	19,0	827	246 ± 18	
20	19,0	594	373 ± 12	377
	21,0	731	326 ± 20	
30	20,0	505	484 ± 14	476
	29,0	620	441 ± 17	
40	21,0	465	52 ± 1	574
	24,0	549	524 ± 15	
50	22,0	386	634 ± 11	643
	26,0	475	603 ± 17	
60	26,0	301	726 ± 7	712
	30,0	396	697 ± 11	
70	30,0	247	776 ± 9	780
	34,0	309	740 ± 19	
80	34,0	196	859 ± 9	849
	38,0	238	801 ± 16	
90	38,0	143	915 ± 7	917
	42,0	190	884 ± 9	
100	42,0	98	986 ± 4	986
	46,0	153	971 ± 9	

Such index as the density of filled composites with reasonable accuracy is calculated by the following formula:

$$\rho_m = \rho_{ms}(1 - \theta_{ms}) + \rho_b \theta_b \quad (2)$$

where ρ_{ms}, ρ_b – the average density of the microspheres and binder, respectively; θ_{cb} – the volume fraction of the binder.

The optimal composition has been considered ones, which density (ρ) was approximately due to the calculated density.

Comparative characteristics of thin-layer syntactic foams (SF) (Table 2) derived from a composition with different viscosities show that the determining parameter for achieving the calculated density SF is the viscosity of the system. In this connection it is necessary to strictly control the viscosity of the composition during the deposition process.

A curing agent has been added composition was deposited using a specialized spray. Spray-productivity is converged layer by layer. The thickness of the first layer is of 90-150 mm, the thickness of subsequent layers is 200-400 microns. Exposure time of each layer in the air at a temperature of 298 K is 0.75 h. Predetermined thickness foam coating has been reached it is matured until all the solvent is removed. The rate of removal of the solvent from the joint venture is largely determined by the content of the glass microspheres in the composition (Figure 1). This is explained by the fact that the introduction of the microspheres increases the rate of diffusion of the solvent. This process can be sped up by using drying at elevated temperatures.

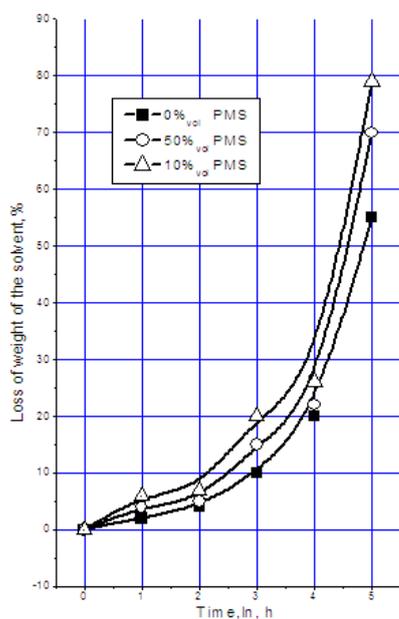


Figure 1. Solvent release during the drying syntactic coverage

In this case, due to the temperature increasing of 60 K, the time of complete solvent removal is reduced by 33 times. Varying in small range, the concentration of hardener can be changed without noticeable deterioration of physical and mechanical properties of the filled material to regulate the time processing of the track from 30 minutes to 3 hours.

3.2. Physical and Mechanical Properties of Building Materials Based on Polydimethylsiloxane

Physical and mechanical properties of the joint venture is defined as natural binder and filler, and production technologies.

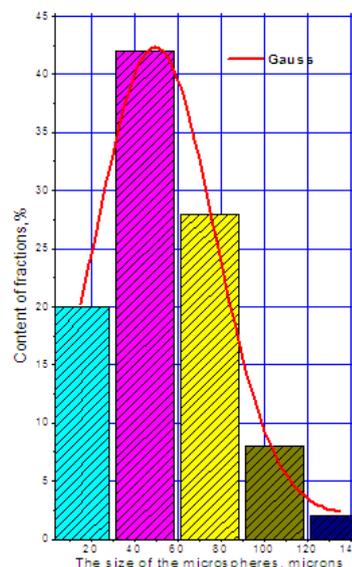


Figure 2. Fractional composition of hollow glass microspheres.

Particle size and size distribution of filler in some way affects the strength characteristics of the filler-binder. Experimental determination of the grain size distribution of PSM is shown in Figure 2. These characteristics indicate that the grain size distribution of PSM is shifted to fines.

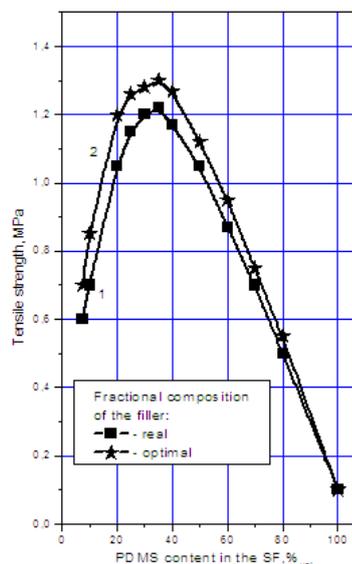


Figure 3. The dependence of the tensile strength of the PDMS content in the SF

Based on theoretical assumptions and numerous studies of strength properties, fractional composition of the investigated PSM batch is not optimal. The optimal size distribution foresees gradual filling Intersectoral space of large filler particles by smaller ones, etc. in accordance with the data [9]. However, when filled elastomers

strength increasing is marked by increasing the filler surface area. Therefore, in this case, you can expect the recouping of the strength loss due to sub-optimal size distribution by increasing of the filler specific surface of. Indeed the study of tensile strength has shown (Figure 3) that the joint venture as a specially prepared optimal fractional composition (curve 2) and the usual (curve 1) is not significantly different from each other.

In this connection further studies in obtaining experimental batches SP filler was used with conventional fractional composition, as in our case, the change of fractional composition of PSM due to their high cost is economically viable and technically not effective.

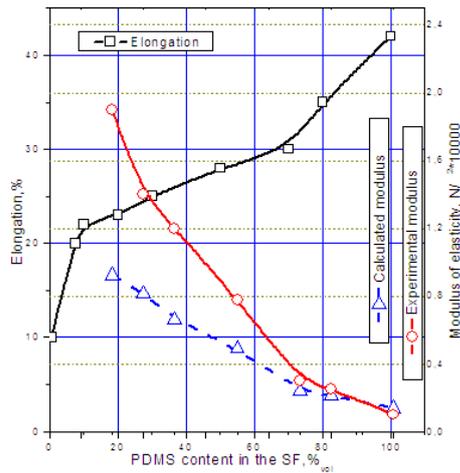


Figure 4. Dependence of elongation and modulus of PDMS content in the SP

With the introduction of the filler in elastomer the increasing of the tensile strength of the material is observed (Figure 4). Hardening can be explained by using a model of slip elastomer molecules along the surface of the filler (Danneberga model [10]). In the absence of filler for the first the rush of short circuit is observed, and in the presence of filler the number of loaded circuits is increased, and accordingly a redistribution of the load is occurred. With the decreasing of the volume fraction of PDMS below 30%, a sharp decreasing of the joint venture tensile strength is observed, due to the lack of binding in the Intersectoral space. In addition, the amplification effect is possible also due to the formation of chemical bonds between the binder and filler, such as unreacted hydroxyl groups of PDMS and silanol groups on the surface of the glass filler.

The elastic modulus of elastomer-a spherical filler is determined, first of all, by the amount of filler increasing the stiffness of the material. The elastic modulus of such compositions can be determined from the equation of Guth and Gold [11]:

$$E = E_0(1 + 2,5C + 14,1C^2) \quad (3)$$

where E and E_0 -modules – filled and non-filled elastomer; C-volume concentration of the filler.

The comparison of experimental and calculated data shows significant differences in modulus values calculated according to equation 4.2 (curve 2 in Figure 4) with the actual values (curve 1 in Figure 4). This is probably due to the significant polydispersity composition PSM. Analysis of the dependence of the modulus of elasticity of

the PDMS content in the joint venture has identified the possibility of describing this dependence with reasonable accuracy the following polynomial relationship:

$$Y = 2,21 - 0,039 * X + 0,0018 * X^2$$

The usage of the binder concentration as an argument, not filler, as it is shown in Equation Guth and Gold, explained the fact that for highly filled systems, as the joint ventures, is more convenient for calculations.

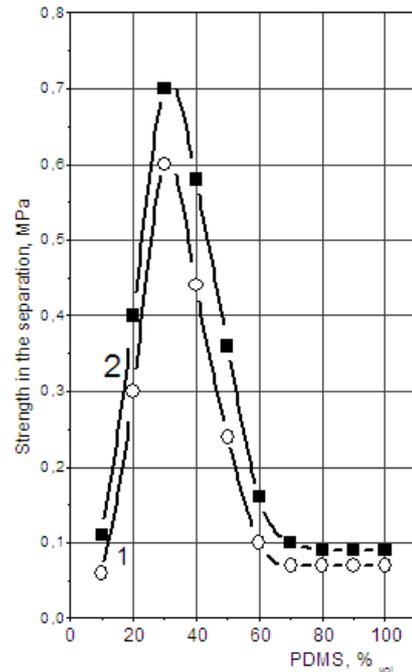


Figure 5. Dependence of the strength of the separation of the content of PDMS in the SF

The examination of the joint venture strength in separation from deposited substrates of different nature has shown that the dependence of this value on the content of the binder has a pronounced extreme nature (Figure 5). Optimal joint venture with the substrate, regardless of its nature, is achieved when the content of the binder is 30 ÷ 45% vol (curves 1, 2). With the introduction of PDMS up to 30% vol the increasing of the strength characteristics in the separation by increasing the tensile strength of the material is observed.

The fracture behavior of the joint venture for given values of cohesive, indicates the high material adhesion to the substrate. With the further increasing in the content of PDMS the character of separation is mostly mixed. The increasing of the PDMS content more than 45% vol leads to the reduction of the strength characteristics in the separation. This can be explained by the fact that in the composition the decreasing of polarized hydroxyl groups formed by the introduction of a filler is observed, and thus the reducing of the number of hydrogen bonds between the SP and the substrate ensures the material adhesion [12,13]. The nature of the separation of material from a substrate in such content is generally adhesive. The strength characteristics of the joint venture in the separation is largely dependent on the substrate material. Since adhesion of the joint venture on a substrate made of steel grade 3 (curve 2), is average higher of 20%, than on a substrate made of aluminum (curve 1) Figure 5. This is

likely due to the presence of the oxide film on the aluminum surface and therefore the difference in the number of hydroxyl groups on the surface of materials.

In order to improve the adhesive properties of the SP on the substrate surface sublayer VIKSINT-28 sealant is pre-deposited. It is a low molecular weight silicone rubber SKTN-1 filled by iron oxide (redoksaydom) [14], with a thickness of 40-50 microns. Sublayer has been deposited by conventional spray in a form of 40% encapsulant solution in toluene with adding curing agent and further

curing at room temperature for 72 hours. The use of an adhesive under layer increases the strength under the separation of an average of 20% irrespective of the substrate materials.

In many cases the impact resistance that characterizes the stability of thin-layer coating to impact is of great importance. The tests have shown that the impact strength of the samples is extremely high and it depends largely on the volume content of the binder in the SP (Table 3).

Table 3. Impact strength of SP

Type of binder	Binder content, % _v	Impact strength, sm/kg
SKTN-1	10	21
-«-	20	37
-«-	30	42
SKTN-1+Aerosil (VIKSITIN-18)	10	28
-«-	20	42
-«-	30	47
SKTN-1+ redoksayt (VIKSITIN 28)	10	32
-«-	20	45
-«-	30	54

High values of impact strength are explained by significant damping capacity of elastomeric binder. Moreover, the use of sealants as binders VIKSINT 18 and VIKSINT 28 leads to the increasing of impact resistance, which is probably due to the reinforcing effect with active fillers: fumed silica and iron oxide (redoksayt).

Thus, varying the ratio of the binder and filler the physical and mechanical properties of the syntactic foam can be widely used.

4. Practical Use

The proposed technologies and compositions can be used in construction, engineering, shipbuilding and other industries where the low density thin-film coatings with high strength characteristics and resistance to adverse factors are required.

5. Conclusions

Thus, to obtain the coating with minimum foamability and according to the highest packing density of the microspheres and the best physical and mechanical properties, the composition should be applied in multiple layers, the thickness of the first layer should not exceed 150 microns. Survivability composition time should be sufficient to prevent premature gelation during the deposition process. Curing temperature should be much lower than the boiling point of the solvent, since material foamability is possible by intensive liquid vapors. It is most expedient to carry out the process at a temperature of 30°C.

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