

EVALUATION OF THE COMPATIBILITY OF POLYORGANYLSILOXANES AND HIGH-MOLECULAR POLYMERS USED AS EMULSIFIERS IN FINISHING WORKS

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ABSTRACT

The compatibility of polyorganylsiloxanes and high-molecular polymers used as emulsifiers was evaluated. The surface and bulk properties of the studied compounds were evaluated using the solubility parameters (δ). It is shown that the copolymers of acrylic acid compound – polyacrylamide and hydrolyzed polyacrylamide, as well as polyvinyl alcohol without residual acetate groups in the macromolecule have the highest degree of incompatibility with polyorganylsiloxanes. It was established that the presence of residual acetate groups in the macromolecule of polyvinyl alcohol leads to an increase in the degree of compatibility of polymers. The calculated data on the fractions of solubility parameters and cohesive energy of polyorganylsiloxanes and emulsifying polymers are presented. The contributions of the components of polymers cohesive energy due to the fractions of dispersion interaction α_d , dipole-dipole interaction α_{dd} , and hydrogen bonding α_h , as well as their influence on the degree of solubility of the polymer – emulsifier system, are shown. The choice of polyvinyl alcohol with residual acetate groups as an emulsifier for polyorganylsiloxanes is theoretically substantiated based on the concept of the solubility parameter as a measure of the affinity of the system components. The developed approach to assessing the compatibility of the polymer – emulsifier system is of practical importance for the creation of polymer compositions in the finishing works.

KEYWORDS

Polyorganylsiloxanes; High-molecular polymers; Emulsions; Compatibility Solubility parameters.

INTRODUCTION

Polyorganylsiloxanes (organosilicon polymers) are widely used in the finishing of textile materials. Due to their unique properties, these compounds are used in the creation of hydrophobic, superhydrophobic and flame retardant textile materials, increase the biocidal properties of fabrics, and change their surface energy. Due to the use of polyorganylsiloxanes, anti-adhesion properties are obtained, which contributes to self-cleaning of fabrics. Polyorganylsiloxanes are often used as crosslinking agents in the implementation of finishing technologies based on the use of polymers, as well as to impart softness, drape, silkiness to textile materials, depending on their purpose.

The choice of polymer components for the preparation of finishing compositions, the method of mixing them, the degree of compatibility (mutual solubility) is dictated by a set of properties that the composition should have, the structure, the properties

of components themselves, the real capabilities of technological equipment for finishing work.

Most organosilicon compounds are insoluble in water, as a result of which they are either pre-dissolved in organic solvents or used in the form of emulsions. The use of organic solvents from the point of view of environmental safety is difficult, since they are not only toxic, but also flammable compounds. Organosilicon emulsions based on surfactants or macromolecular compounds (usually water-soluble polymers) are not always stable over time.

The use of such water-soluble polymers as polyvinyl alcohol and polyacrylamide for the formation of emulsions does not cause any particular environmental hazard due to their low toxicity. The use of these compounds as emulsifiers for the preparation of polyorganylsiloxane emulsions is also justified by the fact that the polymers used are film-forming substances that increase the strength (fixation) of composite film on the surface of textile material during the finishing processes.

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The unbound emulsifier migrates as a result of leaching from the polymer film, which leads to a decrease in transparency, an increase in crispness, and a deterioration in the adhesion of the film to the substrate. In the applied coating, this process leads to a deterioration in water resistance and aesthetic defects, the so-called "snail trails". The issues of assessing the compatibility of polymers are relevant for the purposeful selection of components that provide the system with operational compatibility. When creating polymer compositions, as well as for mixtures of polymers and little used polymers, for which there are no data on the degree of solubility, the calculation method for estimating the mutual solubility of polymers is effective.

In the world, there are several theoretical methods for calculating the solubility parameters δ , as well as experimental methods for assessing the compatibility of polymers or a polymer with a solvent [1-3], namely Hansen, Hildebrand-Sketchard, Van Crevelen, Hoftizer-Van Crevelen, Hoy, Small, Panayot, Flory-Huggins, as well as computer programs HSPiP и HSPStudio [4].

The solubility parameter δ is originally based on cohesive energy and is used to evaluate the ability of polymers to dissolve in a solvent, and it is also a measure of the ability of any two kinds of components to mix. In practice, two main theories of polymer solutions are most often used: Hildebrand-Sketchard and Hansen in the form of the concepts of a three-dimensional solubility parameter and Flory-Huggins. The Flory-Huggins theory is mainly used in the study of polymer systems to evaluate the thermodynamic affinity of a polymer and a solvent using the Flory-Huggins constant. The presence of several theories indicates that all of them are not without flaws and have a number of limitations.

The article [5] provides an assessment of the compatibility of hydrophobic polydimethylsiloxane with hydrolyzed polyvinyl acetate (with 0%, 86% and 100% degree of hydrolysis) for mixtures in various ratios, their surface and bulk properties are determined, based on the calculation of the Flory-Huggins interaction parameter (χ) the compatibility of mixtures and phase transitions are evaluated using atomistic molecular dynamics.

In the study [6] the physical affinity between the epoxy matrix and the carbon fibers was evaluated using Hansen Solubility Parameters (HSP), high physical compatibility of the polymers was found because their respective HSPs are close.

In [7], the authors announced the development of a new approach using the solubility parameters (δ) calculated by the group contribution method as an indicator of the extraction of additives from plastic.

Considering the process from a thermodynamic point of view, it can be noted that there is practically no information in the literature on the use of solubility

parameters for evaluating the interaction of polyorganysiloxanes and high molecular weight emulsifiers. Almost all publications refer to the description of emulsions as colloidal systems created from immiscible liquids and do not take into account the degree of affinity between them.

In this regard, the issues of assessing compatibility are relevant for the targeted selection of the most effective emulsifier that provides a stable structure and operational properties of the emulsion.

The goal of the study is to theoretically substantiate the choice of the most effective high-molecular emulsifier for creating polyorganysiloxane emulsions, based on the assessment of the thermodynamic parameters of polymers and the calculation of the thermodynamic compatibility criterion as a measure of the affinity of the components.

MATERIALS AND METHODS

The following polyorganysiloxanes were studied in the work: polyethylhydrosiloxane with degree of polymerization $n=8$, $n=15$, $n=20$ (PEHS), polymethylhydrosiloxane (PMHS), polydimethylsiloxane (PDMS).

The high-molecular surfactants were studied as emulsifiers for organosilicon polymers: polyvinyl alcohol (PVA), polyvinyl alcohol with residual acetate groups (PVA_{ac.gr.}), polyacrylamide (PAM) and hydrolyzed polyacrylamide (HPAM).

Emulsifiers, including high-molecular ones, which include the above, being adsorbed on the surface of droplets, reduce the surface tension at the "droplet – dispersion medium" interface due to the adsorption-solvation factor and give the system stability.

The compatibility of polymers, their surface and bulk properties were calculated from the solubility parameters (δ). The determination of the solubility parameter δ of polymers was carried out using the increment method, which consists in choosing repeating units of the polymer and finding the increments of the cohesive energy $\Delta E_0 = \sum \Delta E_i$, and the increments of Van der Waals volumes $\Delta V = \sum \Delta V_i$ of individual atoms and groups. The volume of each atom depends on its environment, i.e. on the type of atoms that are chemically bonded to it. The values ΔE_i and ΔV_i known for many groups of atoms, atomic groupings, and intermolecular interactions were used in the calculation. To calculate the solubility parameters, we used the data by increments given in [8, 9] and extended to polar substances as well. In Table 1 presents not only the cohesive energy $\sum \Delta E_i^*$ as an additive sum, but also the molar volumes $\sum \Delta V_i$ calculated for each atom and various atomic groups.

The values of the solubility parameter δ for the polymers under study were determined by calculation

using an equation (1) that allowing to calculate the cohesive energy and its fractions:

$$\delta^2 = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta V_i} = \frac{\sum_i (\Delta E_i^*)_d + \sum_i (\Delta E_i^*)_{dd} + \sum_i (\Delta E_i^*)_h}{N_A \sum_i \Delta V_i}, \quad (1)$$

where δ is the Hildebrand solubility parameter for the polymer; $\sum \Delta E_i^*$ is the contribution of each atom and type of intermolecular interaction to the cohesive energy, reduced as many times as the Van der Waals volume of the molecule is less than the molar volume, and is an additive value; $\sum \Delta V_i$ is the occupied (Van der Waals) volume of molecules, which consists of the Van der Waals volumes of individual atoms; N_A is Avogadro's number.

The fractions of cohesive energy due to dispersion interaction α_d , dipole-dipole interaction α_{dd} and hydrogen bonding α_h were calculated from relations (2)–(4), respectively:

$$\alpha_d = \frac{\sum_i (\Delta E_i^*)_d}{\sum_i \Delta E_i^*}; \quad (2)$$

$$\alpha_{dd} = \frac{\sum_i (\Delta E_i^*)_{dd}}{\sum_i \Delta E_i^*}; \quad (3)$$

$$\alpha_h = \frac{\sum_i (\Delta E_i^*)_h}{\sum_i \Delta E_i^*}. \quad (4)$$

In this case, the sum of the fractions of the cohesive energy is equal to 1 (5):

$$\alpha_d + \alpha_{dd} + \alpha_h = 1. \quad (5)$$

RESULTS AND DISCUSSION

Since emulsions are heterogeneous systems, they are thermodynamically unstable. The lack of thermodynamic compatibility of polymers leads to the formation of a two-phase structure; their mixtures are dispersions of particles of one polymer in another. However, the thermodynamic incompatibility of polymers is not an obstacle, and vice versa, in some cases, it is thanks to the incompatibility of polymers that it is possible to obtain a unique structure. The solubility parameters, sometimes referred to as the cohesion energy parameters, are responsible for the value of the cohesive energy. As mentioned above, the solubility parameters are three initial molecular forces that control the dissolving activity of polymers: dispersion force α_d , polarity α_h and hydrogen bonding, dipole-dipole interaction energy α_{dd} . – i.e. forces that hold the molecule together and therefore control the interaction between polymers.

The values of the Van der Waals volumes of the studied polymers calculated from the volume increments ΔV_i of all atoms in the repeating polymer unit, as well as the value of the cohesive energy and

its fractions, the solubility parameter and surface tension of the polymers are presented in Table 1.

To improve the compatibility of polymer blends, the value of the dipole-dipole interaction and hydrogen bonds should be sufficient to cover the contribution of dispersion interactions.

Let us consider the change in the structural and thermodynamic parameters of polyorganylsiloxanes and polymers used as emulsifiers: polyacrylamide and hydrolyzed polyacrylamide. With a practically insignificant change in the proportions of dipole-dipole, dispersion interactions, and hydrogen bonds, the cohesive energy doubled from 54000 kJ/mol to 101000 kJ/mol for hydrolyzed polyacrylamide. The values of the structural parameters of hydrolyzed polyacrylamide changed, namely, the Van der Waals volume increased significantly from 0.0643 nm³ to 0.1240 nm³.

A somewhat different situation develops with the values of the structural and thermodynamic parameters of polyvinyl alcohol and polyvinyl alcohol with residual acetate groups. With regard to the structural parameters of polymers, it can be noted that the presence of residual acetate groups in the molecular chain of polyvinyl alcohol, compared with polyvinyl alcohol without acetate groups, is accompanied by an increase in the Van der Waals volume by more than 2 times: from 0.0415 nm³ to 0.1210 nm³.

With regard to thermodynamic parameters, the cohesive energy of polyvinyl alcohol compared to polyvinyl alcohol with the presence of acetate groups increases by almost 100%. The change in the cohesive energy is due to a change in the values of the fractions of its components: dipole-dipole, dispersion interaction and hydrogen bonds. As can be seen, in polyvinyl alcohol without residual acetate groups, the greatest contribution to the cohesive energy is made by hydrogen bonds. In the presence of residual acetate groups in the macromolecule of polyvinyl alcohol, a significant influence is made by the dispersion component, the high value of which 0.431 compared to 0.267 characterizes the weakening of the bond between electrons and the nucleus, i.e. promotes better solubility. The fraction of hydrogen bonds decreases from 0.733 to 0.403.

Table 1. Structural and thermodynamic parameters of polymers.

Polymer	Solubility parameter, δ [J/cm ³] ^{1/2}	Surface tension [mN/m]	Van der Waals volume, $\varepsilon_s\Delta V$, [nm ³]	Cohesive energy, ΔE [kJ/mol]	Fractions of the cohesive energy		
					α_d	α_h	α_{dd}
Emulsifier polymers							
PVA	30.0	46.6	0.0415	33000	0.267	0.733	0.000
PVA _{ac.gr.}	23.7	38.4	0.1210	60000	0.431	0.403	0.166
PAM	30.8	50.7	0.0643	54000	0.368	0.447	0.185
HPAM	30.3	63.6	0.1240	101000	0.326	0.477	0.197
Polyorganylsiloxanes							
PEHS _(n=8)	14.2	19.4	0.620	137000	1.000	0.0000	0.000
PEHS _(n=15)	15.0	26.3	1.140	262000	0.893	0.1070	0.000
PEHS _(n=20)	14.8	28.2	1.510	339000	0.917	0.0826	0.000
PMHS	13.7	16.7	0.501	103000	1.000	0.0000	0.000
PDMS	14.6	20.2	0.612	142000	1.000	0.0000	0.000

Table 2. The values of the components of the solubility parameter of polyorganylsiloxanes and emulsifiers and the degree of their compatibility.

Pairs of polymers under study	δ value	Indicators				
		ϕ value	Constant 2ρ	σ value	Interfacial tension γ [dyn/cm ²]	Solubility condition $\mu=2\rho\delta$
PAM + PEHS _(n=8)	0.07	0.85	1.374	0.88	16.99	4.70>0.09
PAM + PEHS _(n=15)	0.14	0.78	1.374	0.75	19.79	4.22>0.19
PAM + PEHS _(n=20)	0.12	0.75	1.374	0.79	22.28	4.33>0.16
PAM + PMHS	0.00	0.87	1.374	1.00	16.78	5.05>0.003
PAM + PDMS	0.09	0.85	1.374	0.82	16.61	4.45>0.13
HPAM + PEHS _(n=8)	0.02	0.91	1.374	0.97	18.84	4.55>0.02
HPAM + PEHS _(n=15)	0.14	0.86	1.374	0.75	19.60	4.08>0.19
HPAM + PEHS _(n=20)	0.13	0.83	1.374	0.77	21.65	4.19>0.18
HPAM + PMHS	-0.08	0.93	1.374	1.17	19.57	4.89>-0.11
HPAM + PDMS	0.05	0.91	1.374	0.90	18.24	4.31>0.07
PVA + PEHS _(n=8)	0.03	0.80	1.374	0.93	18.11	4.46>0.05
PVA + PEHS _(n=15)	0.09	0.73	1.374	0.83	21.85	4.00>0.13
PVA + PEHS _(n=20)	0.07	0.69	1.374	0.87	24.54	4.11>0.10
PVA + PMHS	-0.02	0.82	1.374	1.05	17.46	4.79>0.03
PVA + PDMS	0.06	0.80	1.374	0.88	17.84	4.22>0.08
PVA _{ac.gr.} + PEHS _(n=8)	0.38	0.91	1.374	0.42	8.08	2.79>0.52
PVA _{ac.gr.} + PEHS _(n=15)	0.43	0.86	1.374	0.39	10.26	2.50>0.59
PVA _{ac.gr.} + PEHS _(n=20)	0.40	0.83	1.374	0.44	12.30	2.56>0.55
PVA _{ac.gr.} + PMHS	0.32	0.93	1.374	0.48	8.03	2.99>0.44
PVA _{ac.gr.} + PDMS	0.41	0.91	1.374	0.39	7.80	2.64>0.56

A contribution to the cohesive energy of the dipole-dipole interaction appears, the value of which is 0.166, which is absent in polyvinyl alcohol without acetate groups.

The change in the ratio of the contributions of the components to the cohesive energy of the studied polymers affects the change in the value of the solubility parameter of polyvinyl alcohol with residual acetate groups and is 23.7 (J/cm³)^{1/2} in comparison with the value of the solubility parameter of polyvinyl alcohol 30 (J/cm³)^{1/2}. The surface tension of polyvinyl alcohol also significantly decreased from 46.6 mN/m to 38.4 mN/m for polyvinyl alcohol with residual acetate groups in the macromolecule.

Thus, we can conclude that the main bonds that determine the cohesive strength of polyvinyl alcohol are hydrogen bonds. In the macromolecule of polyvinyl alcohol with residual acetate groups, the number of hydroxyl groups is less, and therefore the probability of formation of intermolecular hydrogen bonds is also reduced. The presence of acetate

groups in the macromolecule contributes to the appearance of weaker hydrophobic interactions that arise between the nonpolar parts of the molecules, which also contribute to the formation of the interfacial layer.

As for the thermodynamic parameters of polyorganylsiloxanes, the greatest contribution to the cohesive energy is made by the dispersion component, which is equal to unity for PEHS with degree of polymerization $n=8$, PMHS and PDMS. Thus, of the three initial molecular forces that control the dissolving activity of polymers in a macromolecule, only the dispersion component is present. With an increase in the degree of polymerization of PEHS to $n=15$ and $n=20$, i.e. as a result of elongation of the polymer macromolecular chain, the dispersion component weakens, and the value of the hydrogen interaction component begins to affect the cohesive energy. Of the structural parameters, an increase in the Van der Waals volume by more than 2 times for PEHS with degree of

polymerization of $n=15$ and $n=20$ can be noted as a result of the growth of the macromolecular chain of polymers.

Changes in the structural and thermodynamic parameters greatly affect the formation and stability of the emulsion. Using these data, the values of the solubility parameters for each polymer were calculated. To assess the degree of compatibility, an improved solubility criterion μ was used, which takes into account the dependence of solubility on the degree of polymerization and the nature of polymer supramolecular structure.

The solubility condition was determined as follows (6) [10]:

$$\mu \leq 2\rho\Phi\left(\frac{\gamma_p}{\gamma_s}\right)^{\frac{1}{2}}, \quad (6)$$

where $\mu = \frac{\delta_p^2}{\delta_s^2}$; δ_p , δ_s – Hildebrand parameters for polymer and solvent, respectively; ρ – constant equal to 0.686; γ_p , γ_s – surface tension of the polymer and solvent, respectively. The value of Φ is calculated as follows (7):

$$\Phi = \frac{4(V_s V_p)^{\frac{1}{3}}}{\left(V_s^{\frac{1}{3}} + V_p^{\frac{1}{3}}\right)^2}, \quad (7)$$

where V_s , V_p – the molar volumes of the solvent and polymer, respectively (per unit).

The calculation of the compatibility of the studied polymers and emulsifiers was carried out according to the following relations (8) – (10):

$$\mu < 2\rho\Phi\left(\Phi - \sqrt{\Phi^2 - 1 + a}\right), \quad (8)$$

where

$$a_1 = \frac{\gamma_{p_1 p_2}}{\gamma_{p_2}}; a_2 = \frac{\gamma_{p_1 p_2}}{\gamma_{p_1}} \quad (9)$$

The interfacial tension was calculated from the relation (10):

$$\gamma_{p_1 p_2} = \gamma_{p_1} + \gamma_{p_2} - 2\Phi(\gamma_{p_1} \cdot \gamma_{p_2})^{\frac{1}{2}}, \quad (10)$$

where γ_{p_1} , γ_{p_2} – surface energies of polymers 1 and 2, respectively.

According to the criterion μ , solubility will be observed if the calculated values $2\rho\Phi(\Phi - \sqrt{\Phi^2 - 1 + a})$ are greater than or equal to the value of $\mu = \frac{\delta_p^2}{\delta_s^2}$. By introducing the notation (11), the solubility criterion μ can be estimated from relation (12):

$$\beta = \Phi\left(\Phi - \sqrt{\Phi^2 - 1 + a}\right). \quad (11)$$

$$\mu < 2\rho\beta. \quad (12)$$

The Table 2 shows the results of the evaluation of the compatibility parameters of emulsifier polymers and polyorganylsiloxanes based on a theoretical calculation of the solubility parameters δ .

According to the data on the solubility of compounds obtained by the calculation method (Table 2), it can be seen that in all cases the left side of the criterion μ is much larger than its right side, i.e. there is an incompatibility of the studied emulsifiers and polyorganylsiloxanes. According to the calculation results, it can be concluded that the copolymers of acrylic acid compound, polyacrylamide and hydrolyzed polyacrylamide, have the highest degree of incompatibility with polyorganylsiloxanes. Polyvinyl alcohol without residual acetate groups in the macromolecule is also characterized by a high degree of incompatibility.

The presence of residual acetate groups in the macromolecule of polyvinyl alcohol significantly affects the decrease in the value of the hydrogen interaction component from 0.733 to 0.403, at the same time, the effect of dispersion interaction increases from 0.267 to 0.431, as a result of which the degree of compatibility of polymers increases almost 2 times.

Considering that emulsions are based on mixtures of incompatible polymers, the improvement in the compatibility of polyorganylsiloxanes and polyvinyl alcohol with residual acetate groups in the macromolecule is accompanied by an increase in the mutual diffusion of their macromolecules at the interface between the contacting phases. As a consequence, a layer of segmental solubility is formed. The formation of an interfacial layer of segmental solubility is an equilibrium phenomenon, due not to kinetic, but to thermodynamic laws [11]. The interfacial layer will be the wider, the more compatible the polymers.

CONCLUSIONS

Based on the concept of the solubility parameter as a measure of the affinity of the system components, the choice of polyvinyl alcohol with residual acetate groups as a high-molecular emulsifier capable of forming a layer of segmental solubility with polyorganylsiloxanes on the phase interface is theoretically substantiated, which ensures the stability of the emulsion due to the structural-mechanical factor.

The developed approach to assessing the thermodynamic compatibility of the polymer – emulsifier system is of practical importance for predicting the stability of an emulsion over time and its operational compatibility in the process of creating finishing compositions.

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