Influence of intermolecular interactions of epoxy binder components on rheological properties and wetting ability

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Abstract. The purpose of this paper is to evaluate the degree of intermolecular interaction of the surfactant and epoxy oligomer ED-20 molecules and to establish regularities of the influence of this interaction on the rheological properties of the epoxy binder. For that purpose computer modeling and quantum chemical calculations of the interaction parameters of modifying additives with ED-20 have been investigated. For the experimental evaluation of the intermolecular interactions degree of the epoxy oligomer with additives, the viscosity rheological properties and wetting ability of binary mixtures were studied. Result of studies have shown that the higher the intermolecular interaction energy of epoxy binders components is the greater its influence on viscosity and the less they will effect on wetting ability of the binder.

1. Introduction and literature review

Rheological processes on the interfacial surface play an important role [1, 2] in the formation of a strong adhesive contact of the binder to the substrate, which in turn determines the exploitation qualities and durability of the protective coatings. The main disadvantages of epoxy oligomer are high viscosity and low wetting ability, which hinder with the formation of adhesive contact of the binder with the substrate [3]. Availability in the epoxy oligomer molecules of such polar groups as hydroxyl (capable of hydrogen bonding), epoxy and ether (dipole-dipole interactions), as well as benzene rings (π-π interactions) cause a high level of intermolecular interactions, and as a result – the high viscosity of the epoxy binder [4, 5].

A perspective method of directional control of wetting ability and viscosity of epoxy oligomer, is the modification of polymer binder by small additives of surfactants [6-8] and organosilicon [9-11]. The polar hydroxyl and ether groups in the chemical structure of the epoxy oligomer are able to interact with the molecules of these additives (their polar and hydrocarbon parts) and to form the intermolecular complexes through hydrogen, Van der Waals bonds and dispersion forces.

The effect of surfactants with different polar groups and hydrocarbon radicals of different length and structure on the structure of resins was studied. It is established that most additives can both weaken and strengthen the structure of the resin, depending on the surfactant content [12-14]. It has been found that the adding of surfactants with different degrees of oxyethylation differentially affects the spreading kinetics, viscosity, surface tension and wetting ability of the oligomer [8, 13].

Modification of polymers by silicone compounds of various nature has a significant effect on the viscosity of the binders, the nature of the inter-chain bonds, the packing density in the interglobular
zones of the polymers, and, accordingly, on the whole complex of physico-mechanical and relaxation properties [9]. Therefore, the use of organosilicon compounds as effective modifiers in the creation of epoxy polymer composites is of great interest.

Despite the large number of studies, including ours [15-18], of the effect of surfactants and organosilicon additives on the improvement of viscosity properties and the wetting ability of the ED-20 oligomer, the mechanism of action due to which the modifying effect of additives is achieved, practically not described. However, it is known that above mentioned properties are very sensitive to intermolecular interaction in the system.

In this regard, it was appropriate to evaluate the degree of intermolecular interaction of the surfactant and ED-20 molecules and to establish regularities of the effect of this interaction on the properties of the epoxy binder. Experimental determination of intermolecular interactions in epoxy oligomers with modifying additives is not possible, so computer simulation methods and quantum chemical calculations have been used to study them.

2. Materials and methods
This research studied an epoxy oligomer ED-20. As the modifying additives were used surfactants of different nature: the cationic: Alkyltrimethylammonium chloride (AMA) and Cetrimonium Chloride (CMC); the anionic: Sodium alkylbenzenesulfonate (ABS) and Sodium laureth sulfate (SLES). As the organosilicon compounds were chosen polymethylsiloxane (PMS).

Determination of intermolecular interactions in the epoxy oligomer with modifying additives was carried out by the semi-empirical calculation of PM3 [19] using the HyperChem software package for computer simulation. Three-dimensional models of intermolecular complexes were constructed. It has been obtained the following characteristics such as intermolecular distance, dipole moments, enthalpy of formation $\Delta H_{\text{form}}$ and the energy of interaction $E_{\text{int}}$ of individual compounds and intermolecular complexes. The interaction energy in complexes ($E_{\text{int}}$) ED-20 + modifier (AB) was determined by the difference between the heat of formation in the complex AB ($\Delta H_{\text{form AB}}$) and the heat of formation in simple substances ED-20 – A ($\Delta H_{\text{form A}}$) and the modifier – B ($\Delta H_{\text{form B}}$):

$$A + B = AB, \quad (1)$$

$$E_{\text{int}} = \Delta H_{\text{form AB}} - (\Delta H_{\text{form A}} + \Delta H_{\text{form B}}). \quad (2)$$

Evaluation of the contribution which each component of the ‘epoxy oligomer-modifier’ mixture made to the effectiveness of intermolecular interactions, and the nature of the structure were carried out by the flow curves using Hoppler viscosimeter [15].

The wetting ability of epoxy compositions is estimated by the method of sitting drop according to the values of the wetting contact angles measured [16]. Plates made of steel were used as the substrate.

3. Results and discussions
The nature of the intermolecular interactions of ED-20 and modifying additives was studied using computer simulation by the method of the semiempirical calculation PM3 in the HyperChem program. As a result of the computer simulation, the next parameters were obtained: the intermolecular distance and dipole moments $\mu$, the enthalpies of the formation $\Delta H_{\text{form}}$ and the interaction energy $E_{\text{int}}$ of individual compounds and intermolecular complexes, which are presented in table 1. Symbols of atoms in molecular models are presented in figure 1.

Figure 2 shows the models of ED-20 molecules interacting. The molecules of the epoxy oligomer are oriented by the epoxy group of one molecule towards the hydroxyl group of another molecule. The distance between the Oxygen and Hydrogen atoms is 7.5 Å, and the energy of interaction of the molecules ED-20 is 65.58 kJ/mol. This energy value is typical for the hydrogen bonds interaction, but the hydrogen bond typically does not exceed 3 Å [20]. This indicates that dipole-dipole interactions, which operate over longer distances, are predominant between the ED-20 molecules. The dipole
The dipole moment of ED-20 intermolecular bond is 5.51 D, which also indicates a rather strong intermolecular bond that usually leads to the association of molecules and to the growth of viscosity.

**Table 1.** Computer simulation parameters of molecular complexes.

| Molecular complex         | $\Delta H_{form}$, kJ/mol | $E_{int}$, kJ/mol | The distance between the molecules, Å | Dipole moment, $\mu$, D |
|---------------------------|-----------------------------|------------------|--------------------------------------|-------------------------|
| ED-20 + ED-20             | -882.35                     | 65.6             | 7.5                                  | 5.51                    |
| AMA + ED-20               | -700.65                     | -11.83           | 11.69                                | 9.16                    |
| CMC + ED-20               | -882.36                     | -11.04           | 14.36                                | 9.11                    |
| ABS + ED-20               | -1343.62                    | -5.06            | 8.39                                 | 6.52                    |
| SLES + ED-20              | -2017.69                    | -5.43            | 10.1                                 | 11.4                    |
| PMS + ED-20               | -7962.82                    | -0.83            | 5.4                                  | 0.23                    |

![Figure 1. Atomic conventions.](image)

![Figure 2. Geometry of molecules ED-20.](image)

In figure 3 the structure of the geometric optimization of the molecular complex of ED-20 and AMA is present. The AMA molecule includes a hydrocarbon radical of eight carbon atoms and a polar trimethylammonium group that is bonded by the ionic bonding to a chlorine atom. It is oriented by the polar part to the ED-20 hydroxyl group. The distance between the hydroxyl group of the molecule ED-20 and the chlorine atom of AMA is 11.69 Å. The dipole moment of the bimolecular complex ED-20 + AMA is 9.16 D, and the interaction energy according to the calculation is $-11.83$ kJ/mol. Such data of intermolecular distance and interaction energy indicate a long-acting dipole-dipole bond.

Cetrimonium chloride differs from AMA by a longer hydrocarbon radical, in the chain of which there are 16 carbon atoms. The dipole moment of the CMC molecule (9.78 D), as indicated in table 1, is practically equal to dipole moment of AMA molecule, which means that the main contribution to the value of the dipole moment is made by the functional group, while the hydrocarbon radical does not significantly influence on the value of $\mu$. The orientation of the CMC molecule to ED-20 is similar to that of the AMA molecule (figure 4). The values of interaction energy between CMC and ED-20, as well as between AMA and ED-20, as shown in table 1, are almost equal are $-11.04$ kJ/mol and $-11.84$ kJ/mol, respectively.
Figure 3. Geometric optimization of the molecular complex of ED-20 and AMA.

Figure 4. Geometric optimization of the molecular complex of ED-20 and CMC.

Figure 5. Geometric optimization of the molecular complex of ED-20 and SLES.

Such data of bond length and energy, as in case of AMA, indicate the presence of long-range orienting forces that can occur between chlorine and hydrogen atoms. Usually such forces are weak and depend on the viscosity of the substance. Since the viscosity of the epoxy oligomer is quite high, the energy of interaction data, combined with a sufficiently large dipole moment value of the bimolecular complex (9.11 D) signified that CMC, as well as AMA can have great affect on the
The structural organization of the oligomer (formation of associates of molecules), and therefore on its viscosity, wetting ability and, accordingly, on the adhesive properties and exploitation qualities of the cured epoxy polymer.

The sodium laureth sulfate molecule (figure 5) is represented as the polyoxyethylene ether of fatty alcohol of sodium sulfate. The energy of intermolecular interaction is \(-5.43 \text{ kJ/mol}\), which is characteristic of orientational forces, taking into account that the SLES molecule oriented by a non-polar hydrocarbon radical to the epoxy group ED-20 at the distance of 10.1 Å. This orientation is quite logical since the sulfate group, as we know, does not form hydrogen bonds with the hydroxyl group and is an electron donor, as is the epoxy group in the structure of the ED-20 oligomer.

The ABS molecule (figure 6), in contrast to SLES, contains an aromatic cycle in its structure. Computer simulation shows that the polar part of the ABS is oriented to the polar epoxy group of the oligomer at the distance of 8.39 Å. The intermolecular interaction energy is \(-5.06 \text{ kJ/mol}\), which is typical for a dipole-dipole bond.

Data from the table 1 shows, that interactions between ED-20 and anionic SLES and ABS molecules are much weaker than between ED-20 and cationic surfactants. Therefore, anionic surfactants will obviously have less influence on the viscosity properties of epoxy oligomer than cationic. Taking into account the weak bond of the investigated anionic surfactants with the epoxy oligomer, the relatively high values of the dipole moment and their electron donor properties, their adsorption on a positively charged solid surface is possible.

Figure 7 shows, that the PMS molecule has a rolled up structure. That structure of the siloxane macromolecule, forming a tangle with exposed hydrocarbon radicals, is explained by the tendency of weak Si-O dipoles to intramolecular compensation as a result that each Si-O dipole has a different dipole with a different orientation O-Si [21].

The dipole moment of complex ED-20 and PMS (table 1) has the smallest value (0.23 D), and the value of the standard enthalpy of formation is \(-7479.27 \text{ kJ/mol}\), which indicates very strong intramolecular interactions of the PMS. At the same time, the intermolecular binding energy of PMS and ED-20 is \(-0.83 \text{ kJ/mol}\), but a relatively small value of the distance between molecules of 5.4 Å means that there is no significant interaction of these substances. So we can conclude that the organosilicons poorly react with ED-20 molecules and have little effect on the structural properties of the epoxy oligomer.

![Figure 6. Geometric optimization of the molecular complex of ED-20 and ABS.](image)

![Figure 7. Geometric optimization of the molecular complex of ED-20 and PMS.](image)
Computer modeling and quantum chemical calculations of the interaction parameters of modifying additives with ED-20 have been investigated. Data of intermolecular bonds and dipole moments of ED-20 and modifying additives complexes were obtained shows that properties of ED-20 are most influenced by the cationic surfactants.

For the experimental evaluation of the intermolecular interactions degree of the epoxy oligomer with additives, the rheological properties of binary mixtures were studied [15, 16].

It is known [22] that the epoxy oligomer is a strongly associative non-Newtonian fluid. Its viscosity is 19 Pa·s and its structure is ruined under such high shear stresses of 2800 Pa. The Newtonian viscosity in that case is 8.5 Pa·s. The decrease of viscosity with the growth of displacement stress at the initial stage can occur due to the weakening of the bonds between the molecule's associative. Higher shear stresses can lead to the breakage of bones between associative and to the destruction of the associations.

Studies of the surfactants effect on the dynamic viscosity changing [15] have determined that the degree of the influence of additives chemical nature on the viscosity is directly related to the level of intermolecular interaction of the oligomer with additives, namely the stronger intermolecular interaction of surfactants with ED-20 additives is the more effectively the Newtonian viscosity (\(\eta_n\)) decrease (figure 8).

Anionic surfactants SLES and ABS, despite the relatively high dipole moment (table 1) of sulfate and sulfonate groups, this additives don’t have much effect on the decrease in viscosity. That is explained due to their electrodonor properties and inability to form hydrogen bonds. Therefore, the initial viscosity of the compositions with the addition of SLES and ABS is quite high and is 13.7 and 12.8 Pa·s, respectively. The structure of oligomer is ruined slowly and the viscosity in the Newtonian region decreases to 5.3 and 4.3 Pa·s, respectively.

Cationic surfactants have the maximum influence on the viscosity in the Newtonian region, as well as on the level of structuring. The introduction of cationic surfactants reduces the epoxy oligomer viscosity more than twice, compared with pure epoxy oligomer: from 19 Pa·s to 7.8-8.4 Pa·s. Similarly, when adding AMA and CMC, there is a lack of a distinct non-Newtonian flow region, and that is typical for weakly structured systems. This is, as have been shown earlier, due to a strong intermolecular interaction of cationic surfactant with ED-20 molecules, which causes intermolecular

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**Figure 8.** Changing the Newtonian viscosity (\(\eta_n\)) and wetting ability (\(\Theta\)) of the binders on the steel surface, depending on the energy of interaction (\(E_{int}\)) of ED-20 with the surfactants.
interactions in the epoxy oligomer to decrease. At the same time, the structure collapses the faster the shorter the hydrocarbon radical in the structure of the cationic surfactant. The Newtonian viscosity is 4 Pa.s.

Studies of the wetting ability of modified binders on the steel surface have shown [16], the chemical nature of surfactants, which determines the energy level of interaction with the oligomer, also affects the wetting ability of the epoxy oligomer. The most effective additives that reduce the wetting contact angle (Θ) on the steel surface are anionic surfactants and organosilicon additive, which improve the wetting ability of epoxy oligomer by 1.5-2 times, compared to cationic ones.

Anionic surfactants have such a great effect, obviously, due to their high dipole moment and the most adsorbable electron-donating sulfonate and sulfate polar groups of anionic surfactants on the steel surface, that have the property of being oxidized.

In the result of studies of surfactants and silicon additive influence on the viscosity properties and wetting ability of epoxy binders we can conclude that the higher the intermolecular interaction energy of additives with ED-20 is, the greater effect of surfactants on the properties in the volume of the binder and the less they will exhibit surface properties (figure 8).

4. Conclusions
Computer modeling and quantum chemical calculations of the interaction parameters of modifying additives with ED-20 have been investigated. Data of intermolecular bonds and dipole moments of ED-20 molecular and modifying additives complexes were obtained. For the experimental evaluation of the intermolecular interactions degree of the epoxy oligomer with additives, the rheological properties of binary mixtures were studied.

The properties of the epoxy oligomer are most influenced by cationic surfactants. Due to a strong intermolecular interaction with ED-20 molecules and the rather large value of the dipole moment cationic surfactants cause intermolecular interactions in the epoxy oligomer to decrease. Therefore cationic surfactants effectively reduce viscosity of epoxy oligomer. Organosilicon additives have strong intra-molecular interactions, they react poorly with the ED-20 molecules and do not have much effect on the structural properties of the epoxy oligomer.

Studies of the wetting ability of modified binders on the steel surface have shown that the most effective additives that reduce the wetting contact angle on the steel surface are anionic surfactants and organosilicon additives, that don’t have strong intermolecular interactions with ED-20 molecules.

The study focuses on the influence of intermolecular interactions of epoxy binder components on rheological properties and wetting ability have found the next regularities: the dynamic viscosity of the oligomers decreases and the wetting ability on the steel surface worsens in the same sequence as the energy of intermolecular interaction of the oligomer with modifying additives increases. It allows predicting the choice of additives to control the properties of epoxy oligomers based on the criterion of energy of intermolecular interaction between the oligomer and additives.

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