

Investigation of the Properties of Epoxy Modified Binders Based on Epoxy Oligomer with Improved Deformation and Strength Properties

Hlaing Zaw Oo, N. Kostromina, V. Osipchik, T. Kravchenko, K. Yakovleva

Abstract—The process of modification of ED-20 epoxy resin synthesized by vinyl-containing compounds is considered. It is shown that the introduction of vinyl-containing compounds into the composition based on epoxy resin ED-20 allows adjusting the technological and operational characteristics of the binder. For improvement of the properties of epoxy resin, following modifiers were selected: polyvinylformalethyl, polyvinyl butyral and composition of linear and aromatic amines (Aramine) as a hardener. Now the big range of hardeners of epoxy resins exists that allows varying technological properties of compositions, and also thermophysical and strength indicators. The nature of the aramin type hardener has a significant impact on the spatial parameters of the mesh, glass transition temperature, and strength characteristics. Epoxy composite materials based on ED-20 modified with polyvinyl butyral were obtained and investigated. It is shown that the composition of resins based on derivatives of polyvinyl butyral and ED-20 allows obtaining composite materials with a higher complex of deformation-strength, adhesion and thermal properties, better water resistance, frost resistance, chemical resistance, and impact strength. The magnitude of the effect depends on the chemical structure, temperature and curing time. In the area of concentrations, where the effect of composite synergy is appearing, the values of strength and stiffness significantly exceed the similar parameters of the individual components of the mixture. The polymer-polymer compositions form their class of materials with diverse specific properties that ensure their competitive application. Coatings with high performance under cyclic loading have been obtained based on epoxy oligomers modified with vinyl-containing compounds.

Keywords—Epoxy resins, modification, vinyl-containing compounds, deformation and strength properties.

I. INTRODUCTION

EPOXY oligomers have been widely used in various fields of the industry due to their high adhesion, chemical resistance and the ability to combine with a variety of substances.

Diane epoxies are the most common epoxy resins. Diphenylpropane and epichlorohydrin are the raw materials for the preparation of epoxydian resins. Epoxy resins are widely used for the manufacture of adhesives, paint systems,

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sealants, as a binder, in the production of composite materials. Fields of their application: electrical and radio engineering, mechanical engineering, aerospace industry, shipbuilding, construction, and repair work.

Diane epoxies are produced in solid and liquid form. Liquid resins are used in the manufacture of injection-molded products, reinforced plastics, paints, adhesives, compounds and other systems with low solvent content or with its absence. Solid resins are usually used for the production of paints and varnishes, various anti-corrosion, and protective compounds. Solutions of epoxy resins, such as ED-20, ED-16, E-40, of various concentrations are used for the manufacture of varnishes, some building materials, enamels, adhesives. Modified epoxy resins are commonly used for sealing, electrical insulating materials, and protective coatings.

Epoxy resin is one of the most widely produced thermoactive resin classes due to their easiness of manufacture, high mechanical and adhesive performance, good electrically insulating properties, chemical durability and relatively low shrinking upon curing. During the exploitation of materials based on epoxy resin genesis and development of microfractures occurs that leads to their premature destruction.

Now increase of the durability is achieved by the introduction of rubber modifier, active diluent and thermoplastic polymers. Diethylene glycol monoethyl ether is one of the active diluents, that involved in curing reaction and helps to achieve viscosity reduction in composite material [1].

In [2] were received and studied epoxy composite materials based on ED-20 resin and derivative from ethylene glycol vinyl glycidyl ether. It was shown that a combination of derivatives from ethylene glycol vinyl glycidyl ether and ED-20 helps to obtain composite materials with a higher complex of strength and deformation, adhesive and thermophysical properties, better resistance of water, frost, chemicals, and impact. The magnitude of the effect depends on chemical structure, temperature and curing time. In concentration range appears composite synergism and the quantity of strength and hardness indicator exceeds similar parameters of a separate compound of composition.

Unfortunately, the use of rubber modifiers, as well as active diluents, leads to a decrease in heat resistance in epoxy matrices. Besides that, use of rubber modifier significantly decreases Young's modulus and tensile strength, increases the viscosity of the system [3], [4].

The addition of thermoplastic common leads to an increase of strength characteristics in the cured system without a

decrease of the glass transition temperature and modulus of elasticity. Based on data of many pieces of research, it can be concluded that improvement of strength and deformation characteristics, increasing crack resistance will appear in system thermoset-thermoplastic due to phase separation.

Applying heat resistant and high-strength thermoplastic for modification of epoxy resin can significantly increase physico-mechanical characteristics of material without decreasing heat resistance, tensile strength and modulus. However there is no certain point of view on the optimal structure of cured epoxy matrix modified by thermoplastic, but the majority of authors assume that phase separation is one of the basic conditions [5], [6], necessary for increasing mechanical characteristics and heat resistance. It is known [7] that high-technology industries commonly apply epoxy-thermoplastic composition which contains polyethersulfone, polyaryletherketone, polyetherimide as a modifier. However, high heat resistance is not always necessary. In this case large and medium tonnage thermoplastic is more efficient as a modifier; they will not impact the price of a modified matrix. Polyvinyl acetal such as polyvinyl butyral (PVB) and polyvinyl formal ethyl (viniflex) (VF) can be successfully applied for this purpose [8], [9].

Several studies are describing their behavior in the composition with an epoxy resin. In [5] mixtures of epoxy resins with PVB cured by phenolic hardeners were used as film coatings. An increase in adhesive properties has been reported, but only with the use of significant quantities of thermoplastic PVB modifier - more than 20 wt.%.

According to the foregoing, this paper aims to study the possibility of regulation physico-mechanical properties and tensile strength characteristics by adding modifiers PVB and VF in epoxy resin. The purpose of this paper was an investigation of the effect on glass transition temperature, toughness, and morphology of cured systems containing modifiers. The possibility of interaction between PVB and VF with hardener Aramin was shown in [6]. The study claims, that applying these modifiers can lead to formation of a matrix with different phase states. Last, but not least aim of this paper is an investigation of hardener impact. In almost all cases epoxy resins were cured by amine hardeners. Applying aromatic polyamines based hardener can lead to obtaining a system with higher heat resistance. Besides that, applying Aramin as a hardener can change the phase state of the system and kinetics of the phase transition process [7].

II. OBJECTS AND METHODS OF RESEARCH

Epoxy oligomer ED-20 (State Standard GOST 10587-84) was used as a base component for developing bonding materials because of its low viscosity, narrow epoxy content limits and stable physicochemical properties. Aramin was used as a hardener. Aramin (Specification TY-2415-164-05786904-02) is a modified aromatic amine designed for curing epoxy resins at room temperature. Aramin has several advantages such as 1) low temperature curing hardener; 2) providing good intermolecular interaction due to the presence of different functional groups.

PVB is obtained by polycondensation of polyvinyl alcohol

with butyraldehyde. PVB has an atmospheric influence, oxygen and ozone resistance and good adhesion. Adding PVB to resins significantly increases their adhesion to materials. VF is a condensation product of polyvinyl alcohol with a composition of formaldehyde and acetaldehyde, has good electrical insulating and anti-corrosion properties.

The curing of the compositions was carried out stepwise: 1 hour at 80 °C, then 3 hours at 120 °C. The curing of a modified binder based on epoxy resin (ED-20), amine hardener (Aramin) and thermoplastics (PVB or VF) is a complex process representing a set of reactions between the interaction of secondary hydroxyl groups ED-20 with hydroxyl groups of polyvinyl acetal and the interaction of functional groups of the amine hardener and epoxy resin, which leads to the formation of a spatial crosslinked structure. The ability of polyvinyl acetal to self-cure at temperatures above 100 °C leads to the formation of structures that affect the physico-mechanical parameters, glass transition temperature and crosslink density of polymer compositions.

The impact strength of cures samples was evaluated by State Standard GOST 14235-69 on the device Dinstat №1893-57-30. Rectangular samples in size 15×10×(2,0-3,0) mm. were applied for testing. Compressive strength was defined by State Standard GOST 4651-82 at a deformation pace of 10 mm. per min. Thermo-mechanical analysis was conducted by the use of Hepler's consistometer for building thermomechanical graphs.

This paper studied effect of PVB and VF on impact strength, bending strength, and compressive strength of a binder based on epoxy oligomer ED-20 and Aramin hardener.

III. RESULTS AND DISCUSSION

A joint applying of epoxy oligomers and polyvinyl acetals can assist in forming more complex cross-links due to their different structure and functionality that in turn can lead to change in properties in final products [8]

Figs. 1 and 2 show the dependences of changes in impact strength and compressive strength on the presence of PVB and VF in an epoxy matrix. The study shows that strength indicators with an increase in the content of modifiers more than 5-7 m.n.(m.n.- mass number) in ED-20 will decrease. However, addition of 5 m.n. PVB increases impact strength by 3 times and with the addition of 7 m.n. VF increases 2.5 times. The compressive strength decreases by 20% by the imposition of the modifier: by the imposition of PVB - from 101.1 MPa to 41 MPa, by the imposition of VF - from 101.1 MPa to 40 MPa. The minimum decrease in compressive strength is observed by the introduction of both PVB and VF in the quantity of 5-7 m.n.

Phase separation in systems epoxy oligomer - polyvinyl acetal can proceed in two ways:

- nucleation of the phase formed by polyvinyl acetate
- the formation of a heterogeneous structure with fragments that contain mainly one of the components

The impact strength of the compositions depends on the phase separation mechanism [6]. The modifier will be a

dispersed phase that is distributed in an epoxy oligomer at a low content of polyvinyl acetals (less than 10 m.n.). A phase inversion occurs with an increase in the modifier content: a phase that contains a large amount of polyvinyl acetal will become continuous. Based on the literature data, we can conclude that the improvement of impact characteristics will appear in systems due to phase separation. Fig. 3 shows the change in the degree of curing of the compositions.

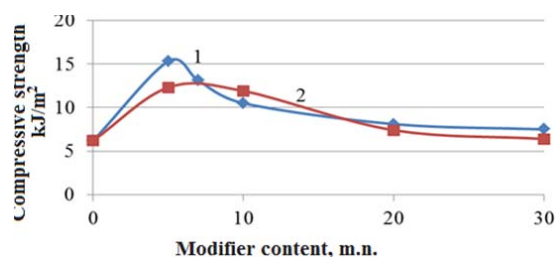


Fig. 1 The dependence of the impact strength of a binder based on ED-20 on the content of the modifier: PVB (1), VF (2)

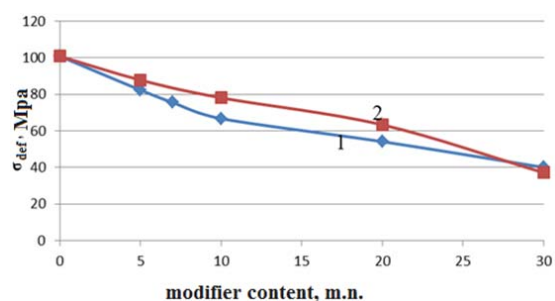


Fig. 2 The dependence of compressive strength of a binder based on ED-20 on the modifier content: PVB (1), VF (2)

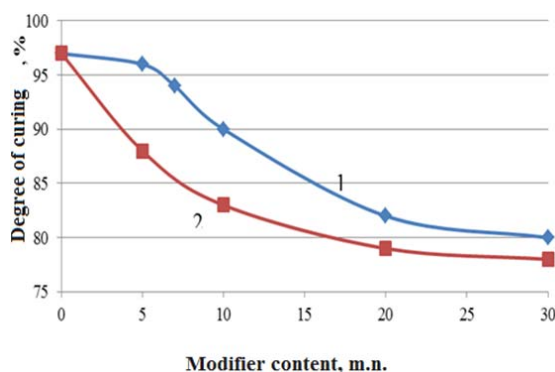


Fig. 3 The dependence of the degree of curing of a binder based on ED-20 on the content of the modifier: PVB (1), VF (2)

The introduction of a large number of modifiers is impractical as it can be seen from Figs. 1-3. Polyvinyl acetals can be represented in the form of copolymers containing three types of functional groups: acetal, hydroxyl, and acetate. According to literature data [8], [9] hydroxyl groups are reactive at elevated temperatures and are capable of interaction with the secondary hydroxyl groups of the epoxy resin, apparently, due to spatial factors. With an increased

content of the modifier in the binder, a decrease in the degree of cure occurs as a result of increasing the viscosity of the systems.

Based on thermomechanical analysis, temperature dependences of the deformation were constructed for samples with different contents of VF and PVB (Fig. 4).

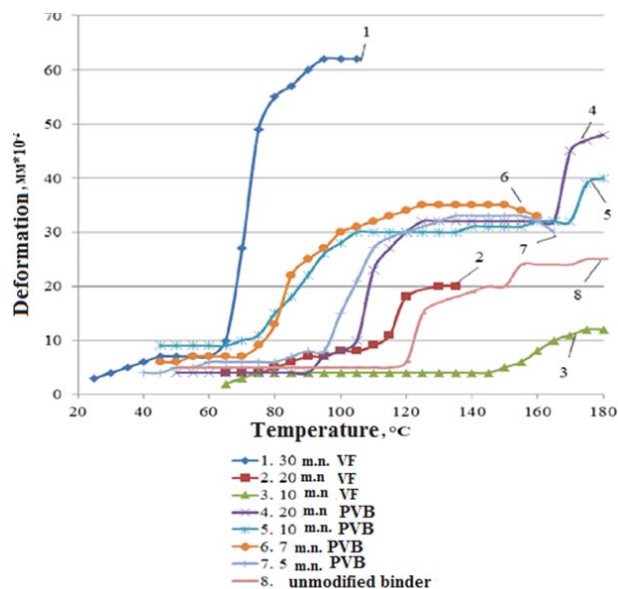


Fig. 4 Thermomechanical graphs of modified binders based on ED-20: 30 m.n. VF (1), 20 m.n. VF (2), 10 m.n. VF (3), 20 m.n. PVB (4), 10 m.n. PVB (5), 7 m.n. PVB (6), 5 m.n. PVB (7), unmodified binder (8)

It was observed, that an increase in deformation happens with an increase in the amount of introduced modifier; the highest values were for binders modified 30 m.n. VF and 20 m.n. PVB. The glass transition temperature (T_g) of the materials was determined from the thermomechanical curves presented in Table I.

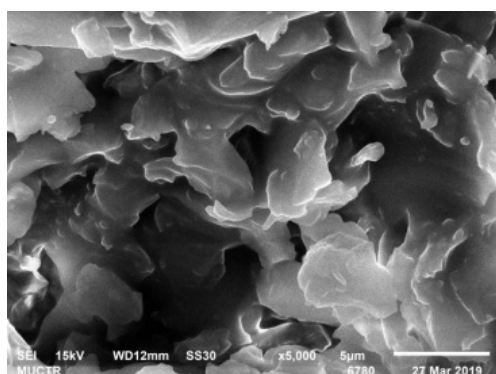
TABLE I
THE DEPENDENCE OF THE GLASS TRANSITION TEMPERATURE ON THE CONTENT OF THE MODIFIER IN THE BINDER

Composition	T _g
ED-20 (100 m.n.) + Aramin (42 m.n.)	120°C
ED-20 + Aramin + 10 m.n. VF	155°C
ED-20 + Aramin + 20 m.n. VF	105°C
ED-20 + Aramin + 30 m.n. VF	65°C
ED-20 + Aramin + 5 m.n. PVB	95°C
ED-20 + Aramin + 7 m.n. PVB	75°C
ED-20 + Aramin + 10 m.n. PVB	77°C
ED-20 + Aramin + 20 m.n. PVB	90°C

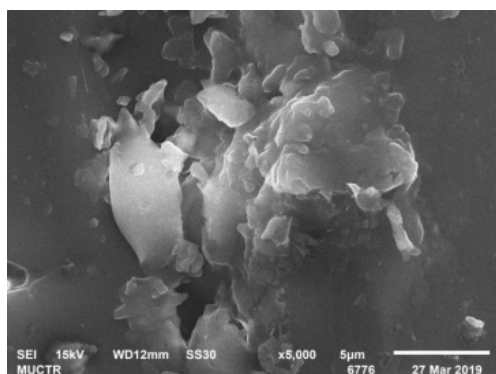
According to the present data, the glass transition temperature increases by 35 °C with the introduction of VF to 10 m.n. The glass transition temperature decreases with higher contents of VF and PVB. The data obtained by the thermomechanical method are in good agreement with physical and mechanical studies and the degree of curing calculated from the content of sol- and gel-fractions.

The production of so-called hybrid or two-phase systems is based on the principle of the incompatibility of modifiers and epoxy oligomers. In the matrix, modifier is spread in the form of a dispersed phase with particles of micron size that provides increased impact resistance. Besides that, cross-linked polymer is formed by the interaction between the reactive groups contained, for example, in the PVB macromolecule and the reactive groups of the binder components (epoxy resin and hardener).

Figs. 5 (a) and (b) show electron micrographs of the distribution of PVB and VF in an epoxy matrix. We can see from the pictures, that the distribution of 10 m.n. PVB is more uniform in the epoxy matrix (Fig. 5 (a)) and the VF distribution (Fig. 5 (b)) contains visible agglomerates.



(a)



(b)

Fig. 5 Electron micrographs of the distribution of (a) PVB and (b) VF in an epoxy matrix (x 5000)

IV. CONCLUSION

Studies of the effect of polyvinyl acetals on the properties of an epoxy oligomer showed that the introduction of modifiers in an amount of up to 10 m.n. improves impact characteristics by about 2 times, while the remaining strength indicators change insignificantly.

Thermomechanical graphs (Fig. 4) show an increase in deformation with an increase in the modifier content and an increase in the glass transition temperature by 35 °C with the introduction of VF up to 10 m.n. A decrease in the glass

transition temperature is observed with a VF content of more than 10 m.n. and with the introduction of PVB.

In some cases, the high viscosity of solutions of polyvinyl acetal and epoxy resin makes the formation of products difficult. Besides that, in the case of using solutions, there is also a need to remove large amounts of solvents. Therefore, in the future, priority should be given to the technology of combining the modifier and the polymer matrix. Thus, the use of mixed compositions based on modified epoxy oligomers has fundamental importance for the creation of structural polymer materials and coatings with high mechanical and thermal properties.

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