The role of thermoactive binders in the structuring of composites

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Abstract

Thermoactive binders are the most widely used form of polymer matrix materials in modern composites. In the production of composites, thermoactive binders are the basis of the matrix structure formation process with different properties. Various thermoactive binders based on epoxy, polyester and other resins compatible with corresponding polymer matrices were examined in the article. The influence of binders on the pre-molding process, various properties of the products, including density, stability and water permeability, as well as the main characteristics of composite materials obtained by various methods, was considered. The most optimal thermoactive binder (epoxy resin) were determined. The influence of thermoactive binders was shown and the advantage of using thermoactive binders in the production of composites was proved on the example of bitumen asphalt.

Keywords: *thermoactive binder, polymer, composite, composite matrix, structure formation.*

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1. Introduction

Within modern materials science research and technological innovation, composite materials have become vital for a wide range of industrial and scientific applications. Their unique properties, combining the advantages of different components, make them particularly relevant for solving a variety of engineering problems. The prerequisite for the emergence of thermoactive binders in modern composite materials was the creation of synthetic resins and fibers. Between 1870 and 1890, a revolution in chemistry occurred, and synthetic (technogenic) resins were developed that could be converted from liquid to solid via polymerization. These polymeric resins are converted from a liquid state to a solid state by cross-linking of molecules. The first synthetic resins were bakelite, celluloid, melamine, polystyrene, phenolic resins, and polyester. World War II shifted the composite industry from research to real production[1].

In recent decades composite materials have become widely used in many industries, including aviation, automotive, construction, and medical industries. One of the key aspects of composites is binders, which determine the quality and properties of the final product. In this context, thermoactive binders play an important role in the structuring of composites, providing not only strength, but also resistance to external factors[2].

Binders in composites play a key role in determining the quality, strength and structure of the final material. However, among the binders, a special place is occupied by thermoactive binders, which provide not only an effective connection of the components of the composite, but also allow to control the process of forming the material[3]. Thermoactive binders are a key element in the structuring composite materials, achieving optimal characteristics and properties of the final product. These binders tend to be activated at certain temperatures, allowing them to react and connect the components of the composite, forming strong and stable bonds[4].

The large-scale use of thermoactive binders in polymer composite materials began in the 1970s. Due to the combination of their opposite properties (high strength but low density), polymeric composites began to compete with steel and other metal products[5]. However, the process of replacing metal products with composites was slowed by the high cost of materials used in their manufacture[6].

The use of thermoactive binders made it possible to create polymer composites with a number of properties, owing to which they were widely used, namely: low viscosity of solutions, high adhesion, and relatively low curing temperatures. When choosing a binder, it is essential to take into account quite conflicting requirements which provides the possibility of obtaining various products as follows: a combination of high strength and heat resistance, cracking resistance under impact load and the necessary processability[7].

Therefore, in addition to assessing the performance of the binder (mechanical properties, heat resistance, dielectric properties), it is necessary to take into consideration its technological properties (viscosity, temperature, curing rate, gelation time). Given the variety of thermoactive binders, it became necessary to consider their correct use in the production of polymer composite materials. One of the central advantages of thermoactive binders is their self-reaction properties under the influence of heat, which allows for efficient structuring of the material without the need for additional chemicals[8]. This makes the production process more efficient and cost-effective. Apart from that, thermoactive binders can be easily adapted to a variety of processing and manufacturing conditions, facilitating control and optimization of composite materials formation. This makes them feasible in the production of large and complex structures where precision and stability are important.

In general, the use of thermoactive binders in the structuring of composites presents new prospects for the development of modern materials with improved mechanical properties, stability, and durability. Thus, a thorough research in this area can lead to the creation of new materials that will meet the requirements of modern industrial production and provide effective solutions for a variety of technical tasks.

Based on the prospect of the wide use of thermoactive binders, the study of the influence of binders on the structure of the composites and its properties is a topical issue[9]. Consequently, the aim of the research is to analyze the influence of thermoactive binders on the structure formation of composites. To that end, the following tasks must be accomplished:

1. Examine the types of thermoactive binders;

2. Analyze the influence of thermoactive binders on the structuring of composites;

3. Determine optimal types of binders for the structuring of composites;

4. Consider the practical impact of optimal thermoactive binder on the composites.

This article is aimed at specialists in the field of materials science, chemistry and engineering, as well as at anyone interested in the development and use of new materials with improved properties.

2. Materials and methods

2.1 General characteristics of thermoactive polymers

Thermoactive polymers are substances consisting of solid glass-like and non-fusible elements. They have the spatial structure of molecules and the ability to solidify when heated. This group of polymers includes phenol formaldehyde, epoxy, polyester resins, and organosilicon polymers[10].

In the initial modelling of polymer binders, the basic requirements were set, namely: the strength and the tendency to uniform distribution in the material used[11]. Phenol formaldehyde oligomers are products of phenols polymerization with linear and branched formaldehyde.

Due to the relative low cost, availability of raw materials and a number of valuable properties, these oligomers are widely used in various industries[12].

The main raw material in the production of phenol formaldehyde resins are phenol and formaldehyde in the form of aqueous solution of formalin. The reaction of phenol to formaldehyde is based on causal and parallel compounds[13]. The properties of the resulting resin depend on their molar ratio and the acidity of the reaction medium. The molar concentration affects oligomer properties. Accordingly, thermoplastic oligomers are called novolacs, whereas thermoactive oligomers are called resols[14]. Phenol-formaldehyde (thermoplastic) polymers are used in the production of composite materials in various areas. Products based on them have high mechanical strength, heat resistance, acid resistance, and do not conduct electricity[15]. They are often formed by phenol formaldehyde resins.

Carbonized and graphite phenol formaldehyde materials are widely used as thermal shields in aeronautical and space technology[16]. The active atoms are connected to hydroxyl groups. Resols are formed when an extra formaldehyde is added and bases are present[17]. In order to produce them, a hardener is introduced into the composition of resol oligomers. The resols are solidified and form a spatially cross-linked structure, which in turn forms a new polymer resite[18].

Furan polymers is another type of heterocyclic polymer. Due to the presence of hydroxyl bonds, furan polymers allow the production of highly dense polymers[19]. Furan oligomers are liquids with high viscosity, which can dissolve in alcohol, benzene, and acetones. They are solidified by opening double bonds in furan cycles and can be formed at 120-140 °C with strong acids of organic origin, and at 20-25 °C with sulfate acids[20].

2.2 Epoxy resins

Epoxy resins are polymers whose main macromolecule chains contain epoxy groups or glycide groups. These groups produce a spatial cross-linked polymer. Epoxy resins is the optimum type of binder for the majority of composites with a fibrous structure, due to the following characteristics[21]:

– the high adhesion to a large number of fillers and reinforcing parts;

– the diversity and accessibility of epoxy resins;

– the absence of by-products and small shrinkage rates when curing;

– chemical resistance and good electrical insulation.

Compounds containing epoxy resins molecules are classified as epoxy resins. Interaction of phenols, alcohols, amines with epichlorohydrin form epoxy compounds (oligomers)[22]. In contrast to mono or diane epoxides, polyepoxides have a greater number of epoxy groups. Due to this, they have a higher cross-linking capacity, can withstand higher temperatures after setting solid, and have the properties of hardeners. They are divided into two groups, namely: cross-linking hardeners, which work with groups of epoxide oligomer, and catalytic hardeners

that are formed during polymerization[23]. The process for cross linking hardeners with amines is shown in Figure 1.

The hardener is formed at temperatures of 0-150 °C when reacting with amines. 1,6-hexamethylenediamine and polyethylene polyamine are mainly used with the following Formula 1:

$$H_2N - (CH_2CH_2NH)_n CH_2CH_2 - NH_2 \qquad (1)$$
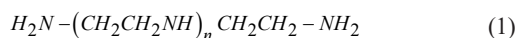
where *n* = 1-4.

These compounds start to react at 20 °C. Aromatic amines are less active and begin to react at 150 °C. Acid hardeners are the aldehydes of carboxylic acids: phthalic, trimellitic, phyromellitic, benzo tricarboxylic anhydride. Their curing occurs at 120-180 °C[24].

2.3 Organosilicon polymers (polyorganosiloxanes)

Organosilicon polymers contain silicon atoms. They have good frost resistance, light resistance, heat resistance, high water and weather resistance, resistance to weak acids and alkalis[25]. The distinctive property of polyorganosiloxanes is high temperature resistance (up to 400-500 °C), which becomes possible with the unique Si-O bond. The raw materials used for the production of polyorganosiloxanes are monomeric silicon and organic compounds in which the silicon atom is directly connected with organic radicals and with chlorine atoms or alkoxy groups. Among these compounds, alkyl(aryl)chlorosilanes and alkyl(aryl)alkoxysilanes were found to be of the most practical use[26].

The hydrolytic polycondensation produced by oligoorganosiloxanes has a relatively low molecular mass. They are soluble in hydrocarbons, compound esters, ketones and limitedly in higher alcohols. Oligoorganosiloxanes are thermoactive oligomers capable of curing due to further polycondensation under harsh conditions (at 200-250 °C within 5-10 hours). In the presence of catalysts (Zn, Fe, Sn) curing occurs in 1-1.5 hours at 100-150 °C[27].

The application of three-functional compounds (silanetriol) leads to the formation of spatial non-polar and insoluble polymers. The properties of organosilicon polymers are determined by the composition and structure of the macromolecule main chain and the chemical composition of the lateral groups. Polyimides are polymers that have clusters with cyclic images. Polyimides have a wide range of temperatures (from –270 to 300 °C) and radiation resistance[28].

Cyanate esters are another equally promising thermoactive polymer matrix that is used in the production of multi-functional polymer composite materials for high-tech industries[29,30]. The relevance of using cyanate esters in the creation of polymer materials is explained by the combination of the processability of processing oligocyanates and the unique complex of properties of the produced polymers[31]. It is necessary to note the thermal resistance of polytriazine polymer matrices, their excellent dielectric properties, radio transparency, low moisture absorption, dimensionality, resistance to ionizing radiation, low smoke separation and gas permeability[32,33].

2.4 Bisphenol-based epoxy resins

The properties of bisphenol A diglycidyl ether epoxy resins are highly dependent on the length of the polymer chains. The low-molecular epoxy resins are in a liquid state, while the epoxy resins with a high molecular mass may be in a solid or jelly-like form. Bisphenol A diglycidyl ether oligomers usually contain a number of specific hydroxyl groups that play an important role in cure kinetics[34,35].

The novolac resins are produced by condensation of phenol and formaldehyde with an acid catalyst followed by condensation results with epichlorohydrin. The high condensation of novolac resins affects the increase in resin functionality that can be achieved by changing the phenol-formaldehyde ratio from 1.49 to 1.72. The formation of novolac resins should occur at 160 °C within 2-4 hours to ensure the formation of a full structure and the release of water vapor as an excess product[36].

The epoxy group in novolac resins facilies high density of transverse bonds. Therefore, the novolac resins have thermal and chemical properties that are ideal for the production of composite glue and the formation of composite matrix. Epoxy resin polymers form a solid, refractory and non-polar mass. The curing process of epoxy resins requires additional substances called hardeners or curing agents[37]. High-performance epoxy resins with low molecular weight will result in high-grade cross-links after curing with amine compounds. Figure 2 shows the chemical structure of amines[38].

The number of hydrogen atoms in an amine molecule determines the functionality of the amine. The main amino group, in which two hydrogen atoms are connected to nitrogen, will react with two epoxy groups, and the secondary amine will react with only one epoxy group. The tertiary amine group that does not have an active hydrogen atom will not react with epoxy groups, but will act as a catalyst that can accelerate the curing process[39]. The advantage of aliphatic amine is that it can cure epoxy resins at room temperature, so it does not require additional energy for reaction.

The second group of amine hardeners require heating during the curing process, which requires not only additional energy, but also cannot be applied for the production of some composites. However, aliphatic amines require a high temperature to obtain a full reaction. The main limitations of the structure formation of epoxy resins with a curing agent are that they cannot form a complete structure at a glass-liquid transition temperature above 120 °C. Aromatic amines require a temperature of 250-300 °C during curing. Many epoxy resins can withstand high temperatures and can therefore be used as a matrix in composites[40].

The epoxy-anhydride thermoactive system typically exhibits low viscosity and long shelf life, low exothermic thermal response and very low shrinkage at high temperature. The curing process takes place slowly at a temperature of 200 °C and is usually catalyzed by a base, acid, tertiary amines or acid compounds[41]. The catalyst concentrate must
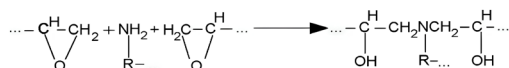

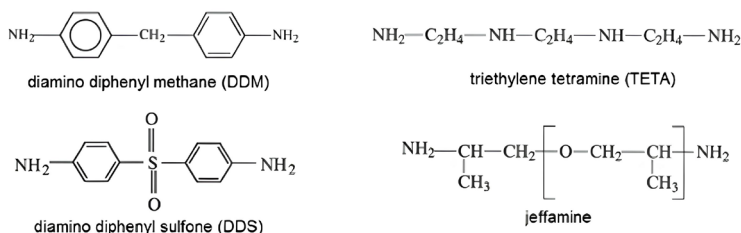**Figure 1.** Curing process of epoxy oligomers.

Figure 2. Chemical structure of amines (hardeners).

be carefully calculated according to the type of anhydride curing agent to produce an epoxy resin resistant to high temperatures[42,43]. Methods for measuring epoxy resins are commonly used by the halogenic acid reaction to open an epoxide ring and produce halohydrins[44,45].

The second hydroxyl group is α-glycol, which is formed from the hydrolysis of the epoxy group and phenolic hydroxyl, which is created by the reaction of phenol imperfection in the production of epoxy resins from high-concentration bisphenol A. The concentration of α-glycol may be determined by the Periodic Acid Schiff (PAS) test or by the lithium aluminum hydride test, which reacts only with active hydrogen. Since α-glycol usually appears in small quantities, it is necessary to be careful when measuring the results[46,47].

In epoxy resins based on bisphenol A, chlorides have a destructive effect on electrical properties when they are applied as a semiconductor[48]. The color and reactivity of the resin can also be affected by the presence of chloride. Active chlorides can block thermoactive reactions of epoxy resins during composite formation. When chloride bonds appear in epoxy resins, they reduce the functionality of epoxy resin and its compounds. Components inside the composite become inefficient[49,50].

The connection process can occur with the input of thermal energy, and some of these compounds occur at room temperature (25 °C) due to the mechanism of epoxy resin curing[51]. The curing process of epoxy resin is an essential factor influencing the guaranteed quality and performance of composites[52]. After an analytical review of thermoactive binders in the structuring of composites, it can be concluded that epoxy resins are the most universal binder.

3. Results

In order to study the influence of thermoactive binder from the practical standpoint, it is necessary to consider the influence of epoxy resin on a composite consisting of bitumen-based asphalt concrete. The shape and structure of bitumen depends mainly on its thermal state as well as on external conditions, which determines its ability to transit from a liquid to a solid state and vice versa. The introduction of epoxy resin into the bitumen itself changes its properties and corresponds to the properties of the material it is composed of[53].

By dissolving bitumen in benzene and subsequently washing with hexane, asphaltenes were isolated, dried and weighed after filtration. At the same time, it was empirically determined that when adding epoxy resins to bitumen, the
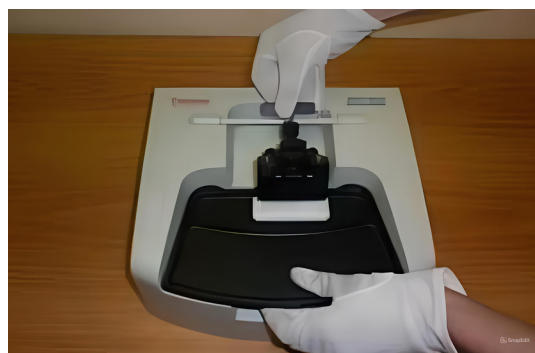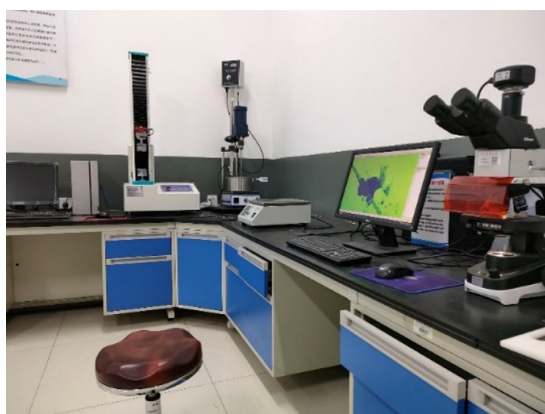

Figure 3. Smart Multi Bounce HATR.

Figure 4. The laboratory at North Minzu University, China.

number of asphaltenes increased. The study applied IR spectrographic analysis, using IR-Fourier spectrometer Nicolet-380 and Smart Multi Bounce HATR (Figure 3).

Bitumen without additives showed the range of hydrocarbons, paraffins, oils, deformation oscillations d(CH2)) and 1377 cm-1 (deformation oscillations d(CH3)). Band 720 cm-1 corresponds to free paraffin chains. Stripes 747, 812, and 870 cm-1 showed aromatic formations[54]. The experiment was conducted in the specially equipped laboratory (Figure 4) at North Minzu University, China.

The interaction of fiber from the fly ash of thermal power plants with road asphalt bitumen[55] is shown in Figure 5.

IR-spectrum of samples of bitumen without additives and bitumen containing epoxy resin showed changes in absorption band 1600cm-1. Oscillations in the region of 3050cm-1 of the original bitumen are attributed to valence oscillations of hydroxyl groups OH-. This change shows the rearrangement of the hydrogen bonds that were influenced by the introduction of epoxy resin (Figure 6).

The change in the structural composition after the introduction of epoxy resin can also be observed after

Figure 5. The interaction of fiber from the fly ash of thermal power plants with road asphalt bitumen.
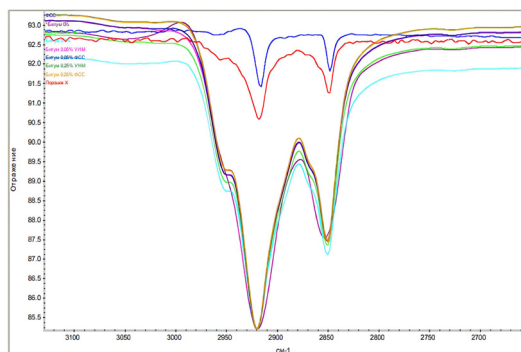

Figure 6. Comparative spectrum of bitumen modification.

considering the absorption band intensity of modifiable epoxy resins, which were determined by IR spectroscopy (Table 1).

The analysis shows the change of chemical composition of modified bitumen. It can be seen that 2.5% of the epoxy resin content has the greatest influence on the composition. Different percentage ratios of additives and different temperature ranges (from 0 °C to 30 °C) were considered for more precise determination of the amount of epoxy resins necessary for the change of bitumen structure. Other properties of bitumen (both modified and original) were tested via the methods recommended by DSTU 4044[54]. Penetration was determined after thermostatic control, which was carried out for 60 minutes in water bath. The activation energy of bitumen (original and modified with epoxy resins) was calculated by the Arrhenius equation.

The activation energy (E_A) and the logarithm of pre-exponential factor is calculated by the Formula 2:

$$tg\alpha = \frac{E_\alpha}{R} \tag{2}$$

It is graphically represented as the tangent of the angle of inclination straight to the axis of the abscissa (Table 2).

The observed reduction in activation energy at 2.0% of epoxy resin introduction could occur when the hydrogen-intermolecular or near-π bonds in the asphaltene molecular subsystem break. The activation energy decreased after less than 2.5% of bitumen was introduced. This may indicate a break of existing links within bitumen and insufficient number of epoxy resin to form new links. Bitumen can be in different states depending on temperature. However, the transition from one state to another depends on a certain temperature. When modifying epoxy resins, bitumen behaves homogeneously at temperature changes, which allows to extend the temperature range in the manufacture of composites and during their subsequent operation[56].

Analyzing the data shown in Figure 7, it is affirmed that the introduction of epoxy resins in the form of a thermoactive binder allows to extend the range of operating temperatures of bitumen, while reducing the temperature of its fragility and

Table 1. Absorption band intensity.

Structural elements	BND 90/130 (original)	Epoxy resin, mass. %		
		2.0	2.5	3.5
Paraffinic naphthenic hydrocarbons	127	20	29	17
C=C cyclical relationship (their valence vibration)	71	128	119	113

Table 2. Definition of the natural logarithm of penetration with the introduction of fullerene-containing modifier.

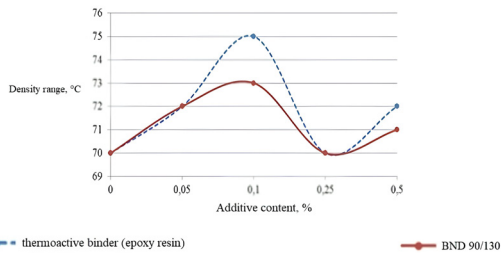| Modifier number in the bitumen ratio	Penetration logarithm at different temperatures (1/T)					
Epoxy resins	0.033	0.04	0.05	0.066	0.1	0.2
0	4,970	4,691	4,174	3,806	3,367	3,258
2.0	4,868	4,644	4,043	3,829	3,611	3,178
2.5	4,970	4,654	4,205	3,850	3,611	3,219
3.5	4,990	4,654	4,174	3,807	3,496	3,258

Figure 7. Influence of epoxy resins on a change in bitumen plasticity interval.

increasing the temperature of its softening. Figure 7 shows that the introduction of 2.0 mass. %. of epoxy resin increases the operating temperature range by 7-10%. The role of epoxy resin as a thermoactive binder consists in the fact that epoxy resin molecules in reactions are energy carriers by attaching radicals to themselves. At the same time, strong bonds are formed around new molecules.

4. Discussion

Epoxy-fibroblastic concrete mixtures are prepared at factories producing asphalt concrete and having epoxy resin and hardeners metering and feeding systems. When preparing epoxy-fibroblastic concrete, the content of the complex binder is up to 10% of the bitumen mass. Partial replacement of bitumen with modifier is possible[57]. The exact content of the epoxy constituents is determined by the selection of epoxy samples with different modifier content based on the results of laboratory tests[58]. The optimal epoxy content of CHS-EPOXY 525 together with the solidifier TELALIT 0800 is 2.5% of the total binder mass. The preparation consists of the following processing steps:

– delivery of BND to the machine for modification and heating up to 125-130 °C;

– step-by-step addition the required amount of curing agent (TELALIT 0800) to BND when mixing;

– combining bitumen with a hardener by mixing for 40-60 min or by passing through the colloid mill (1-2 cycles);

– preparation of a sand-gravel mixture at a temperature of 70-85 °C;

– introduction of bitumen, which contains a hardener, into the mineral mixture with constant stirring;

– introduction to the mixture of mineral powder with constant stirring;

– introduction of epoxy resin (CHS-EPOXY 525) into the asphalt concrete mixture and mixing for 10-15 sec.;

– unloading the epoxy-asphalt concrete mixture from the asphalt mixer into the storage hopper or car.

When preparing epoxy-fibroblast asphalt concrete, it is necessary to strictly adhere to the temperature regime of heating the mineral mixture and bitumen. Over temperature leads to rapid reaction between epoxy and fiber. As a

consequence, the hardening of the mixture and the loss of its plasticity occur because after the repeated dissolution of the mixture, the epoxy is destroyed and the effect of modification is lost).

In case of long-term pauses in the epoxy and fiber feed, and at the end of the working shift, it is necessary to rinse the feed system with organic solvent (toluene) to prevent it from clogging with the polymerized product. After each shift, the asphalt mixer must be thoroughly cleaned of the residue of the mixture by loading the gravel into it and stirring it for 3 minutes, after which the rubble is unloaded from it[59]. The epoxy-asphalt concrete mixtures are placed in the upper layers of pavements on motorways, sections of roads with high traffic intensity, bridges and overpasses, and heavy goods transport parking areas in accordance with the requirements of DBB B.2.3-4 and other normative documents in all road and climatic zones of Ukraine.

5. Conclusions

The main types of thermoactive binders are considered. The analytical review of the studies made it possible to identify the most optimal thermoactive binder in the form of epoxy resins for use in various fields of composite production. The asphalt concrete composition with the addition of epoxy resin as a thermoactive binder was developed. The developed asphalt concrete with epoxy resins showed better deformation and strength characteristics in comparison with the original asphalt concrete.

The use of epoxy resins for bitumen modification was analyzed. Thus, it was proved that the introduction of epoxy resins as a thermoactive binder reduces the number of paraffins by redistributing hydrogen bonds, which results in the formation of benzene rings and new structural elements. When the amount of additive is increased to 2.5% by weight, the epoxy resin is evenly distributed, while thermostability is enhanced. At the same time, the activation energy during the introduction of the epoxy resins forms the non-ferrous films (at the introduction of 2.5%). With less additives, no such structures are formed.

Moreover, the introduction of epoxy resins changes the structure at the macro level, which is confirmed by the increase in plasticity of the composite. It was also established that when used as an additive in the amount of at least 2.5%, the resulting composite epoxy material gains in strength at an increased temperature range. Furthermore, it was determined that the epoxy asphalt concrete preparation requires a hardener that provides a long reaction time with the epoxy resin.

6. Author's Contribution

• **Conceptualization** – Meiyu Shao; Shilin Yang; Viacheslav Trachevskyi.

• **Data curation** – Mingyang Ta.

• **Formal analysis** – Meiyu Shao; Viacheslav Trachevskyi.

• **Funding acquisition -** Andrii Bieliatynskyi.

• **Investigation** – Shilin Yang; Andrii Bieliatynskyi; Meiyu Shao.

- **Methodology** – Meiyu Shao; Viacheslav Trachevskyi; Mingyang Ta.

- **Project administration** – Andrii Bieliatynskyi.

- **Resources** – Andrii Bieliatynskyi; Viacheslav Trachevskyi; Mingyang Ta.

- **Software** – Meiyu Shao; Shilin Yang.

- **Supervision** – Viacheslav Trachevskyi.

- **Validation** – Andrii Bieliatynskyi.

- **Visualization** – Shilin Yang.

- **Writing – original draft** – Shilin Yang; Mingyang Ta.

- **Writing – review & editing** – Meiyu Shao; Viacheslav Trachevskyi.

7. Acknowledgements

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