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A. V. Buketov

Doctor of Technical Sciences, professor
Kherson State Maritime Academy
orcid.org/0000-0001-9836-3296
buketov@tntu.edu.ua

Yu. M. Shulga

Kherson State Maritime Academy
Danube Institute of the National University" Odesa Maritime Academy"
orcid.org/0000-0003-4144-1956
e-mail: yuriyshulga70@gmail.com

TRANSPORT TECHNOLOGIES RELATED TO THE RESTORATION OF SHIP CARGO MECHANISMS WITH THE LATEST MODIFIED EPOXIES

Introduction

The problem of meeting the needs of the southern region and Ukraine as a whole in improving the efficiency of ship loading mechanisms has not been solved, since research into optimising traffic management, clarifying logistics, improving the efficiency of the use of vehicles and their maintenance and repair is of key importance for the country and the region. The development of transport technologies today requires not only the creation of foundations for the optimal technical use of vehicles, their technical operation, but also their maintenance and repair, the study of patterns of changes in the technical condition of vehicles, the development of technical measures to improve the reliability of functional and energy transport systems, and the creation of conditions for the highly efficient use of vehicles in compliance with environmental protection requirements. This will help to significantly reduce the material costs of building new vessels and operating existing ones, improve the level of safety of navigation and contribute to saving energy and resources.

Statement of Problem

One of the main tasks of Transport Technologies is to search for new promising scientific directions and their implementation in practice, as well as to ensure the effective use of the latest technologies and innovative methods for the construction or rehabilitation of water transport facilities. In this respect, the use of epoxy-based polymer composites is promising. They are characterised by improved adhesive and cohesive properties compared to other known oligomers, which determines the wide range of their application in water transport.

Analysis of the Latest Studies and Publications

As shown by the authors of [1–9], the use of such polymer composite materials (PCMs) in the form of coatings for ship loading mechanisms is currently relevant. In order to improve the properties of adhesives based on an epoxy matrix, additives of different physical nature are introduced into it at the initial stage of formation [10–15]. In this way, not only the mechanical properties of protective coatings can be improved, but also their resistance to thermal stress. In this context, the filling of the epoxy matrix with modifiers introduced in small amounts into the epoxy oligomer is considered promising [16–18]. With this in mind, it was considered appropriate to carry out tests to investigate the effect of the modifier d-ascorbic acid (DAA), which is chemically active for epoxy resin. At the same time, it was important to study the behaviour of the modified materials under the influence of temperature, which is important for the operation of water transport mechanisms.

The aim of the work

Is to study the effect of the modifier d-ascorbic acid on the thermophysical properties of epoxy resins in order to obtain a material intended for the restoration of ship cargo mechanisms.

Materials and Investigation Procedure

An ED-20 grade epoxy resin (ISO 18280:2010), which is widely used in practice worldwide, was used to form the polymer matrix. To improve the properties of the polymer matrix, a modifier in the form of d-ascorbic acid (DAA) was additionally introduced into the epoxy binder at a content of 0,1...2,0 pts.wt. per 100 pts.wt. of ED-20 epoxy resin. Molecular formula of the modifier: $C_6H_8O_6$.

Polyethylene polyamine PEPA (TU 6-05-241-202-78) was the hardener for the epoxy binder.

The following properties of the CM were investigated in the work: thermal coefficient of linear expansion (TLCE) and heat resistance (T).

The heat resistance (Martens) of the CM was determined in accordance with GOST 21341-75. The method of testing consists in determining the temperature at which the specimen was heated at a rate of $v = 3$ K/min under a constant bending load $F = 5 \pm 0,5$ MPa, as a result of which it deformed by a given value ($h = 6$ mm).

The thermal coefficient of linear expansion (TCLE) of the materials was calculated from the curve of relative strain versus temperature, approximating this dependence with an exponential function. The relative strain was determined from the change in sample length with increasing temperature under steady state conditions (GOST 15173-70). Dimensions of specimens used in the study: $65 \times 7 \times 7$ mm. The rate of temperature increase was $v = 2$ K/min.

Results and Discussion

Initially, the heat resistance of the original epoxy matrix was investigated and found to be $T = 341$ K (Fig. 1). Subsequently, the heat resistance of the modified CMs was determined by varying the concentration of the DAC modifier in the range of 0,25 pts.wt. to 2 pts.wt. It has been shown that the modifier improves the heat resistance of the epoxy

matrix, since its introduction in a small amount (0,25...1,0 prt.wt.) allows its increase compared to the unfilled matrix from 341 K to 347...351 K. According to the dynamics of the heat resistance as a function of the DAC concentration, the optimal content of the additive in the epoxy compound was determined, which is 1,25...1,50 prt.wt. per 100 prt.wt. of epoxy resin (Fig. 1). It is this modifier content that ensures the production of composites with the highest heat resistance values of all the materials studied. Such CMs are characterised by the following heat resistance values – 352...354 K. Further increase of the additive concentration (1,75...2,00 prt.wt.) leads to a decrease of the heat resistance of the materials to 352 K.

The mechanism by which the heat resistance of the epoxy matrix is increased in the presence of a modifier can be explained as follows. It is well known [5, 6, 12] that the properties of epoxy composites are primarily determined by the structure of the reticulated polymer formed during cross-linking of the epoxy matrix. The kinetics of the reaction of an epoxy oligomer with a polyethylene polyamine hardener is rather complex. However, it should be noted that it occurs without the formation of by-products according to the scheme of diepoxide addition to polyamine with simultaneous opening of the epoxy ring. As a result of such chemical interaction processes, the spatial network of the polymer is formed, which has an amorphous structure.

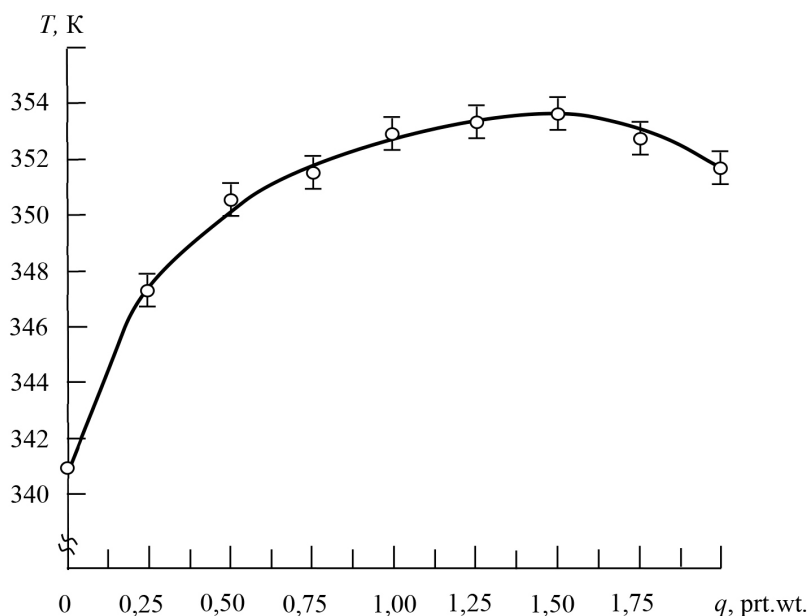


Fig. 1. Dependence of CM heat resistance on DAC concentration

At the same time, it should be noted that globular formations are one of the important elements of the supramolecular structure of amorphous polymers. To date, scientists have carried out a wide range of studies on the directions of globule opening in order

to increase the density of the three-dimensional polymer network. This involves increasing the degree of gel fraction and, as a result, improving the cohesive properties of the materials. In particular, research has been carried out to modify the chemical structure of

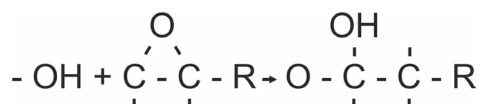
the epoxy oligomer or hardener, to develop new polymer moulding technologies and to investigate the effect of thermal and mechanical fields after polymerisation of the epoxy matrix. At the same time, it can be stated that no significant effect has been observed in changing the shape of the beads or their opening after cross-linking the materials.

The authors of [5, 19] have shown that a significant effect in increasing both the cohesive and thermophysical properties of polymers is achieved by their structural modification. It should be noted that there are three main methods of modifying lattice polymers: chemical, physicochemical and physical. In our case, we used d-ascorbic acid as a modifier, which contains hydroxyl, carbonyl and other functional groups in its structure. In other words, we envisaged a physicochemical method of modifying the epoxy oligomer by introducing a modifying additive.

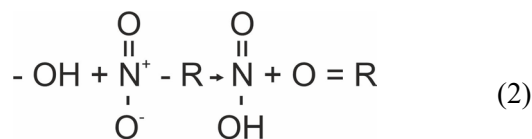
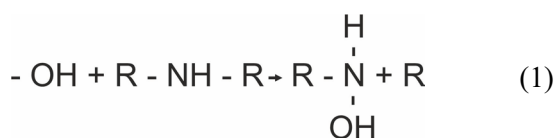
Based on the theory of polymer formation at the macro, meso and micro levels [19], it is necessary to determine and predictably regulate the structure of the initial polymer, including the supramolecular structure, at each level. This requires the existence of thermally and hydrolytically stable bonds between the components of a homogeneous system (in our case, between the epoxy oligomer and the modifier). It is obvious that the modifier must have functional groups in its initial structure capable of participating in the cross-linking reaction with the active groups of the epoxy oligomer. Only the fulfilment of this condition will ensure the production of a material with stable chemical bonds, which will further determine its cohesive strength.

As mentioned above, the structure of the modifier contains hydroxyl and carbonyl groups that can catalyse or inhibit polymerisation reactions. Based on the analysis of the IR spectra of the modifier, epoxy oligomer and modified matrices at different DAC contents, several possible mechanisms of interaction between the epoxy resin and the additive at different concentrations can be identified.

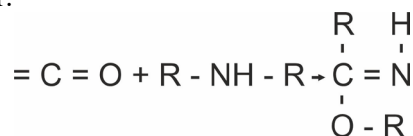
1. Reaction of hydroxyl OH groups of d-ascorbic acid with epoxy groups:



2. Reaction of hydroxyl OH groups of epoxy oligomer and d-ascorbic acid modifier with hardener:



3. Reaction of carbonyl C=O modifier groups with a hardener:



4. Reaction of the carbonyl C=O groups of the epoxy oligomer with a hardener.

As a result of the above-mentioned possible reactions of structure formation of a compound based on an epoxy oligomer and a modifier in the presence of a polyethylene polyamine, mainly strong chemical bonds of the C-O, NH₂, O-NH₂, N=O, N-O-H, C=N type are formed, which largely determine the increase in the cohesive strength of the newly formed modified epoxy matrices. It should be noted that it is the cohesive strength of the matrix that determines the heat resistance of the material under the influence of elevated temperatures.

In addition, the glass transition temperature and shrinkage of the modified CMs were studied as a function of the amount of modifier. It was found (Fig. 2) that the glass transition temperature of the epoxy matrix is T_c = 327 K. The introduction of a modifier increases this indicator to 330 K for materials containing DAC in the amount of 0,5...1,0 pts.wt. The maximum glass transition temperature (333 K) was observed for the modified material containing 1,5 % by weight of DAC. Subsequently, a decrease in this indicator was observed as the additive content increased, as a glass transition temperature of 331 K was observed for the CM with a modifier in the amount of 2.0 pts.wt. At this additive level, the maximum values of both heat resistance and glass transition temperature were observed. It is at this concentration of DAC that the cross-linking of the compound forms the most cross-linked structural network of an amorphous polymer with the highest number of chemical bonds, the mechanism of formation of which is described in detail above.

It is known [6, 7, 12] that during polymerisation of an epoxy oligomer the intermolecular distances decrease from 0,3...0,5 nm to 0,15 nm. This undoubtedly causes a reduction in the volume of the polymer compound after cross-linking, which implies its shrinkage. At the same time, it should be noted that shrinkage deformations lead to additional residual stresses in the polymer composite. This leads to a deterioration of the cohesive and, consequently, the

thermal and mechanical properties of the material during its service life.

It is known [17, 18] that the rate of increase of shrinkage deformations in the CM is maximum in the first hours of polymerisation. After 3...5 days, depending on the nature of the oligomer, the shrinkage dynamics stabilise. Depending on the degree of filling, the type of modifier or plasticiser, the shrinkage of composites during this period can reach values of 0,02 %...0,15 %. Thus, the authors of [5, 17, 18] demonstrated that the introduction of additives can reduce the amount of shrinkage.

In this study (Fig. 2) it was found that the shrinkage of the epoxy matrix (after 3 days of polymerisation) was $\varepsilon = 0,14$ %. The introduction of a modifier at a content of 0,5...1,0 pts.wt. reduces the shrinkage of the materials to 0,10...0,12 %. This suggests a positive effect of the modifier in improving this property of the materials. It should be noted, however, that residual stresses occur

during crosslinking in any case. During the service life of the coating or product they can cause a breakdown in the integrity of the CM due to the formation of cracks in the micro and macro volumes of the matrix (including supramolecular structures). This leads to premature ageing of materials and failure of water transport parts.

It has been shown (Figure 2) that the optimum solution for reducing shrinkage is to add a modifier to the epoxy compound in the amount of 1,25...2,0 pts.wt. In this case, materials with a shrinkage value of 0,07 % are formed. We believe that a further reduction in shrinkage can be achieved by introducing a micro-dispersed filler at a low level. Such an introduction of the optimum level of microparticles will reduce the intrinsic deformations of the clusters on the one hand and reduce the probability of crack initiation under static and dynamic critical loads of transport parts on the other.

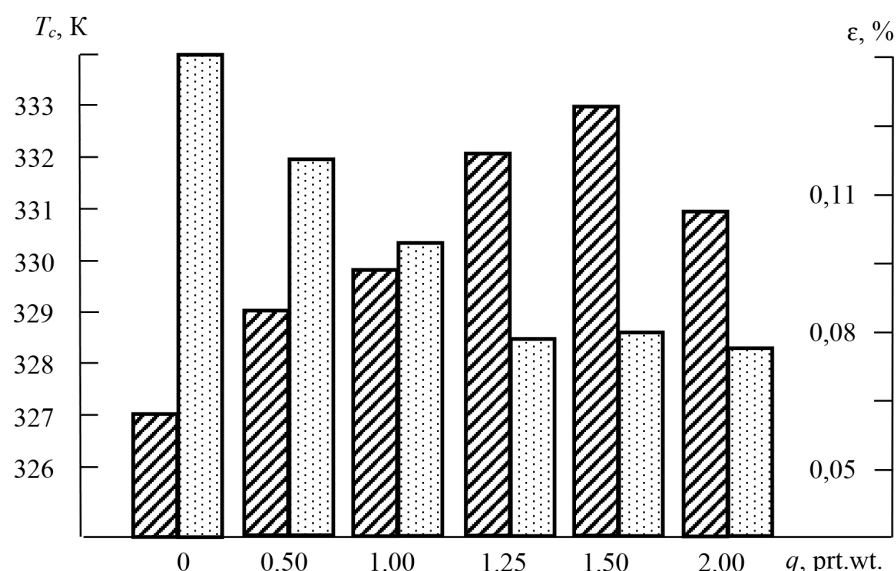


Fig. 2. Dynamics of glass transition temperature (T_c) and shrinkage (ε) of CM on the content of DAC modifier:

▨ – glass transition temperature (T_c); ▤ – shrinkage (ε)

In order to obtain a CM with a densely cross-linked structure, it is necessary to ensure the effect of maximum mobility of the macromolecules during structure formation with their subsequent tight packing in the compound under selected thermal and time polymerisation conditions. These factors depend on the viscosity of the binder, the amount of modifier, the temperature and the time of polymerisation. It should be noted that these criteria, together with the structure-forming activity of the additive, determine the degree of cross-linking of the matrix. The latter parameter is important for assessing the thermophysical properties of materials and their dynamics during the operation of transport parts. It can be estimated indirectly by knowing the dynamics of the thermal coefficient of linear expansion (TCLR) of the cementitious materials as a function of

temperature. The results of these tests are given in Table 1.

It was found (Table 1) that the TCLR of CM increases with increasing temperature regardless of the modifier content. In particular, for the epoxy matrix, an increase in this indicator of 1.7 times was observed with an increase in the temperature range from 320 K to 370 K. At the same time, it can be observed that in selected temperature ranges (the latter corresponding to the operating modes of vehicles), the introduction of a modifier leads to a decrease in the TCLR of the modified matrices compared to the original one. In particular, in the temperature range 300...320 K, a decrease of this indicator from $6,3 \times 10^{-5} \text{ K}^{-1}$ to $(3,8...4,8) \times 10^{-5} \text{ K}^{-1}$ was observed. In the temperature range where the

glass transition temperature of the materials is located (300...420 K), the TCLR of CM decreases from $9.9 \times 10^{-5} \text{ K}^{-1}$ to $(5,4...6,7) \times 10^{-5} \text{ K}^{-1}$.

It should be noted that the minimum values of TCLR were observed for the matrix modified with DAC in the amount of 1,5 pts.wt. In the selected temperature ranges, the coefficient of linear expansion decreases by 1,3...1,8 times compared to the original matrix. The results obtained can be explained as follows.

Analysis of the results shows that the DAC modifier has a plasticising effect on the formation of the epoxy matrix. As shown (Table 1), this dependence (additive content - TCLR values) has a clearly expressed extreme character. The reduction in TCLR at the optimum DAC content ranges from 55 % to 78 %. The results obtained (Table 1) can be explained on the basis of the micro- and nanostructure formation patterns of the modified matrices. As

mentioned above, the original and modified epoxy polymers contain supramolecular globular formations whose end chains can intertwine at the molecular level during structure formation. This creates the reticulated structure of the polymers. The introduction of a small amount of modifier into the epoxy oligomer reduces the frictional forces between the globules and the branched macromolecules of the epoxy oligomer. This results in a significant reduction in the dynamic viscosity of the compound. In the early stages of polymerisation, fibrillar aggregates are also formed from the macromolecules of the epoxy oligomer and modifier. This slows down the growth rate of the plasticity of the compound. In the final stages of curing, the formation of a three-dimensional amorphous polymer network leads to the formation of an interbundle structure of the compound. Accordingly, the dynamic viscosity of the homogeneous system decreases sharply.

Table 1

Dynamics of the thermal coefficient of linear expansion (TCLR) of CM from the test temperature ranges

№	Concentration of the DAC modifier, <i>g</i> , prt.wt.	Thermal coefficient of linear expansion, $\alpha \times 10^{-5}, \text{K}^{-1}$			
		Test temperature ranges, $\Delta T, \text{K}$			
		300...320	300...370	300...420	300...470
1	0	6,3	6,8	9,9	10,9
2	0,5	4,8	5,6	6,7	9,3
3	1,0	4,4	5,2	6,0	8,9
4	1,5	3,8	4,2	5,4	8,5
5	2,0	4,1	4,8	5,8	9,0

Based on the above, it can be argued that the introduction of a modifier into the epoxy oligomer at an optimal concentration (1,25...1,5 pts.wt) promotes the formation of additional cross-links in the network structure of the polymer matrix. At the same time, it is necessary to consider the additional formation of physical bonds in the modified matrix due to the influence of ionic and van der Waals forces. Ultimately, this leads to an increase in the polymerisation rate of the compound and an improvement in the thermal properties of the modified material.

In addition, the following is noted. The problem of globule opening during matrix cross-linking has been described above and is solved by structural modification of the polymers. Based on the results of a series of tests on the thermophysical properties of materials, it can be stated that the plasticising effect of the modifier introduction causes a significant percentage of globular formations to be levelled. This leads to the formation of small clusters compared to fibrils due to a decrease in energy potential.

The second important reason for introducing a modifier is that the modified system has a lower viscosity compared to the original epoxy resin. In the

future, this will make it possible to increase the degree of filling of composites with improved performance characteristics.

Conclusions

Based on the results of the study, the following conclusions can be drawn:

1. Based on the dynamics of the heat resistance as a function of the concentration of d-ascorbic acid, the optimum content of the additive in the epoxy compound was determined, which is 1,25...1,5 prt.wt. on 100 prt.wt. of epoxy resin. The introduction of a modifier into the epoxy oligomer provides composites with the highest heat resistance values of all the materials studied. The heat resistance values increase from 341 K (for the epoxy matrix) to 352...354 K.

2. The mechanism of increasing the heat resistance of the epoxy matrix in the presence of a modifier, which involves the interaction of epoxy resin with the additive and hardener as a result of the following reactions, is substantiated:

– reaction of hydroxyl OH groups of *d*-ascorbic acid with epoxy groups;

- reaction of hydroxyl OH groups of epoxy oligomer and d-ascorbic acid modifier with hardener;
- reaction of carbonyl C=O modifier groups with the hardener;
- reaction of carbonyl C=O groups of the epoxy oligomer with the hardener.

As a result of the above reactions of the structure formation of the compound based on an epoxy oligomer and a modifier in the presence of polyethylene polyamine, mainly strong chemical bonds of the C-O, NH₂, O-NH₂, N=O, N-O-H, C=N type occur, which largely determine the increase in the cohesive strength of the newly created modified epoxy matrices. It should be noted that it is the cohesive strength of the matrix that determines the heat resistance of the material under conditions of elevated temperatures.

3. It was found that the maximum glass transition temperature (333 K) was observed for the modified material containing d-ascorbic acid at 1,5 pts.wt. At this level of additive, the maximum values of both heat resistance and glass transition temperature were observed compared to the original epoxy matrix (327 K). At this modifier concentration, the cross-linking of the compound forms the most cross-linked structural network of an amorphous polymer with the highest number of chemical bonds.

4. It has been shown that the optimum solution for reducing shrinkage is to fill the epoxy compound with a modifier in the amount of 1,25...2,0 pts.wt. In this case, materials with a lower shrinkage value (0,07 %) are formed compared to the epoxy matrix (0,14 %). A further reduction in shrinkage can be achieved by introducing a small amount of micro-dispersed filler. This introduction of the optimum level of micro-particles reduces both the intrinsic deformation of the clusters and the probability of crack initiation under critical static and dynamic loads of transport parts.

5. It has been substantiated that the minimum values of TCLR were observed for the matrix modified with d-ascorbic acid in the amount of 1,5 prt.wt. In the selected temperature ranges (300...470 K), the TCLR of the composite, compared to the original matrix, decreases by 1,3...1,8 times. The results obtained can be explained on the basis of the patterns of formation of the micro- and nanostructure of the modified matrices. The modified epoxy polymers contain supramolecular globular formations, the end chains of which can intertwine during structure formation at the molecular level. This creates the mesh structure of the polymers. When an optimal amount of modifier is added to the epoxy oligomer, the friction forces between the globules and branched macromolecules of the epoxy oligomer are reduced. This leads to a significant reduction in the dynamic viscosity of the compound.

At the initial stage of polymerisation, fibrillar aggregates are also formed from the macromolecules of the epoxy oligomer and modifier. This slows down the growth rate of the plasticity of the compound. At the final stages of curing, the formation of a three-dimensional amorphous polymer network results in the formation of an interbundle structure of the compound. Accordingly, the dynamic viscosity of the homogeneous system decreases sharply.

Based on the above, it can be argued that the introduction of a modifier into the epoxy oligomer at an optimal concentration (1,25...1,5 prt.wt.) promotes the formation of additional transverse bonds in the mesh structure of the polymer matrix. At the same time, it is necessary to take into account the additional formation of physical bonds in the modified matrix due to the influence of ionic and van der Waals forces. Ultimately, this leads to an increase in the polymerisation rate of the compound and an improvement in the thermal properties of the modified material.

In the next stages, the authors plan to conduct tests to determine the effect of dispersed fillers of different physical nature on the structure and properties of modified epoxy composites.

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Букетов А. В., Шульга Ю. М.

ТРАНСПОРТНІ ТЕХНОЛОГІЇ У КОНТЕКСТІ ВІДНОВЛЕННЯ СУДНОВИХ ВАНТАЖНИХ МЕХАНІЗМІВ НОВІТНІМИ МОДИФІКОВАНИМИ ЕПОКСИПЛАСТАМИ

Розвиток транспортних технологій на сьогодні обумовлює необхідність не лише створення основ оптимального технічного використання засобів транспорту, їх технічної експлуатації, але й технічного обслуговування і ремонту. Одним із основних завдань транспортних технологій є пошук нових перспективних наукових напрямів та їх впровадження у практику, а також забезпечення ефективного застосування новітніх технологій та інноваційних методів для формування чи відновлення об'єктів водного транспорту. У цьому плані перспективним є застосування полімерних композитів на основі епоксидної смоли. Вони відрізняються покращеними показниками адгезійних та когезійних властивостей порівняно з іншими відомими олігомерами, що визначає широкий спектр їх застосування на водному транспорті.

З метою поліпшення властивостей адгезивів на основі епоксидної матриці у неї на початковій стадії формування вводять добавки різної фізичної природи. У роботі досліджено вплив модифікатора d-аскорбінової кислоти на теплофізичні властивості епоксипластів для отримання матеріалу, призначеного для відновлення суднових вантажних механізмів. За динамікою теплостійкості від концентрації d-аскорбінової кислоти визначено оптимальний вміст добавки у епоксидному компаунді, який становить 1,25...1,50 мас.% на 100 мас.% епоксидної смоли. Уведення у епоксидний олігомер модифікатора забезпечує отримання композитів з максимальними значеннями теплостійкості серед усіх досліджуваних матеріалів. При цьому значення теплостійкості зростають від 341 К (для епоксидної матриці) до 352...354 К.

Обґрунтовано механізм підвищення теплостійкості епоксидної матриці у присутності модифікатора, який передбачає взаємодію епоксидної смоли з добавкою і твердником внаслідок перебігу хімічних реакцій. У результаті перебігу реакцій структуроутворення компаунду на основі епоксидного олігомеру та модифікатора у присутності поліетиленполіаміну виникають в основному міцні хімічні зв'язки типу C-O, NH₂, O-NH₂, N=O, N-O-H,

$C=N$, які значною мірою обумовлюють підвищення показників когезійної міцності новостворених модифікованих епоксидних матриць. Зазначимо, що саме показники когезійної міцності матриці визначають теплостійкість матеріалу в умовах впливу підвищених температур.

Встановлено, що максимальні показники температури склування (333 K) спостерігали для модифікованого матеріалу, який містить *d*-аскорбінову кислоту у кількості 1,5 мас.%. За такого вмісту добавки спостерігали максимальні значення як теплостійкості, так і температури склування порівняно з вихідною епоксиматрицею (327 K). Саме за такої концентрації модифікатора при зшиванні компаунду формується максимально зшита структурна сітка аморфного полімеру з найбільшою кількістю хімічних зв'язків.

Ключові слова: композит; теплостійкість; модифікатор; деструкція; властивості.

Buketov A. V., Shulga Yu. M.

TRANSPORT TECHNOLOGIES RELATED TO THE RESTORATION OF SHIP CARGO MECHANISMS WITH THE LATEST MODIFIED EPOXIES

The development of transport technologies today requires not only the creation of bases for the optimal technical use of vehicles, their technical operation, but also their maintenance and repair. One of the main tasks of transport technologies is the search for new promising scientific directions and their implementation in practice, as well as ensuring the effective use of the latest technologies and innovative methods for the construction or repair of water transport facilities. In this respect, the use of epoxy-based polymer composites is promising. They are characterised by improved adhesive and cohesive properties compared to other known oligomers, which determines the wide range of their application in water transport.

*In order to improve the properties of epoxy-based adhesives, additives of different physical nature are introduced into the epoxy matrix at the initial stage of moulding. This paper investigates the effect of the modifier *d*-ascorbic acid on the thermal properties of epoxies to obtain a material intended for the restoration of ship loading mechanisms. Based on the dynamics of heat resistance as a function of *d*-ascorbic acid concentration, the optimum content of the additive in the epoxy compound was determined, which is 1,25...1,50 pts.wt. for 100 pts.wt. of epoxy resin. The introduction of a modifier into the epoxy oligomer provides composites with the highest heat resistance values of all the materials studied. The heat resistance values increase from 341 K (for the epoxy matrix) to 352...354 K.*

The mechanism of increasing the heat resistance of an epoxy matrix in the presence of a modifier is substantiated, which involves the interaction of epoxy resin with an additive and a hardener as a result of chemical reactions. As a result of the reactions of structure formation of the compound based on epoxy oligomer and modifier in the presence of polyethylene polyamine, mainly strong chemical bonds of C-O, NH₂, O-NH₂, N=O, N-O-H, C=N type are formed, which largely determine the increase of cohesive strength of the newly formed modified epoxy matrices. It should be noted that it is the cohesive strength of the matrix that determines the thermal resistance of the material at elevated temperatures.

*It was found that the maximum glass transition temperature (333 K) was observed for the modified material containing *d*-ascorbic acid at 1,5 pts.wt. At this level of additive, the maximum values of both heat resistance and glass transition temperature were observed compared to the original epoxy matrix (327 K). At this modifier concentration, the cross-linking of the compound forms the most cross-linked structural network of an amorphous polymer with the highest number of chemical bonds.*

Keywords: compound; heat resistance; modifier; destruction; properties.

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