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Investigation of electrospark hydraulic shock influence on adhesive-cohesion characteristics of epoxy coatings

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The reasonableness of preliminary electrospark alloying of the aluminum base and simultaneous electrospark treatment of the epoxy composition with the subsequent formation of the coating is substantiated. The relevance of the application of dispersed particles with ferromagnetic nature as fillers is experimentally substantiated. Such additives, irrespectively of their chemical, thermodynamic and kinetic activity, significantly affect the degree of binder cross-linking in the surface layers around the fillers and significantly increase physical-mechanical properties of the materials and protective coatings formed on their basis.

Keywords: epoxy composite, interaction mechanism, electrospark treatment, degree of cross-linking, substrate, adhesive strength, phase separation interface.

Дослідження впливу електроіскрового гідроудару на адгезійно-когезійні характеристики епоксидних покриттів. *О.В.Тотосько, П.Д.Стухляк, А.Г.Микитишин, В.В.Левицький*

Обгрунтовано доцільність проведення попереднього електроіскрового легування алюмінієвої основи та одночасної електроіскрової обробки епоксидної композиції з подальшим формуванням покриття. Експериментально підтверджено доцільність використання, як наповнювачів, дисперсних частинок феромагнітної природи. Такі добавки, незалежно від їхньої хімічної, термодинамічної та кінетичної активності, суттєво впливають на ступінь зшивання в'яжучого у поверхневих шарах навколо наповнювачів, що дозволяє суттєво підвищити фізико-механічні властивості матеріалів та захисних покриттів, сформованих на їх основі.

Обоснована целесообразность проведения предварительного электроискрового легирования алюминиевой основы и одновременной электроискровой обработки эпоксидной смолы с последующим ее нанесением на субстрат. Экспериментально подтверждена целесообразность использования, в качестве наполнителей, дисперсных частиц ферромагнитной природы. Такие добавки, независимо от их химической, термодинамической и кинетической активности, существенно влияют на степень сшивания вяжущего в поверхностных слоях вокруг наполнителей, позволяют существенно повысить физико-механические свойства защитных покрытий.

1. Introduction

The current stage in the development of materials science is associated with the creation of protective coatings with a wide range of physical-mechanical properties. At the same time, protective coatings should increase the reliability and operational life of equipment, as well as improve the maintainability of parts and mechanisms of machines. At present, composite materials (CM) based on epoxy binders are widely used. Such materials are characterized by high physical and mechanical properties, high adhesive strength, and also have significant corrosion resistance to aggressive media. However, the potential of epoxy composites is not completely realized. First, not enough attention is paid to the study of interaction at the interface in the "binder — filler" system. Improving the interaction in this system will enhance the overall performance of the composite.

In order to improve the material properties, various methods of processing the composite materials are used, for example, their processing by external fields. The pre-processing of matrix components by the method of electrospark hydraulic shock (ESHS) is one of the most promising in this direction.

It should be noted that the creation of new CMs and improvement of the operational characteristics of composites based on epoxy matrices, requires further investigations of the stages of combining components and forming composites into products. The solution of problems of operation reliability of machine parts having a complex geometric shape is closely related to the analysis of the stress-strain state of their protective coatings. At present, little attention is paid to the development of modern calculation methods for such investigations [1]. This is primarily due to the difficulties occurring during the assessment of the stress state of real objects with protective coatings during operation. In this regard, the problem of developing new and improved modern methods of experimental studying the strength and fracture of materials with polymer coatings is very important.

2. Experimental

Polymer composite materials based on epoxydiane oligomer ED-20 (GOST 10587-84) were selected as the object of the investigation; these are characterized by high adhesive and cohesive strength, insignificant shrinkage and manufacturability when applied to extended surfaces of complex profiles and have a developed raw material base [2]. Taking into account the large size and weight, complex surface profiles of machine parts, as well as the technology of coating, a polyethylene polyamine (PEPA) hardener was used for cross-linking epoxy compositions. It makes it possible to solidify the composite at room temperature. 101P ferrite is used in this investigation. The following temperature-time modes of CM formation are used: combination of components, sample formation, exposure for 24 h at room temperatures, and heat treatment at 413 K for 2 h. The stabilization of samples is performed at room temperature for 24 h, followed by experimental investigations. The uniform distribution of components in the material is ensured by the hydrodynamic combination of components. Before forming samples, the composition is vacuumized. The dispersion is controlled by sieving through sieves of an appropriate size. The appropriate material formation parameters ensure the formation of a three-dimensional grid with the maximum degree of cross-linking. In order to determine the stoichiometric ratio of the components of the filler system, various cross-linking stages are simulated and investigated by introducing a hardener into the composition from 8 to 15 parts by weight. The stoichiometric ratio for these components is determined as follows: 100 weight parts of ED-20, 10 weight parts of PEPA [3, 4]. Previous studies on determination of sedimentological processes during the formation of coatings using optical microscopy have shown that the structure was homogeneous during the formation of samples. The beginning of the sedimentological processes was observed for the filler dispersion of 63 μm, at room temperatures by the difference in the composition transparency after 10-12 days [3].

Taking into account the multifactorial nature of technological modes and statistic errors of the experiment during samples manufacturing, it is reasonable to obtain several characteristics from each sample for one investigation.

Adhesive strength is one of the most important operational characteristics of coatings [1, 5–8]. To study the adhesion properties of protective coatings to the metal surface, the effects of amount, magnetic and chemical nature of filler in the composite on the fracture stress are taken into consideration. Aluminum samples for tensile strength tests were made of 1 mm thick strip. Coatings with a length of 40 mm are applied to aluminum samples with a working part width of 5 mm. Elastic characteristics and relative deformations of aluminum and coatings are determined during the tensile deformation; the amount of the main filler is changed from 30 to 150 weight parts, and fine powders — from 5 to 50 weight parts per 100 weight parts of the epoxy matrix (hereinafter the filler concentration is given in weight parts per 100 weight parts of the binder).

The research technique used makes it possible to determine the value of deformation, adhesion and cohesion strength, modulus of elasticity for the coating and the base, as well as to characterize the type fracture of the composite when testing one sample [9–11].

The modulus of elasticity is determined by the elastic area of the tensile curves by the following formula:

$$E_n = \left(\frac{\varepsilon_o}{\varepsilon_n} - 1\right)\frac{\delta_o}{2\delta_n} \cdot E_o, \tag{1}$$

where indices "o" and "n" denote the characteristics related to the base and coating, respectively. Cohesive strength or normal stresses:

$$\sigma_n = \frac{2\varepsilon_o}{hk^2} \cdot \frac{G_o/G_h \cdot G_h/G_h}{G_o/G_h + G_h/G_h}\left(1 + \frac{chkz}{chkl}\right) \tag{2}$$

dhesive strength or tangential stresses:

$$\tau = \frac{\varepsilon_k}{t\left(\frac{1}{E_nF_n} + \frac{2}{E_oF_o}\right)} thkl \tag{3}$$

where:

$$k^2 = 2tl\left(\frac{1}{E_nF_n} + \frac{2}{E_oF_o}\right) \tag{4}$$

$$L = \frac{G_o/G_h \cdot G_n/G_h}{G_o/G_h + G_n/G_h}, \tag{5}$$

This experimental-calculation technique makes it possible, when testing one sample, to determine a set of values characterizing physical-mechanical properties of the system "base-coating": the modulus of elasticity of the base and coating, the value of composite critical deformation, stress levels within it and in the area of adhesive contact, as well as to define the type of the system fracture (cracking or separation).

3. Results and discussion

Deformation curves of the investigated materials are constructed by averaging the results of three experiments; here the discrepancy of the experimental curves does not exceed 3%. The curves of the dependences of relative deformations on stresses constructed for epoxy resin modified by electrospark hydraulic shock are shown in Fig. 1. It should be noted that the strength properties of epoxy composites are evaluated by the maximum stresses occurring in the material when critical deformations are reached according to the method [9, 10].

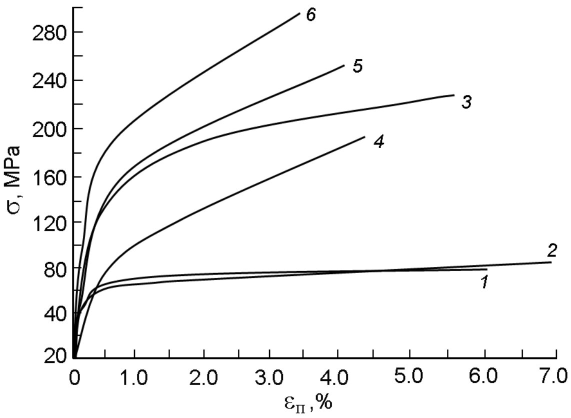

Fig. 1. Dependences of stresses on relative deformations in the base (*1*, *2*) and in the coating (*3–6*): *1* — base modified by electrospark alloying; *2* — unmodified base; *3* — base unmodified by electrospark alloying, unprocessed by ESHS resin in the coating; *4* — base unmodified by electrospark alloying, processed by ESHS resin in the coating; *5* — modified by electrospark alloying base, unprocessed by ESHS resin in the coating; *6* — base modified by electrospark alloying, processed by ESHS resin in the coating.

Analysis of the investigation results shows that the pre-processing of both oligomer and base causes the decrease in the maximum relative deformations of the material (Fig. 1). Particularly, it is shown that due to electrospark alloying the base, the reduction of the maximum relative deformations of aluminum by 14 % occurs (curves *1*, *2*). It is assumed that this is caused by an increase in the cohesive strength of the base due to the formation of transition layer in the base after electrospark alloying.

Note that the base is processed by the spark method, in the capacitor discharge mode in the range of 30–60 V [12]. As a result, a layer of copper oxide forms on the surface of the material, and an intermetallic compound with the crystal structure of the Al_2Cu_3 alloy is formed under it. (Fig. 2).

Analysis of the results of stress dependence on the relative deformations of samples alloyed and modified by the ESHS method, as well as samples without alloying and modification shows that the preliminary treatment provides a significant decrease in the maximum relative deformations, as well as an increase in the maximum stresses in the coatings. The presence of maximum stresses in epoxy resin coatings has been established, which after alloying of the base and ESM modification of the matrix are 1.5...2.0 times higher. These results are ex-

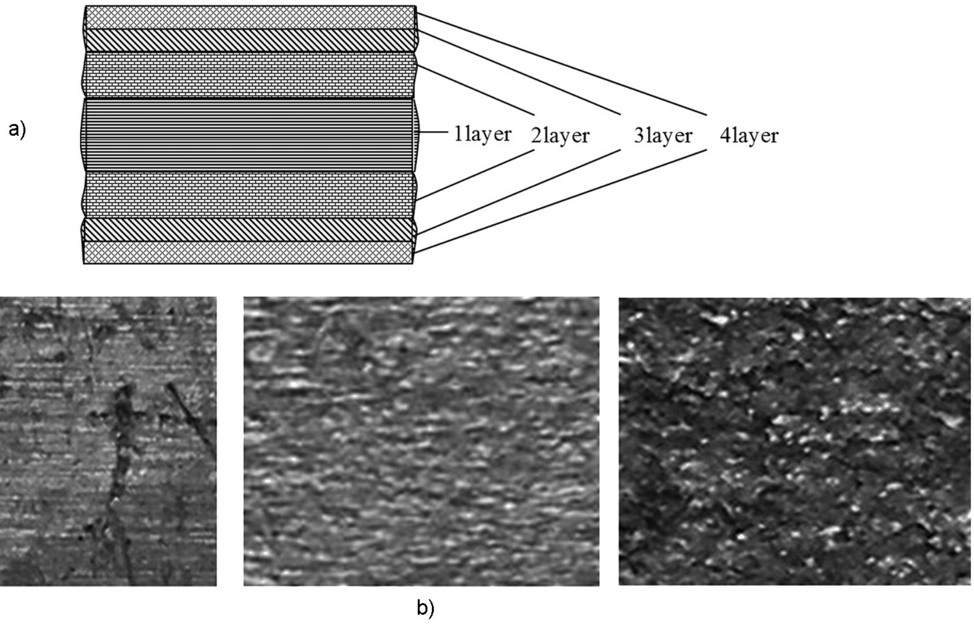

Fig. 2a. Structural diagrams of the coating layers after electrospark alloying of the aluminum base: 1st layer — aluminum; 2nd layer — Al_2Cu_3; 3rd layer — copper oxide; 4th layer — epoxy coating. (b) Optical microphotographs of layers after base alloying: a) aluminum; b) Al_2Cu_3; c) copper oxide.

plained by an increase in the degree of matrix cross-linking during the coating formation after modifying the epoxy resin by the ESHS method, as well as an increase in interfacial interaction at the interface between the polymer matrix and the alloyed base.

These assumptions are confirmed by the results of experiments and calculations of the adhesive and cohesive strength in the composites (Table 1). It should be noted that the experimental dependences of the adhesive strength (τ, MPa) for protective coatings, both original and modified by ESHS, were calculated from the instantaneous stresses in the aluminum sample and protective coatings. It was found experimentally (Table 1) that the modification of epoxy resin by the ESHS method, as well as the preliminary electrospark alloying of the base, provides a significant increase in the adhesive and cohesive strength of the "coating-base" system. Nevertheless, we note that the complex modification of the base and coating provides an increase in the abovementioned characteristics by 1.5...1.8 times as compared to the initial materials. An increase in the degree of matrix cross-linking, as well as better interaction at the "coating base" interface, results in an increase of strength and rigidity of the coatings. This is confirmed by the results on the modulus of elasticity and the magnitude of maximum absolute deformation of the coatings. It is established (Table 1) that after

Table 1. Physical-mechanical properties of epoxy matrix

Material	ESHS processing		Adhesive strength, τ_{max}, MPa	Cohesion strength, τ_c, MPa	Modulus of elasticity, E_p, GPa	Maximum deformation*, L_{pmax} on the basis of L_{base} = 45 mm
	Base	Oligomer				
Matrix	–	–	43.04	29.12	1.51	0.0056
Matrix	–	+	49.45	41.67	2.74	0.0044
Matrix	+	–	56.33	33.7	1.84	0.0041
Matrix	+	+	62.91	45.08	3.02	0.0034

Note. "–" without electrospark hydraulic shock processing; "+" — after electrospark hydraulic shock processing; "*" — the maximum value of standard sample tensile deformation at which the epoxy polymer coating is destroyed by aluminum base deformation.

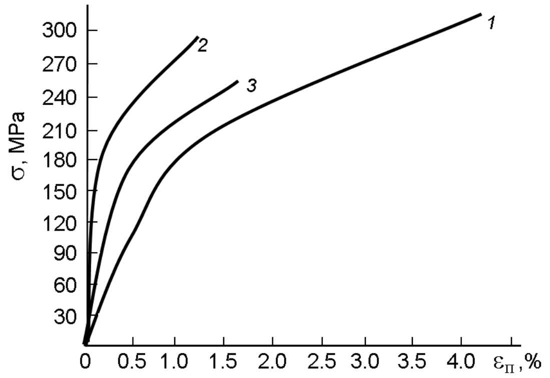

Fig. 3. Stresses depending on relative deformations in coatings based on epoxy matrix, containing: *1* — ferrite + SC; *2* — B_4C + Cr_2O_3; *3* — SiC + Al_2O_3.

modification, the modulus of elasticity increases by 1.6...2.0 times, and the absolute deformation decreases by 18...24 %. Therefore, it can be concluded that after alloying of the base and modification of the matrix by the ESHS method, the formed coatings are characterized by high adhesion and cohesion strength; and they are more rigid in comparison with original (untreated) coatings. It should be noted that during operation, the stresses at the "base-coating" interface decrease. In this case, we should expect an increase in the reliability and operational life of machine parts and mechanisms. This is especially important when parts have complex shapes and operate under thermal cycling conditions.

The next stage of the investigation is to test the "base—coating" systems using a disperse filler. The optimal concentrations of the bidispersed filler in the matrix material depending on the magnetic nature of dispersed particles were determined in previous studies [14]. Further, the complex characteristics of coatings made of filled materials are investigated under stress-strain state conditions.

It was found (Fig. 3) that the previous ESHS treatment of epoxy composites containing bidispersed particles of B_4C and Cr_2O_3, as well as SiC and Al_2O_3 reduces the relative deformation of the coating material by 3.0...3.5 times in comparison with the original epoxy matrix. It should be noted that after the ESHS processing, the deformation characteristics of composites containing particles of ferrite and soft carbon (SC) increase almost twice and reach the values of deformation characteristics of unmodified coatings (Fig. 1, Fig. 3). In addition, it is noted that the maximum stresses in coatings with ferrite and SC particles are the highest of all the samples studied, which indicates the high cohesive characteristics of these coatings.

According to the results of deformation studies, it is interesting to analyze the calculated values of adhesive and cohesive strength of the coatings. It has been established (Table 2) that the introduction of a bidispersed filler after modification of the composition by an electrospark hydraulic shock and after alloying of the base provides an increase in the adhesive strength of the coatings to the base by 1.8...2.0 times. The maximum values of adhesive and cohesive strength (77.6 MPa and 63.54 MPa, respectively) were measured in the coatings containing ferrite and soft carbon. Here we note that the modulus of elasticity of these coatings is 3.54 GPa, which is lower in comparison with other filled coating materials. The obtained results confirm the assumption that after modification of the matrix by the ESHS method, the introduction of ferrite and SC fillers causes the formation of the structure with low rigidity, but with high adhesion and cohesion characteristics. High rates of absolute deformation confirm the above statements (Table 2).

Table 2. Physical-mechanical properties of epoxy composite coatings

Material		Adhesion strength, τ_{max}, MPa	Cohesion strength, σ_c, MPa	Modulus of elasticity, E_p, GPa	Maximum deformation, L_{pmax} on the basis of the base = 45 mm
Main filler	Additional filler				
SiC	Al_2O_3	70.44	56.57	3.86	0.0016
B_4C	Cr_2O_3	72.13	62.72	4.30	0.0013
Ferrite	GC	77.6	63.54	3.54	0.0045

Note: Concentration of composite material components: matrix (ED-20: PEPA—100:10:11 (weight parts)); concentration of the main filler is 80 wt.p. per 100 weight parts of epoxy resin; concentration of additional filler is 80 wt.p. of chromium oxide, 80 wt.p. of aluminum, 50 wt.p. of soft carbon per 100 wt.p. of epoxy resin ED-20.

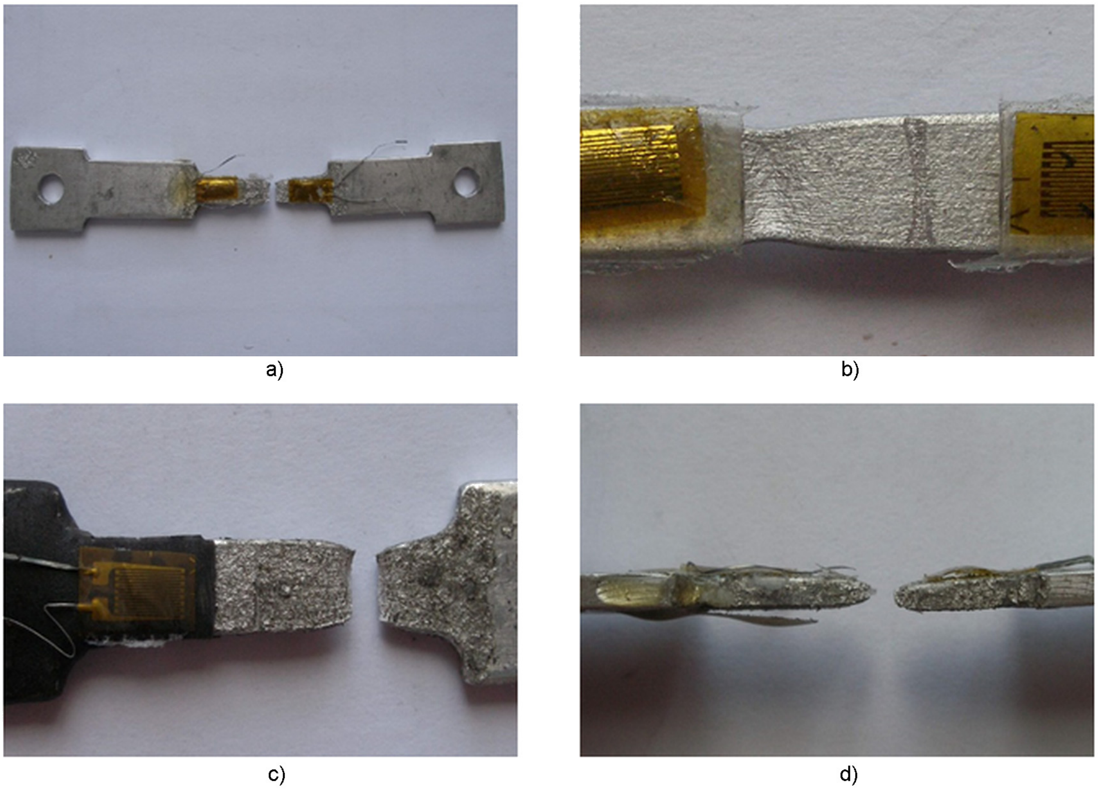
a) b) c) d)

Fig. 4. General view of samples after deformation: a) general view of the sample; b) the beginning of fracture in the non-alloyed aluminum base; c) the view of base alloyed surface; d) separation of adhesive coatings at the end of testing.

Thus, the analysis of the experimental results on elastic-plastic characteristics in the "coating-base" system allows us to conclude that the developed coatings with the bidispersed filler (ferrite and SC) show high complex cohesive and adhesive properties. This, in turn, can ensure the operation of the developed coatings under conditions of alternating loads and significant deformations of the coating material.

Note: concentrations of composite material components: matrix (ED-20: PEPA-100: 10: 11 (weight parts)); concentration of the main filler is 80 wt.p. per 100 weight parts of epoxy resin; concentrations of additional fillers are 80 wt.p. of chromium oxide, 80 wt.p. of aluminium, 50 wt.p. of soft carbon per 100 wt.p. of epoxy resin ED-20.

Also we note, that the increase in the adhesion of the composite to ferromagnetic fillers after ESHS processing is explained by the chemical and thermodynamic activity of the surface of dispersed particles. The magnetic properties of the filler affect the globules of macromolecules, which act as domains with respect to the magnetic field of the filler. In this case, in the subsurface layers of the filler, the cross-linking conditions change. Such an orientation effect improves the adhesive strength due to the improvement of cohesive strength of the coating material [13]. This significantly affects the degree of cross-linking of the epoxy oligomer, including at the interface with the base. The obtained results can be explained by the fact that the adhesive strength depends on the duration of physicochemical processes in the structure of the material and is determined by the following factors: nature and concentration of composition ingredients, temperature and time parameters of material formation, as well as methods of base and composition modification [14]. In this regard, the obtained results on the effect of the base material and the coating treated with an external field on the improvement of adhesive and cohesive strength is in good agreement with the results of [15, 16]. Particularly, the results on adhesion, cohesion strength and the modulus of elasticity of the composites after treatment of the matrix and the base with an electrospark hydraulic shock show an increase in the cohesive characteristics of the systems with a simultaneous increase in adhesion (Table 1, Table 2).

The nature of fracture of the coatings at different stages of deformation of the "base-coating" system was established. The fracture of the base material was observed (Fig. 4a, b) by the method of optical microscopy in all systems without exception, in which the electrospark alloying of the base was not carried out. It is also noted that the coating material remained without cracks, but separated. After modification of the base (Fig. 4c) and treatment of the coating matrix by the ESHS method, the fracture adhesive nature retained; separation of the coating from the base was observed (Fig. 4d). At the final stages of deformation of the "coating — base" system, the plastic deformation of the base is observed; this is the primary cause of adhesive destruction of this system.

4. Conclusions

In this paper, the relevance of preliminary electrospark alloying of an aluminum base and simultaneous electrospark processing of an epoxy resin with its subsequent application to the substrate is for the first time substantiated on the basis of the comprehensive approach to the investigation of adhesive and cohesive properties of epoxy composite materials. It has been established experimentally, that, as the result of such processing, the strength of adhesion and cohesion in the "coating — base" system increases 1.5...1.8 times in comparison with the initial material. The expediency of using dispersed particles of ferromagnetic nature as fillers has been experimentally confirmed. Such additives, regardless of their chemical, thermodynamic and kinetic activity, significantly affect the degree of the binder cross-linking in the surface layers of the matrix, improving the physical-mechanical properties of protective coatings. The introduction of ferrite dispersed filler (80 weight parts per 100 weight parts of ED-20) and soft carbon (50 weight parts per 100 weight parts of ED-20) provides a 1.8-fold increase in cohesion strength.

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