



The Effect of Modifiers on the Strength and Impact Toughness of Carbon Fiber Reinforced Plastics

Laura Mustafa, Marat Ismailov, Indira Tashmukhanbetova*, Ilyas Ablakatov, Venera Zhumakanova

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Abstract

This study utilized epoxy resin, three types of fabric (carbon fiber, glass fiber, and Kevlar), and two plasticizers – tricresyl phosphate (TCP) and oleic acid (OA) – to enhance the impact toughness of carbon fiber-reinforced plastics (CFRP). The polymer matrix used in the experiments was a hot-cured epoxy compound "Etal Inject-T" consisting of two components: A – epoxy resin and B – hardener, in a mass ratio of 100:49.9. For the fabrication of CFRP plates, both manual and vacuum molding techniques were employed. Combined reinforcement of carbon fiber was achieved using one of two types of fabrics: Ortex 360 glass fiber or Kevlar. Accordingly, two compositions were prepared for the experiments: carbon fiber/glass fiber and carbon fiber/Kevlar. Layer stacking in each composition was performed at ratios of 10:10 and 14:6, consisting of 20 layers in total. The greatest strengthening effect for CFRP in the case of carbon fiber/glass fiber was observed with a layer ratio of 14:6 and matrix modification using 10% TCP plasticizer. The strength of the CFRP increased from 425 to 451 MPa, and the impact toughness (α) improved from 192 to 280 kJ/m². A key feature of this technology is the achievement of high-performance dual-purpose CFRP. This enables the reduction of CFRP structures in aerospace applications by 3 to 5 times, while simultaneously enhancing resistance to impact loads.

Keywords: Carbon fiber reinforced plastics, epoxy resin, heat treatment, impact toughness, modifiers, plasticizers, strength, thermoplastics.

1. INTRODUCTION

Carbon fiber-reinforced plastics (CFRP) are widely used as structural materials where their primary target quality is strength. The reinforcement of CFRP can be achieved through the modification of epoxy resin (ER) and combined reinforcement of carbon fiber (CF). The ERs have limited application as polymer matrices due to their three-dimensional cross-linked network structure, which makes them brittle and complicates load absorption and distribution. Given the significant brittleness and stiffness of ER, the issue of enhancing their elasticity while maintaining satisfactory levels of other physico-mechanical characteristics becomes particularly relevant. Co-curing of ER with compounds containing functional groups that react with the epoxy group is one of the most common and effective methods for producing

flexible epoxy compositions. The impact strength of inherently brittle ERs can be improved by introducing modifiers [1]. One method of modifying CFRP is plasticization, which involves altering the properties of the polymer by adding a low-molecular-weight additive—plasticizers. Plasticizers modify the viscosity of the system, as well as the flexibility and mobility of molecular structures. Many plasticizers can enhance the impact toughness of the polymer without compromising strength or modulus of elasticity, and they can also improve fire, light, and thermal resistance. These additives can, in turn, react with functional groups formed at various stages of polymer formation. Moreover, modification also occurs during the curing process of composite materials. Various types of plasticizers are most commonly used as modifying additives [2]-[4].

The properties of epoxy compositions based on ED-20 epoxy dian resin and PEPA hardener, with the addition of buckwheat and millet husks, trichloroethyl phosphate, and TCP, were investigated. TCP was used as a plasticizer and flame retardant. The composition 70 ED-20 + 30 TCP + 15 PEPA yielded the most optimal combination of properties. The physico-mechanical and thermophysical properties of this composition are as follows: the impact toughness increased from 9 to 14 kJ/m² compared to the composition without TCP modification, and the flexural strength

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Table 1. Epoxy resin with PEPA hardener.

	Flexural Strength, MPa	Impact Toughness, kJ/m ²	Brinell Hardness, MPa
Composition (PEPA, 15 parts by weight)			
100 ED-20	17	3	225
70 ED-20+30 TCP	34	13	84
Composition (40 parts by weight PO-300)			
100 ED-20	76	13	185
70 ED-20+30 TCP	8*	36	-

Note: * - no failure observed during testing.

doubled, reaching 98 MPa [5].

The compositions based on ED-20 resin with TCP modifiers have been also developed [6]. PEPA was used as the hardener for the resin. Samples were produced in the form of pressed tablets with a thickness of 1 mm, containing 70% ED-20 by mass, 15% PEPA, and 30% TCP. The samples were tested for flexural strength, impact toughness, and key parameters such as gelation time, curing time, and curing temperature of the epoxy compositions were determined. The results showed that the addition of TCP plasticizer to the resin significantly improves impact toughness by 3 times (10 kJ/m²), flexural strength by 3 times (57 MPa), and hardness by 59% (197 MPa). Additionally, the gelation time increased from 24 to 60 min, the curing time from 39 to 115 min, while the curing temperature decreased from 125 to 44 °C.

The effect of modifiers on the mechanical properties of the resin was investigated [7]. The materials and components used to create the composite included unsaturated polyester resin, hardeners (methyl ethyl ketone peroxide and cobalt naphthenate), and TCP as a modifier. The concentration of TCP in the composition was 5%, 10%, and 15% by mass of the resin. The analysis of mechanical properties showed that the addition of 5% TCP increased the tensile strength by 1.3 times (98 MPa). The addition of 15% TCP improved the impact toughness by 12% (1.47 kJ/m²). On the other hand, epoxy composites based on ED-20 resin with plasticizers were developed and investigated. An amine-type hardener, PEPA, was used for curing the resin. Oleic acid (OA) was used as a

plasticizer, with concentrations of 10%, 15%, and 20% by mass of the resin. The results of the property analysis show that the addition of OA significantly increases flexural strength by 6 times (105 MPa) and impact toughness by 5.5 times (17 kJ/m²) [8].

Oligoxypropyleneglycol, OA, and δ -chlorobutylether- β -chloropropionic acid were investigated as plasticizers for ED-20 ER with PEPA as the hardener. The optimum results were obtained when the polymer was modified with 15% by mass of OA, which resulted in an increase in impact toughness from 3 to 17 kJ/m² and flexural strength from 17 to 105 MPa [9]. The effect of plasticizers on ED-20 resin was investigated also, including diglycidyl ether of diethylene glycol (DEG-1), TCP, and trichloroethyl phosphate (TCEP). The most effective plasticizer, DEG-1, increased the flexural strength of the epoxy resin by 6.5 times, while the impact toughness increased by only 1.5 times [10][11].

In the previous study, the effect of additives on the physical properties of the resin was investigated. Unsaturated polyester resin with the addition of triethyl phosphate and TCP was used. After mixing and ultrasonic treatment, the samples were cured in an oven for 3 h at 70 °C, 1 h at 100 °C, and 1 h at 150 °C. The samples were tested to determine flexural strength and modulus of elasticity. The flexural strength increased from 88 to 94 MPa, while the modulus of elasticity increased from 0.63 to 0.70 \times 10⁶ kgf/cm² [12].

However, in these studies, the widely used "cold"-cured ER ED-20 was utilized [13], which

cures at room temperature. Meanwhile, in CFRP production technology, "hot"-cured ERs are of great interest. One representative of this class is the ER Etal-Inject-T, which cures at temperatures of 150–180 °C [14]. At these temperatures, the resin has low viscosity and very effectively wets and impregnates the carbon fiber reinforcement, improving the quality of the resulting CFRP. At room temperature, this ER with hardener remains in a liquid state, which is highly convenient for molding products. For the ER "Etal-Inject-T" there is a lack of experimental data on modifiers that enhance impact toughness and strength. Research in this area would be of great interest for the technology of producing impact-resistant CFRP.

Composites that incorporate two or more types

of reinforcing materials within a single matrix are typically referred to as hybrid composites. The primary objective of hybridization is to create a material that combines the benefits of its individual components while mitigating some of their limitations. Depending on the desired properties of the hybrid composite, various combinations of reinforcements can be utilized, including the hybridization of carbon fiber with fiberglass and/or aramid fabric. The combination of glass and CF in polymer composites has been shown to yield optimal mechanical properties [15]-[17]. Rajpurohit et al. examined the fracture behavior of hybrid composites, focusing on two-fiber systems [18]. The inclusion of fiberglass alongside carbon fiber was found to enhance the material's toughness, with

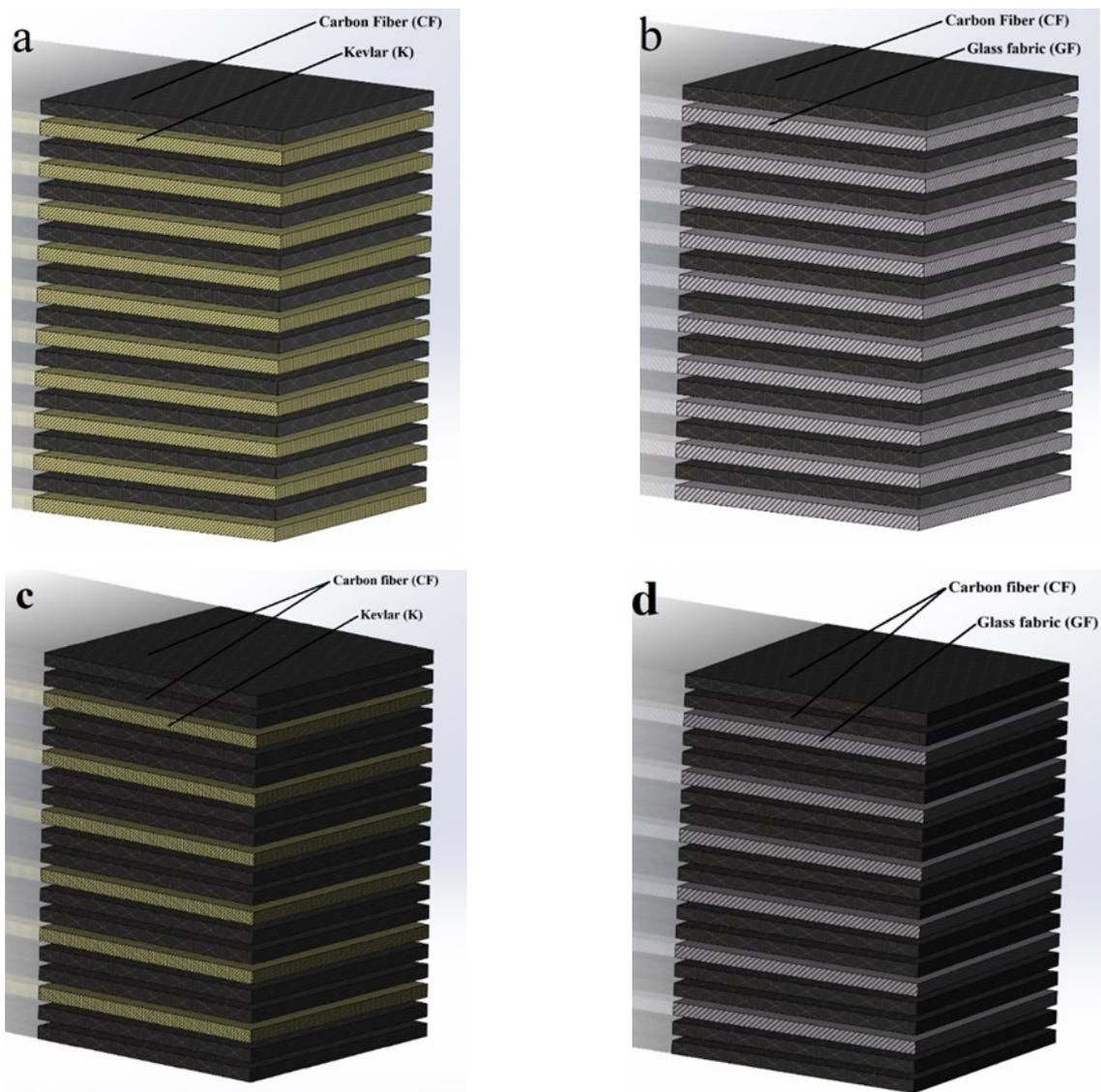


Figure 1. The schematic of fabric layup with different layer ratios (a) the ratio of CF/K is 10:10; (b) the ratio of CF/GF is 10:10; (c) the ratio of CF/K is 14:6; (d) the ratio of CF/GF is 14:6.

Table 2. The effect of combined reinforcement and plasticizers on impact strength and tensile strength during manual molding of CFRP.

Type of laying and reinforcement*	σ (MPa)			a (kJ/m ²)		
	ER	ER+TCP	ER+OA	ER	ER+TCP	ER+OA
CF-14, GF-6		360	346		200	198
CF-10, GF-10		354	331		260	240
CF-14, K-6	425	375	363	192	166	161
CF-10, K-10		362	351		160	153

Note: * CF – carbon fabric, GF – glass fabric, K-kevlar, 6:10;14 – number of layers.

increasing fiberglass content resulting in higher load-bearing capacity and impact energy absorption. Studies on the mechanical properties of hybrid composites reinforced with both carbon and glass fibers have demonstrated that hybrid composites can exhibit compressive strengths up to 8% greater than those of pure CF composites [16]-[22]. The effect of reinforcing ER with CF and carbon-aramid fiber was explored, with samples tested for compressive, tensile, shear, and impact strength. The results indicated that the presence of aramid fiber in the hybrid composite improved toughness by up to 37.9% compared to conventional CF composites [23]. Additionally, aramid fiber contributed to a 19.5% increase in compressive strength, offering a more ductile response compared to carbon reinforcement alone [24]. The aim of this study is to determine the effect of plasticizers, combined reinforcement, and molding techniques on the strength and impact toughness of CFRP.

2. MATERIALS AND METHODS

2.1. Materials

The materials used in this study included ER and three types of fabric (CF, fiberglass, and Kevlar). To enhance the impact toughness, two types of plasticizers, TCP and OA, were utilized in the experiments. The ER compound "Etal Inject-T," a hot-cured system, was used in the study. It consists of two components: A – epoxy resin and B –

hardener, mixed in a mass ratio of 100:49 with the hardener. Curing was carried out using a combined schedule of 4 h at 150 °C followed by 1 h at 180 °C. Due to its low viscosity, the resin ensures rapid and thorough impregnation of the fabric. The technological advantage of this process lies in the fact that, during the layup and high-temperature curing up to 150 °C, the resin maintains its viability, and its viscosity decreases (becoming more fluid), thereby improving the impregnation of the carbon fabric. These factors contribute positively to the uniformity and quality of the composite.

In the previous study, the influence of tricresyl phosphate (TCP) on the properties of an epoxy composite based on ED-20 ER using two types of hardeners—polyethylene polyamine (PEPA) and low-molecular-weight polyamide PO-300—was investigated. The results of the research showed that for compositions cured with PEPA, the addition of 30 parts by weight of TCP resulted in a twofold increase in flexural strength and a fourfold increase in impact toughness, as presented in Table 1 [25]. When TCP plasticizer is introduced into the epoxy resin and cured with PO-300, the impact resistance increases by 2.5 times, reaching a value of 36 kJ/m². In the case of flexural tests, no specimen failure occurs (Table 1) [25].

Plasticizers, used as modifying additives, are liquid organic compounds that enhance the flexibility of polymers and expand the range of

their elastomeric behavior at room temperature. To increase impact toughness, the following additives were employed in the experiments: TCP and OA. TCP is a colorless, transparent, viscous liquid that is virtually non-volatile and odorless. Its composition consists of 2% to 37% *o*-isomers, with the remaining portion being *m*- and *n*-isomers. TCP is insoluble in water but dissolves readily in organic solvents, fats, and certain oils. Its boiling point is approximately 290 °C, although the processing temperatures typically do not exceed 160 °C, preventing harmful evaporation of TCP into the workspace. OA is a monounsaturated fatty acid containing a single double bond, classified as an Omega-9 fatty acid. In terms of its physical

properties, OA is a colorless, viscous liquid with a melting point ranging from 13.4 to 16.3 °C, a boiling point of 286 °C, and a density of 0.895 g/cm³.

For combined reinforcement, the following materials CF, Twill 3K-1200-200 (3K – number of rovings, K=1000; 1200 – roll width in mm; 200 – surface density in g/m²), an organic material characterized by high tensile strength, a low coefficient of thermal expansion, chemical inertness, and low specific weight. Kevlar plain weave for ballistic protection, 460 g/m² – a heat-resistant and durable synthetic fiber. The aramid (Kevlar) fabric for ballistic protection, with a density of 460 g/m², is known for its thermal

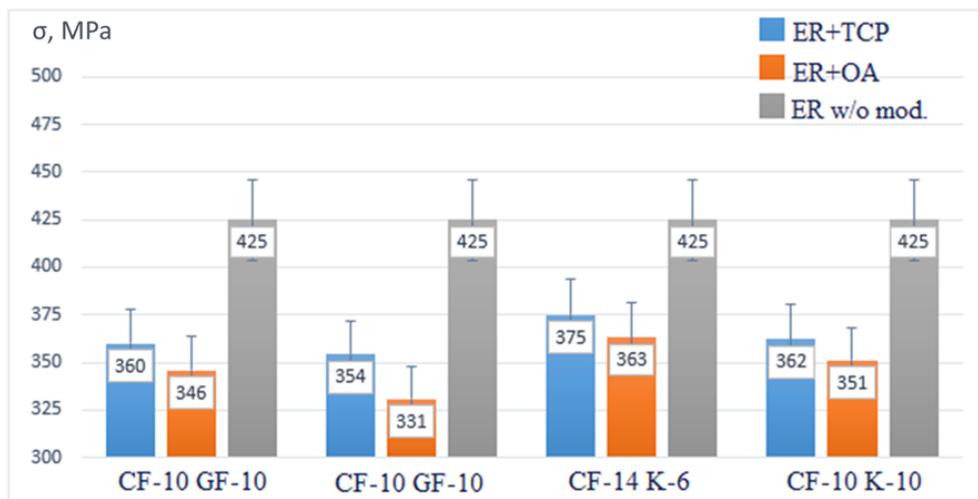


Figure 2. Influence of combined reinforcement and plasticizers on compression strength of manually molded CFRP.

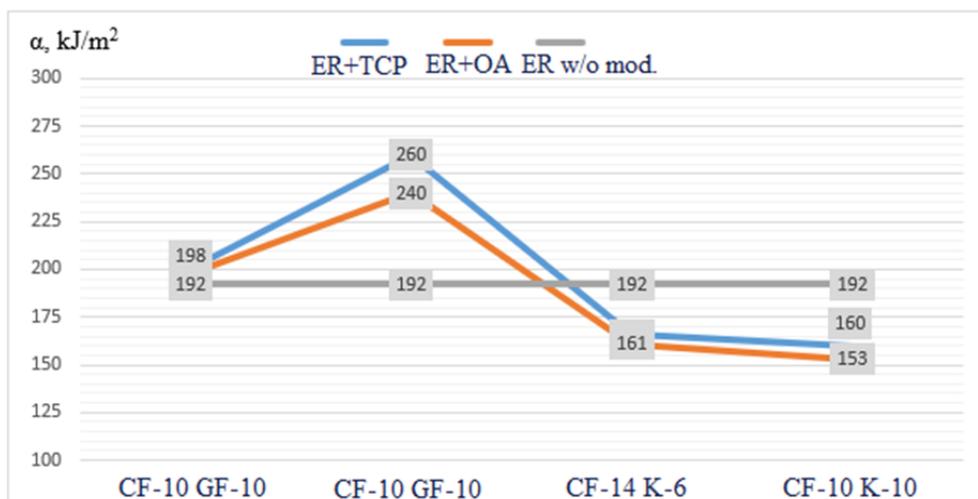


Figure 3. Influence of combined reinforcement and plasticizers on impact toughness of manually molded CFRP.

Table 3. Influence of combined reinforcement and plasticizers on impact toughness and strength in vacuum molded CFRP.

Type of laying and reinforcement*	σ (MPa)			a (kJ/m ²)		
	W/o mod.	TCP	OA	W/o mod.	TCP	OA
CF-14, GF-6		451	423		280	277
CF-10, GF-10		440	404		290	281
CF-14, K-6	425	426	397	192	315	302
CF-10, K-10		403	386		346	316

Note: CF– carbon fabric, GF – glass fabric, K-kevlar. 10:10; 14:6 – number of layers.

resistance and high strength. Fiberglass Ortex 360, 300 g/m² – produced using German technology.

2.2. Methods

The production technology of CFRP with enhanced mechanical properties (impact toughness and tensile/compressive strength) requires a comprehensive approach to the fabrication process, as improving one strength parameter can negatively impact other mechanical properties. To simultaneously increase both strength and impact toughness, the following conditions, experimental selection of the optimal modifier for the epoxy matrix and its percentage content; Experimental determination of the optimal reinforcement for combined layer reinforcement of CFRP and the number of layers is the selection of the optimized molding method for CFRP production.

In the experimental work, the fabrication of CFRP plates utilized both manual and vacuum molding methods with mechanical pressing. This technique is cost-effective, requires minimal labor, and uses fewer materials compared to other molding methods. The process involves laying CF or other reinforcing materials in layers within a glass mold, where each layer is impregnated with resin. Vacuum molding differs from manual molding in that, after the dry fabrics are laid in a vacuum mold, the tool must be carefully sealed, and the resin must be infused into it. Vacuum molding enhances the manufacturability and quality of the product while also reducing porosity. The molding process consists of several stages.

2.2.1. Mold Preparation

A mold is prepared for layup, and in this case, a glass plate was used. A release layer is applied to the mold to allow for the easy removal of the composite later. Loctite 330 NS release agent was used as the release layer.

2.2.2. Layup of Carbon Fabric

Carbon fabric measuring 100 × 100 mm is layered into the mold.

2.2.3. Preparation of The Modified Resin

A modified resin component is prepared by adding the plasticizer to the epoxy oligomer (without hardener). The effect of each plasticizer on the properties of the epoxy component was studied separately. The plasticizer content in the epoxy component was 10% by weight for each composition. The mixture of plasticizers was stirred using an ultrasonic disperser at a frequency of 65 kHz for 20 min. This ultrasonic treatment helped reduce the number of air bubbles, decrease viscosity, degas the mixture, and generally modify the structure, ensuring the monolithic nature of the composite.

2.2.4. Reinforcement Layers

Between the layers of CFs, layers of one of the reinforcing materials—glass fiber (GF) or Kevlar (K)—were added. Accordingly, two compositions were prepared for the experiments: CF/GF and CF/K.

2.2.5. Layer Ratio

The layer stacking in each composition was performed in the following ratios: CF/GF and CF/K. The layer ratios were 10:10 and 14:6, consisting of 20 layers in total. [Figure 1](#) schematically illustrates the fabric layup methods.

To determine the compressive strength of CFRP, specimens were tested using an Instron Universal Testing Machine. The samples for compression tests were prepared in accordance with GOST 33519–2015, with the following dimensions: length $l = 80 \pm 2$ mm; width $b = 10 \pm 0.5$ mm, thickness $h = 4 \pm 0.2$ mm. Composite materials like CFRP often exhibit anisotropic properties, meaning their mechanical characteristics can vary depending on the direction of the applied force. In our study, the specimens were positioned in the testing machine to apply force along the composite's layup plane, which is considered the weaker direction. This approach ensures that the material's behavior under service conditions is accurately assessed. Testing along the layup plane provides information about the strength of the material in a direction most relevant to its actual application. The impact strength of CFRP was measured using the Charpy method, in accordance with GOST 4647–2015, which specifies the procedure for determining the impact strength of plastic specimens with and without a notch. Manual molding followed by pressing was used to fabricate experimental CFRP samples for impact toughness tests ($80 \times 10 \times 4$ mm) and compression tests ($60 \times 20 \times 4$ mm).

3. RESULTS AND DISCUSSIONS

3.1. Influence of Combined Reinforcement and Plasticizers on Impact Toughness and Strength in Manually Molded CFRP

The results of strength tests by manual molding are shown in [Table 2](#) and [Figures 2](#) and [3](#). Based on the test results for the CF/GF composition, it is evident that increasing the number of layers of GF improves the impact toughness of CFRP while simultaneously reducing compression strength. For instance, in samples with a layer stacking ratio of 10:10, impact toughness increased from 192 to 260 kJ/m² (by 35%) while compression strength decreased from 425 to 354 MPa (by 17%). Conversely, in samples with a GF layer stacking

ratio of 14:6, there was only a slight increase in impact toughness from 192 to 200 kJ/m² (by 4%) with a reduction in compression strength from 425 to 360 MPa (by 15%). The potential reasons for such deterioration in mechanical properties may include heterogeneous surface adhesion of ER to different types of fibers, weak diffusion bonding between components due to insufficient pressure during manual molding, which collectively contributes to reduced composite monolith city. This significant finding prevented further increases in the number of reinforcing layers in the sample, prompting the decision to stop at a layer stacking ratio of 10:10, as the project's goal of achieving an impact toughness of 260 kJ/m² for CFRP was achieved. The next objective was to maintain the achieved impact toughness and regain lost compression strength.

3.2. Influence of Combined Reinforcement and Plasticizers on Impact Toughness and Strength in Vacuum Molded CFRP

To minimize the negative impact of combined reinforcement on the strength of CFRP, vacuum molding was employed, which enhances matrix adhesion to various types of fabrics, eliminates the possibility of air pockets in the composite, and improves material uniformity. Results of the tests are presented in [Table 3](#) and [Figures 4](#) and [5](#). The results of the mechanical characteristics of CFRP using vacuum molding showed that introducing the TCP plasticizer into the epoxy matrix and combining carbon and aramid fabric layers in a 10:10 ratio significantly increased impact toughness. Moreover, the loss of compression strength compared to unmodified CFRP was only 8%. This indicator demonstrates the appropriateness of the vacuum molding method, as manual molding resulted in a 13% decrease in compression strength. Using Kevlar as the reinforcing fabric allowed achieving a sufficiently high impact toughness of 346 kJ/m² for CFRP. Additionally, good results were obtained with a reinforcement ratio of 14:6 and modification with TCP. Compression strength reached 451 MPa with impact toughness α at 280 kJ/m². Thus, this section examined the influence on the strength characteristics of CFRP by the influence of plasticizers: TCP and OA; the influence of reinforcing materials: GF, K; the

influence of the ratio of layers of reinforcing material; and the influence of molding method: manual and vacuum. Based on the results, it was determined that TCP is the most promising modifier for the epoxy component, as OA as a modifier can positively affect increasing impact toughness but negatively impacts strength data. Changing the reinforcing material does not affect strength enhancement.

The physicochemical mechanism of plasticization involves altering the viscosity of the system and increasing molecular flexibility, leading to a decrease in glass transition temperature and flow resistance, as well as changes in the strength and brittleness of the material. Small amounts of

plasticizer can enhance both strength and modulus of elasticity, but further additions tend to reduce these properties. The reduction in strength with increasing plasticizer content is related to the decrease in brittleness temperature, which comes at the expense of significantly reduced heat resistance and strength at lower temperatures. The initial increase in strength with the addition of plasticizer can be attributed to the increased mobility of supramolecular structures, which align under tensile stress, thereby contributing to the reinforcement of the polymer. A comparative analysis of the strength characteristics of reinforced carbon fiber plastics showed that GF and K are the most promising reinforcements for obtaining impact-resistant

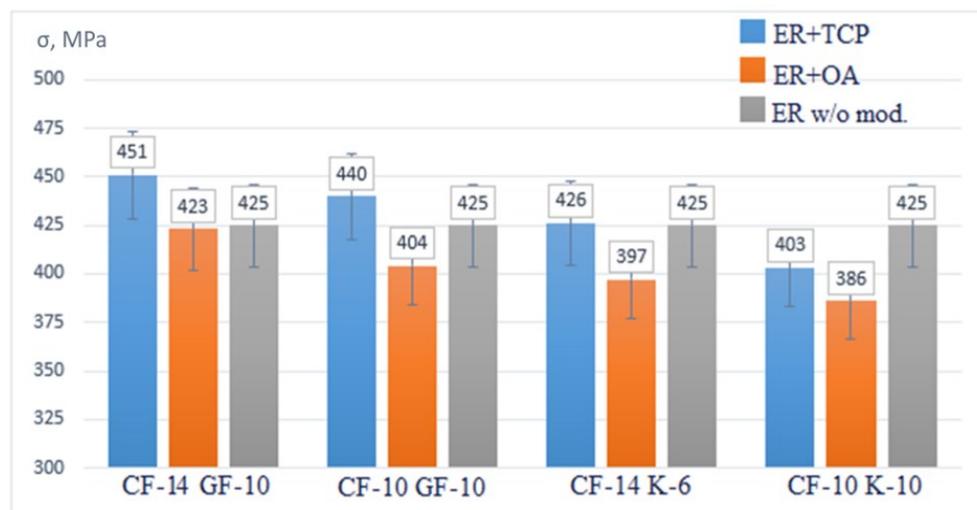


Figure 4. Influence of combined reinforcement and plasticizers on compression strength of vacuum molded CFRP.

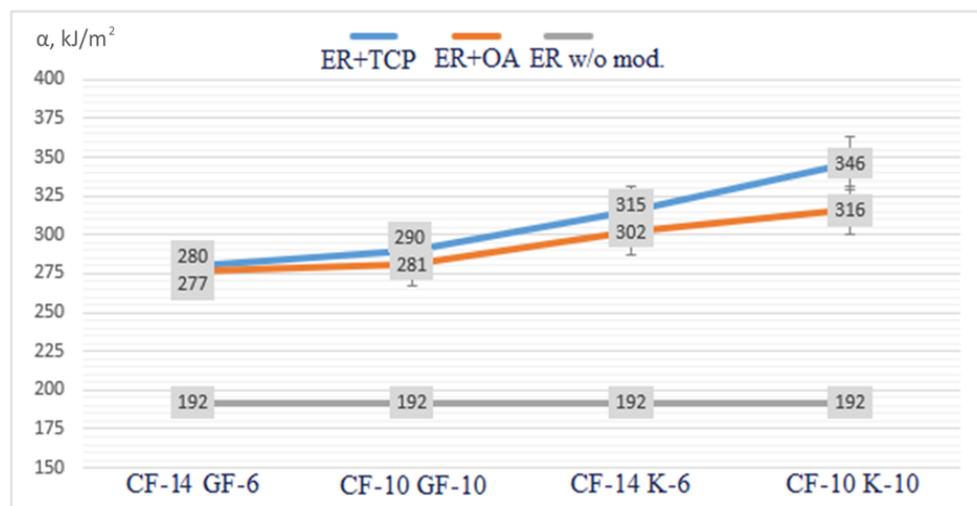


Figure 5. Influence of combined reinforcement and plasticizers on impact toughness of vacuum molded CFRP.

CFRP. It was established that the greatest strengthening effect for CFRP in the case of CF/GF is achieved with a 14:6 layer ratio and modification of the matrix with TCP at 10%. The strength of CFRP increased from 425 to 451 MPa, and impact toughness α increased from 192 to 280 kJ/m².

For the combination of CF/K in a 14:6 ratio, the strength of CFRP increased to 426 MPa, and α reached 315 kJ/m². In the case of carbon fabric/Kevlar in a 10:10 ratio, the strength of CFRP was 403 MPa, and α reached 346 kJ/m². Compression strength slightly decreased (which is not critical for the achieved value), but a sufficiently high impact toughness was obtained. Based on the strength tests, it was determined that vacuum molding is the most acceptable method for obtaining high-strength impact-resistant CFRP.

4. CONCLUSIONS

High impact toughness CFRP consists of ER modified with TCP and reinforcement using CF/K in a 10:10 ratio. It has the following characteristics: σ – 403 MPa, α – 346 kJ/m². CFRP with balanced strength and impact toughness consists of ER modified with TCP and reinforcement using CF/GF in a 14:6 ratio, has the following characteristics: σ – 451 MPa, α – 280 kJ/m². The main feature of this technology is the achievement of high, competitive properties in dual-purpose CFRP. The developed technology enables the production of CFRPs with a compressive strength limit of 450 MPa and impact toughness up to 346 kJ/m². This allows for the reduction of the weight of CFRP structures in aerospace applications by 3–5 times while simultaneously increasing their resistance to impact loads.

AUTHOR INFORMATION

Corresponding Author

Indira Tashmukhanbetova — LLP International Educational Corporation, Almaty-050043 (Kazakhstan);

 orcid.org/0000-0002-4066-8238

Email: indiraberkinbaykyzy@gmail.com

Authors

Laura Mustafa — JSC National Center of

Space Research and Technology, Almaty-050010 (Kazakhstan);

 orcid.org/0000-0002-9779-0007

Marat Ismailov — JSC National Center of Space Research and Technology, Almaty-050010 (Kazakhstan);

 orcid.org/0000-0002-1111-4658

Ilyas Ablakatov — JSC National Center of Space Research and Technology, Almaty-050010 (Kazakhstan);

 orcid.org/0000-0003-4912-9289

Venera Zhumakanova — JSC National Center of Space Research and Technology, Almaty-050010 (Kazakhstan);

 orcid.org/0009-0005-9041-6003

Author Contributions

Conceptualization, L. M. M., I. B. T., M. B. I., I. K. A., V. R. Z.; Methodology, L. M. M.; Software, I. B. T.; Validation, L. M. M., I. B. T., M. B. I., I. K. A., V. R. Z.; Formal Analysis, L. M. M.; Investigation, L. M. M.; Resources, M. B. I.; Data Curation, L. M. M.; Writing – Original Draft Preparation, L. M. M.; Writing – Review & Editing, L. M. M.; Visualization, I. B. T.; Supervision, L. M. M.; Project Administration, I. B. T.; Funding Acquisition, I. B. T., V. R. Z.

Conflicts of Interest

On behalf of all the authors, the correspondent author declares that there is no conflict of interest.

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