STUDY ON THE EFFECT OF PLASTICIZERS AND THERMOPLASTICS ON THE STRENGTH AND TOUGHNESS OF EPOXY RESINS

**Purpose.** To increase the strength and toughness of epoxy resins of “cold hardening” and “hot hardening” by using modified plasticizers and thermoplastic polymers.

**Methodology.** Epoxy resins of “cold hardening” of ED-20 and “hot hardening” of Etal Inject-T, modified with three types of plasticizers and four types of thermoplastic polymers, were investigated. The toughness and compressive strength of unmodified and modified resins were determined with the help of the Charpy impact test at various modifier contents.

**Findings.** Among all studied plasticizers, tricresyl phosphate has the most significant effect on the strength and toughness of both types of resins. The best combination of strength and toughness of ED-20 resin is obtained with 5% tricresyl phosphate content, whereas its higher content reduces the strength of the material. For Etal Inject-T, high values of these properties are obtained with 15% tricresyl phosphate content, whereas adding a smaller amount of a modifier does not change the material strength. The modification with thermoplastic polymers has a less obvious effect on the properties of epoxy resins than the modification with plasticizers does. The most effective additives to ED-20 are high-temperature polycarbonate (5%) and polysulphone (10 and 15%), the addition of which causes a simultaneous increase in both properties. A significant increase in the toughness of Etal Inject-T is observed by adding 5–15% polycarbonate, but the strength of the resin hardly changes. The complex modification of resins with a mixture of plasticizer and thermoplastic leads to a decrease in the toughness and compressive strength of both types of resins.

**Originality.** When the polymer mixture hardens, plasticizer molecules dispersed into the environment of epoxy macromolecules weaken the rigid spatial crosslinking of macromolecules and make them more active. As a result, toughness increases; in certain cases so does resistance due to directed re-orientation of macromolecules under deformation. The change in mechanical properties of epoxy resin when modified with thermoplastics is defined by the bonding strength of the resin and dispersed particles of thermoplastic polymer as well as by the degree of heterophase of the produced mixture.

**Practical value.** The results of changing the mechanical properties of epoxy resin while being modified with plasticizers and thermoplastics can be used to produce impact-resistant composite materials for structural purposes, including those for aviation and space-rocket technology.

**Keywords:** epoxy resin, modifiers, plasticizers, thermoplastics, thermal treatment, toughness

© Mustafa L. M., Ismailov M. B., Sanin A. F., 2020
Mechanical properties of the components of carbon fiber [4, 5]

| Material          | Strength, MPa | Modulus of elasticity, GPa | Toughness, kJ/m² |
|-------------------|---------------|---------------------------|------------------|
| Carbon fiber      | 2500–6000 stretching | 200–600                   | –                |
| Epoxy resin       | 100 stretching/compression | 10                      | 3–40             |

Table 1

Properties of composites based on ED-20 epoxy resin [7]

| Content of modification, % mass | Toughness, kJ/m² | Bending strength, MPa |
|--------------------------------|------------------|-----------------------|
| TCP                            | 10               | 17                    |
| DEG-1                          | 10               | 86                    |
| DEG-1                          | 15               | 110                   |
| TCEP                           | 13               | 34                    |
| TCP                            | 8                | 34                    |

Table 2

Experimental part and research methodology. In the experiments, 2 epoxy resin types were used as a polymer binder:
- Etal Inject-T [11] with hardener at a mass ratio of components 100:49. Hardening was carried out according to the combined mode 150 °C 4 hours + at 180 °C 1 hour;
- ED-20 with hardener PEPA; the mass ratio of the components is 85:15; a hardening mode 48 hours at a room temperature.

To increase the toughness, the following modifying additives were used in the experiments:
- plasticizers such as tricresyl phosphate (TCP), trichloroethyl phosphate (TCEP) and glycidyl methacrylate (GDMA) [6] in a liquid state at a room temperature;
- thermoplastics such as polysulfone (PSF), polycarbonate (PC), polystyrene (PS) and high impact polystyrene (UPS). These polymers are in a solid state at a room temperature; when they are heated, they transform into a highly elastic or viscous flow state, and they have rather high temperatures of a viscous flow and decomposition. For example, for polysulfone, these temperatures are about 300 and 420 °C, respectively [10].

The modification of resin was carried out as follows: in epoxy resins (ED-20, “Etal Inject-T”) modifiers were introduced in the amount of 5, 10 and 15 % of the total mass for each composition. Since the plasticizer is in a liquid state, its addition into epoxy resins is not difficult. Thermoplastics were added into the resin in the form of a dispersed material with a diameter of granules from 1 to 2.5 mm, obtained by mechanical grinding without deep cooling. A modifier was added (total volume of the mixture was 1.5 l) in a cylindrical container with a diameter of 110 mm and a height of 180 mm with an epoxy oligomer (without hardener), then the components were mixed until a homogeneous mass was formed using a two-row mixer propeller stirrer at a speed of 150 rpm. The hardener was added after the formation of a homogeneous mass and it was mixed for 20 minutes. The finished mixture was poured into molds to obtain the samples of materials in the form of cylinders with a diameter of 15 mm and a height of 30 mm to determine the compressive strength and plates for impact testing with a length of 80 mm, a width of 10 mm and a thickness of 4 mm. Etal Inject-T resin samples were hardened in an electric furnace. Analyzing the surface of hardened epoxy resin, we found that the material structure was homogeneous, but heterogeneity of the structure was observed when modified with thermoplastics, and granular polymers acted like fillers. While polycarbonate was used, its particles were stored in ED-20 resin after cold hardening, but in Etal-Inject-T obtained by hot polymerization, there were no dispersed particles of the modifier, the material was completely homogeneous.

The toughness of unmodified and modified epoxy was determined by the Charpy impact test according to industry standard 4647-2015 [12] using a pendulum MK-15, the compressive strength – by using a universal testing machine MUP-200.

Results. Figs. 2 and 3 show the experimental data on the effect of TCP, GDMA, TCEP plasticizers on the toughness ($\sigma_t$) and compressive strength ($\sigma_c$) of the epoxy resin studied. Moreover, Table 3 shows the values of the plasticizer content at which the highest toughness of the modified epoxy resin is achieved when the level of unmodified strength is constant, the greatest compressive strength when the level of the toughness is constant, and a balanced increase in the toughness and strength of epoxy resin is observed.

It can be concluded that the investigated types of epoxy resin have close values of compressive strength; however, the toughness of Etal Inject-T is twice as high as the toughness of ED-20. The examined plasticizers have a significant effect on the toughness of resins causing an increase in their values up to 100 %, and, to a far less degree, contribute to the increase in the strength of ED-20 by 35 % and Etal Inject-T by 15 %.

ED-20 resins containing tricresyl phosphate 5 % TCP and Etal Inject-T with 15 % TCP have balanced mechanical properties.
Taking into account the observed insignificant increase in the toughness of the hardened ED with an increase in the number of liquid plasticizers, we can conclude that in this case there is intrastructural plasticization. Plasticizers have high compatibility both with ED and the polymer chains of the spatial framework formed during its hardening. That is why the regulatory effect of plasticizers becomes apparent during the entire process of formation of the spatial network.

Adding plasticizer makes it possible to increase the toughness of ER and, in some cases, improve the strength due to the directed reorientation of macromolecules during deformation [8].

The second part of the experiments is devoted to the study of thermoplastics modifiers’ impact on mechanical properties of epoxy resin. The experimental data are shown in Figs. 4 and 5 and Table 4.

All the thermoplastics considered increased both the toughness and the compressive strength of ED-20 resin. The best result concerning increasing the toughness (by 85 %) was obtained for ED-20 resin with a content of 15 % thermoplastic...
The maximum strength of ED-20 was increased by 47% with a content of 5% PS. For Etal Inject-T was by 65% with a content of 10% PCF, Etal Inject-T was by 21% with a content of 5% TCP. The plasticizer and thermoplastic mixture of plasticizer and thermoplastic does not provide an additional increase in the mechanical properties compared to using only a TCP modifier. On the contrary, the plasticizers being used together with thermoplastics, apparently, prevent the formation of a reinforcing interfacial layer “thermoplastic-epoxy resin”.

Due to the high elasticity of thermoplastics particles, their presence in the matrix of the hardened composite promotes to reduce the level of stresses arising in the material under mechanical loading. The complex modification of Etal Inject-T resin with a mixture of plasticizer and thermoplastic for further improvement of the properties is of interest. The experimental results are shown in Table 5.

The analysis of the results presented in Table 5 allows us to conclude that the modification of epoxy resin with a mixture of tricresyl phosphate plasticizer and thermoplastic does not provide an additional increase in the mechanical properties comparing to using only a TCP modifier. On the contrary, there is a slight decrease in both toughness and compressive strength.

Thus, there is no additive effect on the properties of ER of plasticizer and thermoplastic dispersed fillers are significantly different, as suggested above. Therefore, the additive effect of factors causing a strengthening effect is not obtained if the additives are used separately. In contrast, the plasticizers being used together with thermoplastics, apparently, prevent the formation of a reinforcing interfacial layer “thermoplastic-epoxy resin”.

As a result, the dispersed particles do not show a strengthening effect, but, like internal defects, they are stress concentrators and can act as crack nucleus in the material.

**Conclusions.** The effect of plasticizers such as tricresyl phosphate, trichloroethylphosphate, glycidyl methacrylate and thermoplastic polymers such as polysulfone, polycarbonate, polystyrene, high impact polystyrene on the toughness and compressive strength of cold and hot hardening of ED-20 and Etal Inject-T epoxy resins was studied.

The most effective modifier to increase the toughness of ER was tricresyl phosphate with a content of 15%. In this case, the toughness of ED-20 resin increased from 20 to 40.2 kJ/m² and Etal Inject-T resin rose from 42.3 up to 80.3 kJ/m² when their level of the compressive strength was constant.

Adding polysulfone thermoplastic had the greatest impact on the compressive strength. If its content was 10%, the strength of ED-20 resin increased from 97 to 142.6 MPa, and the strength of Etal Inject-T rose from 106 to 128 MPa with a content of 15%, when the level of the toughness was constant.

The modification of epoxy resins with a mixture of plasticizers and thermoplastics is not effective due to the difference in the mode of the hardening action of plasticizers and thermoplastic dispersed fillers, as well as the prevention of plasticizers from the formation of a strengthening interfacial layer at the epoxy-thermoplastic interface.

**Acknowledgements.** The work was carried out as part of the RBP 008 BR0533683 target program of the Aerospace Committee of the Ministry of Defense and Aerospace Industry of the Republic of Kazakhstan “Development of a technology for the production of impact-resistant carbon plastics for defense and aerospace products” (2018–2020).

---

**Table 4**

| Epoxy resin | Epoxy resin with maximum toughness | Epoxy resin with balanced properties |
|-------------|-----------------------------------|-------------------------------------|
| ED-20       | a = 97 MPa, σ̄ = 20.1 kJ/m²        | a = 97 MPa, σ̄ = 37 kJ/m² |
|              | a = 97 MPa, σ̄ = 26.5 kJ/m²        | a = 97 MPa, σ̄ = 142.6 kJ/m² |
| “Etal Inject-T” | a = 97 MPa, σ̄ = 42.3 kJ/m² | a = 97 MPa, σ̄ = 43.6 kJ/m² |
|              | a = 106 MPa, σ̄ = 70 kJ/m²        | a = 106 MPa, σ̄ = 128 kJ/m² |

---

**Table 5**

| Epoxy resin | Modifier content | Toughness, kJ/m² | Compressive strength, MPa |
|-------------|------------------|------------------|---------------------------|
| “Etal-Inject T” | –               | 42.3             | 106                       |
| –            | 15 % TCP         | 80.3             | 122                       |
| –            | 15 % TCP + 5 % PS | 72               | 108.4                     |
| –            | 15 % TCP + 5 % PC | 75.8             | 112.3                     |
| –            | 15 % TCP + 5 % IPS | 69               | 118.4                     |
Дослідження впливу пластикаторів і термопластів на міцність та ударну в'язкість епоксидних смол
Л. М. Мустафа1, 2, М. Б. Ісмаілов1, 2, А. Ф. Санин 3

1 – АТ «Національний центр космічних досліджень і технологій», м. Алматы, Республіка Казахстан
2 – Satbayev University, м. Алматы, Республіка Казахстан, e-mail: mustafa@mail.ru
3 – Дніпровський національний університет імені Олеся Гончара, м. Дніпро, Україна, e-mail: afedsa60@gmail.com

Мета. Підвищення ударної в'язкості і міцності епоксидних смол "гарячого" та "холодного" отверджень з використанням модифікуючих пластикаторів і термопластичних полімерів.

Методика. Досліджували пластифікати смол холодногого й гарячого отверджень ЕД-20 і Етал Інжект-Т, модифіковані пластикаторами трьох видів і термопластичними полімерами чотирьох видів. Визначали ударну в'язкість методом Шарпи і міцність на стиск немодифікованих і модифікованих смол за різного вмісту модифікаторів.

Результати. Із досліджених пластикаторів найбільш виражений вплив на міцність і ударну в'язкість обох типів смол надає трикрезилфосфат. Крім сполучення міцності та ударної в'язкості смол ЕД-20 досягається при вмісті трикрезилфосфат 5 %, при більш високому вмісті різко знижується міцність матеріалу. Для смол Етал Інжект-Т високі значення даного характеристик отримані при вмісті 15 % трикрезилфосфату, при введені меншої кількості модифікатору міцність матеріалу практично не змінюється. Модифікаторами термопластичних полімерів чи не менший вплив на властивості епоксидних смол, ніж модифікування пластикаторами. Найбільш ефективними добавками до ЕД-20 є високотемпературні полікарбонат (5 %) і полісульфон (10 та 15 %), уведення яких призводить до однорічного підвищення обох характеристик. Для Етал Інжект-Т помітне збільшення ударної в'язкості відбувається при введені 5–15 % полікарбонату, але міцність смоли майже не змінюється. Комплексне модифікування смол суттєвою пластикатора і термопласта призводить до зниження як ударної в'язкості, так і міцності на стиск для обох типів смол.

Наукова новизна. При затвердінні полімерної суміші молекули пластикатора, дисперgowани в середовище макромолекул, послаблюють жорсткість просторове зшивання макромолекул, роблять їх більш рухливими. У результаті підвищується ударна в'язкість і, у деяких випадках, міцність ускладнює спрямованої переорієнтації макромолекул при деформації. Зміна механічних властивостей епоксидної смоли при модифікуванні термопластами визначається міцністю адгезійного зв'язку смоли й дисперсних частинок термопласта, а також ступенем гетерофазності утвореної суміші.

Практична значимість. Результати змін механічних властивостей епоксидної смоли при модифікуванні пластикаторами і термопластами можуть бути використані для виготовлення ударних матеріалів, карбонних шарів чи в конструкціях космічних та авіаційної техніки.

Ключові слова: епоксидна смола, пластикатори, термопластичні полімери, ударна в'язкість.

Исследование влияния пластикаторов и термопластов на прочность и ударную вязкость эпоксидных смол
Л. М. Мустафа1,2, М. Б. Исмаилов1,2, А. Ф. Санин3
1 – АО «Национальный центр космических исследований и технологий», г. Алматы, Республика Казахстан
2 – Satbayev University, г. Алматы, Республика Казахстан, e-mail: mustafa@mail.ru
3 – Днепровский национальный университет имени Олеся Гончара, г. Днепр, Украина, e-mail: afedsa60@gmail.com

Цель. Повышение ударной вязкости и прочности эпоксидных смол «горячего» и «холодного» отвержения с использованием модифицированных пластикаторов и термо пластичных полимеров.

Методика. Исследовали эпоксидные смолы холодного и горячего отвержения ЕД-20 и Етал Инжект-Т, модифицированные пластикаторами трех видов и термопластичными полимерами четырех видов. Определяли ударную вязкость методом Шарпи и прочность на сжатие немодифицированных и модифицированных смол при различном содержании модификаторов.

Результаты. Из исследованных пластикаторов наиболее выраженное влияние на прочность и ударную вязкость обоих типов смол оказывает трикрезилфосфат. Лучшее сочетание прочности и ударной вязкости смолы

References.
1. Levchenko, I., Bazaika, K., Belmonte, Th., Keidar, M., & Xu, Sh. (2018). Advanced Materials for Next-Generation Spacecraft. Advanced Materials, 30(50), 1–13. https://doi.org/10.1002/adma.201802201.
2. Ghidini, T. (2018). Materials for space exploration and settlement. Nature Materials, (17), 846–850. https://doi.org/10.1038/s41563-018-0184-4.
3. Gaidachuk, V.E., Kondratiev, A.V., & Chesnokov, A.V. (2017). Changes in the thermal and dimensional stability of the structure of a polymer composite after carbonization. Mechanics of Composite Materials, 52(6), 799–806. https://doi.org/10.1007/s11029-017-9631-6.
4. Gunyaeva, A.G., Sidorina, A.I., Kurnosov, A.O., & Klimenko, O.N. (2018). Polymeric composite materials of new generation on the basis of binder VSE-1212 and the filling agents alternative to ones of Porcher Ind. and Toho Tenax. Aviation Materials and Technologies, (3), 18–26. https://doi.org/10.18577/2071-9140-2018-0-3-18-26.
5. Dunn, B.D. (2016). Materials and Processes for Spacecraft and High Reliability Applications. Springer. ISBN: 10.3319233610. https://doi.org/10.1007/978-3-319-23362-8.
6. Mustafa, L.M., Yermakhanova, A.M., Iismailov, M.B., & Sanin, A.F. (2019). Study of the effect of plasticizers and thermoplastics on the mechanical properties of epoxy and carbon fiber reinforced plastic (Review). Complex Use of Mineral Resources, (4), 48–56. https://doi.org/10.31643/2019/6445.37.
7. Mostovoy, A.S. (2015). Modification of epoxy polymeric materials with oleic acid. Prospective materials, (4), 33–37.
8. Mostovoy, A.S. (2015). Prescription modification of epoxy resin using new high-performance plasticizers. Modern High Technologies, (7), 66–70.
9. Marakhovsky, K.M., Osipchik, V.S., Vodovozov, G.A., & Papina, S.N. (2016). Modification of an epoxy binder with enhanced characteristics for the production of composite materials. Advances in Chemistry and Chemical Technology, 30(10), 56–58.
10. Krutko, E.T., & Prolopchuk, N.R. (2017). Melaminealdehyde and epoxy resins chemical modification. Polimerne materialy i technologii, (3), 47–59.
11. Epoxy compound Eial-Inject T (n.d.). Retrieved from http://www.epital.ru/yacht1/inject.html.
12. GOST 4647-2015 Plastics. Charpy Impact Test Method (n.d.). Retrieved from http://internet-law.ru/gost/gost/62398/ (date of treatment 01/15/19).
ЭД-20 достигается при содержании трикрезилфосфата 5 %, при более высоком содержании резко падает прочность материала. Для смолы Этил Инжект-Т высокие значения данных характеристик получены при содержании 15 % трикрезилфосфата, при введении меньшего количества модификатора прочность материала практически не изменяется. Модифицирование термопластичными полимерами оказывает менее выраженного влияние на свойства эпоксидных смол, чем модифицирование пластикаторами. Наиболее эффективными добавками в ЭД-20 являются высокотемпературные поликарбонат (5 %) и полисульфон (10 и 15 %), введение которых приводит к одновременному повышению обеих характеристик. Для Этил Инжект-Т заметное увеличение ударной вязкости происходит при введении 5–15 % поликарбоната, но прочность смолы почти не изменяется. Комплексное модифицирование смол смесь пластикатора и термопласта приводит к снижению как ударной вязкости, так и прочности на сжатие для обоих типов смол.

Научная новизна. При отверждении полимерной смеси молекулы пластикатора, диспергированные в среду макромолекул эпоксидной смолы, ослабляют жесткую пространственную сшивку макромолекул, делают их более подвижными. В результате возрастает ударная вязкость и, в некоторых случаях, прочность вследствие направленной переориентации макромолекул при деформации. Изменение механических свойств эпоксидной смолы при модифицировании термопластами определяется прочностью адгезионной связи смолы и дисперсных частиц термопласта, а также степенью гетерофазности образованной смеси.

Практическая значимость. Результаты изменения механических свойств эпоксидной смолы при модифицировании пластикаторами и термопластами могут быть использованы для получения ударопрочных композиционных материалов конструкционного назначения, в том числе авиационной и ракетно-космической техники.

Ключевые слова: эпоксидная смола, модификаторы, пластикаторы, термопласти, термообработка, ударная вязкость

Recommended for publication by Ye. A. Dzhour, Doctor of Technical Sciences. The manuscript was submitted 09.01.20.