

Operation of polymer composite materials modified in a MW electromagnetic field under low temperatures conditions

I. Zlobina^{1,2*}, N. Bekrenev^{1,2}, and A. Egorov^{2,3}

¹Yuri Gagarin State Technical University of Saratov, 77 Politechnicheskaya street, 410054, Saratov, Russia

²National Research Center «Kurchatov Institute-IREA», Bogorodsky Val str., 3, 107076, Moscow, Russia

³National Research Center «Kurchatov Institute», Akademika Kurchatova sq., 1, 123182, Moscow, Russia

Abstract. Tests of control and microwave-modified samples of carbon- and glass-reinforced plastic were carried out according to the scheme of three-point bending. The sample's temperature was -200C. It has been established that microwave exposure on to these materials for two minutes in the cured state at an energy flux density of (17-18) x104 and (22-25) x104 μW/cm2, respectively, contributes to an increase in bending strength by 12% and 15% with an increase in the uniformity of the parameter in a batch of samples from 1.5 to 4.9 times. It has been established that the accumulation of destructive damage in the prototypes occurs over a 2.5-3.5 times longer period of time than the control ones. The difference in the mechanisms of destruction of control and experimental samples is noted. If the destruction of the control samples has a brittle nature, then for the prototypes there is a tendency to the appearance of a plastic component. Key words: polymer composite materials, microwave exposure, carbon reinforced plastic, glass reinforced plastic.

1 Introduction

Polymer composite materials (PCM) reinforced with fabrics based on carbon, glass and aramid fibers are widely used in transport systems, construction and energy complexes. In particular, there was a sharp increase in the consumption of PCM in housing and communal services and transport infrastructure (12 and 19%, respectively), especially in the production of elements of bridge structures [1-3]. There is a growing interest in the use of materials based on carbon fiber. According to analytical studies, it is expected that the consumption of carbon fiber in the world will actively grow and reach \$ 8 billion in 2026 [4, 5]. The increase in consumption of PCM in various areas of production and economy is determined by their high specific strength and corrosion resistance compared to known metals and alloys, as well as compared to single-component polymers [6, 7].

* Corresponding author: irinka_7_@mail.ru

The development of the Far North and the Arctic shelf infrastructures is one of the priority tasks for ensuring the economic and military security of Russia. At present and in the future, an expanded use of polymer composite materials (PCM) is predicted for energy, construction and transport systems used in these areas. Wind loads typical for these regions, combined with temperature gradients, seasonal fluctuations in temperature and humidity, and prolonged exposure to solar radiation during the “polar day”, lead to aging of the PCM matrix and loss of the initial strength characteristics of the material [8–10].

Temperature gradients, as well as the effect of impact loads (micrometeorites and space debris) and ionizing radiation are also typical for the spacecraft operation, significant part of the structural elements of which are made of PCM. In accordance with the foregoing, conducting comprehensive studies on the development of design and technological methods for improving the performance of PCM seems to be relevant.

The study of the behavior of PCM structures in extreme conditions of outer space, the Arctic and Antarctic revealed the particular importance of their thermal stability in a wide temperature range under conditions of periodic heat changes caused by the movement of an object through the shadow parts of the orbit, periodic exposure to direct rays of the active Sun and low temperatures when continuous clouds appear in high latitudes. Thermally stable structures are created using PCM with low linear thermal expansion coefficient (LTEC) and high thermal conductivity. It is believed that CFRPs are best suited for this purpose, however, their use in large building structures is associated with high costs. The problem of creating heat-conducting composite structures is complicated by the fact that the actual physical and mechanical properties of PCM can be determined only after the manufacture of a specific part, i.e. in cured state. In addition, the scatter coefficients of PCM properties are much higher than for metals and their alloys, and with multi-stage optimization of design parameters, this factor can affect the reliability of data [8–13]. Structural features of PCM and significant differences in the chemical and physical properties of matrices of various compositions and reinforcing components make it difficult to predict the final set of properties due to the multifactorial nature of synthesis processes. The last factor reduces the accuracy of determining the properties of the designed PCM by the methods of mathematical and computer modeling.

Improving the existing technologies for manufacturing components and molding PCM in order to increase their resistance to external factors and, in particular, negative temperatures, by introducing the majority of chemical and physical modification methods at these stages, requires a serious and costly technical re-equipment of production. An effective method of modifying PCM in order to improve the mechanical properties of products made from them is the use of exposure to a microwave electromagnetic field, which makes it possible to form a set of properties specified by technical conditions in the bulk of the material based on thermal and non-thermal effects [14, 15]. The greater part of successful examples of the practical application of microwave exposure to dielectric materials relates to the preliminary modification of the initial components and the increase in the efficiency of the stage of matrix curing during the formation of PCM. This approach reduces the reproducibility of the results and the positive effects obtained as a result of the impact of subsequent operations of machining and assembly of the product.

Therefore, one of the alternative ways to form the required set of PCM properties can be a modifying effect on the finally cured material in the composition of the formed product, which will eliminate or significantly reduce the influence of technological heredity factors on the characteristics of the object.

The authors of the article and a number of other researchers [16-19] believe that these shortcomings can be minimized by using a microwave electromagnetic field to modify PCM during the impact on the final product. This possibility was confirmed by studies conducted by the authors in 2015-2021. However, at the same time, the effect of processing cured PCMs

in a microwave electromagnetic field on the change in their strength characteristics under the action of low temperatures was not studied.

The aim of the research was to identify the possibility of improving the functional characteristics and expanding the range of operating conditions as a result of modifying structural elements made of PCM reinforced with fabrics based on carbon and glass fibers in a microwave electromagnetic field by comparatively assessing the strength at low temperatures.

It is assumed that an increase in the elasticity of the matrix at certain temperatures [20] caused by microwave dielectric heating and the skin effect (for carbon fibers), as well as an increase in elastic properties due to an increase in the number of mechanical bonds in the interfacial zone caused by conformational rotations of polymer molecules, will ensure the stability of the material to the action of negative temperatures, and will prevent the growth of microcracks.

2 Materials and methods

In the experiments, we used samples of carbon- and fiberglass produced by Evrokomplekt LLC, Kaluga, in the form of plane-parallel plates with dimensions of 70x10x5 and 70x10x5.5 mm, respectively. The samples were divided into control and experimental groups. Microwave processing was carried out simultaneously for 5 samples on experimental equipment created on the basis of the Zhuk-2-02 installation (LLC NPP AgroEcoTech, Obninsk, Kaluga region) with a beam-type camera with an unlimited volume of radiation into open space) at frequency of 2.45 GHz and energy flux density when modifying carbon fiber (17-18) $\times 10^4 \mu\text{W}/\text{cm}^2$ and fiberglass - (22-25) $\times 10^4 \mu\text{W}/\text{cm}^2$ for 2 minutes. In these modes, the maximum strengthening effect of microwave exposure is provided [18, 19].

After processing, both groups of samples were cooled to a temperature of -200C at a humidity of 50% in a climatic chamber. For mechanical tests, the samples were removed one at a time and subjected to tests for a time not exceeding 30 s to minimize the effect of the room temperature, which was +220C. Both batches of control and prototype samples were tested according to the three-point bending scheme in accordance with GOST R 56805-2015 on a special computer installation with tensometric force sensors with LabWiev software (IE Mayorov, Orel). The loading rate was 350 mm/min.

Based on the test results, the values and the mathematical expectation of the ultimate bending stresses, the change in the magnitude of the stresses of the prototypes σ_{Fp} in comparison with the control ones σ_{Fc} - ($\Delta = \sigma_{Fref} / \sigma_{Fc}$) were determined. The effect of microwave modification on the uniformity of the values of this parameter was evaluated by calculating the coefficient and range of variation.

3 Results and discussion

The results of statistical processing of data obtained during testing of samples are shown in the diagrams (Fig. 1-3). It can be seen that at negative test temperatures, the prototypes show a (12-15) % higher bending strength compared to the control ones, which can be considered a significant value. In this case, their loading kinetics significantly changes up to destruction, namely, the time before the onset of irreversible damage increases by a factor of 2.5–3.5. The increase in load occurs gradually and can be described by a power law. For control samples, we can state a rapid increase in the load according to a dependence close to a straight line. The noted features may indicate a predominantly brittle fracture mechanism for control samples. In prototypes, a certain proportion of plastic deformation with a gradual accumulation of damage is noted. In general, the effect of an increase in breaking stresses

and an increase in the time to destruction of prototypes is manifested to a much greater extent for samples made of carbon fiber.

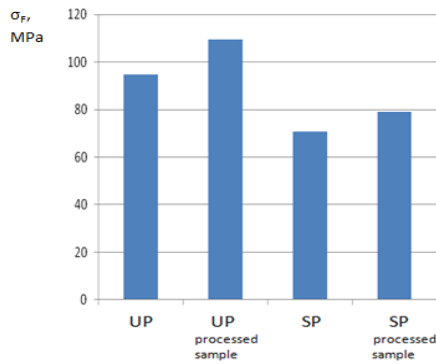


Fig. 1. Ultimate stresses of three-point bending of control and prototype samples of carbon and fiberglass.

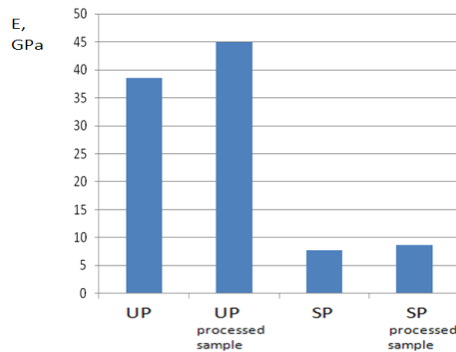


Fig. 2. Transverse modules at three-point bending of control and prototype samples of carbon and fiberglass.

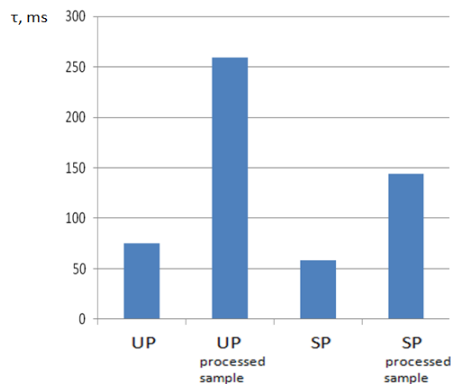


Fig. 3. Average time before destruction of control and prototype samples of carbon and fiberglass.

A significant increase in the uniformity of the parameters characterizing the damage and destruction of the samples was noted. The coefficient of variation of the breaking stresses of carbon and fiberglass decreases from 6.5% to 4.29% and from 8.36% to 1.7% respectively. An increase in the uniformity of strength with respect to three-point bending stresses by 1.5

and 4.9 times is observed. The range of variation also decreases from 17.09 to 9.45 MPa and from 14.3 to 3.18 MPa. In general, both the greater initial uniformity of the strength of fiberglass in comparison with carbon fiber and the greater effect of microwave exposure achieved in this direction are stated.

The strength characteristics of PCM are mainly determined by the "matrix-fiber" interfacial layer (IPL), which is defective due to the presence of pores (voids) formed due to shrinkage of the matrix during the curing of PCM, the components of which have different thermal expansion coefficients. This creates incomplete contact between the reinforcing fibers and the matrix. Accordingly, the large sizes of supramolecular formations, as well as their small number in the presence of voids, will cause a decrease in the strength of the mechanical contact between the fibers and the matrix, worsen the conditions for redistributing the load between the fibers through the matrix when some of the fibers are destroyed. Reinforcing fibers, having a much higher magnitude and elasticity compared to the matrix, bear the main load while ensuring the rigidity of the PCM structure. Accordingly, the larger the area of contact between the fibers and the matrix and the more evenly the indicated areas are distributed over the volume of the PCM, the higher the rigidity of the PCM structure, the greater the values of the moduli of longitudinal and transverse elasticity, the higher the strength characteristics, and also the more uniform the values of this parameter in batches of products. When exposed to negative temperatures, the following changes occur in the PCM structure. Due to the significant hydrophilicity, the voids formed during curing are filled with moisture, moisture is also adsorbed on the surface of the material, filling cracks and microroughnesses. In the process of freezing, the accumulated moisture expands and, accordingly, wedging of voids and the formation and growth of microcracks occurs. At the same time, embrittlement of the amorphous structure of the matrix occurs, and the ability to deform under load decreases. Shrinkage of the matrix with decreasing temperature also leads to deformation of the fibers associated with it, which have significant elastic properties. Due to these reasons, defect formation in the PCM structure increases and internal stresses increase, the value of which, after curing, even under normal conditions, according to a number of data [6, 7, 20], can reach more than 80% of the ultimate strength. Therefore, the brittle nature of the fracture of the studied control PCM samples at a negative temperature, is observed. The effect of modification in a microwave electromagnetic field may consist in inhibition of negative phase-structural changes in the matrix and PCM MFS, caused by exposure to a temperature factor, for the following reasons. It is known [20] that when a cured epoxy resin is heated to a temperature of (50-70)0C, some increase in plasticity occurs. Microwave dielectric heating of PCM to the specified temperature leads to partial plasticization and restoration of the amorphous structure of the epoxy matrix, and wave processes stimulate vibrations of macromolecules in the restored plasticized amorphous structure of the MFS and their conformational rotations, activation of the finished surface of the fibers, promote the movement of defects and their exit to the surface from the structure. A greater number of active centers are formed on the activated surface of the fibers. They interact with the turned links of the chains of macromolecules. Therefore, upon repeated curing, the percentage of the ordered phase in the MFS increases, but the sizes of its fragments (supramolecular formations) are smaller due to the invariance of the initial volume of the matrix. Accordingly, the area of the "matrix-fiber" contact interaction surfaces increases and the sizes of voids (pores) in the MFS decrease. It reduces the volume of moisture absorbed from the environment and, accordingly, reduces the amount of damage caused by the wedging effect when it freezes under the influence of negative temperatures. An increase in the number of contact surfaces of the matrix with the fiber, as well as a smaller temperature gradient, reduces the stress concentration during its shrinkage in process of cooling. A larger volume of "working" fibers contributes to an increase in the deformation capabilities of the structure, which makes it possible to increase the time before the

appearance of irreversible damage. The initial internal stresses that have arisen during the curing of PCMs relax with a temporary increase in the elasticity of the matrix in a microwave electromagnetic field and can significantly decrease with additional curing after the cessation of microwave exposure. Accordingly, the strength of PCM increases.

It is advisable to continue research in this direction in order to obtain an expanded database of the impact made by lower negative temperatures as well as temperature gradients on experimental PCM.

4 Conclusion

A positive effect of finishing treatment in the microwave electromagnetic field of cured carbon and fiberglass was established. It consists in an increase of the limiting stresses of three-point bending by (12-15)%, the uniformity of this parameter up to 4.9 times and an increase in the time period until the destruction of the structure up to 2.5- 3.5 times.

As a mechanism for the formation of these changes in the phase composition and structure of PCM, a temporary restoration of the plasticity of the interfacial layer structure as a result of matrix microwave dielectric heating to a temperature of (50-70) 0C with a subsequent increase in the number of centers for the formation of an ordered structure with a smaller pore size, preventing the penetration of moisture from the outer environment, which reduces defect formation at low temperatures. The number of contact areas (surfaces) in the MFS, which provides an increase in the number of reinforcing fibers in the process of receiving the load, increases with the activation of their surface and conformational rotations of macromolecules under the action of wave processes caused by a microwave electromagnetic field, and allows increasing the elasticity of PCM and, accordingly, increasing the time to material failure.

Acknowledgement

The research was carried out within the framework of the project SP-5946.2021.3 "Method for improving the functional characteristics of spacecraft elements from cured polymer composite materials under the influence of a temperature gradient."

The scientific equipment provided by shared research facilities «Scientific Research Analytical Center» of National Research Center «Kurchatov Institute» – IREA” was used.

The research work was provided with support of National Research Center «Kurchatov Institute».

References

1. V.N. Studentsov, V.A. Kuznetsov, N.V. Zubtsova, I.V. Cheremukhina International Conference Part 1, 357-359 (2009)
2. A.I. Ovchinnikova, *New materials and products of bridge building: textbook* (allowance state tech. un-t., Sarat., 2004)
3. E.N. Kablov, *Aviation materials and technologies* **1** (34), 3-33 (2015)
4. *Electronic resource. Available at: <http://xn--80aplem.xn--p1ai/analytics/Mirovoj-rynok-uglerodnogo-volokna/> (accessed 25.02.2022)*
5. M.S. Doriomedov, *Proceedings of VIAM* **6-7** (89), 29-37 (2020)
6. Yu.A. Mikhailin, 2010 *Structural polymeric composite materials Nauchnye osnovy i tekhnologii* (2010)

7. S. Brinkmann et al., *International Plastics Handbook the Resource for (Plastics Engineers Ed., Hanser., 2006)*
8. I.V. Gorynin, *Ecology and Economics* **3 (19)**, 82-87 (2001)
9. V.M. Buznik, E.N. Kablov, A.A. Koshurina, *Scientific and technical problems of the development of the Arctic*, 275-285 (2015)
10. V.M. Buznik, E.N. Kablov, *Bulletin of the Russian Academy of Sciences* **87 9**, 831-843 (2017)
11. V.A. Kovalenko, A.V. Kondratiev, *Aerospace Engineering and Technology* **5(82)**, 14-20 (2011)
12. I.S. Deev, E.F. Nikishin, *Space model. T. 2. Impact of the space environment on spacecraft materials and equipment* (Ed. L.S. Novikova, KDU. 2007)
13. Yu.V. Polezhaev, S.V. Reznik, E.B. Vasilevsky et al., *Materials and coatings in extreme conditions. A look into the future V. 1. Forecasting and analysis of extreme impacts* (Ed. S.V. Reznik Publishing house of MSTU im. N.E. Bauman, 2002)
14. Yu.S. Arkhangelsky, *Reference book on microwave electrothermy: reference book Scientific book* (2011)
15. S.G. Kalganova, *Electrical technology of non-thermal modification of polymeric materials in a microwave electromagnetic field. Dis. ... doctor of technical sciences* (State those. un-t., Saratov, 2009)
16. S. Inderdeep, K.B. Pramendra, M. Deepak, K.Sh. Apurbba, K. Pradeep, *Akademeia* **1(1)**, 1-6 (2011)
17. I.V. Zlobina, *Metrological Support of Innovative Technologies*, 42045 (2020)
18. I.V. Zlobina, N.V. Bekrenev, *New design and technological methods for increasing the strength of structural elements from non-metallic composite materials* (monograph state tech. un-t., Sarat., 2017)
19. I.V. Zlobina, I.S. Katsuba, N.V. Bekrenev, *Proceedings of the Volgograd State Technical University* **3 (238)**, 20-22 (2020)
20. L. Moshinsky, *Epoxy resins and hardeners Arcadia-Press, LTD* (1995)