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STUDY OF PREPREGS LIFETIME BASED ON EPOXY RESIN WITH AROMATIC AMINE HARDENER

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Today, there is a steady trend in the use of carbon fiber-reinforced plastics in the aerospace and defense industries, mainly based on using pre-impregnated semi-finished products - prepregs. Producing carbon fiber parts from prepregs often requires a long manufacturing time, during which the prepreg must maintain its performance properties. Therefore, one of the main characteristics of prepreg is its viability. This work developed a suitable resin composition with optimized properties and a methodology for studying the viability of prepreg samples, based on determining the stickiness and degree of curing of the prepreg depending on storage time. The influence of prepreg storage time on the strength characteristics of cured laminates was studied. Prepreg samples with long-term viability of up to 60 days were obtained. The experimental data obtained are of practical significance in the industrial production of carbon fiber products, as they establish a connection between the performance properties of the prepreg and storage time.

Keywords: polymeric composite material, prepregs, resin, hardener, polymeric matrix, carbon fiber, viability.

1. Introduction

The use of carbon fiber materials is growing more urgent in the aviation and aerospace industries. Compared to conventional structural materials in the form of metal alloys, carbon fiber-reinforced plastics provide the high-strength/weight ratio. The specific strength of carbon fiber reinforced plastic reaches up to 53-112 km, aluminum alloys up to 21 km, steels up to 27 km, titanium alloys up to 28 km [1-5].

The present-day production of aerospace products from carbon fiber-reinforced plastics is mainly based on prepreg technology. The core of this technology is to obtain a pre-impregnated reinforcement fiber by the system of thermally-reactive matrices- prepreg. The use of prepreg provides an opportunity to obtain the large-sized parts and guarantees a stable and good quality of product. However, this technology results in long production cycles. The manufacture of composite parts from prepregs often requires time for laying and preparation over several days or even weeks, during which the chemical reactions after completion of which the prepreg loses all of its performance properties take place in the prepreg, that adversely affect the strength properties of the final prepreg product. Therefore, one of the main characteristics of prepreg is its viability.

The viability of prepreg is the preservation of its technological properties (adhesiveness, drapability) during storage until processing (from several days to several months) [6-8]. As evidenced by analysis of scientific publications and patents, viability of the prepreg directly depends on the type of hardeners used. The use of anhydride hardeners makes it possible to obtain prepregs with viability of up to 5 days, hardeners, binders with aromatic amine hardeners diaminodiphenylsulfone and dicyandiamide have the greatest viability of up to 360 days [9-12].

In this study, a resin composition suitable for prepregs with optimized properties for prepreg production was developed. It is expected that change in the adhesiveness of prepreg due to aging will be its main disadvantage, which directly affects the quality of manufacture and the final mechanical properties. The works [13-17] contains the studies of the effect of prepreg storage time on physical properties, such as adhesiveness, degree of cure, volatile matter content, jelling time, viscosity, establish a good correlation between storage aging time when stored and conversion in curing, which indicates a decrease in the generated reaction heat, fluidity, and increase in the degree of curing, viscosity. However, the prepreg

composition is often not reported, that is crucial for a substantial understanding of the prepreg properties dependence on storage time.

Furthermore, most references indicate a change in adhesiveness, but there is still insufficient data on the effect on laminate quality [18-20], there is no generalizing disadvantage of changing prepreg properties in the literature. In that regard, the study of mechanical properties and quality of laminates depending on viability is of high research interest.

The purpose of work is a study of prepregs viability based on epoxy resin with aromatic amine hardener to assess manufacturability and determination the dependence of adhesiveness, degree of cure and mechanical properties on the prepreg storage time.

2. Experimental procedure

The prepregs used in the study have been obtained by impregnating a one-directional carbon woven reinforcing filler 12K-300-230 with an epoxy binder with the following composition: 100 weight parts modified epoxy-diane resin; 20 weight parts aromatic amine hardener 4,4'- diamino diphenyl sulfone, 10 weight parts plasticizer tricresyl phosphate [21-24].

The epoxy resin and hardener were loaded into a 300 ml beaker and combined under intensive stirring at 500 rpm and 100 °C in a magnetic stirrer for 30 minutes, then a plasticizer was added to reduce the viscosity. The components were mixed until a homogeneous mass was obtained.

The prepreg impregnation was performed on a laboratory prepreg preparation unit (Figure1), by passing the carbon fabric through the binder bath heated to a temperature of 60 °C while pulling the fabric at a speed of 0.5 m/min. The prepreg samples with a fabric/resin ratio of 65/35 have been obtained (Figure 2). Ingredient control the mass ratio of fabric to resin in the prepreg is adjusted by changing the thickness of the gap between the squeeze rollers to remove excess resin from the impregnated fabric. Fabric wetting width 300 mm. The ratio 65/35 was obtained with a gap thickness of 0.3 mm.

Fig.1. Laboratory unit for preimpregnation

a) *b)*

Fig.2. Roll of experimental prepreg sample (a), experimental prepreg sample (b)

There is no standard method for determining the viability of prepregs, therefore, this article discusses various methods widely used in the global industry. The viability of prepreg samples has been determined by evaluating its adhesiveness, degree of cure, and strength characteristics of cured prepreg laminates. The samples were stored at room temperature 25 ± 1 °C. The prepreg samples have been aged under ambient conditions and tested periodically. The adhesiveness s is an important feasture of prepreg, the loss of which indicates the expiry of its viability time.

The sounding method was used to measure adhesiveness. The adhesive capacity of the material to the surface of the probe was determined under the ASTM D2979 standard [25]. The sample tests for adhesiveness have been performed on a texture/mechanical properties analyzer with TA. XTplus Stable Micro Systems sensitive force sensor. A diagram of measuring is shown in Figure 3.

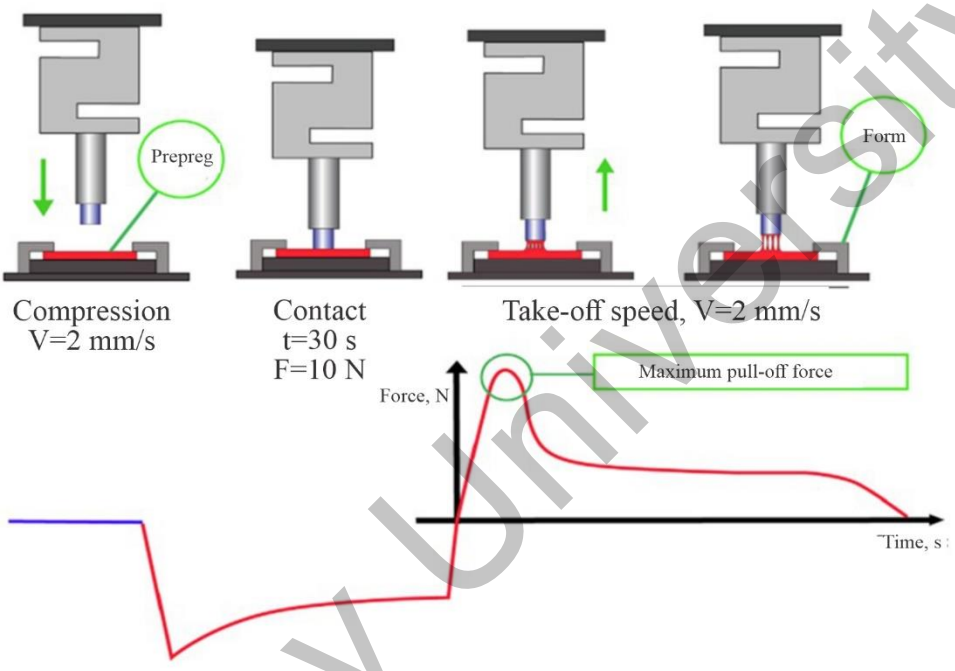

Fig.3. Scheme of measuring the adhesiveness of prepreg samples

The principle of this method is measuring the adhesiveness of adhesive-like materials, which include epoxy prepregs using a probe that separates under driving force the prepreg (adhesive) from the cylinder (substrate). The adhesiveness was measured as follows. The test sample was placed on a cylinder with a hole. A weight was placed on top of the sample for contact pressure. The testing machine drives the probe and returns the probe to its original position after contact with the sample, measuring the force required to separate (detach) the probe from the prepreg. The adhesiveness is expressed as the maximum value of this force. One of the indicators for assessing the viability, in addition to the adhesiveness of the prepreg, is its degree of cure. Since it is important to have data on the degree to which prepregs cure and lose its adhesiveness and draping properties [26].

The degree of cure of the tested (partially cured) prepreg is determined by the ratio of its heat of reaction to the total heat of reaction of the uncured prepreg. Knowing the heat of reaction of 100% unreacted material, it is possible to calculate the degree of curing of the sample using the following equation:

$$\alpha = \left(1 - \frac{H_S}{H_T}\right) * 100 \quad (1)$$

where H_S – total heat of reaction of the tested (partially cured) prepreg J/g; H_T – total heat of reaction of uncured prepreg J/g [27].

The thermal effect of the curing process was studied on a DSC131 EVO Setaram differential scanning calorimeter in the temperature range of 25-175 °C with the heating rate of 10 °C/min.

To study the effect of prepreg storage time on the strength characteristics of cured laminates, samples of carbon fiber reinforced plastic have been obtained from 8 layers of prepreg in the form of plates. For obtaining the prepreg laminates, a hand-molding method with subsequent vacuum treatment evacuation was employed. From the obtained carbon fiber laminates, the samples for tensile tests (GOST 32656-2014) with dimensions 250 x 25 x 2 mm and compression (GOST 33519-2015)] with dimensions 150 x 15 x 2 mm were prepared. The samples were tested on RMG-100MG4 electromechanical testing machine.

3. Results and discussion

The dependence of the degree of cure on the storage time of prepreg was studied. To calculate the degree of cure of the testing samples, the total heat of reaction of the uncured prepreg was determined (Figure 4). As shown by the Figure 4, the total reaction heat of the uncured prepreg was H_T=1024 J/g. The heat release reaction of the sample starts on the fifth minute, the duration of the exothermic reaction is about 80 minutes.

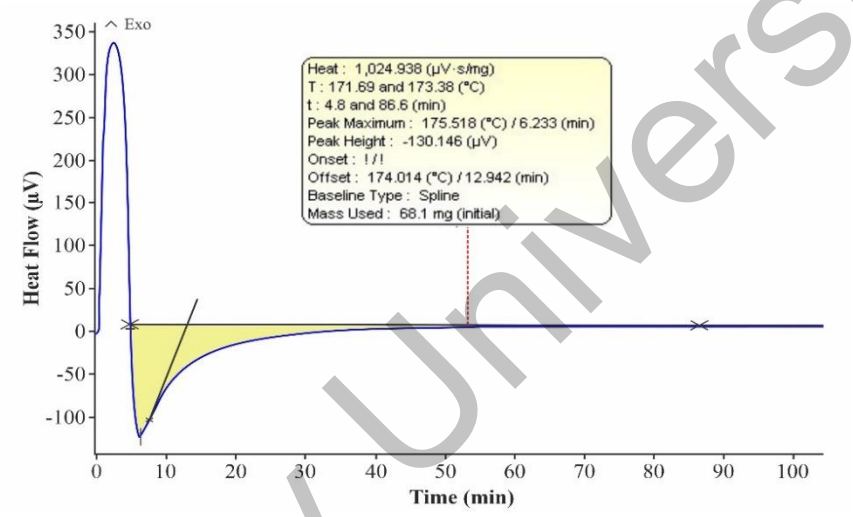

Fig.4. Total reaction heat of the uncured prepreg

Next, the heat of the curing reaction of prepreg samples after storage for up to 60 days was determined. By way of example, the figures show the heat of reaction of prepreg samples after storage for 30 (figure 5) and 60 days (Figure 6).

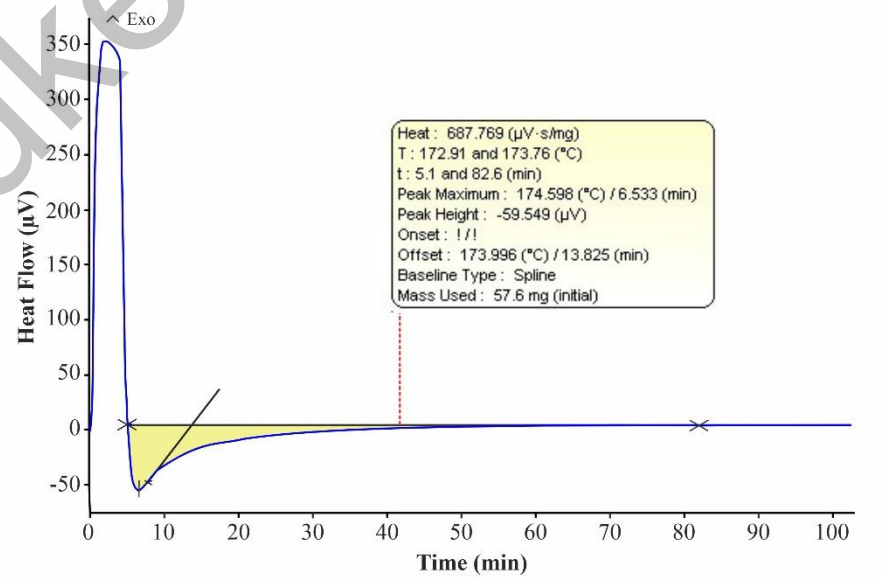

Fig.5. Heat of reaction of the prepreg samples after 30 days storage

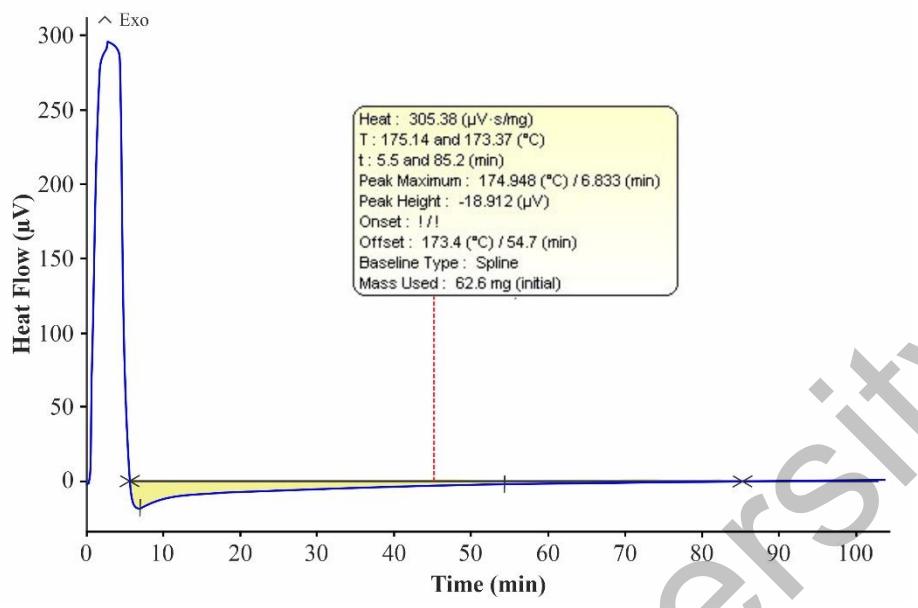

Fig.6. Heat of reaction of the prepreg samples after 60 days storage

According to the experimental results, the total heat of reaction of the prepreg sample after 30 days of storage was H_{S1} = 687 J/g, and the heat of reaction of the prepreg sample after 60 days of storage was H_{S5} = 305 J/g. According to test results, it was found that the peak exotherm decreases with increasing storage time of prepreg samples, this trend is the result of gradual partial curing of the matrix and phase separation during shelf aging. The degree of cure of the partially cured prepreg samples was determined by the ratio of its reaction heat H_s to the total reaction heat of uncured prepreg H_T. The degree of cure α % was calculated according to the formula (1).

The adhesiveness of the prepreg was investigated depending on the storage time at room temperature. The prepreg samples were tested until they lost all of its adhesiveness. The results of the study of the degree of cure and adhesiveness are shown in Figure 7.

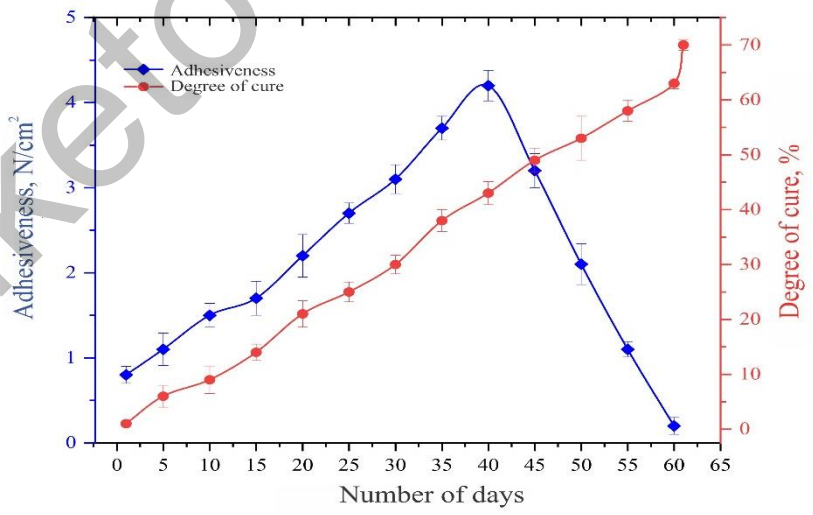

Fig.7. Dependencies of the degree of cure and adhesion of the prepreg samples on storage time

According to results of the study, the prepreg samples have retained its adhesiveness up to 60 days, and the degree of cure of this sample was 63 %. When working with prepregs having a very high adhesiveness of 4.2 N/cm^2, resin distribution and fiber orientation are severely disrupted or clots of reinforcing material are formed. The ratio of components turns out to be inconsistent since the removal of separating foil or substrate

from the prepreg always removes an indefinite amount of resin. A maximum adhesiveness depending on the degree of cure is generated at a conversion of 43 % on day 40 of storage. With further storage a gradual decrease in adhesiveness is observed, such prepreg performance is associated with an increased degree of cure and increased viscosity of the prepreg matrix. After 61 days of storage, the prepreg samples completely lose its adhesiveness with 70 % degree of cure. If the prepregs have no adhesiveness, it means that its preparation has reached too high a stage and their shelf life has expired. Such materials can no longer cure properly.

Therefore, the viability of prepreg samples was determined, which was up to 60 days. This long-term viability achieved with the 4.4-Diaminodiphenylsulfone hardener is caused by availability of amine groups with an aromatic ring; such amines slowly cure epoxide resines at room temperature. At room temperature, the curing practically stops at the reaction with primary amine.

The average shelf life of commercially available prepregs at room temperature is about 30-42 days [28]. In the research work [29], the authors obtained prepregs with a pot life of 4 to 20 days. The authors of [30] report that epoxy prepreg samples containing a cycloaliphatic amine can be stored at room temperature for at least 50 days. In work [31], epoxy prepregs were obtained with the presence of protective polymers in the curing system, which prevented the interaction of the hardener with the resin under storage conditions, allowing the viability of prepregs to be increased to 10 days.

In order to establish the optimal limits of the adhesion indicators, a degree of prepreg samples cure and to identify the relationship between these indicators and strength characteristics of the prepreg laminates, dependence of its strength on storage time have been studied (Figure 8).

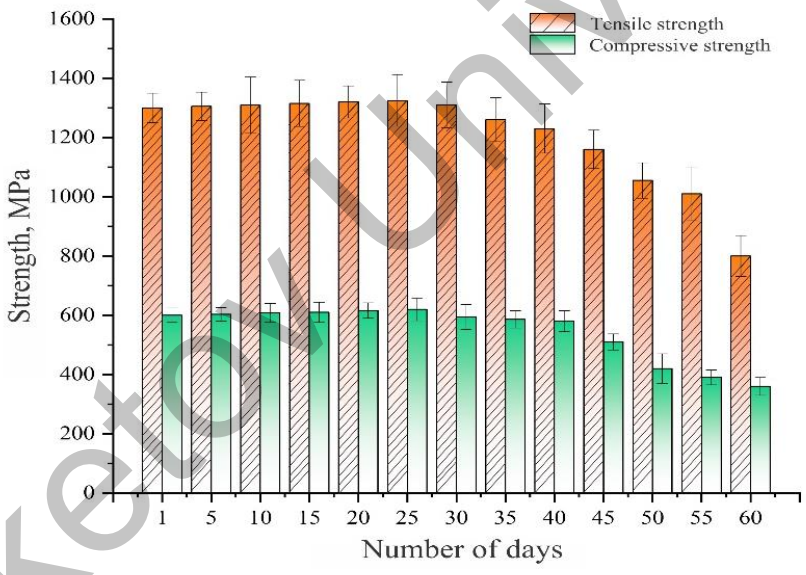

Fig.8. Effect of the prepreg storage time on the strength characteristics of the laminate

The analysis of the results obtained, has demonstrated that within 25 days, the strength has increased by 19 %, with adhesion and curing values were 2.7 N/cm^2 and 25 %, therefore, these parameters can be taken as optimal for prepreg based on epoxy resin with aromatic amine hardener. With further increase in storage time of more than 35 days, strength factor decreases significantly. The reduction of laminates strength is probably due to the fact that when the prepreg degree of cure is increased, the chemical activity of the matrix decreases, which results in decrease in the interlayers hardness between layers at the matrix-matrix interface. This trend of strength reduction after one month of prepreg storage is also observed in the studies [32-34], the authors attribute this to decrease in fluidity and growth of viscosity and degree of cure of the binder in the prepreg.

There are not many similar studies on the effect of storage time on tensile and compressive strength indicators. In [35], prepreg laminates with a tensile strength of 921 MPa were obtained; storing the prepreg for 60 days leads to a decrease in tensile strength by 33 %. As given in [18], based on the results of tensile tests, it can be noted that there are no significant changes in strength after storage time after 60 days, a decrease in strength from 1780 MPa to 1750 MPa.

As a result of the data obtained, the dependences of processibility and mechanical properties on prepreg storage time have been established. The degree of cure is constantly increasing throughout the storage time which is associated with a continuous continuation of the cross-linking reaction of the matrix. After 40 days, the adhesiveness gradually decreases, after 45 days there is a significant decrease in adhesivenes, and the degree of cure at this time is about 50 %. This is probably due to the fact that, as in all prepregs with tthermally-reactive matrix with degree of cure 50-60 % resin reaches the gelatinous state (jellification), where the resin behaves as a semi-solid gelling agent, and the adhesiveness reduces [36]. With a degree of cure of $\alpha > 60$ %, the resin gradually transforms into a solid state and the prepreg completely loses its adhesiveness and the running ability to drape.

4. Conclusions

The viability of prepregs based on epoxy resin with diaminodiphenylsulfone hardener was studied using a method to evaluate the adhesiveness, degree of cure, strength of cured laminates as a function of storage time at room temperature. The prepreg samples with viability up to 60 days were obtained. It has been established that an increase in the prepreg curing rate >40 % negatively affects the strength characteristics of the prepreg laminates obtained by reducing the chemical activity of the matrix, which results in decrease in the interlayer hardness between the layers at the matrix-matrix interface. The highest strength values of laminates were obtained from prepreg samples with adhesiveness 2,7 N/cm^2 and degree of cure 25 %, after 25 days of storage. As a result of the data obtained, the dependences of processibility and mechanical properties on prepreg storage time have been established.

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References

1 Nelyub V.A. Technologies for obtaining prepregs. *All materials. Encyclopedic reference book.* 2013, No. 3. pp. 12–17. [in Russian]

2 Perepelkin K.E. *Reinforcing fibers and fibrous polymer composites*. St. Petersburg, Scientific foundations and technologies. 2009, 380 p. [in Russian]

3 Belova N.A. Composite materials based on carbon fibers. *Young scientist*, 2015, No. 24.1, pp. 5–7. [in Russian]

4 Meyirbekov M.N., Ismailov M.B., Manko T.A., Kozis K.V. Study of the influence of rubber on stremgth properties of carbon plastic. *Space Science and Technology*, 2022, Vol. 28, No. 5, pp. 67–74. doi:10.15407/knit2022.05

5 Ospanali A.T., Kenzhegulov A.K., Zhumadilov B.E., Suyundykova G.S., Medyanova B.S., Partizan G., Aliev B.A. Obtaining of carbon nanofibers based on polyacrylonitrile by the method of electrospinning. *Eurasian Physical Technical Journal*, 2020, Vol. 33, No. 1, pp. 35–38. doi:10.31489/2020No1/35-38

6 Ma Y., Gu Y., Li Y., et al. Interlaminar properties of carbon fiber composites laminates with resin transfer molding/prepreg co-curing process. *J. Reinf. Plast. Compos.*, 2014, Vol. 33, pp. 2228 – 2241. doi:10.1177/ 073168441455706

7 Mangalgiri P.D. Composite materials for aerospace applications. *Bull. Mater. Sci.*, 1999, Vol. 22, pp. 657–664. doi:10.1007/bf02749982

8 Suzuki T., Takahashi J. Prediction of energy intensity of carbon fiber reinforced plastics for massproduced passenger cars. *Proceedings of the 9th Japan International SAMPE Symposium*, Tokyo. 2005, pp.14 – 19.

9 Ashcroft, W.R. *Curing agents for epoxy resins.* Springer. 1993, 37-71 p. doi:10.1007/978-94-011-2932-9_2

10 Olin epoxy, Transportation-Composites (Resins & Systems). Available at: https://olinepoxy.com/industries /transportation/transportation-composites-resins-systems / (March22, 2022)

11 Specialchem company, Epoxy Resins for Adhesives and Sealants. Available at: https://adhesives.special chem.com/selection-guide/epoxy-resins-for-adhesives-and-sealants/examples-of-elevated-temperature- (March11,2022)

12 Niazi M., Beheshty M.H. A new latent accelerator and study of its effect on physical, mechanical and shelflife of carbon fiber epoxy prepreg. *Iranian Polymer Journal*, 2019, Vol.28, pp.337–346. doi:10.1007/s13726-019-00704-8

13 Ji K.J., Wei C.Y., Deng W.H., et al. Evaluation of glass fibre/epoxy prepreg quality during storage. *Polym. Compos.*, 2002, Vol. 10, pp. 599–604. doi:10.1177/096739110201000803

14 Jones R.W., Yeow N., McClelland J.F. Monitoring ambient-temperature aging of a carbon-fiber/epoxy composite prepreg with photoacoustic spectroscopy. *Compos. Part A.*, 2008, Vol. 39, pp. 965 – 971. doi:10.1016/j.compositesa.2008.03.015

15 Grunenfelder L.K., Nutt S.R. Prepreg age monitoring via differential scanning calorimetry. *J. Reinf. Plast. Compos.*, 2012, Vol. 31, pp. 295–302. doi:10.1177/0731684411431020

16 Gu Y., Li M., Zhang Z, et al. Effects of resin storage aging on rheological property and consolidation of composite laminates. *Polym. Compos.*, 2009, Vol. 30, pp.1081–1090. doi:10.1002/pc.20659

17 Budelmann D., Detampel H., Schmidt C., Meiners D. Interaction of process parameters and material properties with regard to prepreg tack in automated lay-up and draping processes. *Compos. A. Appl. Sci. Manuf.*, 2019, Vol. 117, pp. 308 – 316. doi:10.1016/j.compositesa.2018.12.001

18 Blass D., Kreling S., Dilger K. The impact of prepreg aging on its processability and the postcure mechanical properties of epoxy-based carbon-fiber reinforced plastics. *J Materials: Design and Applications*, 2017, Vol. 231(1-2), pp. 62–72. doi:10.1177/1464420716665413

19 Smith A.W., Endruweit A., Choong G.Y.H., et al. Adaptation of material deposition parameters to account for out-time effects on prepreg tack. *Composites Part A*, 2020, Vol. 133, pp. 105835. doi:10.1016/j.compositesa. 2020.105835

20 Endruweit A., Choong G.Y.H., Ghose S., et al. Characterisation of tack for uni-directional prepreg tape employing a continuous application-and-peel test method. *Compos A Appl. Sci. Manuf.*, 2018, Vol. 114, pp. 295 – 306. doi:10.1016/j.compositesa.2018.08.027

21 Meiirbekov M.N., Ismailov M.B., Manko T.A. The effect of the modification of an epoxy resin by liquid oligomers on the physical-mechanical properties of composites. *Voprosy khimii i khimicheskoi tekhnologii*, 2020, Vol. 3, pp. 122-127. doi:10.32434/0321-4095-2020-130-3-122-127

22 Yermakhanova A.M., Baiserikov B.M., Kenzhegulov A.K., Meiirbekov M.N., Zhumadilov B.Y. Study on methods to improve the mechanical properties of aramid/epoxy composites. *Journal of Elastomers & Plastics*, 2023, Vol. 55, No. 2, pp. 331-346. doi:10.1177/00952443221147645

23 Mustafa M., Ismailov M.B., Sanin A.F. Study on the effect of plasticizers and thermoplastics on the strength and toughness of epoxy resins. *Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu*, 2020, No. 4, pp. 63-68. doi:10.33271/nvngu/2020-4/063

24 Yermakhanova A.M., Kenzhegulov A.K., Meiirbekov M.N., Samsonenko A.I., Baiserikov B.M. Study of radio transparency and dielectric permittivity of glass- and aramid epoxy composites. *Eurasian Physical Technical Journal*, 2023, Vol.20, No. 2(44), pp. 60-68. doi: 10.31489/2023NO2/70-78

25 ASTM D2979-01 Standard Test Method for Pressure-Sensitive Tack of Adhesives Using an Inverted Probe Machine. Available at: https://www.astm.org/d2979-01.html (March11, 2022)

26 Stark W., Jaunich M., McHugh J. Cure state detection for pre-cured carbon-fibre epoxy prepreg (CFC) using Temperature-Modulated Differential Scanning Calorimetry (TMDSC). *Polymer Testing*, 2013, Vol. 32, No. 7, pp.1261 – 1272. doi:10.1016/j.polymertesting.2013.07.007

27 Hale A. *Thermosets.* Handbook of thermal analysis and calorimetry. 2002, Vol.3, pp. 295 – 354.

28 Schmidt C., Weber P., Hocke T., Denkena, B. Influence of prepreg material quality on carbon fiber reinforced plastic laminates processed by automated fiber placement. *Procedia CIRP*, 2018, Vol. 67, pp. 422–427. doi:10.1016/j.procir.2017.12.236

29 Yang, et al. A novel bio-based, flame retardant and latent imidazole compound-Its synthesis and uses as curing agent for epoxy resins. *Journal of Applied Polymer Science*, 2022, Vol. 139, pp. e53079. doi: 10.1002/app.53079

30 Kuznetsova I.O., Grebeneva T.A. Regulation of the viability of epoxy SMC prepregs. *Bulletin of Science*, 2020, Vol. 2, No. 1(22), pp. 210 – 217. [in Russian]

31 Cheremukhina I.V. Features of diffusion processes when producing prepregs by layer-by-layer application of components. *Vestnik VGUIT*, 2021, Vol. 83, No. 2, pp. 224 – 229. doi:10.20914/2310-1202-2021-2-224-229. [in Russian]

32 Cole K.C., No Ёel D., Hechler J-J., et al. Room-temperature aging of Narmco 5208 carbon-epoxy prepreg. Part II: physical, mechanical, and nondestructive characterization. *Polym. Compos.*, 1991, Vol. 12, pp. 203-212.

33 Scola D.A., Vontell J., Felsen M. Effects of ambient aging of 5245C/graphite prepreg on composition and mechanical properties of fabricated composites. *Polym. Compos.*, 1987, Vol. 8, pp. 244–250.

34 Ji K.J., Wei C.Y., Deng W.H., et al. Evaluation of glass fibre/epoxy prepreg quality during storage. *Polym. Compos.*, 2002, Vol. 10, pp. 599–604. doi:10.1177/096739110201000803

35 Rabby M.M., Das P.P., Rahman M., Vadlamudi V., Raihan R. Prepreg age monitoring and qualitative prediction of mechanical performance of composite using dielectric state variables. *Polymers and Polymer Composites*, 2022, Vol. 30, pp. 09673911221145053. doi:10.1177/09673911221145053

36 *Degree of cure - A104*. Available at: https:// compositeskn.org/KPC/A104 / (March22, 2023)

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