The use of inhibited layers to improve mechanical properties of thermoset composite materials

A E Protsenko, V V Telesh and A K Potkalov
Komsomolsk-on-Amur State University, Komsomolsk-on-Amur, Russia

E-mail: protsenko.ae@yandex.ru

Abstract. The present paper discusses the research data on strength properties of polymer composite materials using fiberglass reinforced plastic (FRP) as an example. During the process of fiberglass reinforced plastic curing with the use of hot molding, a thermal gradient inevitably appears throughout the material thickness. This phenomenon results in uneven curing of prepreg layers. Internal stress consequently occurs in the material. It is proposed to control the kinetics of binder curing throughout the material thickness by introducing an inhibitor into the various prepreg layers. Multichannel dielectric analysis was used to study the curing kinetics of fiberglass reinforced plastic. It has been found that the time spread for gelation is 8.6 min in the 15-layer sample. The study of strength properties of the obtained samples demonstrates an increase in flexural strength of PCM-modified samples by 12.7%–17.7% and a reduction in their anisotropy.

1. Introduction
Today, polymer composite materials (PCM) are indispensable in machine building, instrument engineering, and other industrial fields [1–5] due to their combination of valuable performance and process characteristics. Vacuum autoclave molding [6,7] is the most widely used process for manufacturing critical structural parts made from polymer composite materials. When manufacturing thick-walled products from polymer composite materials using a hot-cured thermoreactive binder, a thermal gradient is observed throughout the prepreg thickness [8], which is caused by the low thermal conductivity of the prepreg material and by the exothermic nature of the curing process. This results in unevenness in the layer-by-layer curing rate and thus leads to uneven shrinkage, formation of residual stresses [9–11], deterioration of strength properties, and their anisotropy [12,13].

To align the curing rates throughout the prepreg thickness, a method of layer-by-layer inhibition of EDT-69N hot-cured binder has been proposed in paper [14]. Its authors have demonstrated that an increase in strength by 10%–12% was observed when using optimal inhibitor content in the prepreg, thus ensuring the simultaneous start of the gelation process.

Papers [15–18] present the results of research on shrinkage in polymer composite materials based on thermosetting resins. Paper [15] shows that the volume shrinkage from the curing time for a binder based on DER-332 bisphenol A at the gelation point was 79% of the entire shrinkage during the curing process.

The gelation point corresponds to the loss of fluidity as well as commencement of solid phase formation, and the substantial shrinkage of the matrix results in internal stress. Thus, the development
of process techniques that contribute to compensating the described phenomena is the pressing challenge. This paper presents research on the potential for controlling the gelation time by introducing a curing inhibitor into the various prepreg layers.

2. Materials and methods

2.1 Materials

Reinforced plastic materials based on a hot-cured thermoreactive binder have been studied and described in the paper. E-glass structural satin weave fiberglass fabric was used as the composite material filler. This fiberglass fabric was used for producing prepregs. EDT-69N multicomponent hot-cured epoxy binder [19] was used for impregnation.

All of the samples were made by vacuum-autoclave method at the curing temperature of 120 °C and pressure of 0.2 MPa.

2.2 Strength tests

The samples were tested for three-point bending under ASTM D790-10. The sample size was 60x15x3 mm. Supports with a 2 mm radius were used for testing. They were installed at a distance of 48 mm. Loading speed is 1 mm/min.

2.3 Dielectric analysis

Changes in the dielectric data [20] were monitored using a NETZSCH DEA 230\10 instrument during the fiberglass reinforced plastic molding process. The excitation frequency of electromagnetic oscillations was 10 kHz. During the stacking, NETZSCH IDEX comb sensors with an electrode spacing of 100 μm were placed on the prepreg.

Fifteen layers in this work suggested to use for four 3-layer packages in the 15-layer prepreg with one prepreg layer containing the inhibitor laid between them (figure 1). This creates the conditions for primary curing of nonmodified prepreg packages followed by curing of the inhibited layers.

2.4 Gelation point

The gelation point was determined as per the curves showing the dependency of the tangent delta on time as the inflection point [14].

3. Experimental part

To evaluate the extent of anisotropy, the nonmodified fiberglass reinforced plastic was produced as per the abovementioned molding process. During the curing process, the dielectric characteristics of the material and temperature of the sample were monitored on the mold side and on the vacuum bag side (figure 2) [21]. The thermal gradient hereby was 8–10 °C.
Figure 2. Dependence of the tangent delta on time in the process of the ST-69N prepreg curing.

The obtained dependency curves demonstrate the substantial time spread for gelation throughout the prepreg thickness; such a spread is the result of a thermal gradient throughout the sample thickness. The positive result of introduction of the inhibitor layer-by-layer [14] was a prerequisite for conducting the experiment on plastic obtained with improved physical and mechanical properties by introducing an inhibitor into the prepreg layers positioned between the basic packages, as shown in figure 1. This prepreg structure provides the conditions for free shrinkage of 3-layer packages during the curing process and thus prevents internal stress from occurring in the plastic sample. The inhibitor was introduced into the layers between the prepreg packages in a quantity that could facilitate the onset of gelation in modified layers later than that in the packages they were located between. Figure 3 shows the dielectric analysis of the curing process of this multilayer prepreg [21].

Figure 3. Dielectric curves of ST-69N prepreg with inhibited interlayers during cure process.
4. Results and discussions
All plastic materials obtained as per the method presented in this paper were subject to destructive testing to evaluate the impact of inhibitor introduction on strength characteristics [21]. Table 1 shows the result of the flexural strength test.

According to the data in Table 1, a conclusion can be made as to the positive influence of the inhibitor on the PCM strength characteristics of the sample. The increase in flexural strength of 8.8%–17.7% can be observed with introducing NiCl2 with using inhibited layers within the prepreg.

| Table 1: Summary table of mechanical test results |
|-----------------------------------------------|
| FGRP  | Flexural strength, MPa | Anisotropy, % |
|-------|------------------------|---------------|
| ST-69N, fig. 3  | 505.7 (510.3)  | 0.9          |
| ST-69N, fig. 2  | 429.6 (468.9)  | 8.4          |

* The values are indicated when the load is applied from above, in brackets - from below.

It is also noted that in the case of applying oppositely directed loads to the noninhibited plastic samples, unevenness of material properties is observed—that is, anisotropy of the strength properties that is equal to 8.37%. The use of inhibiting layers results to decrease of the strength properties anisotropy under the flexural load to 0.9%.

5. Conclusion
Based on the research conducted, the potential for improving the physical and mechanical properties of polymer composite materials—that is, flexural strength and anisotropy of strength properties — as a result of curing inhibitors has been demonstrated.

The method is creates the conditions for free shrinkage of the individual prepreg packages that are undergoing the curing process. This method is promising as it requires less inhibitor than the other method, and it is less sensitive to observation of the temperature-time curing regime.

Acknowledgement
The research has been carried out with the financial support of the Russian Science Foundation within the framework of research project No. 20-13-00397.

References
[1] Mangalgiri P D 1999 Composite materials for aerospace applications Bull. Mater. Sci. 22 657–64
[2] Fleischer J, Teti R, Lanza G, Mativenga P, Möhring H C and Caggiano A 2018 Composite materials parts manufacturing CIRP Ann. 67 603–26
[3] Mitchell B S 2004 An introduction to materials engineering and science for chemical and materials engineers (John Wiley)
[4] Koushyar H, Alavi-Soltani S, Minaie B and Violette M 2012 Effects of variation in autoclave pressure, temperature, and vacuum-application time on porosity and mechanical properties of a carbon fiber/epoxy composite J. Compos. Mater. 46 1985–2004
[5] Kablov E N 2012 Strategical areas of developing materials and their processing technologies for the period up to 2030 Aviation 7–17
[6] Bhat M R, Binoy M P, Surya N M, Murthy C R L and Engelbart R W 2012 Non-destructive evaluation of porosity and its effect on mechanical properties of carbon fiber reinforced polymer composite materials AIP Conf. Proc. 1430 1080–7
[7] Kumar K V 2016 an Approach To Optimize Autoclaves for Curing Frp Int. J. Eng. Res. Adv. Technol. 597–604
[8] Xie G N, Liu J, Zang W H, Lorenzini G and Biserni C 2013 Simulation and improvement of
temperature distributions of a framed mould during the autoclave composite curing process

[J] Jan K J and Lee D G 1997 Development of an autoclave cure cycle with cooling and reheating steps for thick thermoset composite laminates J. Compos. Mater. 31 2264–82

[10] Stone M A, Schwartz I F and Chandler H D 1997 Residual stresses associated with post-cure shrinkage in GRP tubes Compos. Sci. Technol. 57 47–54

[11] Hahn H T 1976 Residual Stresses in Polymer Matrix Composite Laminates J. Compos. Mater. 10 266–78

[12] Whitney J M and Nuismer R J 1974 Stress Fracture Criteria for Laminated Composites Containing Stress Concentrations J. Compos. Mater. 8 253–65

[13] Tsai S W and Azizi V D 2008 Strength of laminated composite materials. AIAA J. 4 296–301

[14] Protsenko A E and Telesh V V. 2015 Inhibition and Cathalisation as a Method to Improve the Mechanical Properties of a Fiberglass-Reinforced Plastic Mech. Compos. Mater. 51 555–60

[15] Simonov-Emel’yanov I D, Surikov P V., Trofimov A N, Kandyrin L B, Zarubina A Y and Apeksimov N V. 2013 Oligomeric epoxy binders with controllable molecular characteristics: Shrinkage upon curing Polym. Sci. Ser. D 6 202–6

[16] Minakuchi S 2015 In situ characterization of direction-dependent cure-induced shrinkage in thermoset composite laminates with fiber-optic sensors embedded in through-thickness and in-plane directions J. Compos. Mater. 49 1021–34

[17] Li C, Potter K, Wisnom M R and Stringer G 2004 In-situ measurement of chemical shrinkage of MY750 epoxy resin by a novel gravimetric method Compos. Sci. Technol. 64 55–64

[18] Billotte C, Bernard F M and Ruiz E 2013 Chemical shrinkage and thermomechanical characterization of an epoxy resin during cure by a novel in situ measurement method Eur. Polym. J. 49 3548–60

[19] Shalin R E 2012 Polymer Matrix Composites (Springer Science & Business Media)

[20] Senturia S D 1986 Epoxy Resins and Composites IV 80

[21] Alexander P and Telesh V 2019 Polymer composites modified via cure inhibitor vol 1 Mendeley Data