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Mechanical properties and damage development in glass-fiber epoxy laminates subjected to tensile loading at sub-zero temperatures

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Abstract. In various structural applications polymer composites are exposed to sub-zero and even cryogenic temperatures which may initiate of microstructural damage. To anticipate these events, one needs to understand the behavior of composites in a sub-zero environment. This study focuses on damage initiation and accumulation, and its influence on the properties of cross- ply glass fibers epoxy composites at sub-zero temperatures. The effect of bromine modification of epoxy, and the dissolution in an organic solvent on the mechanical performance of the produced composite is also investigated. To evaluate the influence of a sub-zero environment on the mechanical performance of glass fiber epoxy laminates, tensile tests in a sub-zero environment of unconditioned specimens were carried out. The quasi-static tensile tests were performed to measure the elastic modulus of the composites while loading-unloading experiments were performed to monitor the initiation (and accumulation) of microstructural damage and its influence on the stiffness of glass fiber epoxy laminates. The results of cryogenic damage and fracture in the laminates are discussed with a focus on the degradation of properties of glass fiber crucial for their use in structural applications: strength and stiffness.

1. Introduction

Epoxy-glass fibre composites (EP/GF) have a diversified use due to their high stiffness, strength, quality, ease of access, and low price [1,2,3]. Because of good desired mechanical properties, scientists considered the use of EP/GF in low-temperature conditions [4,5,6]. Bhavya et al. [3] developed an epoxy glass laminate using various curing agents, which was tested for tensile, flexural, shear and impact properties. Analyzing the mechanical, dielectric and thermal parameters, it can be concluded that the composite with diethyltoluenediamine hardener is a better choice than triethylenetetramine as a hardener for use as an electromagnetically transparent mechanical coating for antenna systems. LeBlanc, [7] conducted research aimed at analyzing the effect of low temperatures on mechanical properties, cracking, impact strength, and dynamics of carbon-glass and epoxy composites. The E-glass/epoxy- based material tested showed minimal dependence on temperature drop in terms of elastic modulus and tensile strength. Specifically, there was an 11% increase in modulus and a 7% increase in strength with decreasing temperature. Thus, an inverse relationship was found between tensile yield and temperature. In this work, a series of tensile tests were performed to study the mechanical behavior of EP/GF laminate at low temperatures. Using an optical microscope imaging system, the increase in damage area in samples at low temperatures was demonstrated. Furthermore, loading-unloading tensile tests at room and sub-zero temperatures allowed investigation of progressive damage accumulation with increasing load. The degradation of the stiffness of the laminates is directly related to the amount of damage induced at each of the loading steps, thus it is possible to analyze damage offset as well as damage tolerance for different materials at different temperatures.

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The overall objective of this work is to select the best epoxy system suitable for working under cryogenic conditions/low temperatures with respect to the high strength and stiffness and minimal damage during the service life.

2. Experimental procedure

2.1. Materials

EP/GF laminate made by stacking successive layers of plain weave glass fiber fabric impregnated with epoxy resin was studied. The matrix in the manufactured composites were the following epoxy resins: YD-128, (Aditya Birla Chemicals) and YDPN 638A80 (Kukdo). The resins were modified with dicyandiamide (DICY), diaminodiphenyl sulfone (DDS) and Nowolak P hardeners. The Joint Company (Połock, Belarus) provided the E-glass reinforcement necessary for the tests. As part of the conducted research, information about the epoxy resin (EP), the type of epoxy resin (X) and the type of hardener (Y) were used to determine the composite materials.

The notation creating the designation looked like this: EP_X_Y_.

Table 1. Designation of selected composite materials.

Symbol	Epoxy resin type (X)	Viscosity (at 25°C) [Pa·s]	Hardener (Y)
EP_2_2	YD -128	0.011-0.013	DICY
EP_2_1	YD -128	0.011-0.013	Nowolac
EP_1_3	YDPN 638 A 80	0.1 – 0.4	DDS

2.2. Tensile tests

Tests were performed using an Instron 3366 universal testing machine equipped with a 10 kN load cell and mechanical grips in an environmental chamber. Axial strains were measured using a standard clip-on extensometer (Instron 2620–601) with a 50 mm base positioned in the middle of the sample's gauge length. For sub-zero temperature, samples were held at -50 °C for about 30 min before starting testing to ensure thermal saturation of the samples. The tests were conducted in displacement control mode at a rate of 2 mm/min. The modulus was determined from stress-strain curves within the linear range of 0.05% to 0.20% strain. In the cyclic loading-unloading tests (L-UL), samples underwent steps of increasing strain starting from 0.25% until failure (or up to maximum strain of 1.20%). After each loading step, the samples were unloaded to 15 N, axial strains were zeroed, and a low-level (up to 0.25%) L-UL step was performed from which modulus was determined.

The schematic representation of the loading history is shown in Figure 1 below. To identify cracks and damages, optical microscopy was used.

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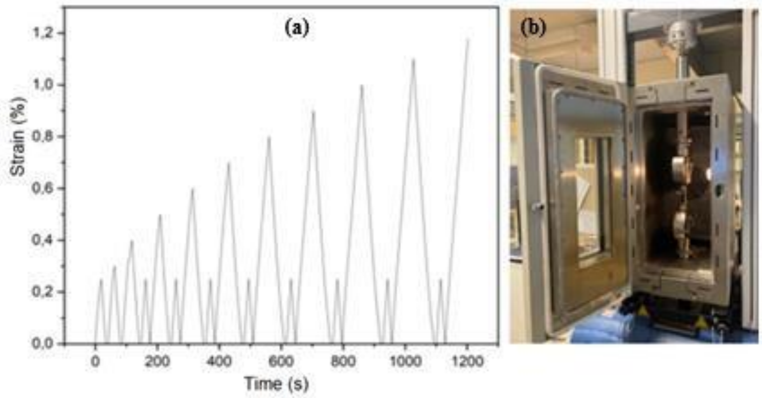


Figure 1. Schematic representation of load application in loading-unloading test (a) and specimen in the environmental chamber (b).

3. Results and discussion

3.1. Tensile properties

The stress-strain curves for all tested materials at room temperature (RT) and at -50°C are presented in Figure 2. The degradation of materials, represented by the reduction in Young's modulus, with increase of applied strain at RT and -50°C are shown in Figure 3. For easier comparison, the numerical values of initial Young's modulus and strength of laminates for all tested composites at RT and -50°C are summarized in Table 2.

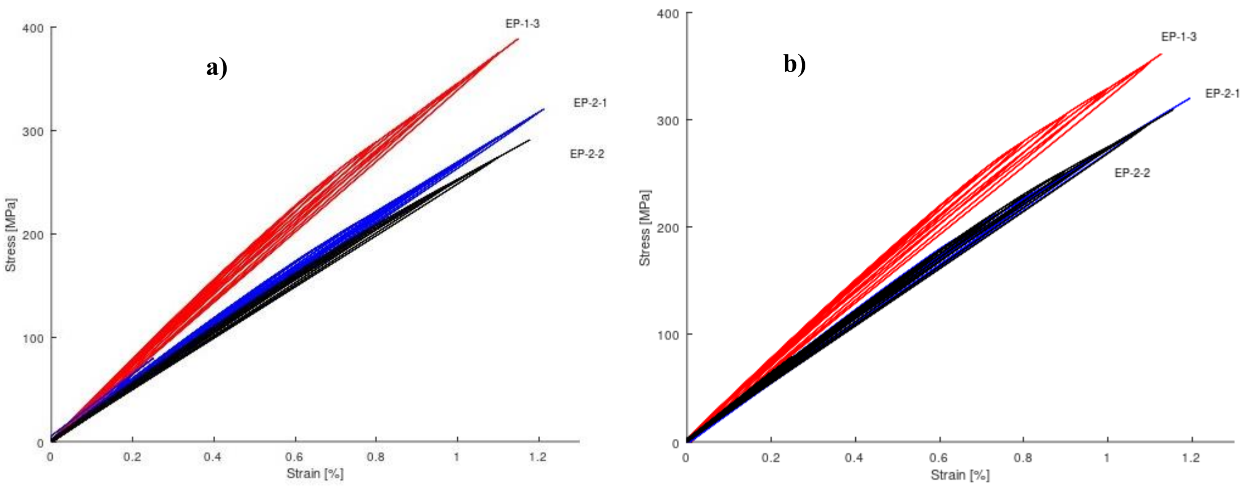


Figure 2. Stress-strain curves of composite laminates at RT (a) and -50°C (b).

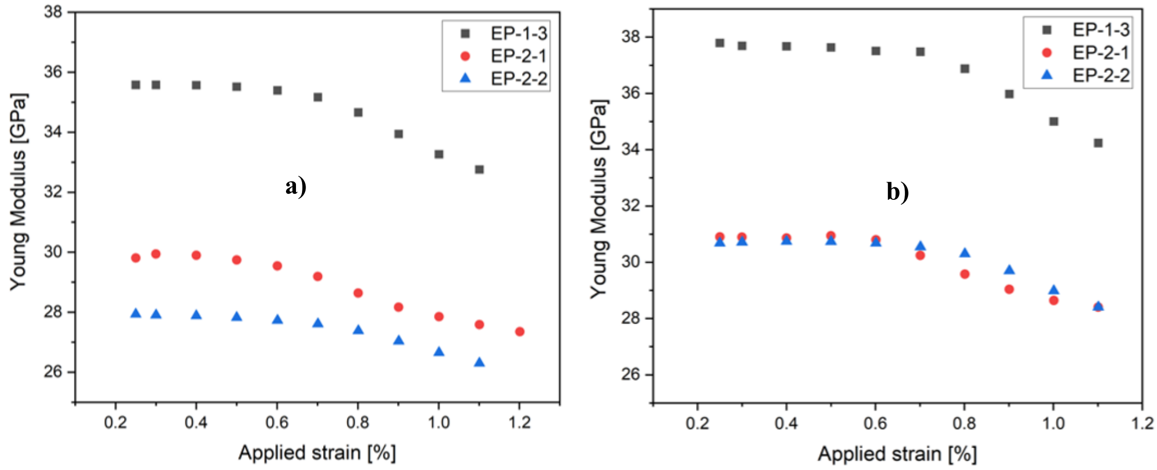


Figure 3. Degradation of Young’s modulus of GF/EP laminates with increase of applied strain at RT (a) and at -50°C (b).

Table 2. Young's modulus and tensile strength of composite laminates in different conditions.

Symbol	E_0 (GPa)		Tensile strength (MPa)	
	RT	-50°C	RT	-50°C
EP_1_3	35.6	37.7	369	361
EP_2_1	29.8	30.9	321	321
EP_2_2	27.7	30.7	291	309

At room temperature, the composite EP_1_3, which utilizes epoxy-bromine resin + DDS, exhibited the highest values of tensile strength, measuring 369 MPa. Conversely, the lowest tensile strength (291 MPa) was observed in EP_2_2, consisting of bisfenol A resin and DICY. This represents a decrease of 21% compared to EP_1_3. The highest and lowest Young's modulus values were also recorded for EP_1_3 and EP_2_2, respectively, with values of 35.6 GPa and 27.7 GPa (22% difference).

The results from testing the samples at -50°C are somewhat intriguing. The laminate EP_2_1 is not affected at all and it is stable in both temperatures. In the case of EP_2_2 and EP_1_3 the decrease of temperature to -50°C causes increase in Young's Modulus by 11% and 6% respectively. While strength of EP_1_3 is almost unaffected by temperature (about 2% decrease) but strength of EP_2_2 increases by 6% as temperature is decreased. In summary, the strength of the tested materials is estimated to be more than 300 MPa.

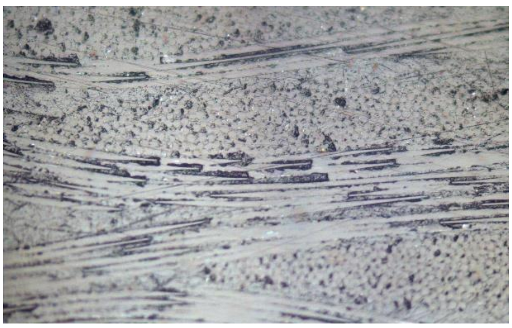
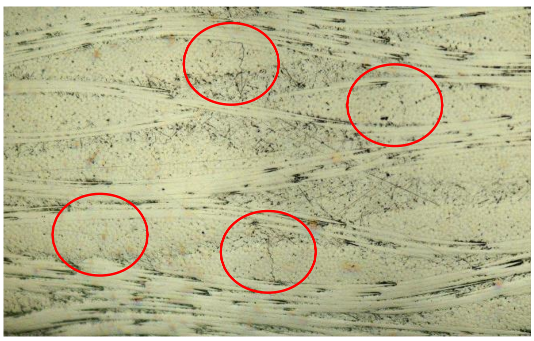
The results obtained in this study compare well with the data published in literature and thus it can be concluded that the tested composite materials show very promising results. For example, Perez et al. [8] studied tensile properties of 1AIUW001-005 composite and obtained tensile strength and Young's modulus of 355.8 MPa and 17.51 GPa respectively. In another study, Kumarasamy et al. [9] investigated the tensile strength of glass fiber-reinforced polymer (GFRP) composites at high and low temperatures. The GFRP laminates were produced using smooth E-glass fabric (800 g/m2) and epoxy resin (Bisphenol-A). At room temperature, the tensile strength and Young's modulus were measured as 275 MPa and 8 GPa respectively. On the other hand, Anjaneyulu et al. [10] fabricated composites using epoxy resin with various orientations of glass fibers and presented studies on the effect of symmetric and non-symmetric fiber orientations on the tensile and flexural properties of epoxy laminates reinforced with unidirectional E-glass fibers. The T-2-S-1 laminate with an orientation of 0°/90°/0°/90° exhibited a tensile strength of 211.73 MPa and a Young's modulus of 20.53 GPa. In terms of the results obtained under cryogenic conditions - liquid nitrogen (LN2), Perez et al. [8] compared the tensile properties of 1AIUW001-005 in the 0° direction at both room temperature (RT) and -196°C. In LN2, both parameters increased, with the tensile strength measuring 468.9 MPa and the Young's modulus measuring 21.30

GPa. This indicates a 24.07% and 17.79% increase compared to RT. Similarly, Kumarasamy et al. [9] observed an increase in tensile strength to 315 MPa under cryogenic conditions. However, there was a decrease in the Young's modulus by 43.75 %.

The degradation of stiffness in all materials is somewhat similar in terms of amount of the decrease of Young's modulus as can be seen from Fig. 3. The decrease of stiffness at around 1.1% of applied strain reaches 10-11% for all materials independently of composition and test conditions. It should be noted that if direct quantification of induced damage (e.g., number of micro-cracks per unit length) is not possible then damage parameter "*d"* can be introduced. Since decrease of stiffness is directly related to the amount of damage in the composite then the damage parameter can be defined as the ratio between the measured stiffness E after each maximum strain level and the initial stiffness E_i of the undamaged sample ($d = E/ E_i$). If there is no damage, then $d = 1$ but once damage is initiated and micro-cracks are present then $d < 1$. It means that at the current decrease of stiffness (10%) the damage parameter $d =0.9$. The data from the literature shows that depending on the thickness of the transverse layer as well as thickness ratio between longitudinal and transverse layers the $d = 0.9$ may correspond to crack densityof 0.1…0.6 mm^{-1} (or 1…6 cracks per 1 cm) [12]. There is of course some variation in the degradation of stiffness between materials/test conditions, but it cannot be properly analysed with limited number oftested specimens. It would be easier to draw conclusions about damage accumulation in those laminatesif crack density was available, but it was not possible to properly quantify damage at this stage of the study. One difference between RT and -50°C tested laminates can be noticed however; the stiffness starts to decrease after 0.6% of applied strain for laminates tested at RT while for materials subjected to -50°C the Young's modulus starts to change after 0.7%. This indicated that offset strain for crack initiation may be higher for laminates tested at -50°C. This is somewhat surprising, since thermal stresses in transverse layers at the same applied mechanical strain should be higher at -50°C than at RT. The polymer also tends to be more brittle at low temperatures thus it would be expected that cracks in laminates at lower temperature should appear easier/earlier. This contradiction with expected/known mechanisms should be investigated further by calculating thermal stresses in different layers and by performing more experimental work on these materials.

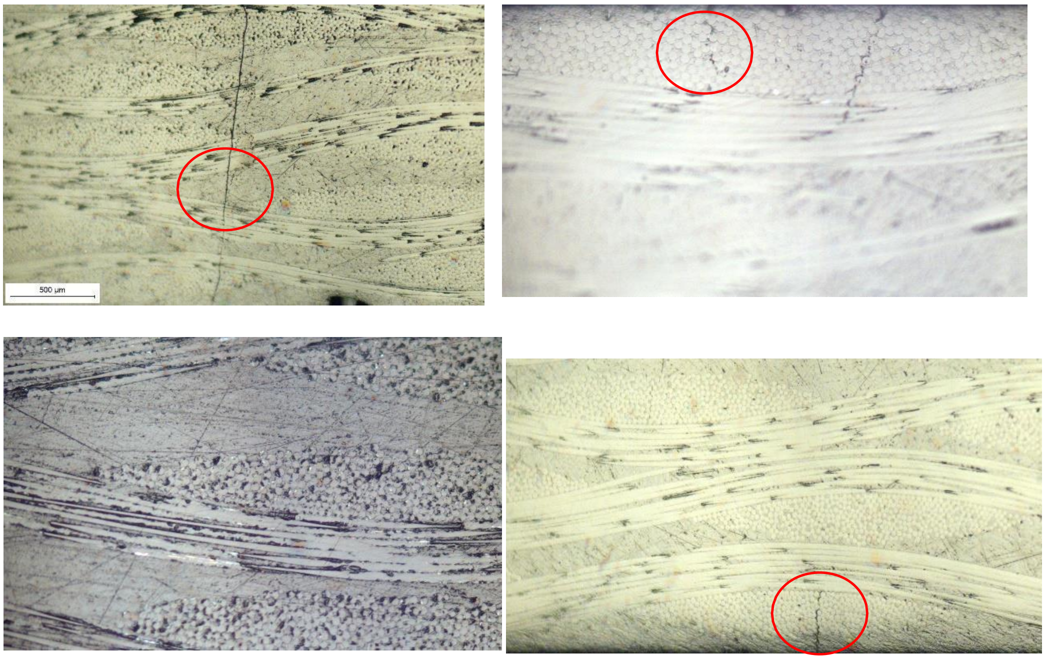
3.2. Microscope observation
Table 3 provides an insight into microstructure of laminates (upper row) with a thickness of 1.5 mm and presence of micro-cracks as seen from optical micrographs. Although the stiffness of laminates is decreasing by approximately 10% as seen from Figure 3, the amount of visible micro- cracks is not so significant as can be observed in those micrographs (damage is indicated by circles in the higher magnification photos on the bottom row in the table).

Table 3. Optical micrographs showing composite microstructure and micro-cracks in transverse bundle.

	RT	-50°C
EP_1_3		

EP_2_1

EP_2_2



4. Conclusions

In this research, loading-unloading tests were performed to investigate the mechanical properties of the GF/EP composite laminates with woven fabric (e.g. cross-ply laminates). The obtained data includes the tensile strength and Young's modulus, which are presented in Table 1. Microscopic images were also captured to visualize the localized damage. The main conclusions are as follows:

- The stiffness degradation was observed in tested laminates (≈10%). This indicates that there may be rather significant amount of damage. Materials with different epoxy matrix show some differences in initial stiffness but not so much in degradation of it during the loading. The laminate tested at - 50°C showed somewhat higher initial stiffness of the laminates compared to RT but only slightly larger (and more rapid) decrease of stiffness.
- The EP_2_1 (YD128 + novolac) exhibits greater strength and stiffness both at RT and -50°C compared to other materials.
- Due to the complex microstructure of laminates as well as challenging test conditions it was not possible at this stage to quantify amount of damage (number of cracks). This part of the study should be carried out in the future.

5. References

[1] Chen W, Meng Q, Hao H, Cui J and Shi Y 2017 Quasi-static and dynamic tensile properties of fiberglass/epoxy laminate sheet *Constr. Build. Mater.* **143** 247–58

[2] Reis J M L, Coelho J L V, Monteiro A H and da Costa Mattos H S 2012 Tensile behavior of glass/epoxy laminates at varying strain rates and temperatures *Compos. Part B Eng.* **43** 2041–6

[3] Bhavya S, Velmurugan R and Arunachalam K 2021 Evaluation of E glass epoxy composite laminate as an electromagnetically transparent aerospace material *Mater. Today Proc.* **46** 4825–34

[4] Sápi Z and Butler R 2020 Properties of cryogenic and low temperature composite materials – A review *Cryogenics (Guildf).* **111** 103190

[5] Chen D, Li J, Yuan Y, Gao C, Cui Y, Li S, Liu X, Wang H, Peng C and Wu Z 2021 A Review of the Polymer for Cryogenic Application: Methods, Mechanisms and Perspectives *Polymers (Basel).* **13** 320

[6] Schutz J . 1998 Properties of composite materials for cryogenic applications *Cryogenics (Guildf).* **38** 3–12

[7] LeBlanc J, Cavallaro P, Torres J, Ponte D, Warner E, Saenger R, Mforsoh I N and Shukla A 2020 Low temperature effects on the mechanical, fracture, and dynamic behavior of carbon and E-glass epoxy laminates *Int. J. Light. Mater. Manuf.* **3** 344–56

[8] Salmeron Perez N, Shaw R M and Gower M R L 2022 *Mechanical testing of fibre-reinforced polymer matrix composites at cryogenic temperatures (-165°C)* (Teddington, UK)
[9] Kumarasamy S, Zainol Abidin M S, Abu Bakar M N, Nazida M S, Mustafa Z and Anjang A 2018 Effects of High and Low Temperature on the Tensile Strength of Glass Fiber Reinforced Polymer Composites *IOP Conf. Ser. Mater. Sci. Eng.* **370** 012021
[10] Anjaneyulu J, Moizuddin M and Chandra kumar P 2020 Evaluation of mechanical behaviour of Glass fibre-epoxy composite laminates *Mater. Today Proc.* **22** 2899–905O.
[11] Rubenis O, Spārniņš E, Andersons J and Joffe R 2007 The Effect of Crack Spacing Distribution on Stiffness Reduction of Cross-ply Laminates *Appl. Compos. Mater.* **14** 59–66

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