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Thermomechanical properties of epoxy and wax matrix composites for superconducting magnets

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Abstract. Thermomechanical properties of epoxy resin systems and paraffin wax for the vacuum impregnation of superconducting magnet coils have been studied at ambient and at cryogenic temperatures. Parameters for the thermomechanical modelling of isotropic pure resins and anisotropic S2 glass fibre reinforced composites, and their stress limits under uniaxial tensile, bending and shear loading have been determined.

1. Introduction

Superconducting magnets contain polymers to provide dielectric insulation and mechanical support. By static stress-strain measurements at room temperature (RT) and 77K we have characterised the effect of different matrix materials and the effect of fibre orientation on the composite mechanical properties. The interlaminar through thickness shear properties were measured by short beam three-point bending tests at RT and at 77K. By Dynamic Mechanical Analysis (DMA) in torsion mode we have measured the anisotropic shear modulus and thermal expansion. Toughness of the composites is compared based on quasi-static tensile and flexural stress-strain measurements. Stress relaxation behaviour of the unfilled and glass fibre reinforced epoxy systems have been characterised under uniaxial tensile loading.

2. Experimental

2.1 The samples

All samples were waterjet cut from 3 mm, 4 mm or 5 mm thick plates produced by vacuum impregnation. The pure epoxy resin systems referred to as CTD101K [1], POLAB Mix, MSUT [2], MY750 and Mix 61 [3] and their processing details can be found in references [4] and [5]. Polarit A55 is a mixture of treated petroleum wax composed of long, straight chain hydrocarbons with chain length C_{20}-C_{50} and paraffin wax product composed of straight chain hydrocarbons (>C_{20}). Composite plates were produced with S2-glass fibre cloth Hexforce 4522 F81 H 27 from Hexcel with S2-glass density of 123 g/m^2 [6], with nominal fibre volume fraction V_f=33%. This volume fraction has been obtained by filling the mould with the maximum number of S2-glass cloths without applying any mechanical stress.

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2.2 Dynamic mechanical analysis (DMA) and thermal expansion measurements

DMA temperature sweeps in torsion mode were performed according to ASTM D7028 [7] with an Anton Paar MCR702e instrument, using samples with nominal dimensions of 4 mm×10 mm×40 mm, at a frequency of 1 Hz with 0.1% shear strain and 2 K/min. For absolute G' measurements the instrument was calibrated using reference samples with known shear modulus (Ti6Al4V G=43.6 GPa, fused quartz G=31.0 GPa and Al 7175 G=25.4 GPa).

Thermal expansion measurements in the temperature range -150 °C to 200 °C have been derived from the sample length change measured during the DMA temperature sweeps according to the procedure described in [5]. Results have been compared to those measured with a laser dilatometer system with a sample holder inside a cryocooled vacuum system [8].

2.3 Tensile stress-strain and stress relaxation measurements

Tensile tests were performed according to ISO 527 [9], with a gauge length of 30 mm, and a distance between grips of 75 mm. The test speed was 1 mm/min while measuring the tensile modulus in the elastic stress–strain region, and 5 mm/min after passing the yield point.

For stress-relaxation measurements the samples were loaded to a pre-stress of either 35 MPa for pure samples or 100 MPa for composites. When reaching the selected pre-stress, the strain, measured with an MTS 632.27F-21 clip-on extensometer with a gauge length of 25 mm, was held constant for at least 24 h.

2.4 Flexural stress-strain measurements

Three-point bending flexural tests were conducted according to ISO 178 [10], with rectangular beams 80 mm × 10 mm, with a thickness between 3 and 4 mm, using Ø = 10 mm loading supports and bending die. The span length was 16 × the nominal sample thickness, and the crosshead speed was 2 mm/min. The flexural modulus is determined as the slope of the linear fit in the strain range 0.05 to 0.25 %. The flexural stress and flexural strain are calculated according to equations (1) and (2) from the load (F), the specimen width (b), the specimen thickness (h), the support span (L), and the displacement (s):

$$Flexural\ stress\ (MPa)\colon \sigma = \frac{3\times F\times L}{2\times b\times h^2} \tag{1}$$

$$Flexural\ strain\ (\%)\colon \varepsilon = \frac{6\times s\times h}{L^2}\times 100\ \% \tag{2}$$

2.5 Shear strength measurements

Three-point bending tests in short beam configuration were performed according to the standard ISO 14130 [11] to determine the apparent interlaminar shear strength. Rectangular beams with nominal dimension of 40 mm x 10 mm x 4 mm have been used for the tests with Ø=4 mm loading supports, Ø=10 mm bending die and a 19.5 mm span (5 × the sample thickness ± 0.3 mm). The crosshead speed was 1 mm/min. The through thickness shear strength is calculated from the load (F), the specimen width (b) and thickness (h), see equation (3):

$$Through\ thickness\ shear\ stress\ (MPa)\colon \tau = \frac{3\times F}{4\times b\times h} \tag{3}$$

3. Results

3.1 Uniaxial tensile stress-strain and stress relaxation at RT

Figure 1(a) compares the RT uniaxial tensile stress-strain curves of V_f=33%, [0°,90°], S2-glass reinforced composites with the epoxy resins CTD101K, POLAB Mix, MSUT, MY750 and Mix61 as matrix materials. The effect of the matrix is comparatively small, only the stress-strain curves of the composite with Mix61 matrix, whose T_g onset is below RT, deviates significantly from the other curves. When the load is applied in the [±45°] fibre orientation σ_m is strongly reduced with respect to the [0°/90°] loading direction. The mechanical anisotropy is reduced when the fibres are oriented in four directions [0°/90°/±45°].

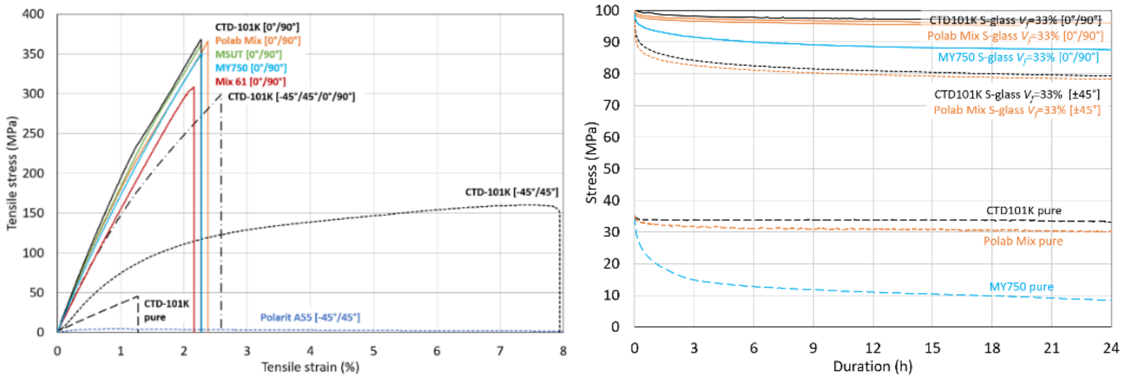

Figure 1. (a) Tensile stress-strain curves acquired at RT of V_f=33% S2 glass fibre reinforced CTD101K, Polab Mix, MSUT, MY750, Mix61 and wax Polarit A55. (b) Stress relaxation as a function of duration at a constant strain of pure epoxy resins at a pre-stress of 35 MPa and of V_f=33% [0°/90°] and [±45°] S2 glass fibre reinforced epoxy resins at RT.

In Figure 1(b) the stress relaxation of the pure epoxy resins CTD101K, Polab Mix and MY750 and [0°/90°] and [±45°] S2-glass composites is compared. The composites and the pure resins have been loaded to a stress of 100 MPa and 35 MPa, respectively. Pure CTD101K shows slightly less stress relaxation than the toughened Polab Mix. The stress relaxation in pure MY750, which is among the toughest epoxy resins, is particularly high, which may influence the pre-stress in a superconducting magnet, but also allow to decrease local stress concentrations originating from manufacturing tolerances of the different coil constituents.

3.2 Flexural stress-strain and shear strength at RT and at 77K

The 77K flexural stress-strain curves of S2-glass reinforced CTD101K with different fibre orientations are compared in Figure 2(a). The composites made with layers of unidirectional [0°/90°] oriented fibres have strongly anisotropic properties, with the highest flexural modulus and ultimate flexural strength in the [0°/90°] configuration, and much smaller modulus and strength, but higher strain at failure measured in the [±45°] fibre direction.

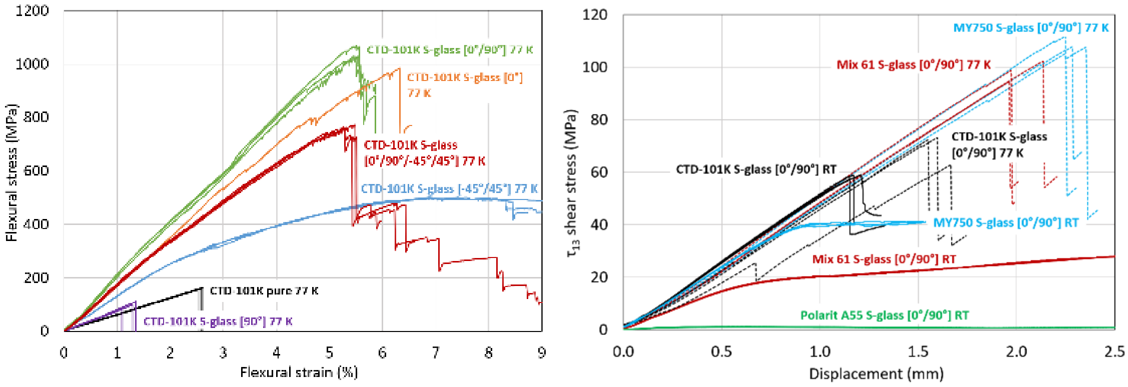

Figure 2. (a) Flexural stress vs strain of S2-glass reinforced CTD101K specimens with fibre orientations [0°/90°], [90°], [0°], [0°/90°/±45°], [±45°], and pure CTD101K at 77K. (b) Shear stress over displacement at RT and at 77K of V_f =33% [0°/90°] S2-glass fibre reinforced CTD101K, Mix61, MY750 and Polarit A55 wax.

Figure 2 (b) compares the through thickness shear stress in the CTD101K, MY750, Mix61 epoxy and Polarit A55 wax matrix as a function of displacement in the centre of the short beam sample at RT and at 77K. At RT the highest fracture force is achieved with the S2-glass fibre-reinforced epoxy CTD101K. At RT the S2-glass reinforced MY750 and Mix61 exhibit plastic behavior, where the build-up in interlaminar shear stress is insufficient to cause shear mode failures. As expected, the wax matrix cannot transmit substantial shear stresses. At 77K, all S2-glass-epoxy composites showed diagonal shear mode failures. The composite with CTD101K matrix fails at lower shear stress than the fibre-reinforced MY750 and Mix61.

3.3 Storage modulus temperature dependence of epoxy resins, wax and fibre reinforced composites

The storage modulus vs temperature evolution *G'*(T) has been determined by DMA temperature sweeps in torsion mode (Figure 3). The glass transition of the epoxy systems is manifested by a strong G' reduction of about two orders of magnitude when the glass transition temperature (T_g) is exceeded. At T<< T_g the shear modulus (G) can be estimated from G'.

The V_f=33.3% [±45°] epoxy composite has the highest G', followed by the V_f= 33.3% [0°/90°/±45°] composite. The V_f =16.6% [90°] composite has the lowest G', only slightly exceeding G' of the pure epoxy, indicating that the [90°] fibres have only a small influence on G'. This shows that the torsional shear properties change from matrix dominated properties towards fibre dominated as more ±45° fibers are added, as would be expected from composite laminate theory. G' of the pure paraffin wax is about 0.5 GPa, and only slightly influenced by temperature, and even with ±45° fibers G' remians below that of pure epoxy resin.

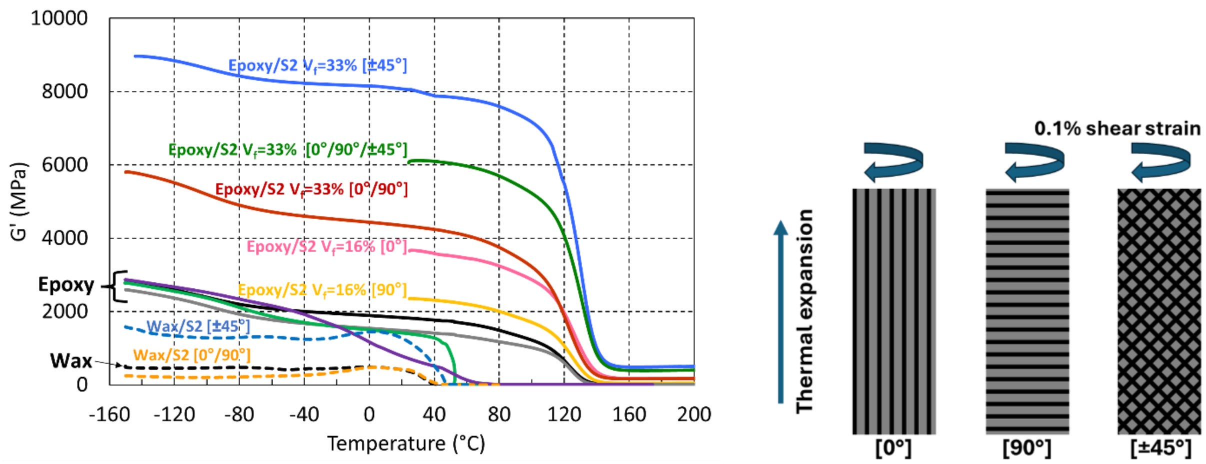

Figure 3. (a) G'(T) of pure epoxy resins and paraffin wax and of V_f=16% and V_f=33% S2-glass fibre reinforced CTD101K and wax with different fibre orientations. (b) Definition of fibre orientations.

3.4 Thermal expansion

In Figure 4 (a) the integrated length change of the pureepoxy resins, paraffin wax and the epoxy and wax composites determined by DMA is plotted with respect to the reference temperature of 25 °C. Below their T_g, the thermal expansion behaviour of the isotropic unfiled epoxy systems is similar. Pure parafin wax has the highest thermal expansion of the materials studied here.

The integrated thermal expansion of CTD101K and MY750 in the temperature range 4.2 K to RT determined previously [8] with a laser dilatometer has been described by a five-degree polynomial fit $(L - L293)/L293= a+b\times T+c\times T^2+d\times T^3+e\times T^4+f\times T^5)$, with the CTD101K coefficients a=-12.10, b=4.27E-03, c=1.90E-04, d=-2.90E-07, e=3.69E-10 and f=-4.27E-13.

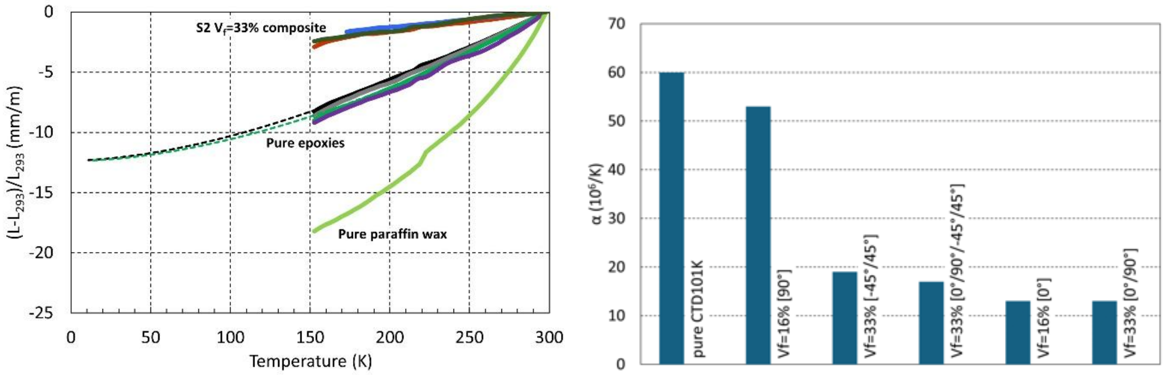

Figure 4. (a) Integrated thermal expansion of pure epoxy resins, wax and composites. (b) Thermal expansion coefficient at 25 °C of pure CTD101K and S2 glass-CTD101K composites with different fibre orientations.

Figure 4(b) compares the linear thermal expansion coefficients (α) of epoxy resin composites with different fibre orientation and the pure epoxy matrix. The smallest thermal expansion of the composite is in the fiber dominated [0°] direction. The [90°] fibres have only a small effect, and in this direction (perpendicular to the fibre meshes) the composite thermal expansion is similar to that of the pure matrix material.

4. Discussion and conclusion

Parameters for the thermomechanical modelling of a typical isotropic pure epoxy resin and paraffin wax and for anisotropic fibre reinforced composites, and their stress limits that have been determined in this study are summarised in Table 1.

Table 1. Young's modulus (E), shear modulus (G), ultimate tensile strength (σ_m), linear thermal expansion coefficient (α) (average in the range 25 °C to 40 °C) and integrated thermal expansion ($\Delta L/L$) in the temperature range 10K-293K, of typical pure epoxy resins with T_g>>RT, of paraffin wax and of epoxy and wax S2 glass composites.

Material	*E* (GPa)		*G* (GPa)		σ_m (MPa)		α (10^{-6} K^{-1})	$\Delta L/L$ (mm/m)
	RT	77K	RT	120K	RT	77K	RT	10-293K
Epoxy resin	3.7	6.0	1.5	2.5	45	90[a]	58	-12 [8]
Epoxy/S2 V_f=16% [90°]	4.8	7.7	2.4	n.m.	40	80[a]	53	-10
Epoxy/S2 V_f=33% [±45°]	9.2	12	7.6	8.8	80	160[a]	19	-4
Epoxy/S2 V_f=33% [0°/90°]	20	23	4.3	5.8	250	500[a]	13	-5
Paraffin wax	0.5	n.m.	0.4	0.5	1	n.m.	300	-30
Paraffin/S2 V_f=33% [0°/90°]	5	n.m.	0.2	0.4	10	n.m.	26	-5

[a] Assuming $\sigma_{m\text{-}77K}=2\times\sigma_{m\text{-}RT}$ (corresponds with the ratio $\sigma_{fm\text{-}77K}=2\times\sigma_{fm\text{-}RT}$ determined by flexural tests)

At RT (below T_g) most pure epoxy resin systems exhibit linear elastic behaviour until fracture, with a Young's modulus between 3 to 4 GPa, and an approximate thermal expansion coefficient of α=60×10⁻⁶ K⁻¹ [12]. Tensile strength is typically in the range 40 to 60 MPa. At 77 K epoxy resins have a Young's modulus of about 6 GPa, and their tensile strength can exceed 100 MPa.

Epoxy resins reinforced with a combination of 0°, 90° and ±45° fibres can provide very high mechanical strength and toughness. The composite mechanical properties are strongly anisotropic, and mainly determined by the fibre properties, volume fraction and orientation with respect to the loading direction. The fibres in 90° direction (perpendicular to loading direction) can reduce the mechanical strength below that of the pure epoxy resin. At cryogenic temperature the mechanical strength of the composites is further increased (the flexural strength is roughly doubled when cooling from RT to 77K).

The through thickness shear properties of composites are heavily influenced by the matrix material. At 77 K the epoxy shear strengths determined for three different epoxy resins are in the range 70-100 MPa. The shear strength of paraffin wax is in the order of 1 MPa.

Since the thermal expansion of the glass fibres ($\alpha_{S2\text{-glass}}=2\times10^{-6}$ K^{-1}, $E_{S2\text{-glass}}$=90 GPa) is much smaller than that of the epoxy matrix, residual stresses in the order of 100 MPa can build up in the composite during cooling from the epoxy curing temperature to the magnet operation temperature. The residual stresses in the composite might facilitate epoxy resin cracking and influence the occurence of training quenches during powering of superconducting magnets [13]. The stress-relaxation behaviour of the different composites may reduce residual stresses, depending on the matrix material.

An approach to reduce superconducting magnet training quenches is the impregnation with wax [14], which fracture toughness is minimal, and therefore cannot release much energy when it is cracking. Additionally, wax may act as a lubricant between coil constituents, reducing energy release from friction and stick-slip effects. The Young's modulus and tensile strength at RT of paraffin wax are typically in the order of 1 GPa, and 1 MPa, respectively [15]. As a result, unlike in epoxy matrix composites, in wax composites residual stresses are marginal because the matrix cannot transmit substantial loads.

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