Interlaminar fracture toughness of low curing temperature vinylester composites exposed to severe service conditions

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Abstract

The effects of high temperature environmental exposition and of soft curing treatment on the interlaminar shear strength for vinylester glass fibre multilayer composites have been studied. The degradation effects on the matrix and fibre-matrix interface are due to scissions of polymer chains, the oxidation process, the weakening of fibre-matrix bonding. Possibility of stabilization of Glassfiber - Vinylester-Bisphenol-A composite for prolonged high temperature service by low temperature curing is established

Keywords: Vinylester, GFRP, fracture, SERR, G_{IIC}, delamination, shear, ageing, toughness, curing

1. Introduction

The vinylester-bisphenol-A (VEBA) poses high chemical and thermal stability, strength and toughness, and is competitive because of lower cost [1]. Glass fibre VEBA composites (VEBA-GFRP) are increasingly used due to their advantages over metals in corrosive environments and at high temperature but the investigation needs to be continued in order to determine the real limits of their possibilities. The alterations in curing conditions are harmful for the mechanical properties of VEBA composites [2]. This is particularly important for in situ manufacturing and repair tasks when the high Curing Temperature (Tc) or the post-curing treatments are impossible. On the other

hand GFRP show weakness out of the sheet plane owing to an anisotropic constitution. Interlaminar delamination is the main drawback because the gradients and stress concentration in composites leads material to catastrophic failure.

This work evaluates the Strain Energy Release Rate in Mode II (G_{IIC}) and shear strength of VEBA-GFRP, exposed to interlaminar shear stresses and elevated temperature, in correlation with low values of Tc.

2. Experimental

The GFRP are fabricated using VEBA resin Basf A430™, adding 2.5% v/v of PMEK resin catalyst and 0.5% v/v of cobalt octoato. The composite is made by alternately placing E-glass fibre plane fabrics oriented at 0-90º and ±45º up to complete 8 layers. The fibre ply density is 440 g/m^2. The pre-crack of the end-notched flexural (ENF) fracture samples for G_{IIC} is an insert of 40 μm thick Teflon®. The samples were cured at Tc 20ºC and 50ºC (both for 48 hours) and then aged at 95 ºC during 0, 1200, 2200, and 5300 hours. G_{IIC}, flexural and interlaminar shear strength (ILSS) were obtained from specific three-point bending tests. The G_{IIC} was calculated applying equation (1) on ENF-test data in accordance with modified beam theory [3-5]:

$$G_{IIC} = C_F \frac{9P^2a^2}{16E_O w^2 h^3} \qquad (1)$$

where P is the maximum load, a the precrack length (25 mm), w the width, and h is the half-thickness. E_O is the elastic modulus when a = 0, no crack. C_F is a factor to correct non-lineal effects in G_{IIC} [5], here it ranges between 0.94 and 0.98. Five coupons per condition were used for all mechanical tests.

Two cycles of modulated differential scanning calorimetry (MDSC) with heating up to 200ºC in N_2 followed by cooling up to 0ºC, enabled the precise determination of the glass transition temperature T_G [3,6]. The weight loss and the thermal stability of the

resin were determined by the thermo-gravimetric analysis (TGA) from room temperature up to 650ºC in N_2.

Fracture surfaces were analysed using scanning electronic microscopy.

3. Results and discussions

According to the Table, the change of Tc from 20ºC to 50ºC makes the properties grows by up to 13% (E), 9% (R), 17% (τ) and 13% (G_{IIC}). ILSS τ is the most influenced. The improvement of these properties is attributed to the increase in cross-linking density [7,8].

R, E, and τ decrease strongly with exposure time at 95ºC (Table) fluctuating between 16% and 19%. ILSS τ falls between 38% and 48% for Tc=50ºC and this reduction increases up to 56% for Tc=20ºC. This behaviour prompted the study about G_{IIC} changes.

Table - Characteristics of composites exposed at 95°C

T_C (°C)	Time at 95ºC (h)	E (GPa) ±5%	R (MPa) ±5%	τ (MPa) ±23%	G_{IIC} (kJ/m^2) ±9%	T_G (ºC)	Volatile % weight	Volatile T (ºC)	Polymer decompos. T (ºC)
20	0	12.6	350	18	3.1	118	2.4	114	388
	1200	10.6	301	9	2.7				
	2200	10.4	292	8	2.2				
	5300	10.8	305	9	2.4				
50	0	14.2	381	21	3.5	126	1.4	130	385
	1200	12.7	346	13	3.1				
	2200	11.5	321	11	2.9				
	5300	11.9	330	12	2.9	127	0.7	130	385

Tc – curing temperature; E - flexural Modulus of elasticity; R - flexural strength; τ – interlaminar shear strength; G_{IIC} - strain energy release rate in Mode II; T_G – glass transition temperature.

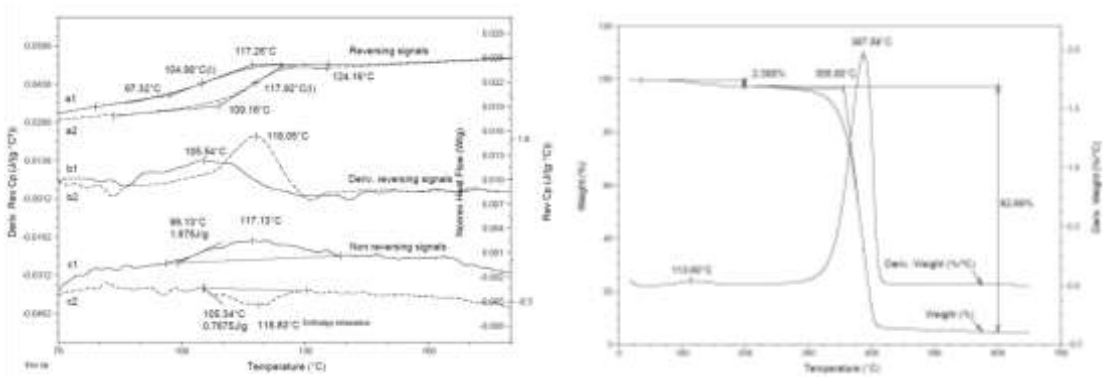
As occurs with static properties, G_{IIC} is very sensitive to high temperatures (Table) and decreases exponentially with ageing time. Tc of 50ºC stabilise G_{IIC} at around 2.9

kJ/m^2 at 2200 h, while 20ºC does not. The differences between the two cured composites reach 45% after 5300 h of exposition.

3.1. Looking for reasons

The data of the Table means that the higher Tc not only influences the resistance to crack propagation due to increase of the polymerisation degree [9] but also reinforce the surface fibre–matrix adhesion. The degradation of properties at 95ºC can be attributed to a weakening of the interaction between matrix and fibre [7]. The surface of E-fibres may catalyse and amplify the degradation reaction of the VEBA matrix [8]. Chain scissions are the first step of degradation in general purpose unsaturated polyester when it is exposed to a high temperature [10]. This will be accelerated by auto-oxidative reactions leading to the formation of oxidised fragments and cross-link breaks [11].

3.1.1. MDSC and TGA tests



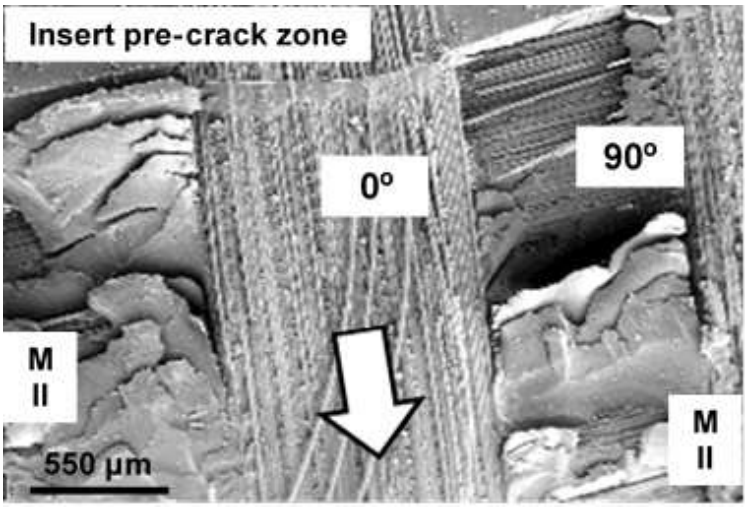
a **b**

Fig. 1. MDSC (a) and TGA (b) for non-degraded sample cured at 20ºC

MDSC and TGA presented in Fig.1 and in Table show that non-degraded coupons have T_G around 105ºC (cured 20ºC) and 122ºC (cured 50ºC). In the second heat scanning, T_G rises up to 118ºC (T_C 20ºC) and 126ºC (T_C 50ºC). The remaining curing enthalpy (ΔH) indicates that lower curing coupons have the post-curing capacity three times higher. MDSC for 5300 h ageing (T_C 50ºC) show the higher values for T_G. Null curing enthalpy was observed and the curing capacity is exhausted. The higher T_G after

5300 h can be justified by an additional post-curing process in such conditions. Light fractions that volatilise at lower temperatures and the curing enthalpy are related to an incomplete curing process during manufacturing. The exposition to high temperature for 5300 h reduce this volatile fraction because a post-curing could take place [12].

3.1.2. Fractography



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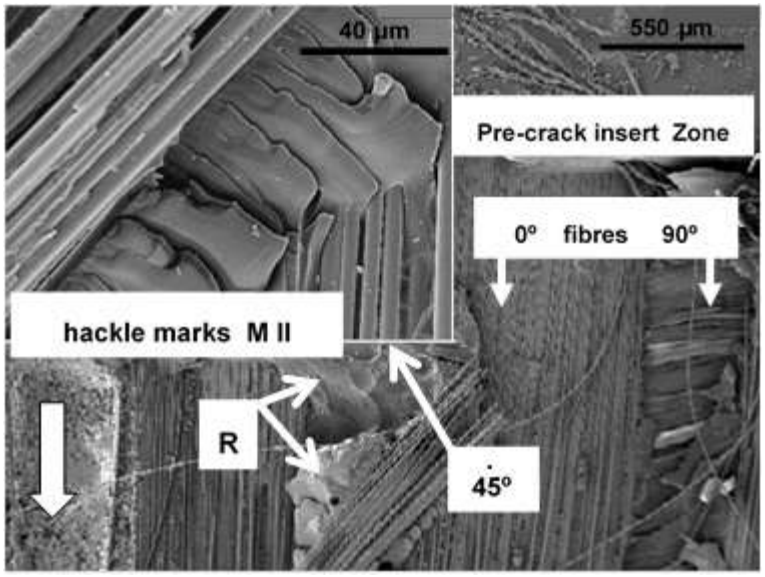
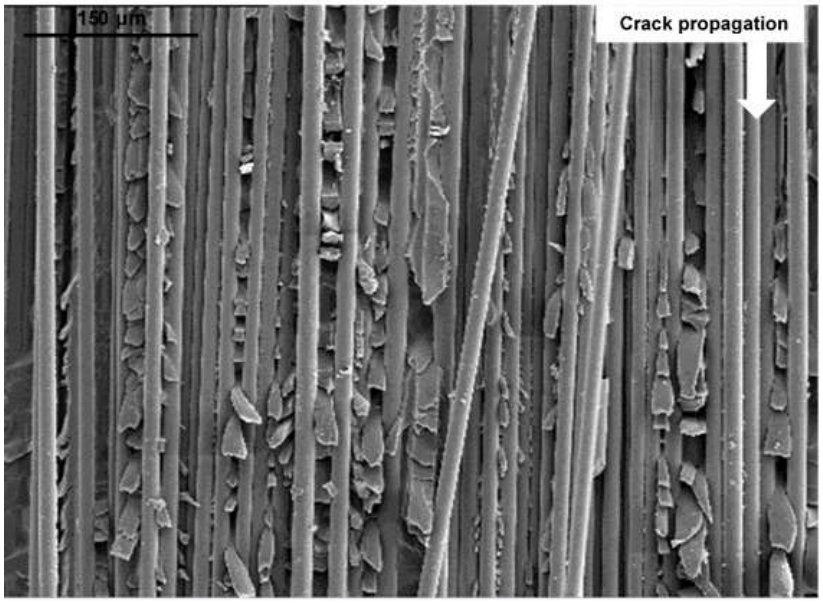


b

Fig.2. Non-aged sample cured at: a) 20°C; b) 50ºC. Fibres at 0º, 90º and 45º. M II - large hackle formations. R - resin rich zone. Arrow - crack propagation direction.

The fracture of the non-aged sample cured at 20ºC (Fig. 2a) is clearly defined by the apparition of larger hackle formations (M II) in the resin rich area that follow the crack propagation direction (arrow). The hackles are wide, near, and large – the evidence of a non-degraded polymer. Fracture of the samples cured at 20ºC occurs among 0-90º fibre layers (arrows). The relative weakness of the resin around the 90º fibres prompts the



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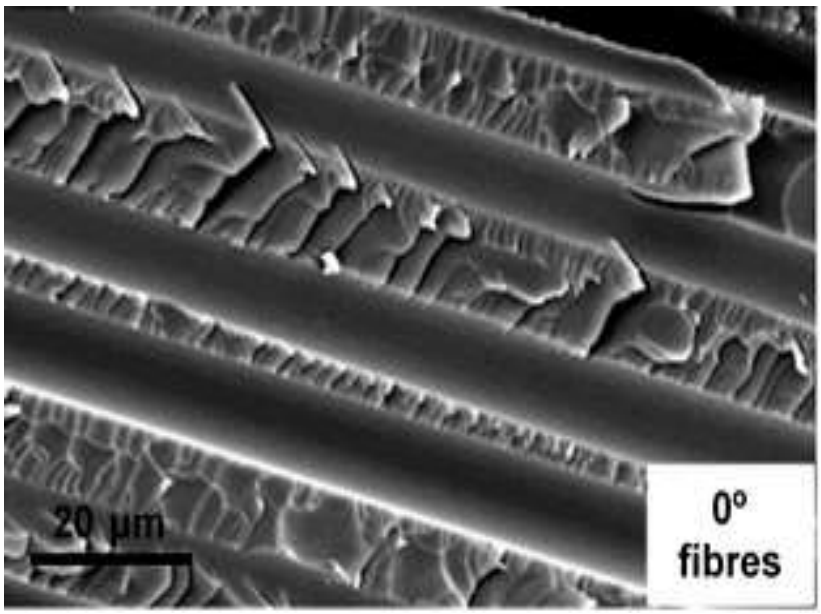

b

Fig.3. Samples cured at 95ºC: a) Tc 20°C, 1200 h exposition; b) Tc 50°C, 5300 hours exposition.

cracks to expand while 0º fibres delay the propagation. At 50ºC (Fig.2,b) there are hackles roughly closed and good adhered to the fibres. The capacity of the resin to stick to the reinforcement further supports toughness [13-15]

The aged sample, Fig.3a, shows an increase in resin embrittlement: a hackle packet reduction, sharp and smooth facets of hackle morphology.

Fracture surface from long-term aged coupons cured at 50ºC are shown in Fig.3b. A higher density of raised but no sharp faceted hackles is noticeable due to partial retaining original toughness and fibre adhesion. Higher Tc improve the fracture toughness for even longer expositions. Above all, residual styrene and non-reacted vinyl groups suffer and contribute to thermal oxidation [2,15-1]. Glass-VEBA interface adherence is also impaired and composite turns brittle.

4. Conclusions

Stabilization of GFRP-VEBA for prolonged high temperature service by low temperature curing is possible.

Long-term exposition at high temperatures (95 ºC) for E-glass VEBA composites causes decrease in τ and in G_{IIC}.

Higher Tc improves initial mechanical properties because of increased chain cross-linking and the fibre-matrix adhesion. Ageing effects are stronger if Tc is lower. Both T_G and curing enthalpies confirm that cross-linking, molecular resin decomposition, and losses in fibre-matrix adherence are responsible for decreases in mechanical properties.

G_{IIC} and τ are sensitive and suitable for ageing degree evaluation

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References

[1] M. Sultania, S.B. Yadaw, J.S.P. Rai, D. Srivastava, Laminates based on vinyl ester resin and glass fabric: a study on the thermal, mechanical and morphological characteristics, Mater. Sci. Eng. 527 (2010) 4560–4570. DOI: 10.1016/j.msea.2010.04.038

[2] A. Valea, I. Martinez, M.L. Gonzalez, A. Eceiza, I. Mondragón, Influence of cure schedule and solvent exposure on the dynamic mechanical behaviour of a vinyl ester resin containing glass fibers, J. Appl. Polym. Sci. 70 (1998) 2595-2602. DOI: 10.1002/(SICI)1097-4628(19981226)70:13<2595::AID-APP5>3.0.CO;2-W

[3] M. Hojo, T. Ando, M. Tanaka, T. Adachi, S. Ochiai, Y. Endo, Modes I and II interlaminar fracture toughness and fatigue delamination of CF/epoxy laminates with self-same epoxy interleaf, Int. J. Fatigue. 28 (2006) 1154–1165. DOI: 10.1016/j.ijfatigue.2006.02.004

[4] D. Stevanovic, S. Kayanasundaram, A. Lowe, P.Y.B. Jar, Mode I and Mode II delamination properties of glass/vinyl-ester composite toughened by particulate modified interlayers, Compos. Sci. Technol. 4 (2003) 1949-1964. DOI: 10.1016/S0266-3538(03)00162-3

[5] M. Salviato, K. Kirane, Z.P. Baant, G. Cusatis, Mode i and II Interlaminar Fracture in Laminated Composites: A Size Effect Study, J. Appl. Mech. Trans. ASME. 86 (2019). https://doi.org/10.1115/1.4043889.

[6] B. Wunderlich, Glass transition as a key to identifying solid phases, J. Appl. Polym. Sci. 105 (2007) 49-59. DOI: 10.1002/app.26110

[7] Siddaramaiah, S. V. Suresh, V. B. Atul, D. Srinivas, S. Girish, Effect of aggressive environments on composite properties, J. Appl. Polym. Sci. 73 (1999) 795-799.
DOI: 10.1002/(SICI)1097-4628(19990801)73:5<795::AID-APP19>3.0.CO;2-5

[8] D. Ray, S. Banerjee, A.K. Mohanty, M. Misra, Thermal and electrical behaviour of vinylester resin matrix composites filled with fly Ash particles, Polym. Comp. 29 (2008) 58-62. DOI: 10.1002/pc.20354

[9] K.S. Jagadeesh, Siddaramaiah, Fibre reinforced composites of multifunctional epoxy resins, Polym. Int. 33 (1994) 367-372 DOI: 10.1002/pi.1994.210330404

[10] J.D. Badia, E. Strömberg, S. Karlsson, A. Ribes-Greus, The role of crystalline, mobile amorphous and rigid amorphous fractions in the performance of recycled poly ethylene terephthalate PET, Polym. Degrad. Stabil. 97 (2012) 98-107
DOI: 10.1016/j.polymdegradstab.2011.10.008

[11] K. Laoubi, Z. Hamadi, A. Ahmed Benyahia, A. Serier, Z. Azari, Thermal behavior of E-glass fiber-reinforced unsaturated polyester composites, Compos. Part B Eng. 56 (2014) 520–526. DOI: 10.1016/j.compositesb.2013.08.085

[12] S. Marouani, L. Curtil, P. Hamelin, Ageing of carbon/epoxy and carbon/vinylester composites used in the reinforcement and/or the repair of civil engineering structures, Composite 43 (2012) 2020-2030.
DOI: 10.1016/j.compositesb.2012.01.001

[13] M. Charambides, A.J. Kinloch, Y. Wang, J.G. Williams, On the analysis of mixed mode, Int. J. Fract. 54 (1992) 269-291. DOI: 10.1007/BF00035361

[14] A. Laksimi, Mode I interlaminar fracture of symmetrical cross-ply composites, Compos. Sci. Technol. 41 (1991) 147-164. DOI: 10.1016/0266-3538(91)90025-K

[15] R. Shrivastava, K.K. Singh, Interlaminar Fracture Toughness Characterization of Laminated Composites: A Review, Polym. Rev. 60 (2020). DOI: 10.1080/15583724.2019.1677708

[16] S. Khare, R.K. Sah, Cure kinetic analysis of unsaturated polyester resin, BTRA Scan. 43 (2013). ISSN: 09728341

[17] P.M. Jacobs, F.R. Jones, The influence of heterogeneous crosslink density on the thermomechanical and hygrothermal properties of an unsaturated polyester resin: 1. Thermomechanical response, Polymer 33 (1992)1418. DOI: 10.1016/0032-3861(92)90116-E

[18] J.S. Yang, J.Y. Xiao, J.C. Zeng, C.Y. Peng, Study on rheological behavior of unsaturated polyester resin system, Cailiao Gongcheng/Journal Mater. Eng. (2009). ISSN: 10014381