Effect of Different Thermal Histories on the Thermo-Mechanical Properties of a Toughened Composite Carbon Fiber-Epoxy Laminate

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Abstract

The effect of postcure treatments on the dynamic mechanical properties of HTA/6376 carbon fiber / epoxy unidirectional laminates was investigated. Postcure at different temperatures for two hours indicate that the residual epoxy groups conversion is practically complete above 190°C. In these treatments E' remains practically constant while T_g increases in correspondence with the residual epoxy groups disappearance. Moreover toughness measurements show an enbrittlement of the postcured laminates. At 175°C the epoxy groups conversion is not complete after six hours treatment. Cyclic postcure is more efficient in modifying the laminates than a single treatment in the same conditions.

Introduction

Carbon fiber - epoxy resin composites provide a high performance material that, after curing in suitable conditions, can be transformed in laminates for structural applications having excellent thermo-mechanical properties, high fatigue and moisture resistance[1-5].

In particular these systems, toughened by introducing a thermoplastic additive, such as polyethersulphone, obtain wide applications in the production of helicopter components. The adopted technology involves the curing of prepregs in standard conditions, at high pressure and temperature, in order to obtain the set of properties required for the helicopter applications.

It is well known that the curing cycles do not assure usually the complete polymerization of all the epoxy groups present in the polymer matrix; therefore residual unreacted groups still remain in the cured material, reaching a value which can be up to 15% of the total groups present[6].

Subsequent material processing operations (such as bonding and assembling) can involve high temperature treatments and induce further reactions of the residual epoxy groups changing the structure and the properties of the final materials[7].

This work aims to evaluate the influence of the different thermal treatments on the thermo-mechanical properties of the composite material. Dynamic mechanical thermal (DMTA) analysis was the main tool used for characterizing the change in the structure and in the properties of the final material. The importance of this technique and its usefulness in composites characterization was previously established[8-11]. The results obtained give indications on the modifications occurring in the material during

postcure treatments: in this way it is possible to simulate what happens in the material during structure assembly operations.

Experimental

Materials:

Unidirectional laminates obtained from Fibredux 6376 toughened carbon fibers/epoxy prepregs (Ciba Geigy products with HTA fiber from Toho) were used. The laminates were cured by means of a standard Agusta Costruzioni Aeronautiche procedure (2 hrs at 175°C at 0.3 MPa pressure). The resin mass content was 0.35. The laminate thickness was 0.9 mm.

Thermal treatments:

The laminates obtained from Agusta were conditioned at 100°C for 24 hrs and stored under dry conditions in a desiccator.
The samples were put in a oven at different temperatures in the range 175-200°C for different times, then stored in a desiccator at room temperature for at least 1 day before performing the thermomechanical characterization. The cyclic heating - cooling treatments were carried out by repeating the previous treatments after a period of at least 4 hrs.

Analyses:

DSC analyses were performed by a Mettler TA 3000 Instr. in the 30-300°C range. The T_g values were obtained by considering the midpoint of the glass transition interval.
DMTA analyses were carried out at 1 Hz frequency and 0.012% strain by using a Polymer Laboratories MK II Instr. at a heating rate usually of 10°C/min. The analyses were performed using a three-point bending device; the dimensions of specimens were 14 x 3 x 0.9 mm. The storage modulus, E', the loss modulus E" and the loss factor, tan δ, were measured from 30 up to 260°C, temperature at which polymer matrix was always in the rubbery state. The T_g value was measured at the maximum of the loss factor curve.
Impact measurements were obtained by Charpy Pendulum Instr., ATS-FAR (25 J impact energy) on unnotched samples having the following dimensions: 6 x 2.5 x 0.9 mm.

Results and discussions

Characterization of the starting laminate

In Fig. 1 a typical DSC thermogram related to the starting laminate is reported. An exothermal peak is evident in the 220-280°C range and a ΔH value of 31.9 J/g is obtained. It corresponds to a concentration of unreacted epoxy groups equal to 6.2% taking into account the ΔH value obtained by working on the prepreg (515 J/g).
By repeating the DSC analysis on the sample after the complete epoxy groups conversion, the thermogram of Fig. 2 is obtained in which a T_g value (midpoint) of 217°C can be observed.

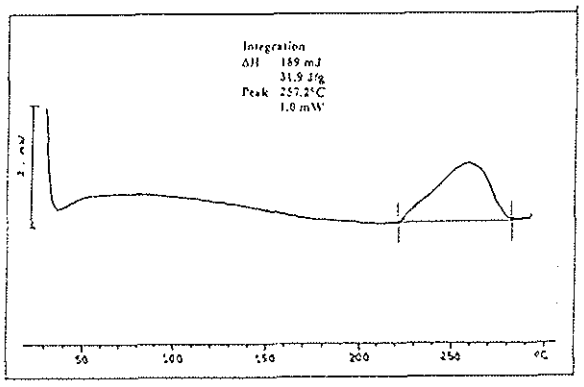

Fig. 1: DSC thermogram of the starting laminate

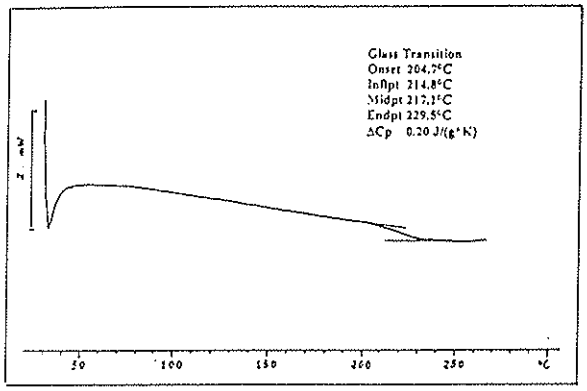

Fig. 2: DSC thermogram repeated on the same starting laminate

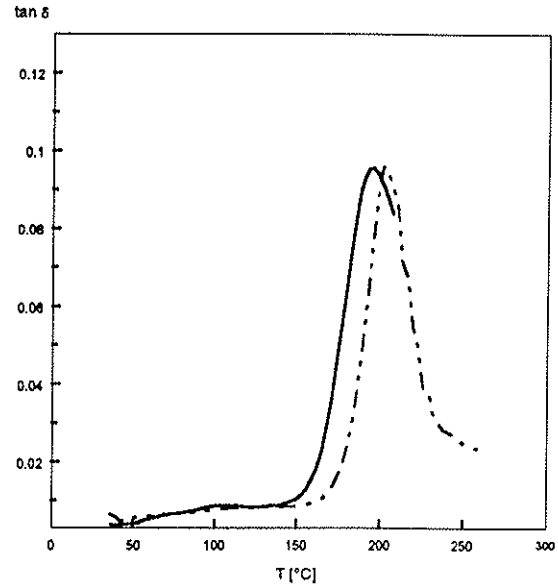

Fig. 4: Tan δ vs T on the starting laminate (——). Analysis repeated on the same laminate (-·-·-·-)

Dynamic mechanical analysis (DMTA) is a powerful technique for evaluating the elastic and viscous component of the modulus of the composite material in a very large temperature interval. Therefore it allows to obtain a better characterization of the thermal and mechanical properties of the material[8-10]. In Fig. 3 the DMTA spectrum of the starting laminate (heating rate = 8°C/min) is reported: a T_g value of 194°C is evident corresponding to the maximum of tan δ curve.

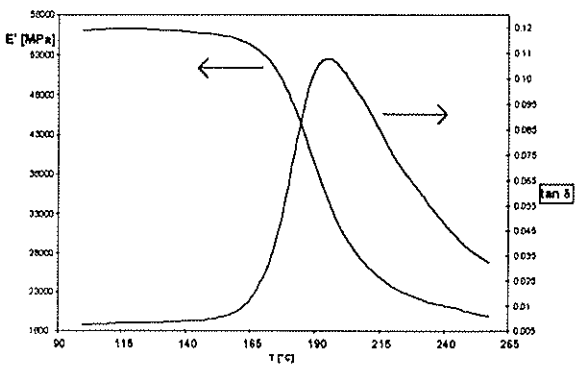

Fig. 3: Typical DMTA spectrum of a toughened composite carbon fiber epoxy laminate

By repeating the DMTA analysis on the same sample heated at a temperature just above the T_g value, we observed a modification of the spectrum with an increase of the T_g value (Fig. 4). This effect can be attributed to a partial curing of the material during the thermal treatment. In Fig. 5 and 6 the same effect is observed considering the E' and E" curves.

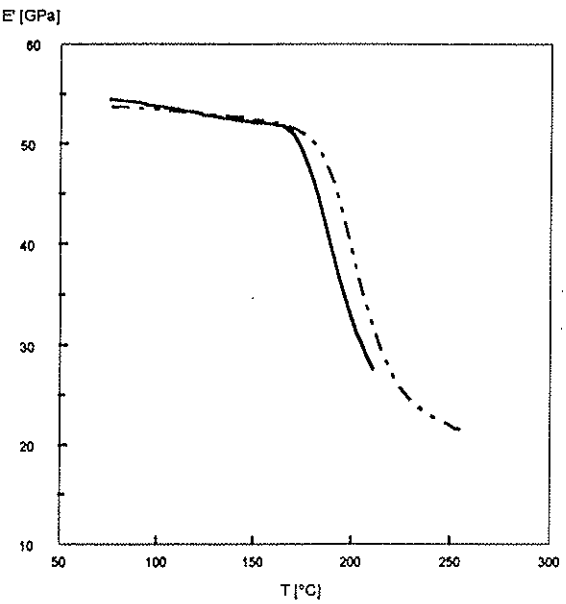

Fig. 5: E' vs T on the starting laminate (——). Analysis repeated on the same laminate (-·-·-·-)

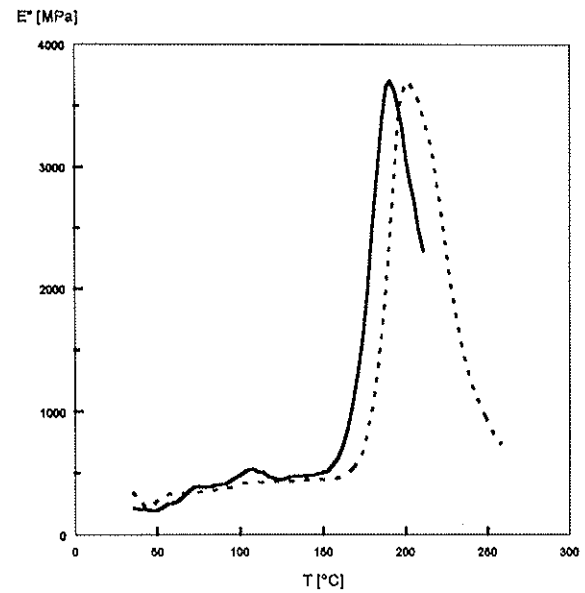

Fig. 6: E" vs T on the starting laminate (——). Analysis repeated on the same laminate (------)

The T_g increment depended on the heating rate imposed to the DMTA analysis, as reported in Table 1.

Table 1: Influence of the heating rate on the T_g value of the laminate determined by DMTA analysis.

Heating Rate [°C/min]	T_g (1) [°C]	T_g (2) [°C]	ΔT_g [°C]
4	198	218	20
8	194	210	16
10	196	208	12
16	195	205	10

(1) T_g value obtained in the first DMTA spectrum

(2) T_g value obtained in the repeated DMTA spectrum

It is evident from the data of Table 1 that, by increasing the heating rate, the ΔT_g value decreases indicating a lower extent of thermal curing during the DMTA analysis. Considering that, by working at higher heating rates, less accurate results are obtained, we chose a medium heating rate (10°C/min). By adopting these conditions, we characterized the laminates by DMTA analysis after the different thermal treatments.

Thermal treatments of the laminates

a - Influence of temperature

The laminates were put in a oven at different temperatures ranging from 175 to 200°C, for a constant time, then the change in the thermal and mechanical properties was measured. DSC analysis allowed to determine the residual heat of polymerization: the obtained values are reported in Table 2 and plotted in Fig. 7 as % of residual epoxy groups. The data indicate that in the adopted conditions, the conversion of the epoxy groups is practically complete above 190°C.

Table 2: Residual epoxy groups in the laminates treated at different temperatures[1)]

T [°C]	Residual epoxy groups [%]
—[2)]	6.2
175	4.1
180	3.3
185	1.9
190	0.4
195	0.1
200	0

1 - Time = 2 hrs

2 - Untreated sample

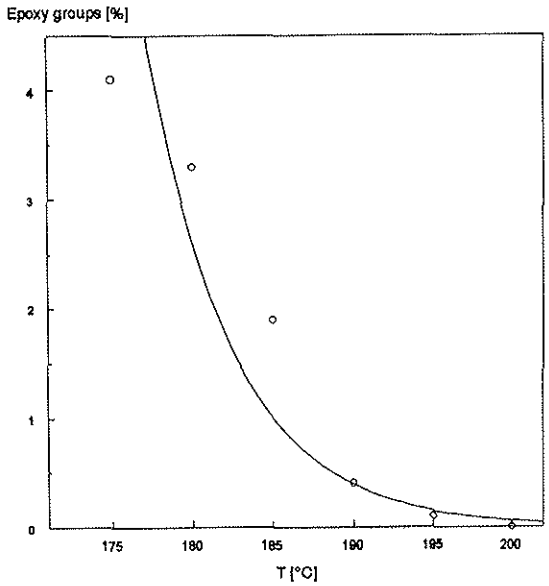

Fig. 7: Residual epoxy groups content vs. temperature (data of Table 2)

DMTA analysis allowed to obtain the values of E' and T_g after the different treatments. The results are reported in Table 3 together with the toughness measurements:

Table 3: E', Tg and toughness of the laminates treated at different temperatures [1)]

Temperature [°C]	E' [2)] [GPa]	T_g [°C]	Toughness [J/cm^2]
— [3)]	52.444	193.7	31.6
175	55.179	215.0	30.4
190	52.538	223.0	29.2
200	54.415	226.7	28.0

1- Time= 1 hr; the data are mean of 5 measurements
2 - Measured at 130°C
3 - Untreated sample

The results of Table 3 indicate that, after the thermal treatments, E' values remain practically constant in the range 52 - 55 Gpa. Therefore E' does not change, at least in our experimental conditions, when the conversion of the low residual fraction of the epoxy groups is completed. Otherwise the T_g values are clearly influenced by the thermal treatments ranging from 193.7 to 226.7°C. It is well known that in the thermosetting systems the T_g value increases deeply when the last reactive groups disappear, thus eliminating the last dangling ends in the network(8). The data of Table 3 indicate also that the toughness of the laminates decreases. The embrittlement of the material can be attributed to the change in the crosslinking density as revealed by the increase of the T_g value(8). This effect was reported previously on unidirectional laminates(7).
It can be noted that the final T_g value obtained by means of DMTA (226.7°C) is higher than that obtained via DSC analysis (217.1°C); this result is in agreement with previous reported data and can be attributed to a frequency effect(8,9).

b - Influence of time

The samples were maintained at 175°C (the standard temperature used in the curing cycles) for different times ranging from 1 to 6 hrs, then the change in the properties of the material was evaluated. The data are reported in Table 4 as residual epoxy groups fraction (by DSC) and T_g values (by DMTA).

Table 4: Residual epoxy groups % and T_g of the laminates as a function of time at 175°C

Time [hrs]	Residual epoxy groups [1)] [%]	T_g [1,2)] [°C]
— [3)]	6.2	193.7
1	4.5	210.2
2	4.1	215.0
4	3.2	216.2
6	2.5	217.2

1 - Mean of 5 measurements
2 - By DMTA
3 - Untreated sample

It can be concluded that at 175°C the conversion of epoxy groups is more evident for low times and does not reach, after a 6 hrs treatment, the complete epoxy groups disappearance.

c - Influence of the repeated cycles

Cyclic heating-cooling treatments were performed at 175°C for 1 hour and repeating the treatment for increasing number of cycles. The results are reported in Table 5: they indicate that the cyclic treatments are more efficient for reducing the % of residual epoxy groups than those performed in a single treatment.

Table 5: Influence of the number of cycles at 175°C on the properties of laminates

N. of cycles	Total time [hrs]	Residual epoxy groups [%]		T_g [°C]
1	1	4.5		210
2	2	2.6	4.1 [1)]	211
3	3	1.8		208
6	6	1.7	2.5 [1)]	210

1 - Residual epoxy groups % when the treatment is performed in one time

Conclusions

DSC and DMTA analyses allowed to characterize the thermo-mechanical properties of a thoughened composite fiber-epoxy laminate used for helicopter applications. It was evidenced that, during the thermal analyses, a partial modification of the material occurs involving an exothermal reaction on the residual epoxy groups present in the polymer matrix. This effect can be reduced by performing analyses at high heating rate.

The postcure reaction carried out at different temperatures for a constant time (2 hrs) causes the disappearance of the residual epoxy groups; the conversion is practically complete above 190°C. In these treatments E' remains practically constant while T_g increases. Toughness values decrease, indicating an embrittlement of the composite material.

Working at 175°C the epoxy groups conversion is not complete even after long time treatments.

The results of the cyclic heating treatments indicate that they are more efficient than a single continous treatment performed in the same conditions.

Acknowledgements

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References

1. "Composite Materials" Ed. L.J. Broutman, R.M. Krack, Acad. Press. N.Y. 1975
2. "Polymer Composites" Ed. B. Sedlacek, N.Y. 1986
3. "Carbon Fibers and their Composites" Springer Verlag, N.Y. 1985
4. "High Performance Fibre Composites" J.C. Morley, Academic Press, London 1987
5. "Fiber Reinforced - Composites" K.H.G. Ashbee, Technomic Publ. Basilea 1989
6. A. Apicella, L. Nicolais, Adv. in Polym Science, Vol 72, Springer Verlag, (1985) p. 69
7. E. R. Lang, S. A. T. Lang, W. D. Collions, S. L. Gray, J. G. Funk, SAMPE Vol.20, No. 3 (1989) p. 9
8. L. Nielsen "Mechanical Properties of Polymer and Composites", Vol 1 and 2, M. Dekker, N.Y. 1994
9. X. Gong, "The Dynamic Mechanical Behaviour of Random-in-Plane Short Fiber-reinforced Epoxy Resin Composites", Polymers for Advanced Technologies 7, 141 (1996).
10. D.I. Green, A.P. Unwin, G.R. Davis, I.M. Word, Polymer, 31, 579 (1990).
11. A. Priola, G. Gozzelino, F. Ferrero "UV-curable coatings on plastic substrate: DMTA and FTIR analysis of the interfacial layer" Int. J. Adhesion and Adhesives 11, 255 (1991)