



# Dynamic Mechanical Analysis of Hybrid Fibre/Glass Microspheres Composites

J. A. M. Ferreira\*, C. Capela<sup>†</sup> and J. D. Costa\*

\*CEMUC, Mechanical Engineering Department, University of Coimbra, Polo II da Univ. de Coimbra, Pinhal de Marrocos, 3030-788, Coimbra, Portugal

<sup>†</sup>CDRsp, Centre for Rapid and Sustainable Product Development, Polytechnic Institute of Leiria, Morro do Lena - Alto Vieiro, 2400-901 Leiria, Portugal

**ABSTRACT:** This article presents the results obtained in a current study of the viscous properties on hybrid short fibre/hollow glass microspheres composites fabricated with epoxy binder. The effect of the filler volume fraction and of the fibre reinforcement on the dynamic stiffness modulus, damping coefficient and glass transition temperature was studied. These properties were determined using dynamic mechanical analysis (DMA) in three points bending mode. The specimens were cut from plates produced by vacuum resin transfer moulding with microspheres weight contents up to 17%. Net resin exhibits storage modulus significantly higher than the 2% in weight of microspheres foam, while negligible effect was observed on the maximum loss modulus, maximum damping coefficient and glass transition temperature. The increase in filler volume fraction tends to decrease significantly storage and loss modulus at stable regions and the maximum damping coefficient, while glass transition temperature is only marginally affected. The addition of low contents of short fibre increases significantly storage modulus, particularly for carbon fibre, while maximum loss modulus does not exhibit a well-defined tendency. Important reduction in the maximum damping coefficient was observed by the addition of both fibre reinforcements.

**KEY WORDS:** *dynamic mechanical analysis, hollow glass microspheres, hybrid composites*

## Introduction

Low-density sheet moulding compounds incorporating hollow glass micro-spheres are being increasingly used namely in automotive industry [1], boats and deep-water submarines [2] and core materials. Compared with traditional metal, these composites exhibit advantages, such as lower weight, less expensive for low volume production, no corrosion effects, a more design freedom, etc. Syntactic foams are potential good materials for applications where impact loads occur in consequence of its ability to absorbing impact energy [3, 4].

As reported by Kim *et al.* [4] and Oldenbo *et al.* [5], the addition of hollow microspheres tends to reduce the Young modulus and ultimate strength. Even the specific values are only increased in terms of impact force and marginally in terms of flexural modulus for high volume fractions of microspheres [4]. Also, the thickness and size of microspheres can produce important changes on the mechanical behaviour [6]. Recent studies report benefits on strength and fracture toughness by using short fibre reinforced hybrid

foams. For example: Wouterson *et al.* [7] observed a concomitant strengthening and toughening on hybrid short carbon fibres/phenolic microspheres and epoxy matrix binding foams; Yi-Jen Huang *et al.* [8] obtained an important enhancement in both compression and tensile strength by small additions of chopped carbon and aramid fibres in foams fabricated with amino resin microspheres and a phenolic resin binder.

Dynamic mechanical analysis (DMA) provides viscoelastic behaviour information extremely useful for material development and quality control, particularly for polymer foams. DMA studies on polymer-based foams were carried out by Sankaran *et al.* [9] obtaining the effect of the temperature on the dynamic modulus and damping coefficient and also the glass transition temperature and maximum use temperature. The same technique was used by Wouterson *et al.* [7] to study the viscous properties also in a hybrid carbon short fibre/ phenolic microspheres with epoxy resin binder and by Chen *et al.* [10] to analyse the influence of the addition of the carbon black into the matrix leads on the damping

ratio magnetorheological elastomers. Also, Backfolk *et al.* [11] used DMA to obtain the glass transition temperatures of two styrene/butadiene latex films and compared their values with results obtained using other techniques.

This paper presents the results of a current study of the viscous behaviour characterisation of hollow glass microspheres filled composites, fabricated with epoxy binder. The influence of the addition of low contents of short fibre reinforcement was investigated by testing specimens in three points bending mode. The effects of both filler volume fraction and the short fibre reinforcement on the dynamic stiffness modulus, damping coefficient and glass transition temperature were also studied.

### Materials Processing and Testing

The filler used in the present study was the hollow glass microspheres K20 manufactured by 3M™ (St. Paul, MN, USA), nominally with 50% of particles with diameter lesser than 55 μm. The binding resin was the epoxy 520 with hardener 523 supplied by

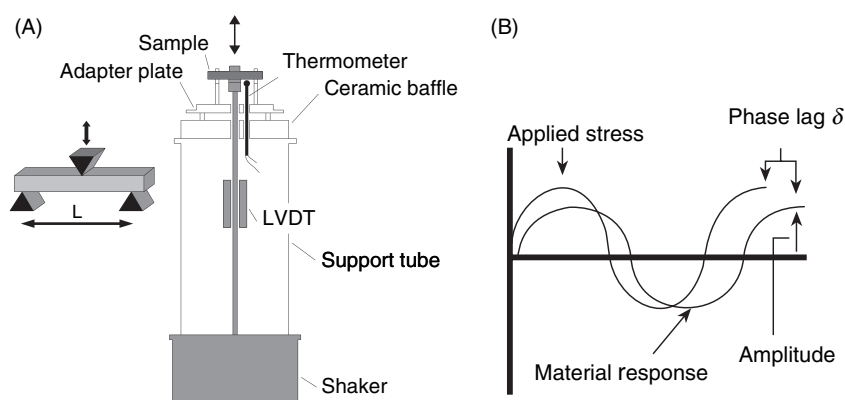
Ashland Chemical Hispania (Benicarlo, Spain). Two types of reinforcement fibres were used: a chopped strand for general purpose of glass E 3313 supplied by PPG with average length of 3 mm and a carbon fibre also with nominal 3 mm length cut from continuous thread T300 supplied from Toray. Resin and hardener were mixed in a pot and afterwards the microspheres (and fibre) were added while stirring. Composite sheets were manufactured by resin transfer moulding in vacuum by using an aluminium mould with a rectangular parallelepiped cavity of 200 × 200 × 10 mm. The mould was cleaned using acetone and treated with a release agent fluid – methylcyclopropane (MCP).

Eleven plates were manufactured with different resins and reinforcement contents. The specimens were cut and machined from the moulded plates. The corresponding mixture densities were calculated according to Archimedes principle and the contents of all formulations studied are summarised in Table 1.

Dynamic mechanical analysis method is widely used to determine relative stiffness and damping characteristics of polymeric and composite materials

Identification number	Reinforcement fibre	% weight of fibre reinforcement, $W_{fr}$	% weight of microballons, $W_{fm}$	Density ( $g/cm^3$ )
F1	-	0	0	1.170
F2	-	0	2	1.071
F3	Glass	1	2	1.074
F4	Glass	3	2	1.103
F5	-	0	6	0.915
F6	-	0	13	0.757
F7	Glass	1	13	0.790
F8	Glass	3	13	0.794
F9	-	0	17	0.690
F10	Carbon	1	13	0.792
F11	Carbon	2	13	0.796

**Table 1:** Materials composition



**Figure 1:** Schematic: (A) DMA set up; (B) Applied force oscillations and materials displacement response

[7, 9–11]. Storage modulus  $E_1$ , loss modulus  $E_2$  and damping coefficient,  $\tan \delta$ , given by the ratio between the loss modulus and the storage modulus, are recorded as a function of temperature. DMA identifies transition regions in composites, such as the glass transition temperature ( $T_g$ ) and recognises small transition regions beyond the resolution of other thermal analysis techniques.

The specimens with  $45 \times 4 \times 4$  mm are fixed between a movable and a stationary clamp fixture and then enclosed in a thermal chamber as shown schematically (Figure 1A). Frequency and load amplitude and temperature range, appropriate for the tested material are inputted. A sinusoidal oscillatory three points bending (3PB) load is applied to the specimen in programmed temperature range, which generates a sinusoidal strain. The viscous load lost in each oscillation is externally compensated every time. By measuring both the amplitude of the deformation at the peak of the sine wave and the lag between the stress and strain sine waves (Figure 1B), quantities like the storage and loss modules and the damping can be calculated. The tests were carried out using a Triton Technology TRITEC 2000 machine.

## Results and Discussion

Figures 2, 3 and 4 show DMA thermograms results. The storage modulus and loss modulus are plotted against the temperature from 20 to 100 °C. Figure 2 shows the results for unreinforced foam with different filler contents and for the net resin, while Figures 3 and 4 intend to show the effect of the fibre reinforcement type and content, for composites with microspheres content of 2% and 13% in weight respectively. In Figure 2, it is observed that both for foams and net resin, storage modulus decreases gradually with increasing of temperature until attaining the region of  $T_g$ , where a sudden reduction in values occurs, which can be associated with the softening of the matrix. The decreasing rate is slightly lower in foams than in net resin. The loss modulus increases only very slightly until reaching the maximum use temperature ( $T_{max}$ ) after which it increases sharply with temperature.  $T_{max}$  temperatures are taken as the temperature at which the storage modulus values start decreasing suddenly in the thermograms. Both storage and loss moduli were significantly affected by filler content: (i) an important decreasing was observed of both parameters on stable region; (ii) the maximum loss modulus decreases with the increase of microspheres content. Table 2 partly summarises the results depicted in

Figures 2–4 and obtained in the DMA thermograms: readings of storage modulus at 25 °C and the maximum use temperatures. Epoxy resin exhibits elastic modulus 29% higher than the 2% in weight of microspheres foam at 25 °C.

Figure 3 shows that the addition of low contents of short fibre increases slightly storage modulus of hybrid composites with 2% of filler. For the case of a content of 13% of microspheres Figure 4 shows that the addition of short fibre produces a much more

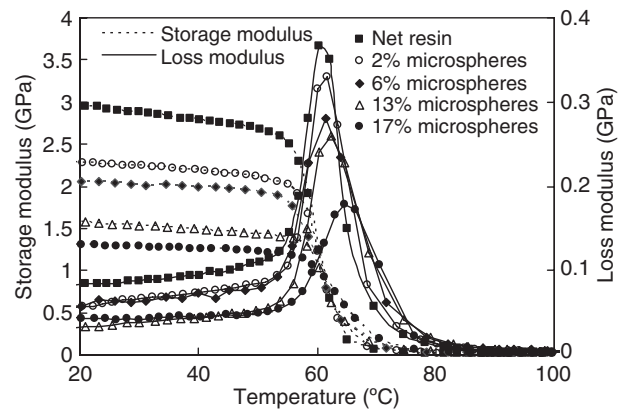


Figure 2: DMA thermograms of the unreinforced syntactic foams

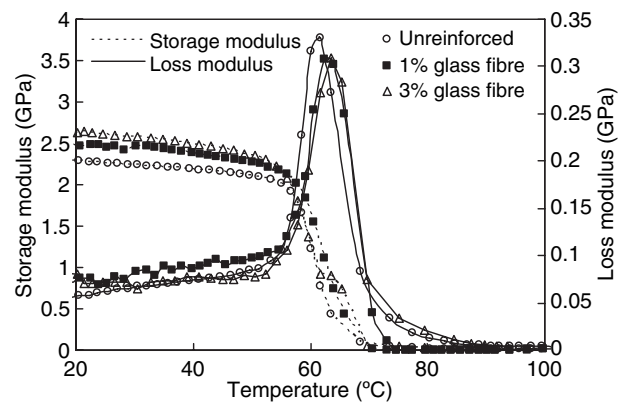


Figure 3: DMA thermograms for the hybrid composites with 2% wt of microspheres

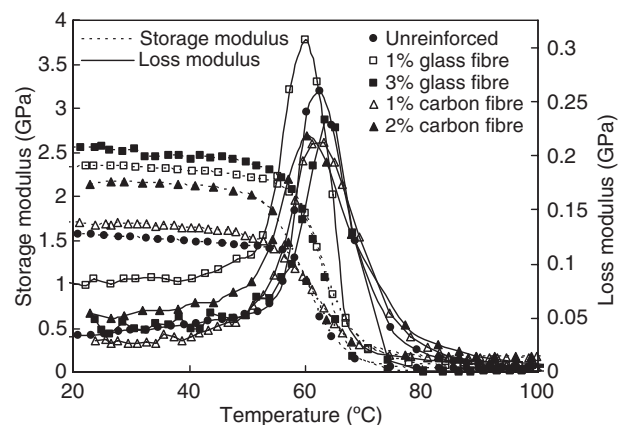
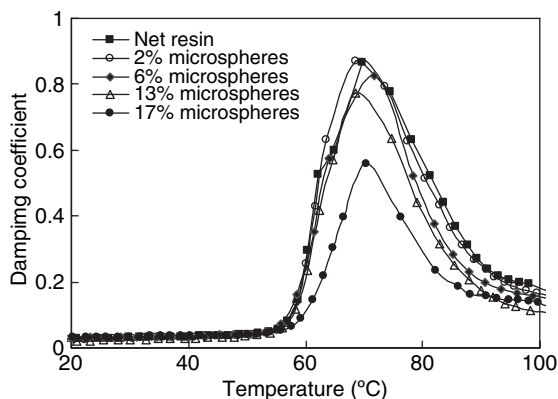


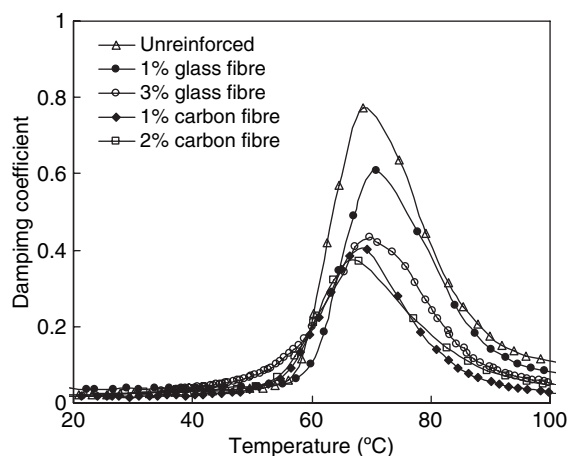
Figure 4: DMA thermograms for the hybrid composites with 13% wt of microspheres

Identification number	Storage modulus at 25 °C (GPa)	Glass transition temperature (°C)	Maximum damping coefficient	Maximum use temperature (°C)
F1	2.921	69.7	0.868	57.5
F2	2.261	68.6	0.872	58.3
F3	2.483	66.8	0.572	58.9
F4	2.617	65.4	0.686	57.9
F5	2.048	71.0	0.826	57.8
F6	1.555	68.6	0.772	59.4
F7	2.338	70.4	0.607	59.7
F8	2.567	69.7	0.432	59.1
F9	1.295	70.5	0.559	60.5
F10	1.689	69.2	0.402	57.5
F11	2.160	68.0	0.372	56.2

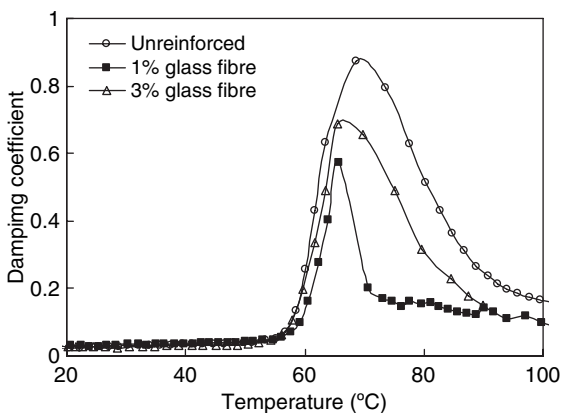
**Table 2:** Elastic modulus, glass transition temperature, maximum damping coefficient and maximum use temperature values



**Figure 5:** Damping coefficients thermograms for the unreinforced syntactic foams



**Figure 7:** Damping coefficients for the hybrid composites with 13% wt of microspheres



**Figure 6:** Damping coefficients for the hybrid composites with 2% wt of microspheres

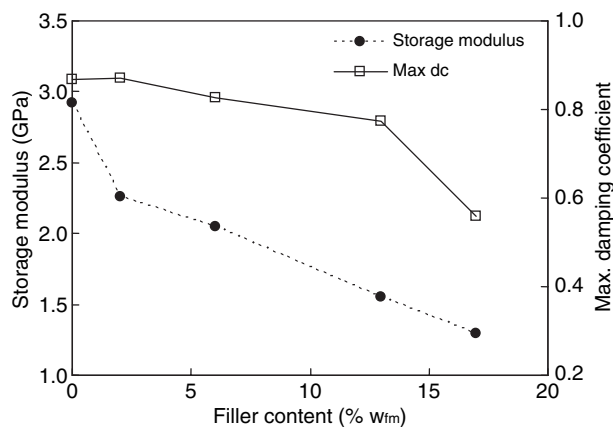
significant increase in the storage modulus. Comparing the storage modulus, obtained for a content of 1% of both glass and carbon fibres, it seems that glass fibre addition is more effective in the increase of this modulus.

Apparently, maximum loss modulus trends to decrease with the addition of the fibre reinforcement, but unfortunately the results show a high scatter in this region which advise caution regarding this conclusion. This scatter can be eventually associated

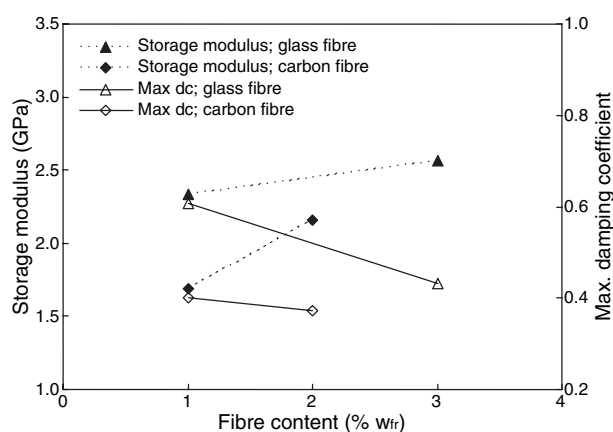
with a high sensibility of this parameter with fibre distribution homogenisation and orientation.

Figure 5 shows the variation in the damping coefficient,  $\tan \delta$ , with temperature for the net resin and unreinforced foams. The temperature at which the damping coefficient reaches its maximum value is interpreted as the glass transition temperature of the material. It was expected that  $T_g$  will be higher for the foams when compared with corresponding resin cast because of the reinforcing effect of the micro-spheres that would reduce the mobility of polymeric chains in the inter-phase region between the matrix and the microspheres [9]. Table 2 summarises also the glass transition temperature and the maximum damping coefficient.

Figures 6 and 7 show the variation in the damping coefficient,  $\tan \delta$ , with temperature for the hybrid composites with 2% wt and 13% contents of microspheres respectively. Figure 8 shows the storage modulus at 25 °C and the maximum damping coefficient (Max dc) against the filler content for unreinforced foams. According with the results obtained by the authors, for the stiffness modulus in quasi



**Figure 8:** Storage modulus and the maximum damping coefficient (Max dc) against the filler content



**Figure 9:** Storage modulus and the maximum damping coefficient (Max dc) against the fibre content

static three points bending, an important decreasing on the storage modulus with filler content was observed. Storage modulus decreases about 43% when filler content increases from 2% up to 17%. Also, an evident tendency to decrease was observed on the maximum damping coefficient values. The foams with 17% of filler exhibits maximum damping coefficient about 35% lower than 2% filled foams.

Figure 9 shows the storage modulus at 25 °C and the maximum damping coefficient against the fibre content for 13% of microspheres filled composites. Important increase on the storage modulus with fibre content was observed for both fibre reinforcements, particularly for carbon fibre, reaching about 28% when 2% reinforcement composites are compared with that of 1%. The other important reduction in the maximum damping coefficient was obtained by the addition of fibre reinforcements.

## Conclusions

Storage and loss moduli, damping coefficient and glass transition temperature, were obtained on

epoxy/glass microspheres foams and also on hybrid epoxy/glass microspheres/fibre reinforced composites, using DMA. In comparison with the 2% in weight of microspheres foam, epoxy resin exhibits 29% higher storage modulus at 25 °C, while negligible effect was observed on the maximum loss modulus, maximum damping coefficient and glass transition temperature. The increase in filler volume fraction tends to decrease storage and loss modulus at stable regions significantly. Storage and loss modulus decrease about 43% and 35% respectively for the foams with 17% of filler when compared with 2% filled foams. Glass transition temperature was only marginally affected. The addition of low contents of short fibre increases storage modulus significantly, particularly for carbon fibre, while maximum loss modulus does not exhibit a well-defined tendency. Important reduction in the maximum damping coefficient was observed by the addition of both fibre reinforcements.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge Project no. PTDC/EME-PME/66549/2006, promoted by Portuguese Foundation to science and Technology, for funding the work reported.

## REFERENCES

- Gregl, B. V. and Khamis, M. A. (1997) Glass microspheres produce lower weight SMC. *Reinf. Plast.* **1997**, 34–37.
- Malloy, R. A. and Hdsen, J. A. (1990) *International Encyclopaedia of Composites*, S. M. Lee (Ed.), VCH Publishers, p. 355.
- Kim, H. S. and Oh, H. H. (2000) Manufacturing and impact behaviour of syntactic foam. *J. Appl. Polym. Sci.* **76**, 1324–1328.
- Kim, H. S. and Khamis, M. A. (2001) Fracture and impact behaviours of hollow micro-spheres/epoxy resin composites. *Composites Part A: Appl. Sci. Manuf.* **32**, 1311–1317.
- Oldenbo, M., Fernberg, S. P. and Berglund, L. A. (2003) Mechanical behaviour of SMC composites with toughening and low density additives. *Composites Part A: Appl. Sci. Manuf.* **34**, 875–885.
- Wouterson, E. M., Boey, F. Y. C., Hu, X. and Wong, S. C. (2005) Specific properties and fracture toughness of syntactic foam: Effect of foam microstructures. *Compos. Sci. Technol.* **65**, 1840–1850.
- Wouterson, E. M., Boey, F. Y. C., Hu, X. and Wong, S. C. (2007) Effect of fiber reinforcement on the tensile, fracture and thermal properties of syntactic foam. *Polymer*. **48**, 3183–3191.
- Huang, Y.-J., Vaikhanski, L. and Nutt, S. R. (2006) 3D long fiber-reinforced syntactic foam based on hollow polymeric microspheres. *Composites Part A: Appl. Sci. Manuf.* **37**, 488–496.

9. Sankaram, S., Sekhar, K. R., Raju, G. and Kumar, M. N. J. (2006) Characterization of epoxy syntactic foams by dynamic mechanical analysis. *J. Mat. Sci.* **41**, 4041–4046.
10. Chen, L., Gong, X. L. and Li, W. H. (2008) Effect of carbon black on the mechanical performances of magnetorheological elastomers. *Polymer Testing*. **27**, 340–345.
11. Backfolk, K., Holmes, R., Ihalainen, P., Sirvio, P., Triantafillopoulos, N. and Peltonen, J. (2007) Effect of carbon black on the mechanical performances of magnetorheological elastomers. *Polymer Testing* **26**, 1031–1040.