The Influence of Glass Bead Content on the Thermal Expansion Coefficient of Epoxy Resins

Fang Wang, Applications Laboratory Shanghai, and Doreen Rapp, Applications Laboratory Selb

Introduction

Epoxy resins have been widely used in the field of building reinforcement and repair due to their excellent adhesion, mechanical properties and chemical corrosion resistance. In particular, epoxy resin is used for crack grouting and surface repair in the restoration of concrete structures, effectively restoring their integrity and durability. However, pure epoxy resin undergoes a certain degree of length change during the curing process and in heated environments. If its thermal expansion coefficient differs greatly from that of the concrete substrate, internal stress is likely to be generated at the interface during temperature changes, which will further lead to debonding or secondary cracking, and ultimately affect the repair effect and long-term stability [1].

To improve the dimensional stability of epoxy resins, inorganic fillers are often introduced into the resin matrix to reduce their thermal expansion coefficient. As a hollow, lightweight micron-sized inorganic filler, glass beads feature low thermal expansion coefficient, high specific strength and good fluidity [2]. Not only can they reduce the thermal expansion coefficient of the composite material, but also the self-weight of the repair material to a certain extent, making them both practical and economical.

The samples used in this experiment were epoxy resins used for repairing building cracks, with phenolic amide as the curing agent, supplemented by cardanol (C) and diethylenetriamine (D) to form a composite curing accelerator system (Figure 1). By adding glass beads (GB) with different mass fractions (0%, 0.5%, 1%, 1.5%, 2%) to the resin (the addition ratio is calculated as the percentage of the mass of epoxy resin), the influence of its content on the average thermal expansion coefficient of the epoxy resin was studied. The test instrument used in this experiment was a NETZSCH TMA 402 ***F1*** thermomechanical analyzer (equipped with a stainless-steel furnace).

Experimental Conditions

The measurement conditions are detailed in Table 1.

1 Epoxy resin samples (left); sample testing arrangement (right)

Table 1 Experimental conditions

Instrument	TMA 402 ***F1*** *Hyperion®*
Sample size	Cuboid, approx. 10 mm x 10 mm x 25 mm
Heating rate	5 K/min
Static force	50 mN
Sample holder	Fused silica compression holder
Temperature range	-50 - 150°C
Atmosphere	Inert gas (70 ml/min)

NGB · Application Note 459 · EN · 0726 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

NETZSCH

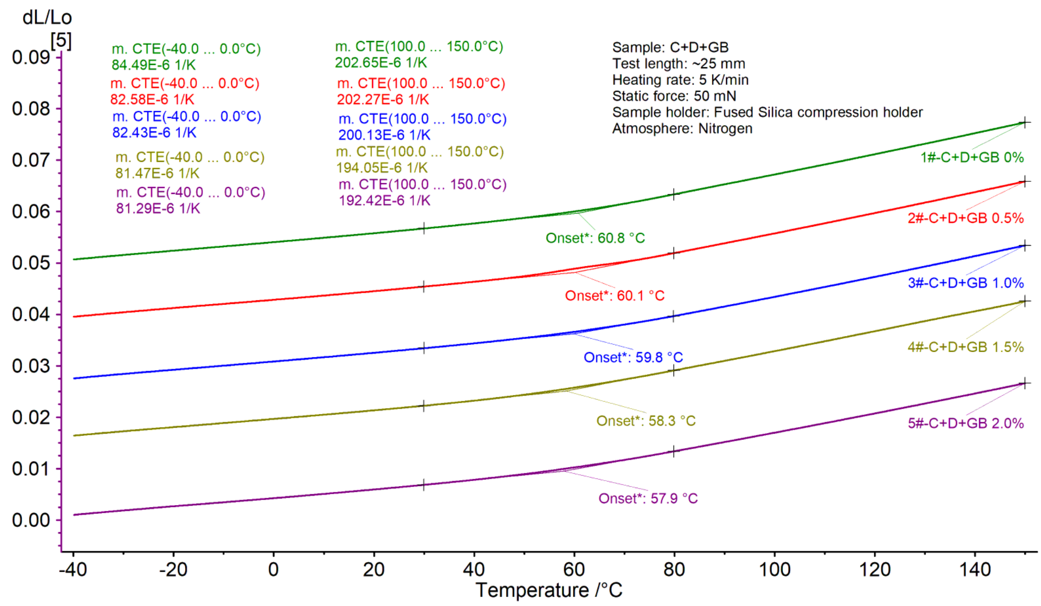
Measurement Results and Discussion

Figure 2 shows the second-run dL/L0 curves of the cured epoxy resin samples with different GB contents. Table 2 summarizes the glass transition temperature (T_g) and the mean coefficient of thermal expansion (mCTE) of each sample in different temperature ranges.

As shown in Table 2, the T_g of the epoxy resin slightly decreases with an increasing GB content. The blank sample (1#) exhibits a T_g of 60.8°C; at 2.0 % GB, the T_g reaches 57.9°C, a reduction of 2.9°C. This marginal decline is attributed to the disruption of the crosslinking network and increased free volume at the interface [3], as well as trace moisture and residual additives that marginally inhibit curing [4].

In the glassy state (-40°C to 0°C), the mCTE decreases from 84.49 $\times 10^{-6}$ K^{-1} to 81.29 $\times 10^{-6}$ K^{-1} as the GB content increases from 0 to 2.0%, corresponding to a reduction of 3.8%. This indicates that rigid GBs constrain thermal expansion even when the matrix is below the T_g. In the rubbery state (100°C to 150°C), the neat epoxy shows an mCTE of 202.65$\times 10^{-6}$ K^{-1} (≈ 2.4 times the glassy value). The addition of 2.0 % GB reduces this value to 192.42 $\times 10^{-6}$ K^{-1} (5.1 % reduction), confirming a more pronounced restriction effect in the rubbery state.

Across the investigated temperature range, the mCTE correlates negatively with the GB content, consistent with literature findings [5].



2 TMA curves of cured epoxy resin samples with different GB contents (second heating run).

Table 2 T_g and mCTE of epoxy resin samples with different GB contents

Sample No.	Glass Bead Content (wt-%)	T_g (°C)	mCTE (10^{-6} 1/K)	
			-40 - 0°C	100 - 150°C
1	0	60.8	84.49	202.65
2	0.5	60.1	82.58	202.27
3	1.0	59.8	82.43	200.14
4	1.5	58.3	81.47	194.05
5	2.0	57.9	81.29	192.42

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

Conclusion

Based on the sample test results obtained with the TMA 402 ***F1***, the thermal behavior of the composites can be precisely characterized. The addition of glass beads significantly reduces the thermal expansion coefficient of epoxy resin, enhances thermal matching with concrete substrates, and lowers the risk of debonding and cracking induced by temperature changes, providing an experimental basis for formulation optimization of concrete repair materials.

References

[1] Yu Z , Du X , Zhu P ,et al. Surface modified hollow glass microspheres-epoxy composites with enhanced thermal insulation and reduced dielectric constant[J]. Materials Today Communications, 2022.DOI:10.1016/j.mtcomm.2022.104046.
[2] Tang H , Zhan Y , Lei F ,et al. Mechanical and thermal properties of epoxy hybrid foams with inorganic and organic microspheres[J].Advanced Industrial and Engineering Polymer Research, 2025, 8(4):531-538. DOI:10.1016/j.aiepr.2025.08.001.
[3] Vukovi F , Swan S R , Reyes L Q ,et al. Beyond the ring flip: A molecular signature of the glass-rubber transition in tetrafunctional epoxy resins[J].Polymer, 2020, 206(29):122893.DOI:10.1016/j.polymer.2020.122893.
[4] Anandakumar P , Kanny K , Mohan T P ,et al. Mechanical behavior of glass fiber-reinforced hollow glass particles filled epoxy composites under moisture environment[J].Polymer Composites, 2024, 45(9):18. DOI:10.1002/pc.28364.
[5] Moradi A , Ansari R , Hassanzadeh-Aghdam M K ,et al. Numerical prediction of thermal conductivity and thermal expansion coefficient of glass fiber-reinforced polymer hybrid composites filled with hollow spheres[J]. Journal of Composite Materials, 2024, 58(9):14. DOI:10.1177/00219983241235857.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com