Survey data on thermal properties of different hyperbranched polymers (HBPs) and on morphological and thermal analysis of the corresponding epoxy matrix nanocomposites

Aldobenedetto Zotti, Simona Zuppolini, Anna Borriello⁎, Mauro Zarrelli

Institute for Polymers, Composites and Biomaterials, National Research Council of Italy, P.le Fermi, 1, 80055, Portici, Naples, Italy

ABSTRACT

The following data describe the thermal properties of two different typologies of Hyperbranched Polymers (HBPs): the first one is a polyester (HBPG – Hyperbranched Polymer Glassy) with a glass transition temperature (Tg) higher than room temperature (~90 °C) whereas the second one is a polyamide ester (HBPR – Hyperbranched Polymer Rubbery) characterized by Tg of about 20 °C. The nanocomposites manufactured using these HBPs as filler were characterized using Optical Microscopy and Differential Scanning Calorimetry. The raw data for the evaluation of fracture toughness properties are reported for the listed materials. This article provides data related to “The effect of Glassy and Rubbery Hyperbranched Polymers as Modifiers in Epoxy Aeronautical Systems” (Zotti et al.).

© 2019 The Authors. Published by Elsevier Inc. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
1. Data

The shared data comprise: a) the thermal stability curve of the synthesised nanofillers investigated by Thermo-Gravimetric Analysis (TGA); b) the thermal characterization of the manufactured nanocomposites by using Differential Scanning Calorimetry (DSC); c) load vs displacement curves related to the performed fracture tests according to. ASTM D5045 [3].

Fig. 1 reports thermal-gravimetrical data relative to the synthesized HBPG and HPBR fillers scanned by using a TGA - Q500 system by TA Instruments - at temperature rate of 10 °C/min from ambient temperature to 700 °C; DSC was performed under nitrogen flux (50 mL/min), with an heating rate of 10 °C/min, from ambient temperature to 250 °C; Flexural Tests were performed by setting a quasi-static displacement rate of 1 mm/min, with SENB samples prepared according ASTM D5045 standard.

Fig. 3 reports the DSC analysis, performed by using a DSC Q1000 by TA Instrument, relative to the nanocomposites loaded with the different synthesized fillers.

In Fig. 4 the optical micrographs of the manufactured nanocomposites are reported: these observations, performed in transmission mode on resin slices with a nominal thickness of about 100 μm, were recorded by using an Olimpus BX51 Instruments. Fracture toughness properties were evaluated according to the ASTM D5045, considering a SENB (Single Ended Notched Beam) specimen in 3-point bending load configuration. Samples are characterized by 3 × 6 × 28 mm³ nominal sizes with a notch length of about 3 mm. An Instron 4301 Universal Testing Machine, equipped with a 250N load cell, was employed to measure the mechanical data shown in Fig. 5.
2. Experimental design, materials and methods

HBPG were synthesized starting by 4,4-Bis(p-hydroxyphenyl) pentanoic acid (diphenolic acid) and Sn(Oct)$_2$ (1:0.01 M ratio). The system was mixed for 3 h at 190 °C and then the temperature was raised up to 225 °C for another 3 h. The crude product was dissolved in tetrahydrofuran (THF) and precipitated in deionized water in order to obtain the pure HBPG. For the HBPR synthesis, equal moles of
**Fig. 3.** DSC thermograms of a) HBPG/RTM6 systems and b) HBPR/RTM6 systems.

**Fig. 4.** Optical microscopy (10x and 20x) of a) neat RTM6, b) RTM6 + 0.1 wt% HBPG, c) RTM6 + 5 wt% HBPG, d) RTM6 + 0.1 wt% HBPR and e) RTM6 + 5 wt% HBPR.
diisopropanolamine and sebacic acid were mixed at 140 °C. After 10 min the catalyst Sn(Oct)$_2$ was added to the system and temperature was raised up 185 °C under vacuum conditions. The product was dissolved in methanol, filtered and finally washed. Both HBP$s$ were dried in oven at 80 °C under vacuum for a night.

In Fig. 1 the TGA thermograms of the synthesized HBP$s$ are reported: it is evident that HBPG shows an higher thermal stability, in term of temperature associated to the maximum degradation rate and weight residual at 600 °C, compared to HBPR; this result could be attributable to the aromatic nature of the glassy polymer.

Fig. 5. Fracture Toughness Load-Displacement Curves for a) neat RTM6, b) RTM6 + 0.1 wt% HBPG, c) RTM6 + 5 wt% HBPG, d) RTM6 + 0.1 wt% HBPR and e) RTM6 + 5 wt% HBPR.
For each HBPs typology two different concentrations were employed, respectively 0.1 wt% and 5 wt %. During nanocomposites manufacturing, the HBPs were dissolved in a proper solvent (THF for HBPG and, dimethylformamide for HBPR) and the solutions were mixed with the epoxy resin. Solvent was removed by rotavapor (80 °C for 30 min) and the system was poured in an aluminum mould: the loaded resin was cured according to RTM6 [2] temperature profile, i.e. 90 min at 160 °C followed by 120 min at 180 °C [4].

Cryogenic fracture surface of HBPR/RTM6 system is reported in Fig. 2. The nanometric size of the nanocomposite is highlighted by the presence of ultra-small cluster, with a maximum diameter of about 200 nm. The formation of small HBP clusters is associated to a phase separation phenomenon during the hosting matrix cure procedure [5].

Fig. 3 reports the nanocomposites thermograms in the temperature range of 100–250 °C. A dramatic reduction of $T_g$ for the system filled with HBPR (up to $\sim$50 °C for the nanocomposite RTM6+5 wt% HBPR) is evident. For what concern the HBPG filled systems, the $T_g$ reduction results smaller, with a larger variation compared to the neat system of about 9 °C. These data are in agreement with the DMA results reported in the main paper [1].

In Fig. 4 the optical micrographs of the investigated nanocomposites are reported at 2 different magnitudes (10× and 20x). The oblique lines are the scratches generated during the sample cut: excluding the latter, no other objects are evident, indicating the absence of HBPs micrometric clusters and consequently the homogeneous dispersion of the fillers in the hosting matrix.

According ASTM D5045, at least 6 samples must be tested for a reproducible fracture toughness test. In Fig. 5 are reported the curve load-displacement for each RTM6+HBPs system, and how it is evident each sample breaks with a brittle fracture (absence of plasticization phenomenon). These samples were tested in a 3-point bending configurations using SENB (Single Edge Notched Beam) specimen. The obtained curves were employed for the evaluation of the fracture toughness parameters, i.e., $K_{IC}$ and $G_{IC}$.

**Acknowledgements**

This study was financially supported from European Project: EXTREME dynamic loading—pushing the boundaries of aerospace composite material structures - GA 636549.

**Conflict of interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Appendix A. Supplementary data**

Supplementary data to this article can be found online at [https://doi.org/10.1016/j.dib.2019.104303](https://doi.org/10.1016/j.dib.2019.104303).

**References**

[1] A. Zotti, S. Zuppolini, A. Borriello, M. Zarrelli. The Effect of Glassy and Rubbery Hyperbranched Polymers as Modifiers in Epoxy Aeronautical Systems. Composite Part B, in press.
[2] RTM6 Technical Datasheet. Excel Corporation.[https://www.imatec.it/wp-content/uploads/2016/05/RTM6_global.pdf](https://www.imatec.it/wp-content/uploads/2016/05/RTM6_global.pdf).
[3] ASTM D5045. Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials.[https://www.astm.org/Standards/D5045.htm](https://www.astm.org/Standards/D5045.htm).
[4] A. Zotti, S. Zuppolini, A. Borriello, M. Zarrelli, Thermal properties and fracture toughness of epoxy nanocomposites loaded with hyperbranched-polymers-based core/shell nanoparticles, Nanomaterials 9 (3) (2019) 418–432, [https://doi.org/10.3390/nano9030418](https://doi.org/10.3390/nano9030418).
[5] G.G. Buonocore, L. Schiavo, I. Attianese, A. Borriello, Hyperbranched polymers as modifiers of epoxy adhesives, Composites Part B 53 (2013) 187–192, [https://doi.org/10.1016/j.compositesb.2013.04.062](https://doi.org/10.1016/j.compositesb.2013.04.062).