

PALS STUDY OF THE NANO HOLE VOLUME DEPENDENCE ON CHEMICAL COMPOSITION AND CURE SCHEDULE IN EPOXY THERMOSETTING NETWORKS

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Epoxy resins are widely used in industrial applications ranging from high performance aerospace composites to encapsulants for microelectronics, as a consequence of high thermal resistance, high tensile strength and modulus and good chemical resistance. The most important factors influencing their performance are molecular architecture, stoichiometric ratio between epoxy and hardener, and curing conditions, as described by several authors¹⁻³. As a matter of fact, by choosing monomers with an appropriate molecular structure the rigidity of epoxy networks can be controlled, while stoichiometry and curing conditions predominantly affect crosslinking density, free volume but also mechanical properties.

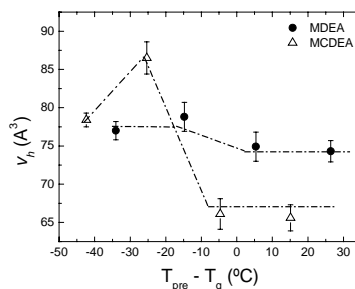
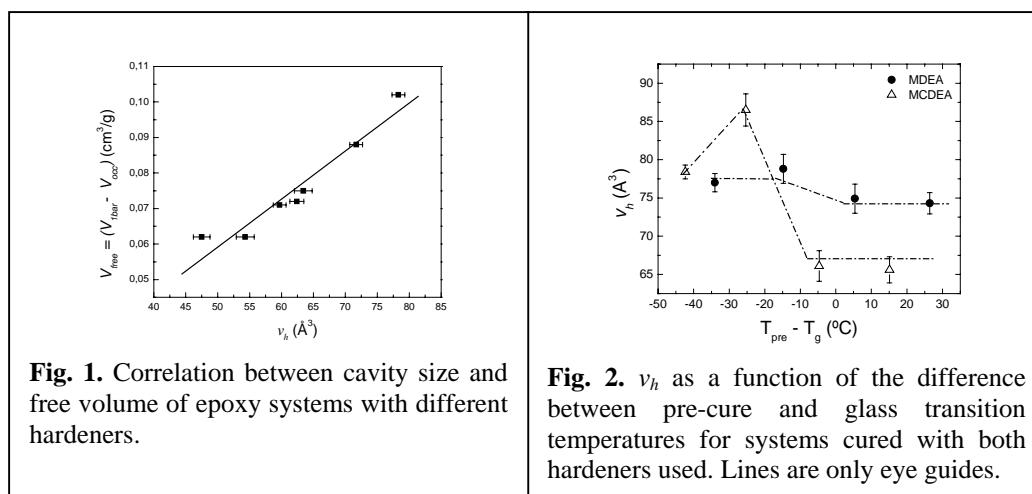
In the present work we have used positron annihilation spectroscopy (PALS) to analyse the variations in local free volume that occur when epoxy pre-polymers are cured with different aminic hardeners⁴. Complementarily, the use of pressure-volume-temperature (PVT) technique has allowed us to measure the changes in the specific volume, relating them to the packing variations of polymer chains of the crosslinked networks.

Hardener	Cure schedule	Molecular structure	v_h (Å ³)	$V_{free(1bar)}$ (cm ³ /g)
DDS	135 °C 6 h / 200 °C 1 h		47.5 ± 1.3	0.062
DDM	110 °C 90 min / 200 °C 2 h		54.3 ± 1.4	0.062
3DCM	50 °C 4 h / 190 °C 4 h		59.7 ± 1.0	0.071
DETA80	140 °C 200 min / 200 °C 2 h		62.4 ± 1.1	0.072
MDEA	140 °C 200 min / 200 °C 2 h		63.4 ± 1.4	0.075
MMIPA	140 °C 260 min / 200 °C 2 h		71.7 ± 1.0	0.088
MDIPA	140 °C 260 min / 200 °C 2 h		78.3 ± 1.0	0.102

Table 1. Cure schedules of the epoxy resin, molecular structures of the different aminic hardeners, the most probable cavity size (v_h) and the free volume ($V_{free(1bar)}$) obtained from PALS and PVT measurements.

As shown in table 1, the value of the cavity size (v_h) increases as chemical structure complexity of hardener does. Such a complexity could hinder good packaging of the molecular structures. As shown in figure 1, when the experimental values of free volume

($V_{free(1bar)}$), from PVT measurements and Simha-Somcynsky modelling, are plotted against v_h for the systems investigated, a linear relationship seems to exist between both parameters.



On the other hand, currently a systematic study on the changes in the volume at nano-scale in epoxy systems cured with selected aminic hardeners (MDEA and MCDEA) at different pre-cure temperatures is being carried out⁵. The values of the glass transition temperature (T_g) and the molecular weight between crosslinks have been obtained by dynamic-mechanical analysis (DMA). Both PALS and DMA techniques are being used to improve the knowledge on these thermoset structures.

Specifically, the experimental results presented in this work show the effect of the applied pre-cure cycle on the nano-size holes, as shown in figure 2. Both the pre-cure temperature and the structure of the hardeners are responsible for the molecular chains packing of the epoxy network. The role of the Cl atom in the chemical structure of MCDEA hardener has been analyzed. The reactivity of the hardener decreases by the presence of Cl. On the other hand, at pre-cure temperatures above the T_g , both systems show a decrease in the hole cavity sizes owing to the formation of shorter length chains. However, the Cl atom presence in the 3-dimensional structure of the DGEBA/MCDEA network reduces even more the hole cavity sizes than in the case of DGEBA/MDEA. Summarizing, it can be concluded that a strong change in the volume and number density of the nanoholes takes place around the glass transition temperature for both systems.

Finally, the results reported also allow to gain information about the conditions in which the hole volume results, measured by PALS, must be compared to the free volume dependent mechanical properties in different thermosetting systems.

References

- [1] L. Yang, H.A. Hristov, A.F. Yee, D.W. Gidley, D. Bauchiere, J.L. Halary, L. Monnerie, *Polymer* **36** (1995) 3997.
- [2] O. Sindt, J. Perez, J.F. Gerard, *Polymer* **37** (1996) 2989.
- [3] A.E. Mayr, W.D. Cook, G.H. Edward, *Polymer* **39** (1998) 3719.
- [4] S. Goyanes, W. Salgueiro, A. Somoza, J. A. Ramos, I. Mondragon, *Polymer* **45** (2004) 6691.
- [5] W. Salgueiro, J. Ramos, A. Somoza, S. Goyanes, I. Mondragon, *Polymer*, **to be published**.