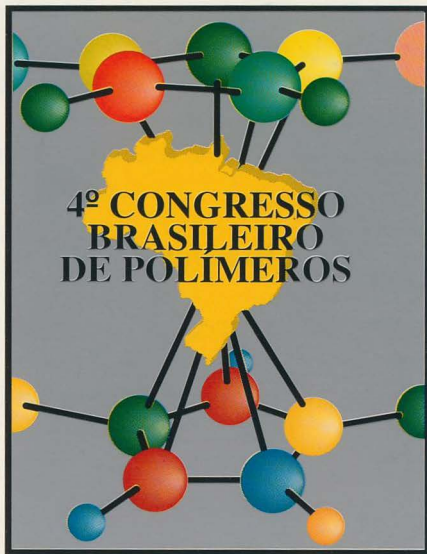


# 4º CONGRESSO BRASILEIRO DE POLÍMEROS

Salvador, 28 de setembro a 2 de outubro de 1997



Promoção:



Associação Brasileira de Polímeros

# PHYSICAL AGING BEHAVIOR OF A DGEBA/DDM SYSTEM STUDIED BY THERMAL ANALYSIS

**Izabel Cristina Riegel, Liane L. Freitas, Dimitrios Samios**

Instituto de Química/UFRGS – Cx. Postal 15003, CEP 91501-970, Porto Alegre, RS, Brasil.  
e-mail: [iriegel@if.ufrgs.br](mailto:iriegel@if.ufrgs.br)

## INTRODUCTION

The epoxy resin network shows two characteristic aspects: one is its crosslinked nature and the other is the glassy state behavior. Amorphous solids can be regarded as solidified supercooled liquids whose volume, enthalpy and entropy are greater than they would be in the equilibrium state. As a consequence, these materials undergo slow processes of structural relaxation which attempt to establish equilibrium, indicating that even below  $T_g$  molecular mobility is not quite zero. This process is generally called physical aging<sup>1</sup> and continuously changes many material properties. The effects of physical aging on the mechanical and thermal behavior of a DGEBA/DDM stoichiometric system were investigated as a function of crosslinking degree and aging time of the samples, using dynamical mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC).

## EXPERIMENTAL

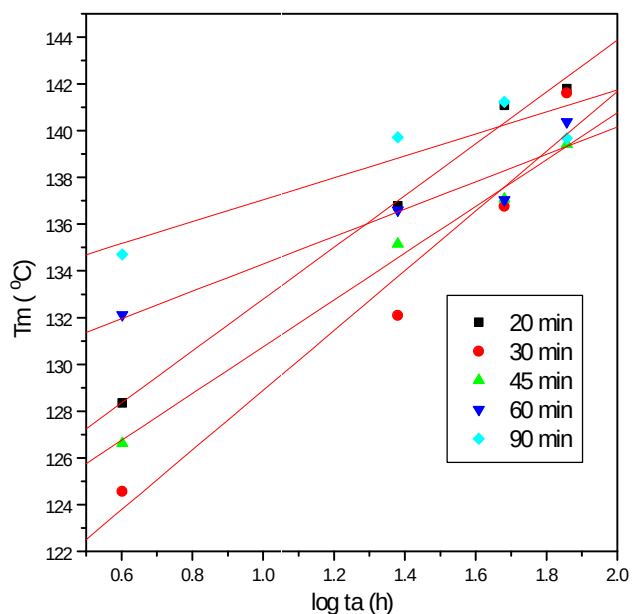
The chemical system used was a difunctional epoxy liquid, diglycidyl ether of bisphenol-A (DGEBA), and a tetrafunctional aromatic diamine, 4,4'-diaminodiphenylmethane (DDM). The reagents were stoichiometrically mixed at 90 °C with vigorous stirring in order to dissolve the amine in the epoxy resin. The resulting viscous liquid was isothermally cured at 115 °C for 20, 30, 45, 60 and 90 min in order to obtain different crosslinking degrees<sup>2</sup>. Next, each specimen was aged at 100 °C ( $T_a$ ) for periods of time ranging from 4 to 72 hours. The DSC experiments were performed with a Perkin Elmer DSC-4 equipment and the dynamical measurements were performed with a PL-DMTA.

## RESULTS AND DISCUSSION

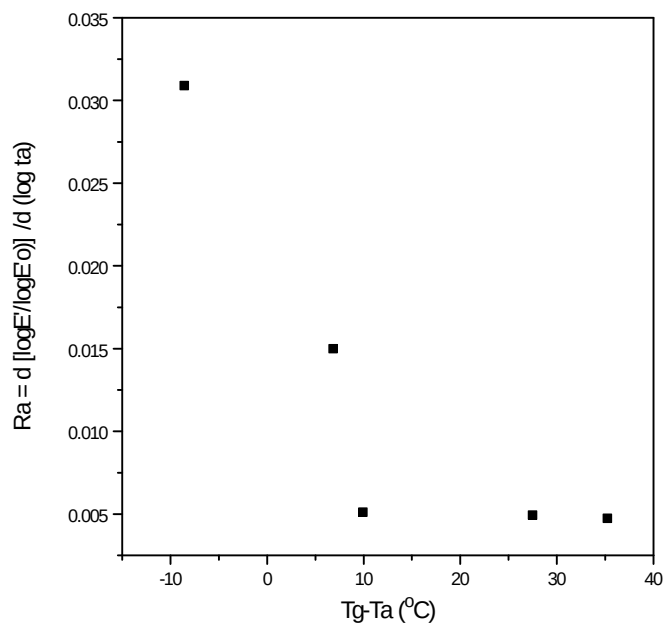
The extent of physical aging has been measured by the area of the endothermic peak (enthalpy relaxation) which appears within the glass transition region according to the aged samples DSC thermograms. The enthalpy relaxation (cal/g) was found to increase with aging time ( $t_a$ ), as well as the temperature of the endothermic peak ( $T_m$ ). The relationship between  $T_m$  and  $\log(t_a)$  is approximately linear (Figure 1) and the effect of  $t_a$  on  $T_m$  is greater at low crosslinking degrees. In a second DSC scan it was verified that the aging process carried out on this study is thermoreversible.

Aging rates and glass transition activation energies were obtained through DMTA parameters and then associated with the different curing and aging histories of the material. The aging rate ( $R_a$ ) (Figure 2), as measured by the normalized dynamic storage modulus<sup>3,4</sup>, decreases with increasing crosslinking degree and the activation energies demonstrate a tendency to increase with curing and aging time. According to the results, as

depicted by aging rates and activation energies, it was concluded that the physical aging stiffens the material in a rate that depends on the crosslinking degree, which is related to the material  $T_g$  <sup>2</sup>.



**Figure 1.** Endothermic peak temperature versus  $\log(ta)$  at different curing times.



**Figure 2.** Physical aging rate (Ra) as a function of  $T_g - T_a$  (a measurement of the departure from equilibrium).

## REFERENCES

1. Struik, L.C.E., *Physical Aging in Amorphous Solids and Other Materials*, Elsevier, Amsterdam, 1978.
2. Miranda, M.I.G., Samios, D., *Eur. Pol. J.*, **33**:3, 325 (1997).
3. Wang, X., Gillham, J.K., *J. Appl. Pol. Sci.*, **47**, 447 (1993).
4. Maddox, S.L., Gillham, J.K., *J. Appl. Pol. Sci.*, **64**, 55 (1997).

➤ The authors gratefully acknowledge CAPES for financial support.