THERMALLY STIMULATED CREEP SPECTROSCOPY FOR THE STUDY OF DGEBA-DDM NETWORKS

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During the past two decades, Thermally Stimulated Creep Recovery (TSCR) has been used successfully to study molecular mobility in polymers. The main feature of this technique is its quite good sensitiveness: the sample undergoes a shear stress, so that the subsequent strain is linear in a range larger than in elongation or compression experiments. Furthermore, the low equivalent frequency of TSCR permits the resolution of normally overlapping peaks.

In this study, the TSCR technique has been used to investigate a series of DGEBA-DDM networks differing from the value of the amine-to-epoxy ratio which was systematically varied below stoichiometric composition. The magnitude of the \( \beta \)-mode (glassy region) is seen to decrease unexpectedly as the network gets looser, while its peak-temperature decreases. This result is interpreted in terms of 'internal antiplasticization'. Moreover, we show that the important shift of the \( \alpha \)-peak associated with the glass transition has an essentially entropic origin.

Introduction

Thermosets based on epoxy resins are widely used as adhesives, coatings and matrices for reinforced composites. The choice of particular pre-polymer or crosslinking agents is dictated by end-use or service requirements.

Despite their good mechanical properties (e.g. high storage modulus), these materials display a disposition to cracking or fracture which still remains a matter of concern for many researchers. The fracture mechanisms involved in the material are obviously related to their molecular structure. It is therefore necessary to correlate the anelastic losses responsible for those mechanisms with the microstructure of the thermoset network. This is the purpose of the present study by carrying out TSCR experiments. The technique has already been utilized to study both amorphous and crystalline polymers [1–3], copolymers [4] and blends [5].
In this work, the epoxy pre-polymer DGEBA (diglycidyl ether of bisphenol A)-average degree of polymerisation: 0.03- was crosslinked with the primary amine DDM (4,4' diamino diphenyl methane). The structural parameter is the amine-to-epoxy molar ratio $r$ which varies between the values 0.5 and 1.

**Thermally stimulated creep recovery (TSCR)**

The TSCR principle and the torsion pendulum used for this work have been extensively described elsewhere [1, 6]. However, the general outlines are mentioned below.

**Principle**

The TSCR principle is shown in Fig. 1. A static shear stress $\sigma$ is applied to the sample at a temperature $T_\sigma$ for a time $t_\sigma = 2$ min to allow polymer chains orientation. The resulting viscoelastic strain is then frozen by quenching the sample to a temperature $T_0 << T_\sigma$. After 2 min at $T_0$, a linear heating run is imposed to the sample:

$$T = T_0 + mt$$

![Fig. 1 Principle of thermally stimulated creep](image-url)