Characterization of crosslinked polyester resins by dynamic mechanical properties

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Dynamic mechanical properties of a series of crosslinked polyester resins have been determined by a freely oscillating torsional pendulum in the temperature range −175 to 270°C. The materials were obtained by adding various amounts of two different flexibilizers, one crosslinkable and the other non-crosslinkable with itself, to a basic polyester resin. The results confirm the indications, derived from previous d.s.c. measurements, that the addition of the crosslinkable flexibilizer gives substantially homogeneous network structures, while the addition of the non-crosslinkable flexibilizer gives heterogeneous polyphasic network structures. It has also been shown that the lowering of the glass transition temperature by the addition of the crosslinkable flexibilizer is attributable partly to a reduction in the degree of crosslinking and partly to the effect of variation in chemical composition.

(Keywords: polyester resins; flexibilization; dynamic mechanical properties; crosslink density; glass transition)

Introduction

In a previous study[1] we investigated the non-linear stress relaxation behaviour in simple tension of a series of crosslinked polyester resins. The materials used were prepared by curing a basic unsaturated polyester resin to which different amounts of two types of flexibilizers were added. The first flexibilizer was polyfunctional, crosslinkable with itself, and therefore also acting as a crosslinking comonomer, while the second was essentially bifunctional, non-crosslinkable with itself, and thus acting as a plasticizer with side groups pendant from the polyester basic network chains. The materials showed a wide range of deformability, depending on type and amount of the added flexibilizer.

The glass transition temperatures (T_gs) of the materials were determined by d.s.c. The addition of the crosslinkable flexibilizer led to mixtures showing, like the cured basic resin, a single glass transition, with temperature values that decreased with increasing amounts of flexibilizer: this indicated the formation of relatively homogeneous network structures. The mixtures obtained by addition of the non-crosslinkable flexibilizer showed three transitions (two in the case of higher flexibilizer content): this clearly suggested the formation of a polyphasic network structure, which may be assumed to be due to the presence in each mixture of a phase of substantially pure flexibilizer, a phase of mixed composition and a phase of substantially pure basic resin.

We thought it of interest to study the characterization of these materials further, in order to verify and improve the indications derived from the d.s.c. measurements. A further way to obtain substantial structural information on the network structure of highly crosslinked polymers may be the analysis of dynamic mechanical properties, by which the effects of the addition of flexibilizers can also be investigated[2–4].

In this paper the results of dynamic mechanical measurements carried out on the same materials using a freely oscillating torsional pendulum will be presented and discussed.

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Experimental

The starting materials were supplied by DSM Italia SpA, Italy.

The basic resin was an orthophthalic unsaturated polyester (DSM Neoxil 256N5) in 67 wt% styrene solution. Both the flexibilizers were styrene solutions of special polyester resins; one was crosslinkable with itself (DSM 12161) while the other was essentially non-crosslinkable with itself (DSM Neoxil 226). Details of the curing and postcuring procedures have been described previously[1].

Seven different materials were considered: the pure cured basic resin (denoted as R in the following), three mixtures (CF15, CF30, CF45) containing 15, 30 and 45 wt% of the crosslinkable flexibilizer, and three mixtures (NF15, NF30, NF45) containing 15, 30 and 45 wt% of the non-crosslinkable flexibilizer.

Specimens for dynamic mechanical testing, with nominal dimensions 65 × 10 × 1 mm, were cut from moulded plates. The measurements were carried out with a freely oscillating torsional pendulum Brabender Torsionsautomat, in a temperature range −175 to 270°C, with an increment of 2°C min^{-1}. The test frequencies were typically adjusted in the range of 0.1–10 Hz.

Results of d.s.c. measurements have been taken from our previous work[1].

Results and discussion

The storage shear modulus and the damping (logarithmic decrement), as a function of temperature, are given in *Figure 1* for the resin R and the CF mixtures, and in *Figure 2* for the resin R and the NF mixtures. The most interesting temperature range (−30 to 220°C) is shown in the figures; at lower temperatures the damping curves of all the materials reveal a secondary relaxation peak around −90°C, which is not detectable in the modulus curves.

The damping curves of the CF mixtures (*Figure 1*) show peaks progressively broadened and shifted towards

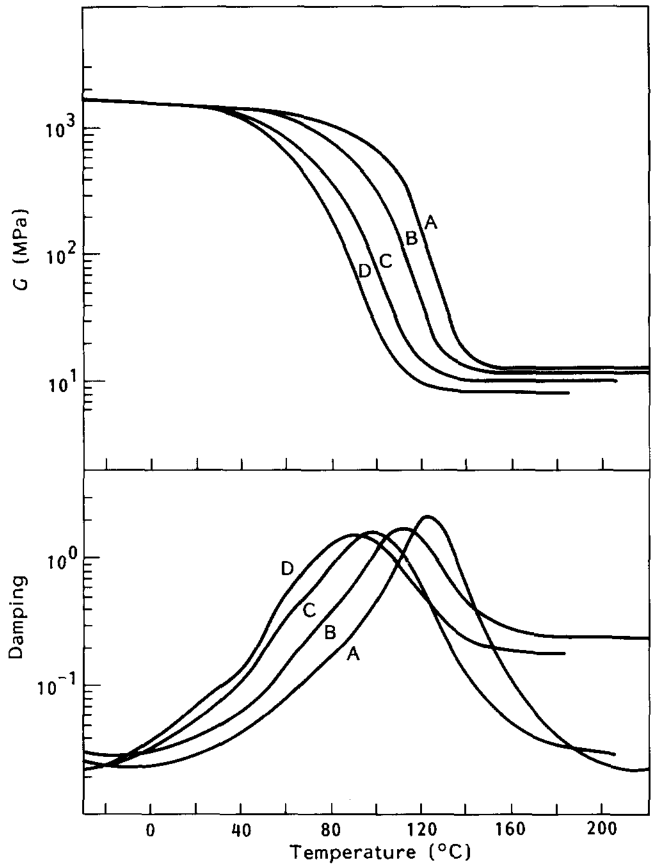

Figure 1 Storage shear modulus G and damping (logarithmic decrement), as a function of temperature, of the resin R (A) and of the CF15 (B), CF30 (C) and CF45 (D) mixtures

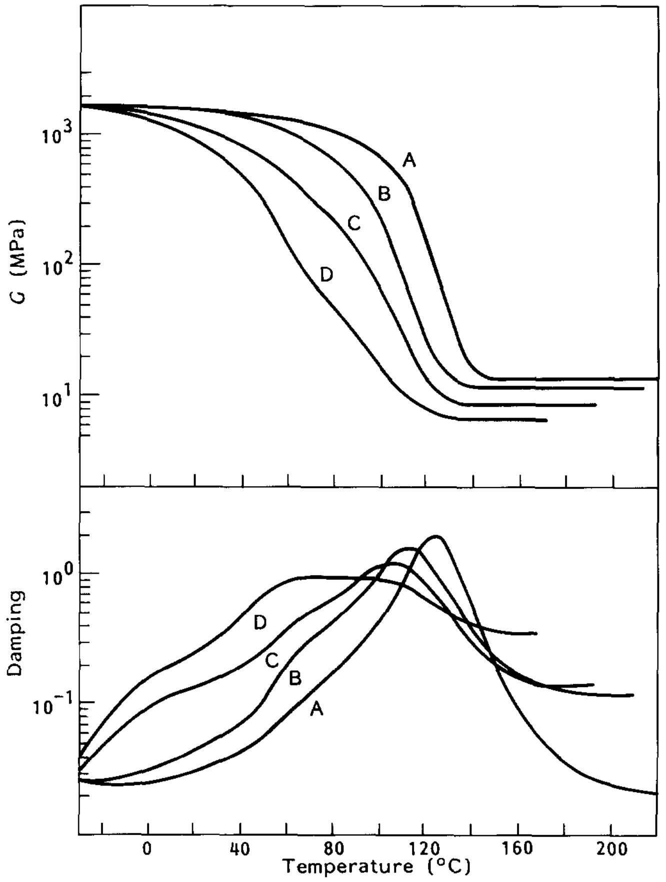

Figure 2 Storage shear modulus G and damping (logarithmic decrement), as a function of temperature, of the resin R (A) and of the NF15 (B), NF30 (C) and NF45 (D) mixtures

Table 1 Characteristics of the materials

Materials	G' (MPa)[a]	M_c[b]	T_g (°C)[c]	T_g (°C)[d]
R	13.8	296	125	124
CF15	12.0	312	114	113
CF30	11.0	324	94	99
CF45	8.0	373	69	90
NF15	11.4	319	−10, 63, 118	– , (60), 113
NF30	8.3	367	−10, 55, 110	(−10), (60), 104
NF45	6.4	418	−5, 55, –	(−10), 55–105

[a] Storage shear modulus values at the rubbery plateau
[b] Calculated from equation (1) (see text)
[c] From d.s.c. measurements (ref. 1)
[d] From dynamic mechanical measurements (this work)

lower temperatures with increasing amounts of added flexibilizer. The broadening of the damping peaks, often observed in crosslinked polymers, has been in general attributed to a distribution of the molecular weight between crosslinks or to heterogeneity in the network structure[2], and both these features should be typical of crosslinked polyesters[5]. As can be seen from the data in *Table 1*, for the pure resin R and for the CF15 and CF30 mixtures the transition temperatures compare well with the T_g values determined by d.s.c. As a matter of fact, at low frequencies, of the order of 1 Hz as in our measurements, the damping peak temperature should correspond to the T_g measured by d.s.c.[6]. For the CF45 mixture a more pronounced shoulder around 60°C appears in the damping peak, and this could explain the difference with the d.s.c. results.

The heterogeneous network structure of the NF mixtures is clearly evidenced by the damping curves in *Figure 2*. The temperatures of the main damping peak are in good agreement with those obtained from d.s.c. measurements (*Table 1*), and can be attributed[1] to the basic resin network phase. Shoulders around 60°C, increasingly more evident for the NF15, NF30 and NF45 mixtures, could correspond to a mixed network phase, and, particularly for the NF30 and NF45 mixtures, a transition around −10°C corresponding to a flexibilizer phase is detectable. For the NF45 mixture the main damping peak is very broad and flat in the region 55–105°C; this could explain the fact that only the transition at 55°C was revealed by d.s.c.

It has been suggested[6] that the shifts of the T_gs in homogeneous crosslinked systems, as a consequence of the addition of a crosslinkable comonomer, are made up of two nearly independent effects: the variation of crosslink density, which is largely independent of chemical composition, and the 'copolymer effect' dependent on the chemical nature of the comonomer. It would be interesting to clarify if, for our homogeneous CF mixtures, besides the actual variation of the crosslink density, a copolymer effect is also effectively working.

The crosslink density of the mixtures can be independently determined from the storage shear modulus values in the rubbery plateau region. Quantitative relationships between the elastic modulus values in the rubbery plateau and density of crosslinks can be derived from the kinetic theory of rubber elasticity, but their validity[6] is limited to lightly crosslinked polymers, with moduli lower than 10 MPa. Modified equations have been proposed by Smith[7] for highly crosslinked networks, but their applicability appears to be questionable for materials, like polyester resins, with a non-uniform crosslink density. For highly crosslinked polymers, Nielsen[6] has proposed an empirical equation that appears to give a reasonable estimate of the degree of crosslinking nearly independent of the chemical composition, as long as the modulus is measured at temperatures well above (30–50°C) the glass transition:

$$\log G' = 6.0 + 0.293\, d\, M_c^{-1} \qquad (1)$$

where G' is the storage shear modulus (Pa), d the density (kg m^{-3}) and M_c the number average molecular weight of polymer chains between crosslinks. The M_c values obtained using equation (1) for each material are given in *Table 1*.

Various equations have also been proposed to account for the shift of the T_g produced only by the variation of crosslink density. Among these, an empirical equation reported by Nielsen[6] has provided a good description of experimental data for a wide range of crosslinked systems[3,8]:

$$T_g - T_{go} = 3.9 \times 10^4\, M_c^{-1} \qquad (2)$$

where T_{go} is the glass transition temperature of the uncrosslinked polymer. Although T_g values obtainable from equation (2) are to be considered as rough estimates, it can be thought that application of equation (2) to a series of homologous materials can provide significant indications. In our case, T_{go}, the glass transition temperature of the pure uncrosslinked basic resin, is actually not measurable; however it can be calculated by introducing into equation (2) the M_c value determined using equation (1). The result is -7°C. Now the T_g values for the CF15, CF30 and CF45 mixtures can also be calculated using equation (2) introducing T_{go} and the proper M_c values. Temperatures of 118, 113 and 98°C, respectively, are obtained, which are higher than those measured by d.s.c. or dynamic mechanical tests (*Table 1*). Hence the crosslink density effect on T_g would lead to values higher than the experimental values, and therefore a copolymer or chemical nature effect, with a consequent lowering of the T_g, needs to be taken into account.

We can conclude that the results of dynamic mechanical measurements confirm the indications, derived from d.s.c. results, that the addition of the crosslinkable flexibilizer gives substantially homogeneous network structures, while the addition of the non-crosslinkable flexibilizer leads to heterogeneous polyphasic network structures. Moreover we have shown that the incorporation of the crosslinkable flexibilizer into the basic network structure produces a lowering of the T_g which seems to be attributable partly to a reduction in the degree of crosslinking and partly to a change in chemical composition.

Acknowledgements

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