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NMR investigation of the miscibility of new antiplasticizers in densely cross-linked epoxy–amine resins

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Abstract

The behaviour of antiplasticized epoxy–amine networks was investigated by variable-temperature determinations of ^{1}H NMR free induction decays. Up to 50 °C, all antiplasticized resins exhibited a solid-like behaviour. At higher temperatures, resins containing the less polar additives were shown to be phase-separated, in contrast to systems containing polar additives. The temperature dependence of the phase composition of the resins, as detected by NMR, supports the conclusions previously deduced from the dynamic mechanical analysis (DMA) study: non- or slightly-polar antiplasticizer molecules are sharply phase-separated in highly cross-linked epoxy–amine networks cured extensively. The resulting morphology mainly consists in nano-scale aggregates of additives entrapped within the polymer matrix.

Keywords: Epoxy resins; Phase separation; ^{1}H NMR

1. Introduction

The first antiplasticizer for epoxy–amine resins was developed by Garton [1] under the name EPPHAA. As shown by nuclear magnetic resonance (NMR) experiments, the EPPHAA molecules and resin chains were mixed at a 5 Å scale, clearly demonstrating the intimate nature of the mixing. Besides, the local chain mobilities of the resin and EPPHAA units were reported [2] to be compatible with the assumption of a dynamic coupling, suggesting that the additive and matrix share rather strong interactions.

In contrast with the miscibility of EPPHAA and epoxy resins, new antiplasticizing additives to be used in densely cross-linked aromatic epoxy–amine resins were prepared by Sauvant et al. [3,4]. These new additives were designed to be fully miscible with the mixture of monomers before cure and to give rise to phase separation during the network formation, in order to obtain small aggregates, rich in additive molecules and dispersed in the polymer matrix. Such a biphasic character should lead to an improvement of the room temperature toughness and modulus with respect to those exhibited by the neat epoxy–amine resins.

The phase separation of the above antiplasticized epoxy resins was first investigated by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) [3,4]. In systems where the antiplasticizers have a poor affinity for the resin and, thus, undergo a phase separation during cure, the viscoelastic response of the cured networks suggested the existence of two phases. Indeed, two distinct relaxations were observed in the high temperature range: at the higher temperature, the α relaxation corresponded to the glass transition of the plasticized matrix, at a lower temperature, the μ relaxation was assigned to the glass transition of additive-rich aggregates. The glass transition temperature associated with the α relaxation was observed by DSC. However, DSC traces did not exhibit any significant change in specific heat around $T\mu$, which indicated that additives and matrix were almost miscible on the DSC spatial scale. Since the length of the smallest heterogeneities observed by this technique is of the order of 10 nm [5], the heterogeneities detected by DMA in these materials should be at a nanometric spatial scale. Therefore, it was of interest to investigate the phase behaviour of the above mentioned antiplasticized systems at a smaller spatial scale, in order to demonstrate the existence of a nano-scale phase separation resulting from curing.

However, the bulk organization of antiplasticized resins based on densely cross-linked epoxy–amine units and

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additives, which are mimetic of the network since they have to be initially miscible with resin monomers, was not accessible by most usual techniques. For example, their morphologies could not be determined by using transmission electron microscopy (TEM) experiments due to the similarities in the chemical structure of the additive and the network units.

NMR is also an interesting technique for investigating small heterogeneities. The spatial scale of the NMR technique has permitted to detect the existence of small interphases in polymer blends [6] or block copolymers [7–9]. In the resins under study, as for TEM experiments, the contrast between the phases cannot originate from differences in the chemical structure. However, since two glass transition temperatures were observed by DMA, there should exist a large difference in phase mobilities in the temperature range between these two glass transition temperatures. Such differences in local mobilities should induce differences in the ^{1}H free induction decays (FID) of the two phases.

Therefore, the present paper is devoted to the NMR investigation of the phase behaviour of representative antiplasticized epoxy–amine resins with high toughness and modulus [3,4]. In the following, we will report results obtained from the variable-temperature determinations of ^{1}H NMR free induction decays and focus on the influence of both the additive nature and additive amount. For comparison, data relative to the neat network and to the resin prepared in the presence of EPPHAA, which is known to be a miscible blend of antiplasticizer and matrix chains, will also be discussed. It must be noticed in the present work that the use of NMR is voluntarily restricted to the analysis of ^{1}H FID shapes since extensive DMA work reported elsewhere [3,4] had provided additional information on the structure and dynamics of the additive rich aggregates.

2. Experimental

2.1. Materials

The formulae and code names of the different antiplasticizing additives used in the present work are given in Fig. 1.

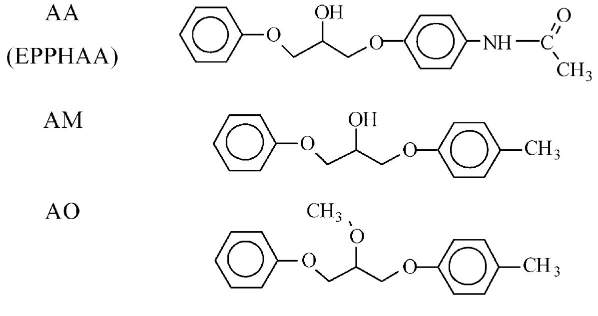

Fig. 1. Code names and formulae of the different antiplasticizing additives.

Table 1
Code names, solubility parameters and glass transition temperatures of neat DGEBA–DDM and additives

Code name	δ^{15} (MPa$^{1/2}$)	T_{gDSC}^{a} (°C)
DGEBA–DDM	26.5	165
AA	26.5	− 14
AM	24.0	− 23
AO	20.8	− 45

[a] Measured at the onset of the sloping portion due to the glass transition phenomenon using a DSC calorimeter Dupont 1090 operating at a heating rate of 10 K/min.

Their synthesis, the preparation of neat and antiplasticized networks based on stochiometric mixtures of diglycidylether of bisphenol-A (DGEBA) and diaminodiphenylmethane (DDM) and the cure cycle used to achieve extensive cross-linking were described previously [3,4].

Table 1 lists the solubility parameters and glass transition temperatures of the neat matrix and antiplasticizers. The code names, composition and transition temperatures, $T\alpha$ and $T\mu$, determined by DMA [3,4] are given in Table 2 for the different networks.

2.2. NMR

^{1}H FIDs were obtained at 100 MHz with a BRUKER CXP 100 spectrometer using the solid-echo pulse sequence [10,11]. The 90° pulse length was equal to 2.8 μs. Measurements were performed as a function of temperature over the temperature range, from 25 to 121 °C.

The ^{1}H magnetization decay can be written as a function of time, t, as:

$$M(t) = \exp\left(-\frac{t}{T_2(\mathrm{H})}\right)^p \tag{1}$$

where p is almost equal to 2 in the solid state and decreases with increasing temperature to reach 1 for liquids.

3. Results and discussion

3.1. DGEBA–DDM

The FIDs of the DGEBA–DDM protons recorded at different temperatures in the range from 25 to 121 °C are shown in Fig. 2 as a function of t^2. They exhibit a rapidly decaying quasi-Gaussian behaviour over the first 25 μs, in agreement with the classical behaviour of a glassy polymer. The spin–spin relaxation times, $T_2(\mathrm{H})_{\mathrm{rigid}}$, calculated assuming a Gaussian decay, are in the range from 17 to 21 μs.

3.2. AM-62

The FIDs of the AM-62 protons were determined over the whole temperature range. Representative data recorded at 25, 86 and 121 °C, are compared on Fig. 3 with the FIDs

Table 2
Code names, compositions and transition temperatures detected by DMA for the samples under study

Sample code	Additive		$^1H_{additive}$ (%)	$T\alpha^a$ (°C)	$T\mu^a$ (°C)
	mol/network unit	wt%			
DGEBA–DDM	0	0	0	186	
AA-62	0.62	17.5	19.0	106	
AM-62	0.62	15.4	18.2	111	61
AO-62	0.62	16.1	19.9	110	50
AM-96	0.96	25.7	25.7	93	50

[a] Determined at the maximum of loss modulus for a frequency of 1 Hz using a servohydraulic testing machine MTS 831.

obtained for the neat resin. Both systems exhibit similar quasi-Gaussian behaviour over the first 25 μs at room temperature, in agreement with the solid character of both resins. At 86 °C and above, the AM-62 FIDs have a more complex behaviour, exhibiting a fast and a slow relaxing component which correspond to rigid and mobile protons, respectively. Indeed, the time dependence of the FID of the slow relaxing component is well-described by Eq. (1) using $p = 1$. The resolution of the FIDs into gaussian and exponential components was performed graphically using the following procedure. The relative amount of mobile protons was determined by extrapolating the slow relaxing component to zero time. The values of $T_2(H)_{mobile}$ and the percentage of mobile protons are listed in Table 3. Then, the short-time component of the AM-62 ^1H FIDs was obtained by subtraction of the slow decaying component. These short time components are compared to their DGEBA–DDM counterparts in Fig. 4. It appears that the AM-62 ^1H FIDs strictly follow the evolution of the DGEBA–DDM ^1H FIDs within the first 30 μs at 25 and 86 °C. At higher temperatures, the rigid component of the AM-62 ^1H FID has a slightly slower decrease than its DGEBA–DDM counterpart, with a $T_2(H)_{rigid}$ value of 24 μs at 121 °C. This small increase in $T_2(H)_{rigid}$ is likely due to the approach of the glass transition phenomenon which occurs at a much lower temperature in the AM-62 resin than in the neat resin, as indicated in Table 2.

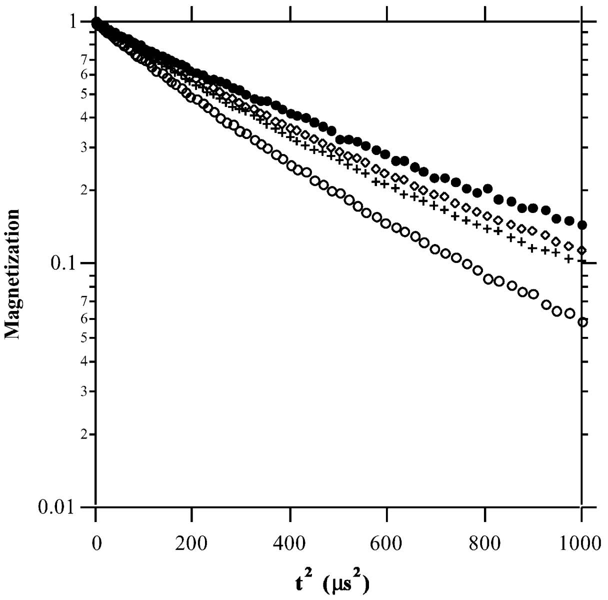

Fig. 2. ^1H FIDs of the DGEBA–DDM resin obtained at various temperatures. (○): 25 °C; (+): 69 °C; (◇): 86 °C and (●): 121 °C.

3.3. Influence of the additive nature

The ^1H FIDs were determined in the AA-62, AM-62 and AO-62 resins as a function of temperature. The separation of the FIDs into gaussian and exponential components was done as described earlier. The percentages of rigid and mobile protons, $\%H_{mobile}$ and $\%H_{rigid}$, respectively, and the spin–spin relaxation times of the two components, $T_2(H)_{rigid}$ and $T_2(H)_{mobile}$, are reported in Table 3. Below 70 °C, during the first 25 μs, each resin exhibits a quasi-Gaussian behaviour characteristic of its solid character. The $T_2(H)_{rigid}$ values, reported in Table 3, are almost similar to those obtained for the neat DGEBA–DDM resin. On the contrary, significant differences can be observed above 70 °C: on the one hand, the AA-62 ^1H FIDs are similar to their DGBEA–DDM counterparts up to 102 °C. At this temperature, $T_2(H)_{rigid}$ is shorter than 21 μs, in agreement with the behaviour of a glassy polymer. At 121 °C, on the contrary, the FID has a slower decay. The change in the time dependence of the FID, that can be separated into a fast and a significant slow component at 121 °C, is evidence for the approach of the glass transition. On the other hand, the AO-62 ^1H FIDs can be systematically analysed in terms of a fast and a slow component, corresponding to rigid and mobile protons, respectively, at temperatures higher than 65 °C. As shown by data given in Table 3, these NMR experiments indicate that the AA-62 resin mainly consists of a unique miscible phase in the temperature range investigated, with a single glass transition, which manifests itself around 121 °C in the NMR data. This result is in agreement with a previous NMR study of EPPHAA antiplasticized epoxy–amine resins [2]. In contrast with the AA-62 behaviour, the AM-62 and AO-62 systems exhibit an additional mobility below their glass transition temperature (as determined from DSC). This additional mobility is a

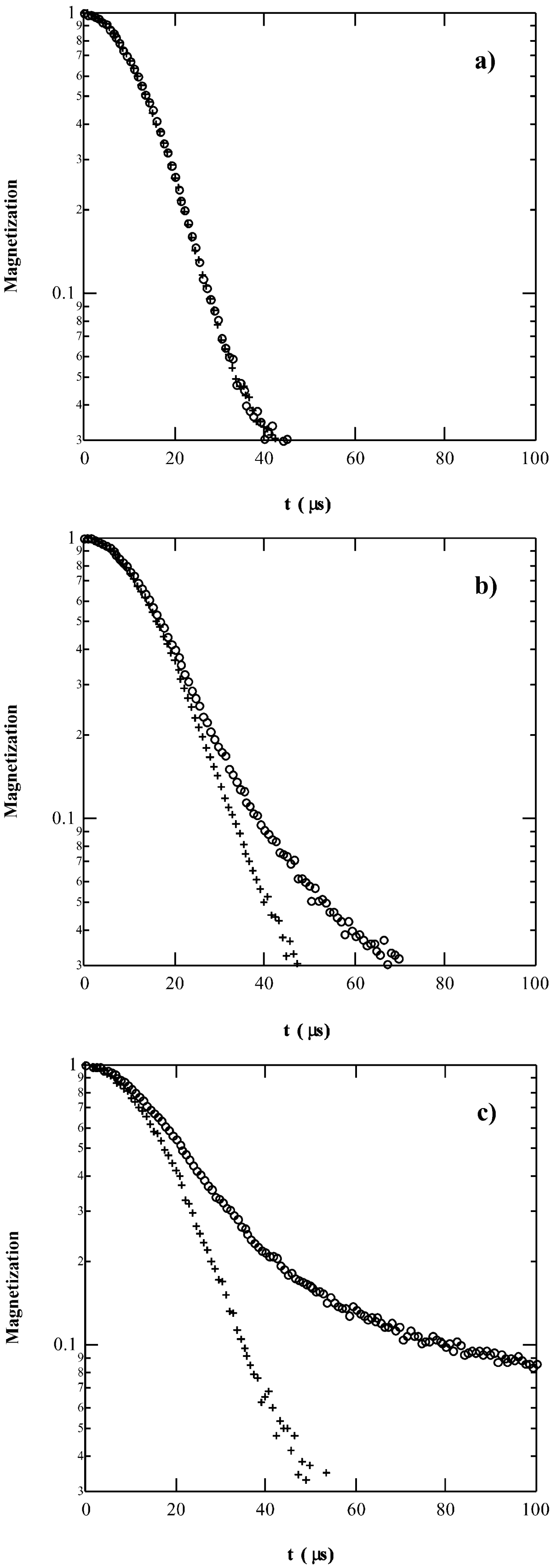

Fig. 3. Comparative study of ^{1}H FIDs: (a) 25 °C; (b) 86 °C; (c) 21 °C. (+): DGEBA–DDM (experimental data); (○): AM-62 (experimental data).

Table 3
FID characteristics as a function of temperature for the systems under study

Sample code	T (°C)	%H_{mobile}	%H_{rigid}	$T_2(H)_{mobile}$ (μs)	$T_2(H)_{rigid}$ (μs)
AA-62	25	1.0	99.0		16.9
	34	1.4	98.6		16.6
	51	1.5	98.5		18.2
	69	1.6	98.4		18.9
	86	1.8	98.2		20.0
	102	2.0	98.0		20.3
	121	8.0	92.0	100	21.5
AM-62	25	0.8	98.2		16.8
	34	2.1	97.9		17.4
	51	2.2	97.8		18.1
	69	3.1	96.9		19.1
	86	4.9	95.1	126	20.4
	102	8.7	91.3	131	21.3
	112	11.4	88.1	152	22.1
	121	14.3	85.7	194	24.0
AO-62	25	1.7	98.3		17.9
	34	1.9	98.1		17.4
	51	2.5	97.5		18.2
	69	5.3	94.7	131	19.1
	86	9.7	90.3	140	20.2
	102	15.5	84.5	196	21.6
	112	18.7	81.3	226	22.7
	121	21.9	78.1	263	24.1
AM-96	25	0.7	99.3		16.7
	34	1.1	98.9		17.5
	51	2.0	98.0		18.4
	69	4.1	95.9	103	19.2
	86	9.0	91.0	105	20.0
	102	16.4	83.6	152	21.4
	112	20.4	79.6	191	22.8
	121	23.5	76.5	244	24.2

good indication that the resins are phase-separated at the molecular scale. These conclusions are in very good agreement with previous DMA analysis [3,4].

For each resin under study, the temperature, T_0, at which 5% mobile protons were observed on the FID, is reported in Table 4. From the comparison between NMR and DMA characteristic temperatures, it can be concluded that the coexistence of regions with different mobilities, observed by NMR, is indicative of: (i) the α relaxation in AA-62 resin and of (ii) the μ relaxation in AM-62 and AO-62 resins. It should be noted that the development of mobility appears at a slightly higher temperature in NMR measurements than in DMA experiments. Indeed, according to the

Table 4
T_0 values corresponding to an amount of 5% mobile protons; $T\alpha$ and $T\mu$ values have been added for comparison

Sample code	T_0 (°C)	$T\mu$ (°C)	$T\alpha$ (°C)
AA-62	~ 115		106
AM-62	86	61	111
AO-62	67	50	110
AM-96	76	50	93

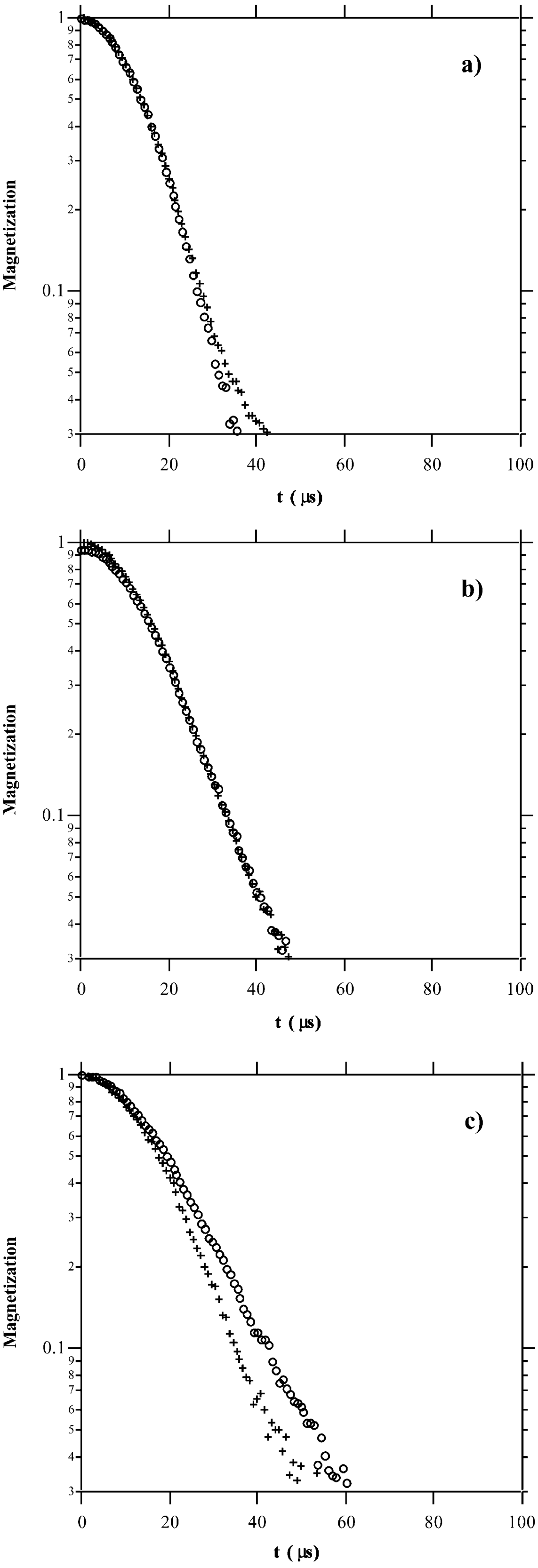

Fig. 4. Comparative study of ^{1}H FIDs: (a) 25 °C; (b) 86 °C; (c) 121 °C. (+): DGEBA–DDM (experimental data); (○): AM-62 (after subtraction of the slowly decaying component).

relaxation map of each resin [4], the frequencies associated to the characteristic temperature T_0 are of the order of 10^3 Hz whereas the DMA data were obtained at a 1 Hz test frequency.

The $T_2(\mathrm{H})_{\mathrm{rigid}}$ values are listed in Table 3 for each antiplasticized resin as a function of temperature. Though they regularly increase on increasing temperature, $T_2(\mathrm{H})_{\mathrm{rigid}}$ values remain shorter than 25 μs, which is a typical solid-like behaviour.

The $T_2(\mathrm{H})_{\mathrm{mobile}}$ values and percentages of mobile protons are plotted versus $(T - T_0)$ in Figs. 5 and 6, respectively. As shown on these figures, the characteristics of the mobile phase have the same $(T - T_0)$ dependence in the two systems considered. This result is in agreement with a WLF description [12] of the additive-rich domains above their glass transition temperature, with the assumption that the viscoelastic coefficients, C_1^{g} and C_2^{g}, associated to the μ relaxation, are independent of the additive nature within experimental accuracy.

Besides, as shown in Fig. 6, at temperatures above T_0, the amount of protons associated to the soft regions regularly increases on increasing temperature, following a similar behaviour whatever the antiplasticizer nature maybe. This continuous increase reflects the existence of a distributed composition within the resins that can be related to the width of: (i) the α relaxation for AA-62, and (ii) the μ relaxations for the AM-62 and AO-62 systems. This result corroborates the conclusions deduced from the DMA data analysis [3,4].

Furthermore, particular attention should be paid to the amount of protons contained in the soft microphases of biphasic systems below the α relaxation, as detected by NMR. Up to 112 °C in biphasic resins, the amount of mobile protons is smaller than the amount of protons belonging to the additives and reported in Table 2, which indicates that all the protons of the antiplasticizer additives are not located in the soft microphases: there is an additive-rich phase and an additive-poor phase. Moreover, according to the strictly additive character of the gaussian and exponential components of the FIDs, the samples must be sharply phase-separated.

3.4. Influence of the additive amount

In order to achieve a better understanding of the biphasic microstructure of epoxy–amine resins fully cured in the presence of non- or slightly-polar additives, variable-temperature ^{1}H FID measurements were performed as a function of the additive amount. The AM-96 resin was selected and compared to the AM-62 sample. The respective compositions and transition temperatures, as detected by DMA, are reported on Table 2 for both resins.

^{1}H FIDs obtained over the whole temperature range for the AM-96 sample are shown in Fig. 7. Above 70 °C, they exhibit a fast and a slow relaxing component which correspond to rigid and mobile protons, respectively, underlying the

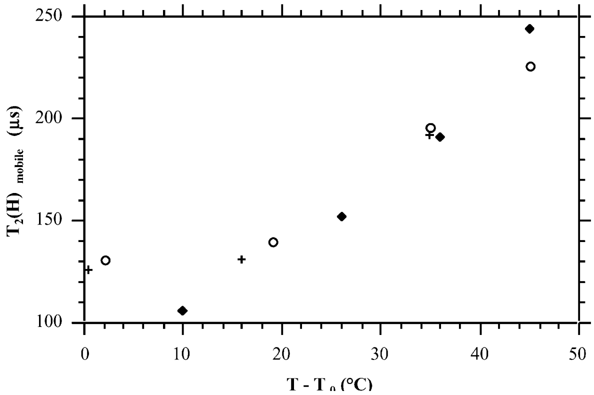

Fig. 5. Temperature dependences of $T_2(\mathrm{H})_{\mathrm{mobile}}$ in AM-62 (+), AO-62 (○) and AM-96 (◆).

biphasic character of the AM-96 resin. The values of $T_2(\mathrm{H})_{\mathrm{mobile}}$, $T_2(\mathrm{H})_{\mathrm{rigid,}}$ and the percentages of mobile and rigid protons, obtained from the FID analysis, are listed in Table 3.

In agreement with results reported in Section 3.3, the extrapolated T_0 value corresponding to 5% mobile protons, around 76 °C, is higher than the temperature of the μ relaxation detected at 1 Hz by DMA.

The spin–spin relaxation times, associated to the rigid phase, $T_2(\mathrm{H})_{\mathrm{rigid,}}$, are listed in Table 2. They are characteristic of a rigid phase behaviour over the whole temperature range covered and exhibit similar values for the AM-62 and AM-96 resins within experimental accuracy.

The variation of $T_2(\mathrm{H})_{\mathrm{mobile}}$ for both AM-62 and AM-96 samples, plotted versus $(T - T_0)$ in Fig. 5, exhibits no particular sensitivity to the additive amount. This result is in agreement with the fact that, as a first approximation, the μ relaxation obeys the classical WLF equation with C_1^{g} and C_2^{g} coefficients that do not depend on the exact amount of antiplasticizer introduced in the network.

Fig. 6 shows the dependence of the percentage of mobile protons as a function of $(T - T_0)$. While both curves exhibit a regular increase above T_0, there is a faster increase in the percentage of mobile protons when the concentration of additives is increased in the resin. This observation can be related to the more dissipating character, as observed by DMA, of the μ relaxation in the AM-96 sample than in the AM-62 sample.

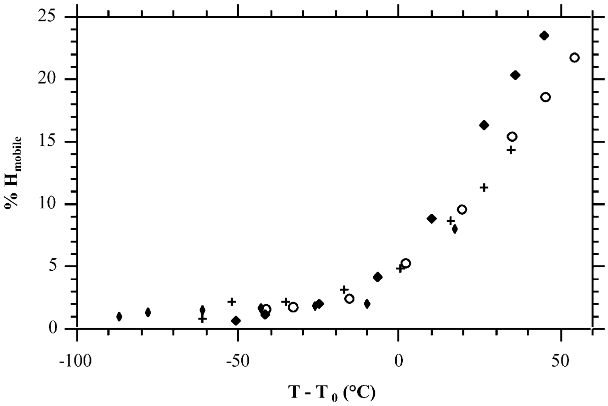

Fig. 6. Temperature dependences of the amount of mobile protons in AA-62 (♦), AM-62 (+), AO-62 (○) and AM-96 (◆).

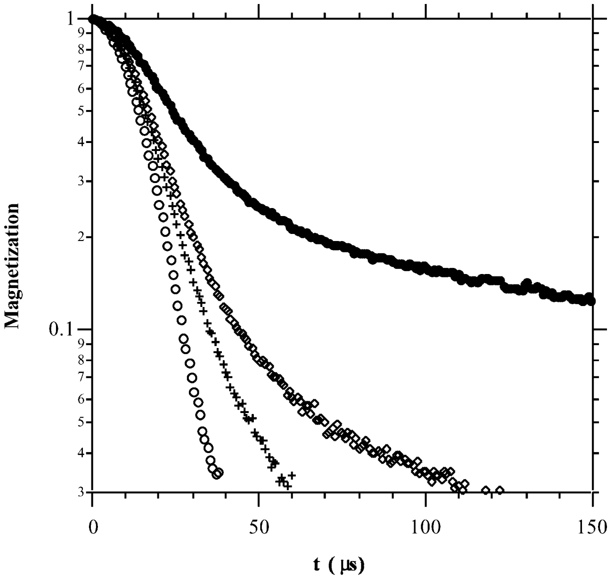

Fig. 7. ^{1}H FIDs of the AM-96 resin obtained at various temperatures: (○): 25 °C; (+): 69 °C; (◇): 86 °C and (●): 121 °C.

4. Conclusions

The EPPHAA antiplasticized resin exhibited a solid-like behaviour at temperatures below its unique glass transition temperature. Since the additives share rather strong interactions with the densely cross-linked matrix and the additive length is of the order of the length of a matrix unit, no further mobility could allow additives to phase-separate at high temperatures, while being fully miscible with the matrix at low temperatures (LCST-type behaviour). The NMR investigations of neat and antiplasticized DGEBA–DDM showed that each fully cured resin exhibits a solid-like behaviour at low temperatures. In contrast, two phases—with different mobilities—were observed in the temperature range between $T\mu$ and $T\alpha$ in resins containing non-polar or slightly-polar antiplasticizers. Therefore, the additional mobility observed below glass transition temperature in resins with high toughness and modulus indicated their biphasic character at the molecular scale. These NMR experiments support the assignment of the two transitions observed by DMA, $T\alpha$ and $T\mu$, to the glass transitions of additive-poor and additive-rich phases, respectively. Moreover, within the sensitivity of the NMR technique, it may be concluded that resins including AM or AO antiplasticizers are sharply phase-separated, a conclusion which could not be drawn from the DSC technique.

As expected, the proportion of each phase depends on the amount of AM antiplasticizing molecules.

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