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Dynamic mechanical investigations of the effects of water sorption and physical ageing on an epoxy resin system

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Abstract

After immersion (3 months) in distilled water, the epoxy–amine (diglycidyl ether of Bisphenol A–4,4′-methylene bis[3-chloro-2,6-diethylaniline], DGEBA–MCDEA) samples were mounted on the dynamic mechanical analyser where the thermal ageing treatment was performed. The influence of both hydrothermal and physical ageing on the viscoelastic properties of DGEBA–MCDEA network was investigated.

Three relaxational processes were evidenced on the mechanical spectra (at 1 Hz) of the samples: the main relaxation (α) at higher temperatures, the secondary relaxation (β) at lower temperatures, and the intermediate ω-relaxation between 300 and 350 K.

The β-relaxation mode was found bimodal, mainly affected by the water sorption, and unconcerned by the structural recovery following the thermal ageing treatment. On the opposite, the viscoelastic characteristics of the ω-relaxation were significantly affected by each step of both hydrothermal and thermal ageing treatments.

Keywords: Epoxy–amine network; Hydrothermal and physical ageing; Viscoelasticity

1. Introduction

Epoxy resins are widely used as matrices for structural composite materials, adhesives, and organic coatings due to their good mechanical properties. Obviously, the knowledge of the evolution of their long-term performance under deleterious conditions is of primary importance. Consequently, numerous studies have been devoted to the relaxations of epoxy–amine systems in the glassy state. However, despite the number of reports and reviews available in the literature, the understanding of the connection between the chemical structure and the mechanical properties of these materials remains limited, sometimes contradictory. Such a point reflects the complexity of the commercial formulations, which are well known to exhibit a complex chemical structure resulting from the addition of epoxy groups onto amine functions.

The mechanism and kinetics of the epoxy–amine curing reaction have been accurately analysed. It is usually reported [1,2] that three principal reactions take place (Fig. 1). The first step, which corresponds to the reaction of the primary amine hydrogen with the epoxy group, is followed by the secondary amine hydrogen reacting with another epoxy group (second step). The occurrence of the etherification reaction (third step) depends on the temperature as well as on the basicity of the diamine. It is generally accepted that the curing reaction occurs by two competitive mechanism: one (rate constants k_1 and k_2) is catalysed by the hydroxyl groups (initially present in the epoxy prepolymer and those generated during the reaction), and the other (rate constants k_1' and k_2') is a non-catalytic mechanism identified by a second-order reaction. As a result of the difficulty to form the complex of ternary transition, the catalytic mechanism vanishes at high temperatures, whereas the non-catalytic reactions take place over the whole temperature range. In addition to the product of these three main reactions, it is often considered that the final network architecture also includes unreacted epoxy and amine functions, and hence dangling chains as well as chemical units due to side reactions. Obviously, the overall mechanical properties of epoxy–amine networks, as well as their long-term performance, are strongly dependent on such details of the chemical structure.

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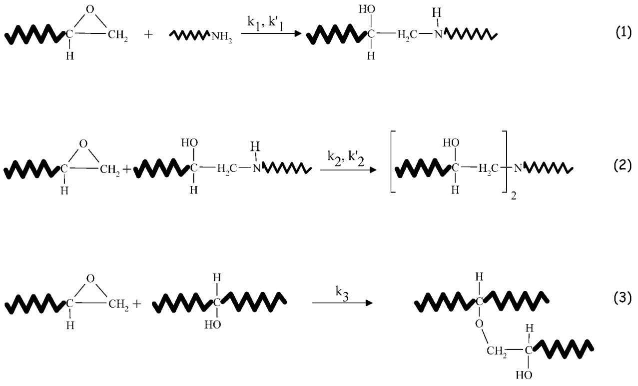


Fig. 1. Principal chemical reactions in epoxy–amine systems.

On the one hand, it is known that these properties can suffer substantial losses following water sorption, which usually cause plasticisation and diminish the mechanical properties. So, both water sorption and water transport in epoxy systems are of great importance [3–26] and have been studied by various characterisation techniques including IR [3,4,7,13], NIR [13], UV [14], NMR [15], dielectric [5,16,17] and dynamic mechanical spectroscopies [3,5,9,16, 18–25]. These studies suggest that the water transport is related to the availability of molecular-sized holes in the polymer structure and the polymer–water affinity. Obviously, the availability of holes mainly depends [18] on the polymer structure, morphology and crosslink density. Furthermore, the polymer–water affinity is related to the presence of hydrogen-bonding sites along the polymer chains, which create attractive forces between the polymer and the water molecules. By studying the nature of epoxy/ water molecule interactions, Apicella et al. [3,26] proposed three different modes for the water sorption of epoxy systems:

- bulk dissolution of water in the polymer network,
- moisture sorption onto the surfaces of holes that define the excess of free volume of the glassy structure, and
- hydrogen bonding between hydrophilic groups of the polymer and water.

As a result, it was also reported [3–5,9,11,14–19] that in epoxy compounds, water exists in two distinct forms: ‘free’ water that fills the microcavities of the network and ‘bound’ water in strong interactions with polar segments.

On the other hand, as amorphous solid materials, epoxy resins are affected by physical ageing [27–29], whose mechanism (1) is assigned to intrinsic phenomena associated with changes of the molecular conformation that occur within the material relaxation times, and (2) depends on the distance to the equilibrium state of the sample when cooled below the glass transition temperature. The free volume decreases over the course of time as a consequence of the tendency of the material to approach the equilibrium state. Obviously, this gradual approach to equilibrium affects [27–33] many properties and is strongly influenced by the preparation as well as the thermal history of the samples. Precisely, for epoxy systems [28,30–33], this phenomenon has been reported as leading to the increase of the density, loss of ductility and decreases of both mechanical damping and stress-relaxation rates.

The goal of the present work is to provide an academic investigation of the influence of both water sorption and physical ageing on the viscoelastic behaviour of an epoxy–amine network.

2. Experimental

2.1. Material

Suppliers and characteristics of the chemicals used in the paper are summarised in Table 1. The epoxy prepolymer, diglycidyl ether of Bisphenol A (DGEBA) with a low dispersity index ($n = 0.03$), was used. The 4,4′ methylene bis[3-chloro-2,6-diethylaniline] (MCDEA) was used as hardener (stoichiometric ratio amino-hydrogen-to-epoxy equal to 1). The cure schedule was 7 h at 408 K followed by post-curing at 458 K for 2 h. The synthesis of the model epoxy network, i.e. the reaction kinetics and further characterisation, was detailed previously [34].

2.2. Characterisation

Differential scanning calorimetry (DSC) analysis was carried out in a DSC 7 Perkin Elmer device. DSC thermograms were recorded under a nitrogen atmosphere from 433 to 483 K. Measurements of the glass transition temperatures and heat flow were conducted at a heating rate of 10 K/min.

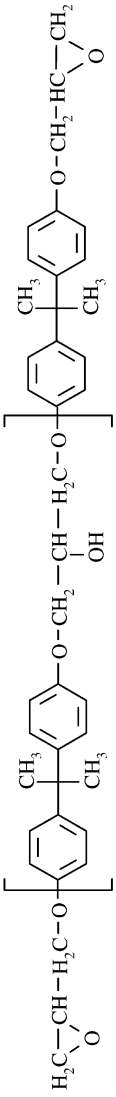
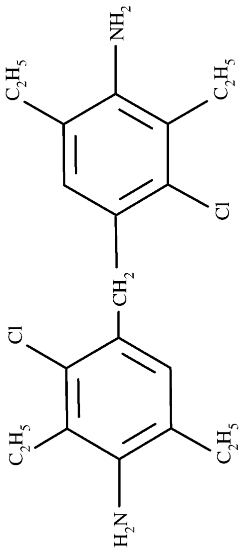
The dynamic mechanical properties of the samples were determined using the analyser Rheometric Scientific DMTA MK III. The viscoelastic spectra were recorded from 143 to 523 K, with a heating rate of 1 K/min under a nitrogen atmosphere. The apparatus was used in a double cantilever mode under isochronal conditions at frequencies of 0.3, 1, 3, and 10 Hz. The samples were approximately 1 mm thick, 6 mm wide, and 27 mm long.

2.3. Presentation of hydrothermal and thermal ageing treatments

The influence of both water and physical ageing on the viscoelastic behaviour of DGEBA–MCDEA network was simultaneously investigated. First, the samples were immersed in distilled water, then mounted on the dynamic mechanical analyser, where the thermal ageing treatment was further performed.

Hydrothermal ageing. The samples were placed 3 months, into distilled water, at ambient temperature. They were weighed periodically using a digital balance (0.1 mg resolution) to determine weight change: it was found that

Table 1
Characteristics of the reactants used

Reactants	Chemical formula	Supplier and characteristics
Diglycidyl ether of bisphenol A, DGEBA $\bar{n} = 0.03$		Dow chemicals DER332 $\bar{M}_n = 348.5\ \mathrm{g\ mol^{-1}}$ $T_{\mathrm{melting}} = 320\ \mathrm{K}$
(4,4′-Methylene bis[3-chloro-2,6-diethylaniline], MCDEA)		LONZA $\bar{M}_n = 380\ \mathrm{g\ mol^{-1}}$ $T_{\mathrm{melting}} = 365\ \mathrm{K}$

after 3 months in water, the samples reached a maximum water gain (0.8 wt%).

Thermal ageing treatment. DSC experiments were used to define the different temperatures concerning the thermal treatment. First, the glass transition temperature, T_g, of the DGEBA–MCDEA network was found at 448 K (onset), and neither an exothermal peak (during the first heating) nor an increase of T_g (during a second heating) was observed. As a result, the epoxy system can be considered as fully reacted (i.e. 448 K is the maximum T_g), and it can be reasonably expected that the thermal treatment based on the following temperatures

- 468 K ($T_g + 20$ K) as a temperature for which the samples are refreshed,
- 428 K ($T_g - 20$ K) as a temperature which leads to structural recovery (physical ageing),

will not induce any chemical changes in the network. Similarly to the choice of both 'refreshing' and 'ageing' temperatures, the samples will be denoted as:

- 'as received' for samples without any hydrothermal or thermal treatment after curing;
- 'wet' for as received samples immersed 3 months in water at ambient temperature;
- 'refreshed' for wet samples treated 30 min at $T_g + 20$ K in the furnace of the DMTA, under nitrogen atmosphere, and then cooled down to 143 K at about 15 K/min;
- 'aged' for refreshed samples treated, under nitrogen atmosphere, for 45 h at $T_g - 20$ K and then cooled down to 143 K with a cooling rate of 1 K/min.

A schematic representation of the hydrothermal and thermal ageing treatments is given in Fig. 2. In addition, the DSC scans of the as received DGEBA–MCDEA sample as well as those obtained after both refreshing and ageing thermal treatments are shown in Fig. 3. Thus, an endothermal peak near the onset of the transition from the glassy state to the rubbery state can be seen on the DSC scans for as received and aged samples. Such an occurrence is well known [10] to reflect the thermoreversibility of the 'physical ageing' phenomenon. This observation also confirms the availability of the chosen thermal ageing treatment.

3. Results and discussion

3.1. Viscoelastic behaviour of the DGEBA–MCDEA network

Fig. 4 gives the experimental dynamic mechanical values of the storage modulus (E') and the loss factor ($\tan\delta$) at 1 Hz for the as received DGEBA–MCDEA sample. With an

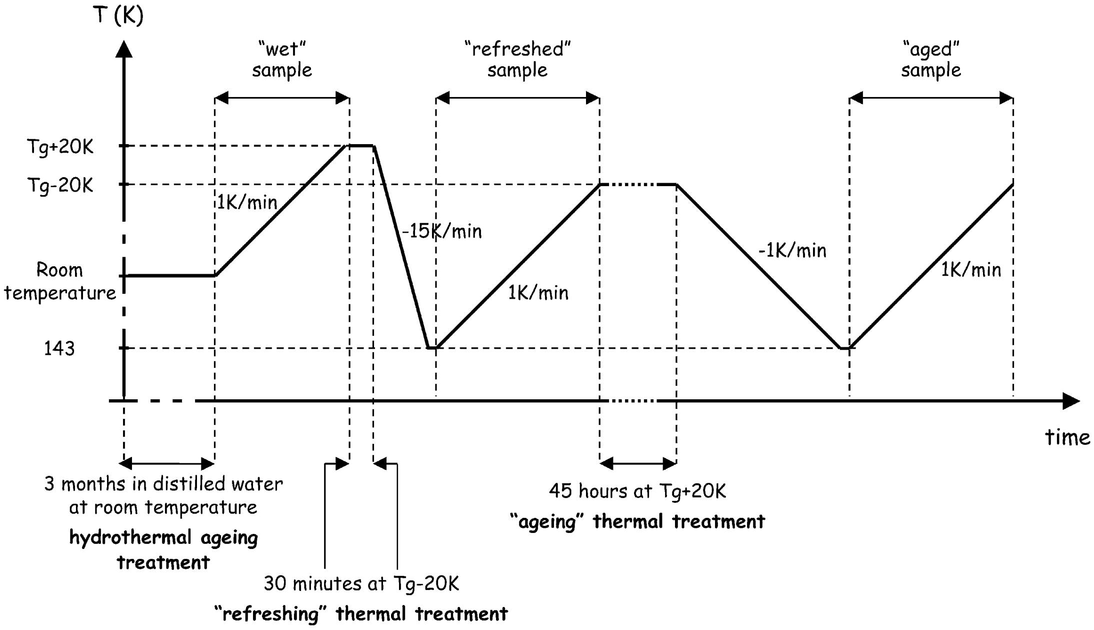


Fig. 2. Schematic representation of hydrothermal and thermal ageing treatments.

increasing temperature, three relaxational processes are evidenced below.

Around 203 K, the first maximum of the tan δ values (at 1 Hz) corresponds to the β-relaxation mode. This secondary relaxational process is associated [19–22,25,31] with motions of small units of the macromolecular chains. In the case of epoxy diamine networks, the β-relaxation was attributed [31] to the sum of localised motions of the glycerol groups and the diphenylpropane units in the network chains. In addition, it is often reported [19,22,25] that motions of the hydroxyether groups are located at higher temperatures than those of the diphenylpropane units.

A slight relaxational process is detected between 300 and 350 K at 1 Hz. There are numerous papers [3–5,7,19–25,31] dealing with the observation of such an intermediate relaxation mode, so-called ω-relaxation, on the viscoelastic spectra of epoxy resin-based composite materials. Unfortunately, in spite of all these investigations, the assessment of the ω-relaxation in terms of molecular mobility remains uncertain. As a matter of fact, in the past, the ω-relaxation was attributed [23,24] to unreacted molecular segments, chain ends and inhomogeneities in the network arising from regions of dissimilar densities of crosslink points. However, nowadays, the epoxy–amine networks are better controlled and well known to be homogeneous [16,17,34]. Other authors associated [22] the ω-relaxation with motions of the *p*-phenylene groups, whereas the intermediate relaxation was also considered [3,5,7,16,17] as a probe of the microstructural rearrangements within the network following the moisture sorption. Thus, the ω-relaxation was reported as significantly sensitive to the moisture sorption: especially, in the presence of water, the increase of the

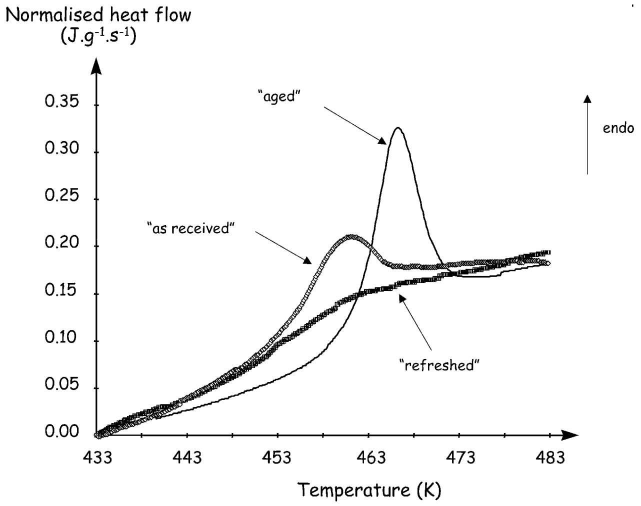


Fig. 3. DSC scans of as received, refreshed and aged DGEBA–MCDEA samples.

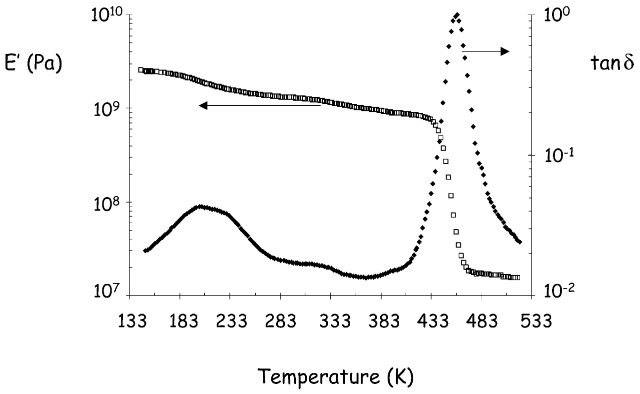


Fig. 4. Viscoelastic properties (storage modulus, E', and loss factor, tan δ) versus temperature at 1 Hz for as received DGEBA–MCDEA samples.

intensity of the corresponding tan δ peak on the viscoelastic spectra was observed.

At higher temperatures, the α-relaxation mode—associated with the glass transition—can be observed at about 459 K (maximum of tan δ values at 1 Hz).

In addition, since our dynamic mechanical experiments were performed in the multifrequency mode (frequency range from 0.3 to 10 Hz), the apparent activation energies of both the main (α) and the secondary (β) relaxations were estimated by considering an Arrhenius dependence of the relaxational processes. The corresponding values (550 ± 50 and 70 ± 2 kJ/mol, respectively) are close to existing data for various epoxy networks in Refs. [19,21,25]. Unfortunately, such estimation was not available for the apparent activation energy of the ω-relaxation, the intensity of the corresponding tan δ peak being too weak to accurately determine the shift of the temperature location of the maximum value with an increasing frequency.

3.2. Consequences of the hydrothermal ageing treatments—influence of water sorption

The dynamic mechanical spectra of the loss factor tan δ (at 1 Hz), for both as received and wet DGEBA–MCDEA samples are given in Fig. 5. The influence of the hydrothermal ageing treatment on the viscoelastic characteristics of the β- and the ω-relaxations is well evidenced. On the one hand, a significant increase of the magnitudes of their corresponding tan δ peaks can be noticed. On the other hand, whereas the width of the tan δ peak corresponding to the ω-relaxation mode is slightly enlarged in presence of water, the splitting of the tan δ peak corresponding to the δ-relaxation mode is strongly amplified.

In order to further explore these results, Fig. 6 shows the difference of the tan δ spectra of the as received and the wet DGEBA–MCDEA samples. First, this representation of the viscoelastic data makes easier the determination of the temperature location of the maximum (around 304 K) of the tan δ peak associated with the ω-relaxation. Subsequently, such a plot is even more relevant in the case of the β-relaxation. As a matter of fact, the spectral difference (Fig. 6) clearly points out the presence of two distinct contributions: one at lower temperatures (around 190 K), the other at higher temperatures (around 246 K). It is interesting to note that such bimodal aspect of the secondary relaxation does not simply result from the presence of water, since a slight splitting of the corresponding tan δ peak was already noticeable on the dynamic mechanical spectrum of the as received sample (Fig. 5). Nevertheless, the presence of sorbed water in the DGEBA–MCDEA network highlights the presence of two distinct relaxational processes. Although numerous studies have been devoted to the relaxations of the epoxy–amine networks, the bimodal aspect of the β-relaxation is rarely reported. In contrast, the β-relaxation is always observed in the viscoelastic spectra of epoxy systems, whatever the complexity of the chemical structure of the network. As a consequence, the motions of the hydroxypropylether units, $O{-}CH_2{-}CHOH{-}CH_2$, must be associated to the β-relaxation, since they are present in all the epoxy systems (as illustrated in Fig. 1). On the basis of the conclusions of a recent investigation [25], including both ^{13}C NMR and mechanical spectrometry, the motions of the hydroxyether groups are considered here as responsible for the contribution occurring at lower temperatures, around 190 K. Concerning the attribution of the high temperature part of the β-relaxation, the situation is more complex, since several motions with various origins, such as the so-called ‘DGEBA-ring flip’ [25] or the existence of cooperative modes [17,18,25] implying several units, might be considered. Indeed, to support our discussion, it has been reported [17,25] that the β-relaxation is broader and more intense in networks prepared in presence of secondary amines than in systems with a same crosslink density by using primary amines. This result was interpreted in terms of motions that have higher intramolecular cooperativity than the cooperativity developed in networks incorporating pending hexamethylene units and a lower spatial extent than the one observed in densely crosslinked networks.

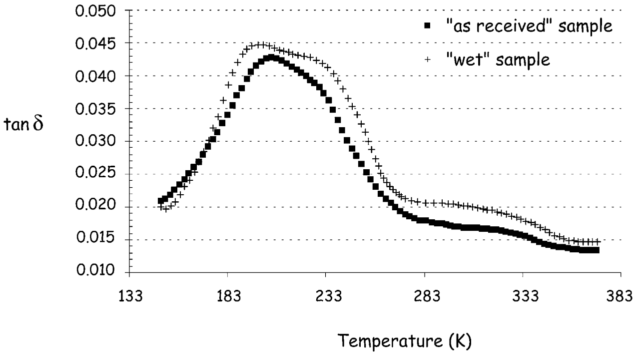


Fig. 5. Loss factor tan δ versus temperature at 1 Hz for as received (■), and wet (+) DGEBA–MCDEA samples.

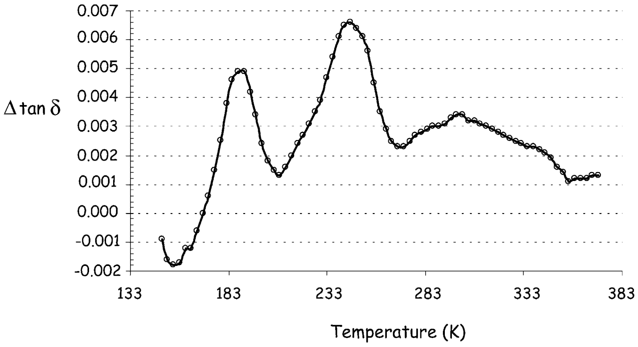


Fig. 6. Difference of tan δ spectra of as received and wet DGEBA–MCDEA samples versus temperature at 1 Hz.

As a partial conclusion related to the influence of the hydrothermal ageing treatment, it can be here suggested that the water acts as a plasticiser into the DGEBA–MCDEA network. As a result, the molecular mobility of the smallest units of the network significantly increases, amplifying the

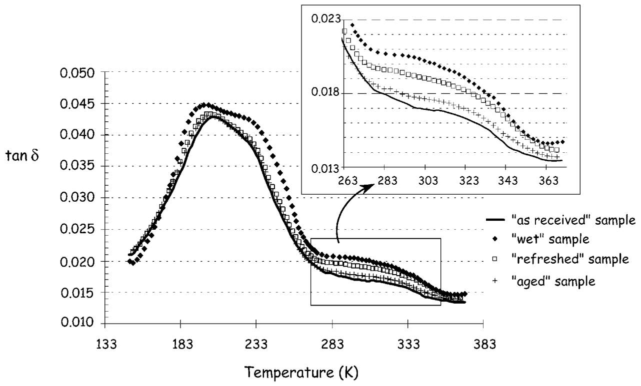


Fig. 7. Loss factor tan δ at 1 Hz versus temperature for the various DGEBA–MCDEA samples during hydrothermal and thermal ageing treatments.

magnitude of both β- and ω-relaxations on the dynamic mechanical spectra. Furthermore, although reflecting the bimodal aspect of the β-relaxation, the splitting of the tan δ peak—associated to the secondary relaxation—can be considered as a probe of the sorbed water.

3.3. Consequences of the thermal refreshing and ageing treatments—influence of physical ageing

Now, it is of interest to investigate the influence of the overall thermal ageing treatment on the viscoelastic characteristics of the β- and ω-relaxations. Fig. 7 gives the dynamic mechanical spectra of the loss factor tan δ (at 1 Hz) for all the samples, denoted as as received, wet, refreshed and aged DGEBA–MCDEA samples, respectively (Fig. 2).

On the one hand, it can be seen that the thermal ageing treatment does not seem to affect the β-relaxation mode. As a matter of fact, as soon as the end of the refreshing treatment (i.e. for the refreshed and the aged samples), the magnitude as well as the temperature location of the secondary relaxation are both found to become close to that of the as received DGEBA–MCDEA sample. Such step-by-step observations are supported by previous discussions [27, 29–31,33] indicating that the physical ageing phenomenon slightly affects the molecular mobility at short distances in most of the amorphous materials. The β-relaxation mode of the DGEBA–MCDEA epoxy–amine network appears, therefore, clearly affected by the sorption of water but remains unconcerned about the volume recoveries following the thermal ageing treatment. In addition, such results also reveal that the effects of sorbed water on the viscoelastic characteristics (i.e. magnitude, temperature location) of the β-relaxation are reversible, at the observation scale of the mechanical spectrometry.

On the other hand, Fig. 7 also shows how the viscoelastic characteristics of the ω-relaxation are influenced by each step of the thermal treatment. A further exploration of the temperature range of the relaxation can be done by means of the enlargement of the loss factor spectra, given in the top right corner of Fig. 7. Thus, it can be noticed that the magnitude of the ω-relaxation gradually decreases when the physical ageing acts. Although the main modifications of the loss factor spectra are found for the refreshed DGEBA–MCDEA sample, such observations lead us to the conclusion that the ω-relaxational mode is not only influenced by the water sorption, but also by the physical ageing phenomenon.

4. Conclusion

In this paper, the influence of both hydrothermal and physical ageing on the viscoelastic behaviour of the DGEBA–MCDEA epoxy–amine network was investigated.

With an increasing temperature, three relaxational processes were found on the dynamic mechanical spectra (at 1 Hz) of the as received DGEBA–MCDEA sample: the secondary β-relaxation at lower temperature (203 K), the intermediate ω-relaxation (between 300 and 350 K), and the main α-relaxation at higher temperature (459 K).

As a result of the plasticisation effect of the water in the epoxy–amine network, the molecular mobility of the smallest units of the wet DGEBA–MCDEA sample significantly increased, amplifying the magnitude of both β- and ω-relaxations on the dynamic mechanical spectra.

The β-relaxation mode was found bimodal and mainly affected by the water sorption, whose influence on the viscoelastic characteristics of the secondary relaxation remains, however, reversible. On the opposite, both hydrothermal and thermal ageing treatments were found to significantly influence the viscoelastic characteristics of the ω-relaxation.

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