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► **To cite this version:**

Romain Delannoy, Emmanuel Richaud, Vincent Tognetti, Blandine Quélenec, Laurent Delbreilh, et al.. Macromolecular Mobility Changes Induced by Thermal Aging of Epoxy-amine Polymer Networks. Macromolecular Symposia, 2022, Times of Polymers and Composites (TOP), 405 (1), pp.2100228. 10.1002/masy.202100228 . hal-04072695

HAL Id: hal-04072695

<https://hal.science/hal-04072695>

Submitted on 18 Apr 2023

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Macromolecular Mobility Changes Induced by Thermal Aging of Epoxy-amine Polymer Networks

Romain Delannoy,* Emmanuel Richaud, Vincent Tognetti, Blandine Quélenec, Laurent Delbreilh, and Nicolas Delpouve

Changes in macromolecular mobility during the thermal oxidation of epoxy-amine thermoset networks are addressed in this study. Three epoxy-amine systems, cured with DGEBA and three similar aliphatic hardeners – ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine (TETA) – aged at 160°C are characterized by dynamic mechanical analysis (DMA). Results show a split of the single initial α relaxation peak with aging, which may imply that chain scissions are preferred at certain oxidizable sites in the network. A β relaxation can be identified around -60°C and does not seem to evolve much with aging, while another sub-glass transition around 30°C decreases with it. Implications of this work both with mechanical fracture properties and with segmental mobility of radical chemical functions involved in bimolecular oxidation reactions have yet to be confirmed.

1. Introduction

Commonly used as a matrix for coatings or fiber-reinforced composite materials, epoxy resins are widely used for their lightweightness, easiness to process, and barrier properties. The thermal oxidation of such resins induces a degradation of their properties, which has been studied over the past decades to predict their lifetime. Previous studies focused on identifying the main degradation trackers, and the structure-properties relationships between oxidation, macromolecular changes, and embrittlement. Pile-up of oxidized products is expected to occur during aging, which depending on the network may lead to a loss of rupture at break properties and

ductility with aging.^[1,2] Relationship between the changes in macromolecular mobility – especially for sub-glass relaxations – and mechanical properties have yet to be thoroughly understood, and recent work have demonstrated the direct correlation between modulus, yield strain, and sub-glass relaxation area.^[3]

2. Experimental Section

Three epoxy-amine systems were obtained from the same epoxide prepolymer DGEBA, cured with three similar amine hardener components, namely, ethylenediamine (EDA, with AHEW 15.0 g eq⁻¹), diethylenetriamine (DETA, with AHEW 20.6 g eq⁻¹), and triethylenetetramine (TETA, with AHEW 24.4 g eq⁻¹) (Figure 1). D.E.R. 332 with EEW 171–175 g eq⁻¹ (provided by Sigma-Aldrich) was chosen to obtain a tightly woven network and a well-defined chemical environment for the oxidizable sites it presents, assuming a single unit of DGEBA is expected between amine crosslinks.

The blends were then set to thicken for up to 3 h in closed vials to avoid any potential hardener evaporation. Epoxy films of about 300 μm – to avoid diffusion-limited oxidation^[4] – were then manufactured using a heating hydropress for 1 h at 50°C, and 1 h at 90°C, and finally post-cured during 30 min at 170°C under vacuum (over the expected glass transition of the polymer). Aging was carried out at 160°C under aerated ovens for up to 20 h.

To ensure the epoxy-amine systems were properly cured (Figure 1), differential scanning calorimetry (DSC) was performed at 10°C min⁻¹ to confirm the absence of any residual exothermic curing peak and to characterize glass transition of unaged

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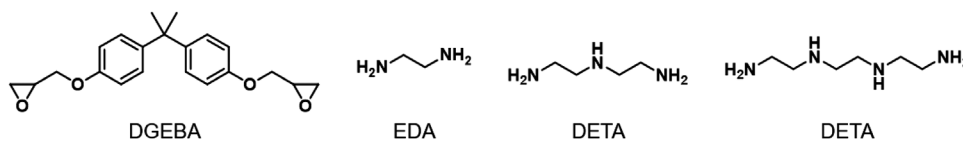


Figure 1. Structure of prepolymers used for the formation of epoxy-amine networks.

Table 1. Identification of unaged epoxy-amine glass transitions.

System	EEW/AHEW ratio	Curing enthalpy [J g^{-1}]	Glass transition temperature [$^{\circ}\text{C}$]	α relaxation temperature [$^{\circ}\text{C}$]	Semi-empirical glass transition temperature [$^{\circ}\text{C}$]
DGEBA-EDA	11.7	449.9	143	145	125
DGEBA-DETA	8.5	531.4	147	147	126
DGEBA-TETA	7.2	436.9	149	147	127

samples. It was carried out using a TA Instruments© DSC Q10 with samples of about 15 mg.

FTIR spectroscopy was subsequently used to check for the disappearance of epoxides and the absence of pre-oxidation before aging (Figure 1), and to assess the pile-up of oxidized products with aging. It was carried out in transmission mode using a Frontier spectrophotometer (PerkinElmer) on films with thickness of up to 50 μm by averaging eight scans at a resolution 4 cm^{-1} between 400 and 4000 cm^{-1} .

Tensile tests were carried out to assess the mechanical properties with aging using an Instron 5881 machine equipped with a 100 N cell, in a controlled environment of 23 $^{\circ}\text{C}$. Dumbbell-shaped samples with effective section of 10 mm in length and 2 mm in width were tested – with thickness not exceeding 100 μm – at a crosshead speed of 1 mm min^{-1} .

Mobility changes were followed with dynamical mechanical analysis (DMA) using a TA Instruments DMA Q800 in tension mode on rectangular samples with effective section of about 2.5

$\times 0.3 \text{ mm}^2$. Tests were carried out at 0.15% strain between -110 $^{\circ}\text{C}$ and 200 $^{\circ}\text{C}$. Points were acquired with temperature ramps of 3 $^{\circ}\text{C min}^{-1}$ at 1 Hz, and a nitrogen flow was used throughout every test to avoid any oxidation during the analysis.

3. Results and Discussion

Glass transition for all three unaged epoxy-amine systems can be identified around 150 $^{\circ}\text{C}$ both with DSC at 10 $^{\circ}\text{C min}^{-1}$ on the second temperature ramp, and DMA with loss modulus maxima at 3 $^{\circ}\text{C min}^{-1}$ and 1 Hz (Table 1), which was confirmed by semi-empirical calculations.^[5]

Below 100 $^{\circ}\text{C}$, two sub-glass relaxations are exhibited by the loss factor plots (Figure 2) for the three epoxy-amine systems. Although hardly visible for DGEBA-EDA, the asymmetry of the relaxation peak suggests an overlapping secondary peak can be observed.

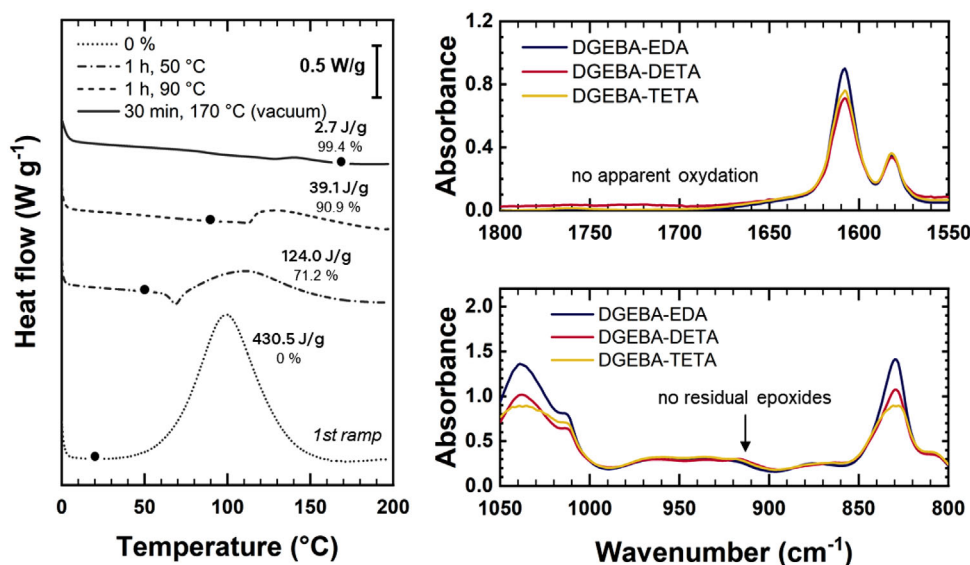


Figure 2. Curing process analysis. (left) DSC ramps at 10 $^{\circ}\text{C min}^{-1}$ after each step show the disappearance of an exothermic curing peak – (right) FTIR spectroscopy show the absence of carbonyl groups between 1650 and 1750 cm^{-1} , and the disappearance of epoxide groups around 910 cm^{-1} .

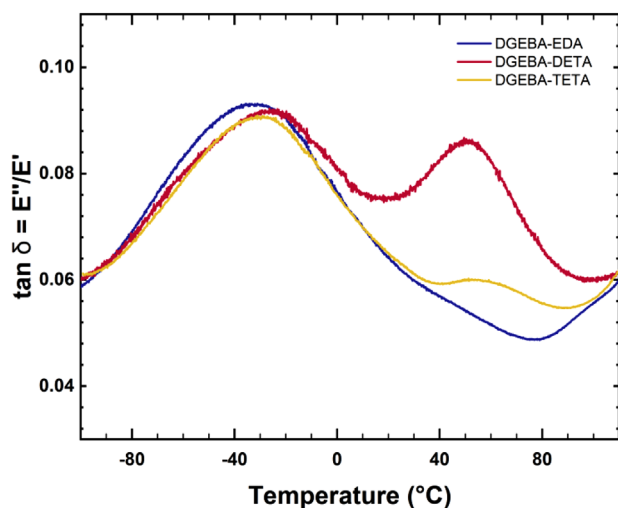


Figure 3. Sub-glass relaxations exhibited between -100°C and 100°C by dynamic mechanical analysis of epoxy-amine systems.

Of the two relaxations, one can be identified as the so-called β relaxation – which is clearly defined with maxima around -30°C – that can be attributed to the hydroxypropyl ether unit motions and aromatic ring flips.^[4] A second relaxation, hereby noted β^* , is observed around 50°C , with origin still undefined although some authors suggest it be the result of chain motions in highly crosslinked areas in the network.^[6]

After 20 h, the samples are expected to be brittle with loss of strain at break caused by oxidative aging (Figure 3). Although the analysis of the molecular network structure through aging shows the progressive pile-up of amide groups – which appear to be the main oxidized products – up to 40 h of aging, the mechanical properties at break seem to drastically decay after only 8 h. This may indicate that tracking of the oxidation through the pile-up of oxidized products may not be sufficient for understanding the rupture behavior of the studied epoxy-amine systems. As such chain mobility changes were then studied with dynamic mechanical analysis.

After aging, the dynamic response of DGEBA-DETA at $3^{\circ}\text{C min}^{-1}$ and 1 Hz (Figure 3) shows a clear split of the initially single α relaxation peak as displayed by the loss modulus plots. The peak around 150°C progressively disappears, and another at lower temperatures appears and evolves towards lower temperatures. This indicates that the network tends to overgo chain scissions rather than crosslinking with oxidation.

After aging, dynamic response analysis was conducted on DGEBA-DETA samples aged for up to 20 h with temperature

ramps of $3^{\circ}\text{C min}^{-1}$ and at 1 Hz (Figures 4 and 5). First observation would be the decrease of the rubbery plateau above the glass transition temperature on storage modulus plots, indicating that we observe a decrease in crosslink density, and as such oxidation mainly operate through chain scissions of the polymer network rather than crosslinking. Loss modulus plots, on the other hand, show a clear split of the initially single α relaxation peak. The peak around 150°C progressively decreases in intensity, and another at lower temperatures appears, increases, and evolves toward lower temperatures as aging progresses.

Looking at sub-glass relaxations, one can observe that the β relaxation centered around -30°C slightly increases in size with aging. The β^* relaxation centered between 50°C and 70°C appears to decrease in intensity through aging. One should also note that the β^* relaxation peak is greatly influenced by the overlapping of neighboring peaks, especially by the α relaxations at longer aging times. The prospect of finding the origin of the loss of this specific mobility is crucial for a better understanding of the mechanisms of rupture in aged polymer networks.

Such behavior may indicate that a population of elastic chains initially present in the network see their mobility shift as chain scissions caused by oxidation operate at preferred oxidizable sites in the molecular structure. As the β relaxation attributed to the mobility of hydroxypropyl ether units appears to increase with aging, it may indicate that scissions are unlikely occurring in these network sections. On the other hand, one could imagine that if chain scissions are more likely to occur within $-\text{C}_2\text{H}_4-$ hardener nodes, the local mobility of hydroxypropyl ether groups increases as local crosslinking is severely depleted. As such, the global mobility of the network may exhibit two mobile populations of populations, exhibited by the split of the α relaxation, as if it were a copolymer.

4. Conclusion

During thermo-oxidative aging, epoxy-amine samples tend to overgo chain scissions in the network allowing for a shift in macromolecular mobility. As such, aged samples exhibit a unique behavior with the appearance of at least two populations of chains with different mobility, that may be caused by scissions in preferred portions of the network. Involvement of this work on the changes of mechanical properties is to be discussed. Further examinations of a possible link between sub-glass transitions and segmental mobility of radicals may allow for a better understanding of the kinetics of some bimolecular reactions involved in oxidation.

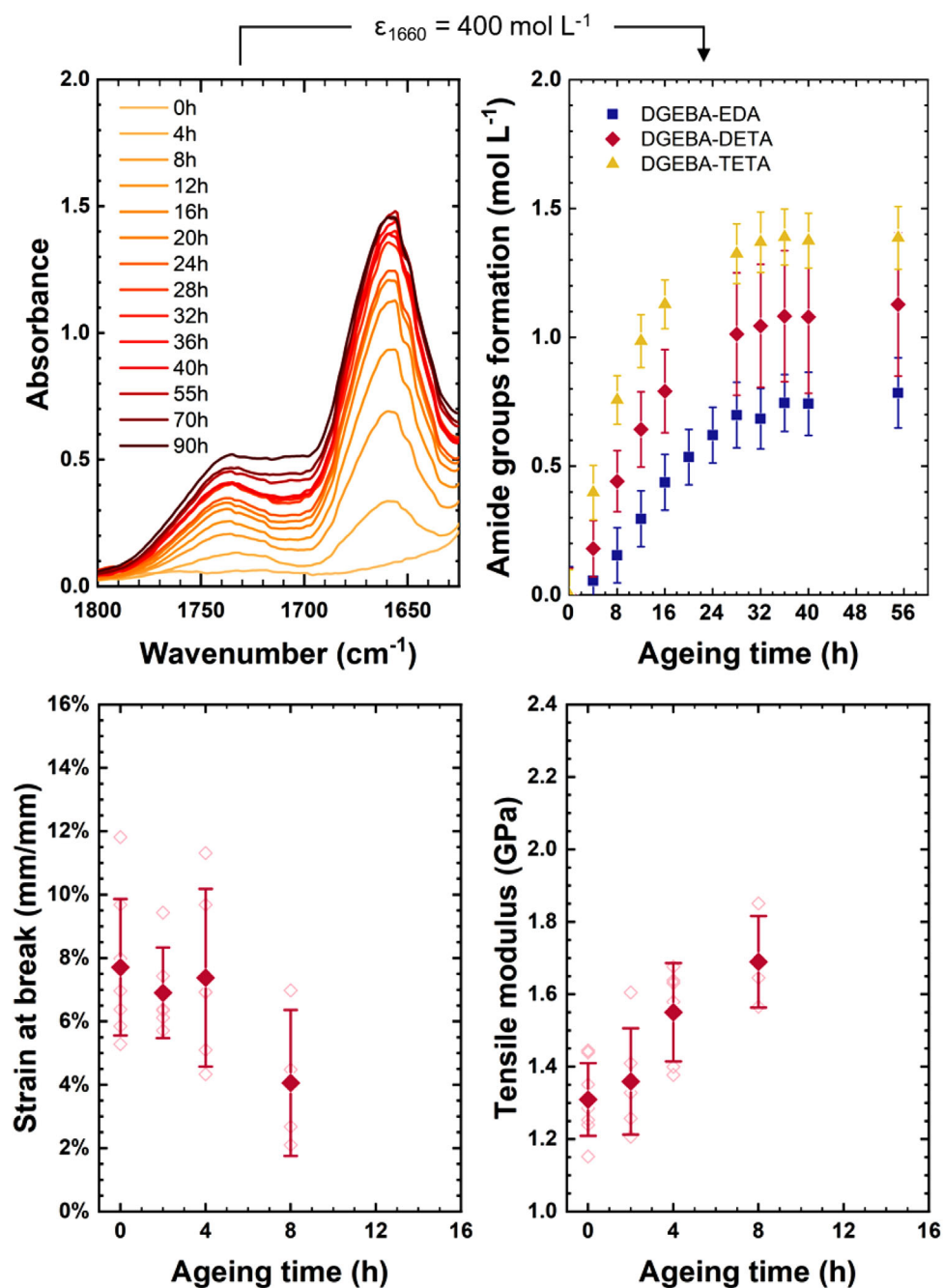


Figure 4. Molecular and quasi-static mechanical analysis of the epoxy-amine systems during aging – (above) FTIR spectrum between 1625 and 1800 cm^{-1} showing the main appearance of 1660 cm^{-1} peak attributed to the formation of amide groups, and calculated concentrations of amides with time – (below) Mechanical response analysis of strain at break and modulus showing the rapid loss of rupture properties.

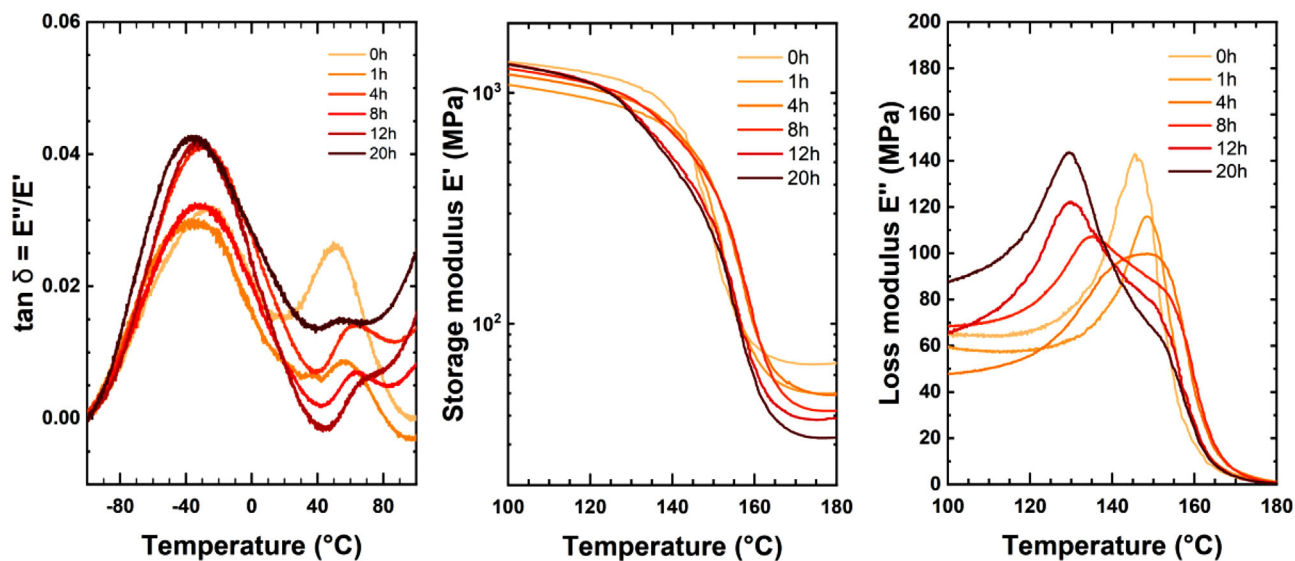


Figure 5. Dynamic mechanical response of DGEBA-DETA system aged up to 20 h at 160°C – (left) Loss factor at 3°C min⁻¹ and 1 Hz exhibiting the two sub-glass relaxations – (center) Storage modulus at 3°C min⁻¹ and 1 Hz displaying the decrease of the rubbery plateau after aging – (right) Loss modulus at 3°C min⁻¹ and 1 Hz displaying the α relaxations.

Acknowledgements

The Agence Nationale de la Recherche is gratefully acknowledged for funding the project ANR DUREVE (2019-2022), and this work.

Keywords

aging, dynamic mechanical analysis (DMA), epoxy, macromolecular mobility, thermosets

Received: June 14, 2021

Revised: October 4, 2021

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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