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Impact of polar groups concentration and free volume on water sorption in model epoxy free films and coatings

G. Bouvet, Nguyen Dang, S. Cohendoz, X. Feaugas, S. Mallarino*, S. Touzain

Laboratoire des Sciences de l'Ingénieur pour l'Environnement (LaSIE UMR-CNRS 7356) Université de La Rochelle, Bâtiment Marie Curie, Avenue Michel Crépeau, 17042 La Rochelle Cedex 1, France

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ABSTRACT

The water sorption characteristics have been determined for two model epoxy systems based on the DGEBA resin and two amine hardeners (TETA and DAMP). A particular attention was paid to the curing protocol to control the macromolecular architectures. Using FTIR, DSC and DMTA measurements, it was demonstrated that both network microstructures differ mainly in the polar groups density, the potential crosslinking nodes and the free volume. DGEBA/DAMP system presents a higher free volume fraction and a lower polar groups concentration compared to the DGEBA/TETA system. Gravimetric measurements on free films and EIS experiments onto coated steel Q-panels were carried out to follow the water sorption kinetics at different temperatures (30, 40, 50 and 60 °C). For both epoxy systems, the diffusion processes follow a pseudo-fickian behaviour with two diffusive stages. Solubility and diffusion processes are discussed in relation with the microstructural specificities of the polymer networks using a thermodynamic framework. The main result is that in DGEBA/DAMP and DGEBA/TETA systems, the water diffusion and solubility are mainly governed by a water polar group interaction mechanism.

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1. Introduction

Epoxy-based paints are widely used to protect metals against corrosion because of their low cost and their efficiency in corrosive environments such as seawater. However, many environmental factors such as water, temperature, UV and oxygen cause degradation and thus affect the durability of the coated systems. The amine-based epoxy resins are particularly sensitive to the absorption of water (1–6% by weight) [1]. Indeed, when these materials are in contact with an aqueous environment, the water enters within the macromolecular structure and modifies physicochemical and mechanical properties. However, the relation between the macromolecular network and the water uptake process is still discussed, as recently reminded by Morsch et al. [2,3].

The diffusion of water molecules in an epoxy matrix has historically been described by two approaches: volumetric and interactional approaches [4]. The volumetric approach considers the water molecule diffusion through the free volume available between the macromolecular chains of the system [5–9], without taking into account the interactions between water and the polar groups [10]. This approach is controlled by the physical state of the

polymer. Unlike this, the interactional approach takes into account these interactions [4,11,12]. Water molecules diffuse into the network through hydrogen bonds established with the polar groups, mainly the hydroxyl and amine groups in the case of epoxy-amine resins. This approach is controlled by the chemical structure. These two above concepts are however generally complementary and can generally occur in the same scales of time and space [13].

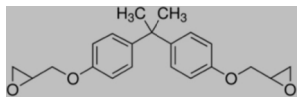
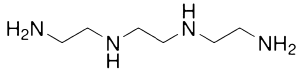
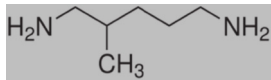
According to Berens et al. [14], there would be a competition between the volumetric approach and the interactional approach of the diffusion, depending on the considered structure. Indeed, for a small amine amount, the diffusion by free volumes would be predominant, whereas when the amine amount increases, interactions with the macromolecular network would be predominant. The network architecture (mass between crosslinking nodes, crosslinking density, free volume, etc.) and the chemical nature of the components (polar groups) are obviously key parameters in these approaches. Thus, the modification of one of these parameters (nature of the co-monomers, curing cycle, stoichiometry, etc.) involves a change of the water sorption mechanisms, favouring either approach.

A previous study [15,16] concerning marine paints highlighted synergies between various degradation factors. However, water diffusion laws inherent in these synergies are difficult to establish because the paint formulations are complex and involve different compounds (binder, mineral fillers, pigments, additives). In order

* Corresponding author.

E-mail address: stephanie.mallarino@univ-lr.fr (S. Mallarino).

Table 1
Structure and characteristics of the products.

Product (supplier)	Formulae	M (g mol ⁻¹)	F	AHEW (g eq ⁻¹)	EEW (g eq ⁻¹)
DGEBA (Aldrich, D.E.R TM 322)		340.41	2	–	170.21
TETA (Aldrich, DEH24 60% assay)		146.23	6	24.37	–
DAMP (Aldrich, 99% assay)		116.2	4	29.05	–

to continue this work, a more fundamental study has been realized by choosing two unfilled model materials, composed solely of the binder. DGEBA/TETA and DGEBA/DAMP epoxy systems have been used. The microstructures differ only in the crosslinking density as well as the number of polar groups. Indeed, the two hardeners are aliphatic and have the same chemical groups. In addition, the curing conditions are identical (stoichiometry and maximum conversion rate). The purpose of this study is to precise the preponderant impact between the polar groups concentration and the free volume fraction in the water diffusion mechanisms in fully cured epoxy networks.

2. Experimental

2.1. Materials

The epoxy resins investigated were prepared from a Diglycidyl Ether of Bisphenol A (DGEBA) cured with triethylenetetramine (TETA) or methylpentanediamine (DAMP). The formulae, supplier, molecular weight (M), functionality (F), Amine-Hydrogen Equivalent Weight (AHEW) and Epoxy Equivalent Weight (EEW) of the products are listed in Table 1. All materials are used as received without further purification.

A stoichiometric amount of DGEBA was added to the amine hardener, mixed at room temperature and degassed under vacuum. In order to create free films, the mixture was transferred to a mould, which consisted of two Teflon sheets which are separated by a spacer of about 120 μm thick. For coated steel panels, the mixture was deposited onto the steel sheet and inserted in the mould used for free films.

A controlled curing protocol was used to create a homogeneous fully cured network, according to Tcharkhtchi et al. recommendation [17]. Two isotherm temperatures were chosen and two intermediary isotherms were used to get a homogeneous crosslinking. Then, a post-curing step above T_g was realized to place the material in a thermodynamic equilibrium state. So, a crosslinking protocol was defined for each system:

- For DGEBA/TETA epoxy systems: 6 h at 30 °C, followed by 18 h at 60 °C, followed by 3 h at 80 °C, followed by 3 h at 90 °C, followed by 1 h at 120 °C, and a postcure period for 1 h at 150 °C;
- For DGEBA/DAMP epoxy systems: 7 h at 30 °C, followed by 3 h at 60 °C, followed by 3 h at 80 °C, followed by 3 h at 100 °C, followed by 3 h at 120 °C, and a postcure period for 1 h at 130 °C.

The two systems were rapidly cooled to room temperature with a rate of 10 °C min⁻¹ to avoid physical ageing which is not negligible in the temperature range [T_g –50 °C; T_g]. The cured specimens were stored in a desiccator containing silica gel desiccant to prevent

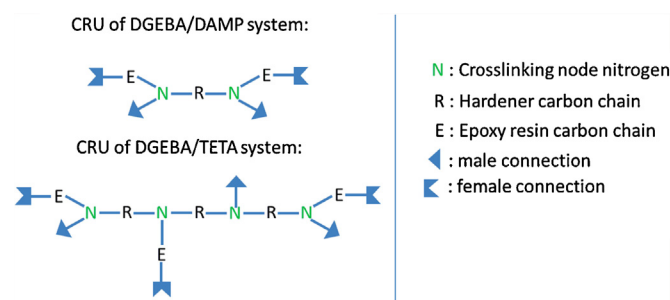


Fig. 1. CRU of DGEBA/DAMP and DGEBA/TETA system.

moisture absorption before immersion. A representation of the network structure can be achieved using constitutive repetitive units (CRU) (Fig. 1) considering theoretical ideal macromolecular systems [18]. Different network characteristics can be calculated for both systems.

The molar mass of CRU is calculated as $M_{CRU} = \sum_i^{CRU} M_i$, with M_i the molar mass of the i group. The theoretical crosslinking densities is related to the molar mass of CRU as $x_{theo} = N/M_{CRU}$, with N the number of crosslinking nodes. The polar group concentration C_{PG} is determined by $C_{PG} = n/M_{CRU}$, with n the number of polar groups (OH and N groups). Only the tertiary amine and hydroxyl groups are considered as significant polar groups in these systems. The values of these parameters are presented in Table 2 for both systems. From these results, it can be noted that the use of a lower AHEW curing agent theoretically enables increasing the crosslinking density of the system, so decreasing molecular weight between crosslinking nodes. Given that the most important polar groups (N, OH) are located close to the crosslinking nodes, the increase of the crosslinking density leads to an increase of the polar group concentration.

2.2. Physico-chemical and mechanical characterization methods

Fourier transform infrared (FTIR) analyses of cured materials were carried out by Thermo-Nicolet Magna IR 760 spectrometer equipped with a Smart MIRacle ATR accessory with a diamond crystal. Spectra were collected over a range 600–4000 cm⁻¹ with a

Table 2
CRU parameters of DGEBA/DAMP and DGEBA/TETA systems.

	DGEBA/DAMP	DGEBA/TETA
M_{CRU}	799 g mol ⁻¹	1167 g mol ⁻¹
Crosslinking density (x_{theo})	2.51 mol kg ⁻¹	3.43 mol kg ⁻¹
Polar groups (n)	6	10
Polar group concentration (C_{PG})	7.51 mol kg ⁻¹	8.57 mol kg ⁻¹

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