THERMAL DEGRADATION MECHANISMS OF NUCLEAR EPOXY COATINGS

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The thermal and radio exposure of industrial epoxy coatings, used with amine hardener, have been the subject of many researches in order to study their degradation mechanisms and to predict lifetime of coatings. However, networks can be hard to study and to characterize. In this paper we propose a simple model system to study the chemical environment of crosslinking nods found in epoxy-amine networks. It can be synthesized by mixing monoepoxy monomer and aliphatic diamine. After reaction, the system is soluble in organic solvents, which give us more access to characterization methods, as GPC, than the ones used with epoxy network.

This model system (A), described in figure 1, is based on the reaction of phenyl glycidyl ether (PGE; 150g/mol; ether group present) with aliphatic diamine hardener (dodecance diamine; 200 g/mol). After reaction of this stoichiometric ratio (R (Amine/Epoxy) = 1), (A) system is a clear solution with high viscosity. Exposed at 110°C in air until 2000 hours, (A) system is characterized using several analytical methods such as FTIR in transmission mode, Gel Permeation chromatography (GPC) and High Resolution Mass spectroscopy (HRMS).
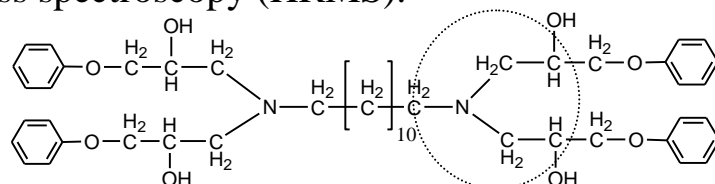

Figure 1. Chemical structure of model system (A) (800 g/mol), showing in the circle same chemical environment of crosslinking nods existing in the industrial coatings (epoxy/amine).

After performing GPC measurements, one can evaluate $[A]_R$, the concentration of (A) system Remaining (fig.2.(a) right axis), using GPC's values of refraction index. These latter are related to the concentration of

correspondent product. The kinetics showed that the consumption of main product is very close to a 1st order reaction with kinetic rate of $k \approx 2.5 \text{ x} 10^{-3}$ h^{-1} at 110°C. In addition to that, GPC measurements has put in evidence the presence of lower molecular weight products formed after chain scission, caused by oxidation.

FTIR spectras, between 1800 and 1600 cm^{-1}, showed the increase of three main pics at 1660 cm^{-1}, 1705 cm^{-1} and 1735 cm^{-1}, attributed to amides and carbonyles (acids, and ketones) respectivley [1-2]. Using Lambert-Beer law, one can study the increase of carbonyl concentration during aging (fig.2.(a) left axis). Combining GPC data and carbonyl formation, we can plot the chain scission number (S) ((S) = $[A]_0 - [A]_R$) as function as carbonyl concentration (Where $[A]_0$ is the initial concentration of (A)).
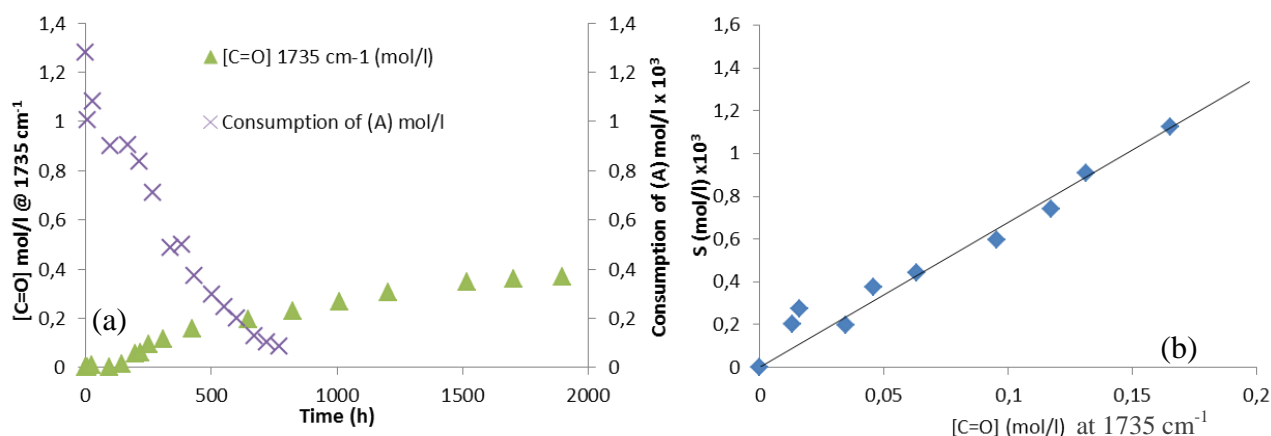
Figure 2. (a) On the left axis: Carbonyl increase during aging; on the right axis: Consumption of (A) system. (b) Chain scission number (S) as function as Carbonyl concentration at 1735 cm^{-1}.

According to these results, carbonyls are responsible of chain scission and probably resulting from α attack of methylene group adjacent to ether group. One of oxidation products have been identified as phenol obtained after β scission from secondary alcohol group in PGE part. (A) system provided better ideas about the oxidation mechanisms formed during aging in industrial epoxy coating used with amine hardener.

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