ENVIROMENTAL UTILITY MATERIALS
An epoxy system as surface protective coating analysis

Lisardo Núñez Regueira[*]*, M. R. Núñez, M. Villanueva and B. Rial*

Research Group TERBIPROMAT, Departamento de Física Aplicada. Facultade de Física, Universidade de Santiago (U.S.C), 15782 Santiago de Compostela, Spain

Abstract

The influence of agents originated in a municipal landfill on the thermal degradation of a polymeric system composed of a diglycidyl ether of bisphenol A ($n=0$) and 1,2-diaminecyclohexane was studied by thermogravimetric analysis (TG) in order to obtain the lifetime of this material before and after being attacked. The different data obtained were analyzed to check the resistance of these materials to chemical attack and the possibility of their use as coating materials in plants where those reagents were present.

At the optimum temperature of service for this material, 373.16 K, the lifetimes obtained from the experimental results were 2633 years and 2135 years, respectively.

Keywords: epoxy-amino system, lifetime, protective coating, TG

Introduction

There were several problems to the successful commercial implementation of solventless two-pack epoxy coatings. One of the problems was the performance limitations of epoxy resins and curing agents available at that time. Limitations of available equipment for applying solventless coating were another problem. A third and predominant problem was the absence of reasons for the industry to move to solventless coatings.

This situation has clearly changed with implementation of regulations mandating the reduction of volatile organic compounds (VOCs) in coatings. In the meantime, means of overcoming the first two problems have also become available. Therefore, it is now possible to formulate and apply commercially viable solventless coatings.

Formulators looked for maintaining ease of application, high levels of performance, competitive cost and the required VOC reductions in the coatings.

Solventless epoxy coatings offer the following advantages:

– ultra-low VOC emissions (<25 g L^{-1}),
– absence of flammable or combustible solvents,

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* Author for correspondence: E-mail: falisar1@uscmail.usc.es

– thick, non-porous films with superior chemical resistance, and
– one-coat application of films from 150–600 μm (around 200 μm for the epoxy system studied).

Although the cost per liter of a solventless coating material may be higher than for a conventional epoxy coating, experience has shown that the overall applied cost of solventless coating is lowered by the following factors:

– single-coat application,
– less overspray losses,
– no coating volume losses due to solvent evaporation, and
– no special VOC [1].

Lifetime prediction [2] is an applied technique, which is frequently needed in industry to find out the probable performance of a new material. The phylosophy of lifetime prediction is to identify the critical reaction which limits the life of a material, then to measure its kinetics quantitatively at high temperature where the reaction is fast. Finally, using proper kinetic expressions, the kinetics for reaction at lower temperatures, at which reaction times are longer, can be extrapolated and thus the time the material will be in service. The used technique is mass loss, despite the fact that the useful life of a material may have ended long before a loss of mass is detected. This technique is a simple and convenient method because of the high sensitivity and baseline stability of electrobalances make them ideal for measuring initial rates, and the volatilization of small fragments is often closely coupled to the kinetics of the degradation processes in the condensed phase which are not directly measurable.

The lifetime is considered when 5% mass loss [3] or 5% conversion [4] is reached from a thermogravimetric analysis experiment (TG).

Kinetic methods

Combining the Arrhenius law with the general rate equation in terms of the degree of conversion, time and temperature, the following relationship for the calculation of the kinetic parameters of a solid-state reaction from dynamic experiments, can be obtained

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) e^{-E/RT} \tag{1}$$

where $f(\alpha)$ is a function depending on the reaction mechanism and $\beta = dT/dt$ is defined as the heating rate.

By integrating Eq. (1) we get

$$g(\alpha) = \frac{A}{\beta} \int_0^T e^{-E/RT} dT \tag{2}$$

where $g(\alpha)$ is the integral function of conversion.

Experimental

Materials

The epoxy resin was a commercial BADGE (*n*=0) (Resin 332, Sigma Chemical Co., St. Louis, USA) with an equivalent molecular mass of 173.6 g eq^{-1}, as determined by wet analysis [5, 6]. The curing agent was 1,2 diaminecyclohexane (DCH) (Fluka, Switzerland) with an amine hydrogen equivalent mass of 28.5.

Sample preparation

Epoxy resin and curing agent were carefully and homogeneously mixed, at stoichiometric ratio and then the samples were introduced in a cylindrical frame.

The curing reaction was programmed according to the isothermal time-temperature-transformation (TTT) cure diagram [7, 8] specially calculated for this material using a differential scanning calorimeter (DSC). This diagram is a very useful tool for studying cure processes of epoxy systems.

The curing reaction consists of two stages: a first step 24 h at 23°C and a second one 16 h at 70°C in a stove. After curing, the samples were removed from the frame.

For thermogravimetric analysis, the samples were cut in the form of 15 to 25 mg in weight and 6 mm in diameter discs and some of them were introduced in lixiviates and HCl during 30 days (Cl$^-$ is one of the most common ions in the composition of the lixiviates used in this study).

Technique

Thermogravimetric analysis was performed using a Thermogravimetric Analyzer (TGA7) from Perkin Elmer controlled by a 1022 computer.

The system was operated in the dynamic mode in the temperature range from 100 to 900°C, at different heating rates: 5, 15, 25, 35 and 45°C min^{-1}.

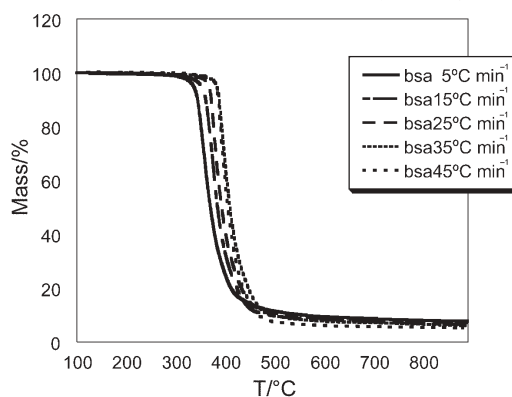All the experiments were carried out under a dry nitrogen atmosphere.

Fig. 1 Thermal degradation curves, at different heating rates, for the BADGE (*n*=0)/1,2 DCH system not immersed in HCl
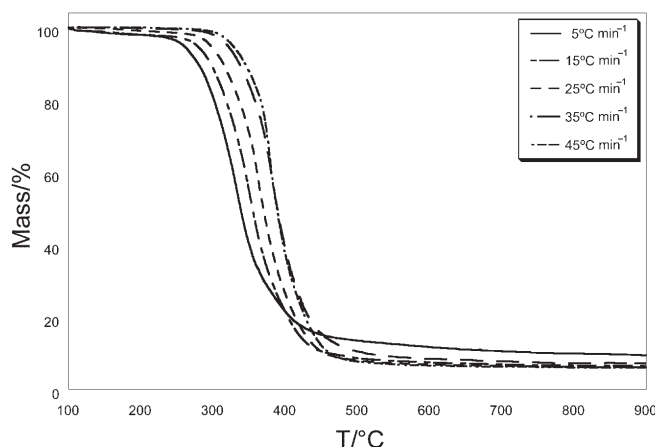
Fig. 2 Thermal degradation curves, at different heating rates, for the BADGE (*n*=0)/1,2
         DCH system immersed during 30 days in HCl

Calculation of lifetime without knowledge of reaction mechanism

Kinetic information can be extracted from a dynamic experiment using Flynn–Wall–
Ozawa [9, 10] method. This involves an approximate integral of the Eq. (2). Equation
(2) was integrated using the Doyle approximation [11] and was rearranged after tak-
ing logaritms in the form:

$$\log\beta=\log\left[\frac{AE}{g(\alpha)R}\right]-2.315-\frac{0.457E}{RT} \tag{3}$$

Thermal degradation was studied, using the dynamic mode, at different heating
rates: 5, 15, 25, 35 and 45°C min^{-1}. Figures 1 and 2 show thermal degradation curves cor-
responding to dynamic experiments carried out at different heating rates for the system
BADGE (*n*=0)/1,2 DCH not immersed in HCl and immersed during 30 days in HCl,
repectively. These curves are C type [12], which correspond to a one-stage decomposi-
tion reaction where the procedural decomposition temperatures (initial and final) are well
defined.

Results and conclusions

To apply Doyle approximation, conversions of 5, 8, 11, 14, 17 and 20% were used. Fig-
ure 3 shows the fit of plots of logβ *vs.* 1/*T* at various conversions for the epoxy system
immersed in HCl . The parallel lines indicate that the activation energies are essentially
the same throughout the reaction and suggest that the single reaction mechanism is opera-
tive [13, 14]. From the fit of a plot of logβ *vs.* 1/*T* at the various conversions, the activa-
tion energy was calculated. The mean value of the activation energy is 148±4 kJ mol^{-1}
[15] for the not immersed system and 81±2 kJ mol^{-1} [16] for the same epoxy system im-
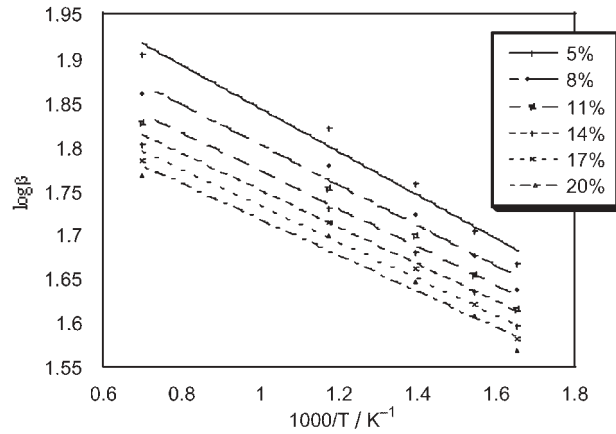mersed for 30 days in HCl.

Fig. 3 Typical plots of logβ *vs.* 1000/*T* at various conversion values in the range
5–20% in steps of 3%

The lifetime at several temperatures can be predicted from dynamic experiments assuming that it is reached at 5% of conversion. Lifetime values corresponding to temperatures, between 373.16–633.16 K for the system with filler are summarized in Table 1.

Table 1 Experimental lifetimes values for the system BADGE (*n*=0)/1,2-DCH not inmersed and inmersed in HCl for 30 days at several temperatures

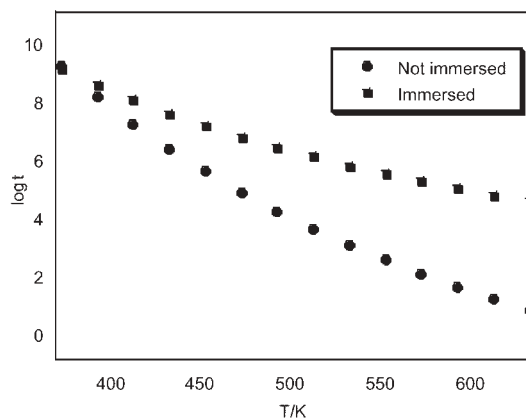| *T*/K	Not immersed t_{exp}/min	Immersed t_{exp}/min
373.16	$1.38 \cdot 10^9$	$1.12 \cdot 10^9$
393.16	$1.25 \cdot 10^8$	$3.04 \cdot 10^8$
413.16	$1.42 \cdot 10^7$	$9.36 \cdot 10^7$
433.16	$1.98 \cdot 10^6$	$3.21 \cdot 10^7$
453.16	$3.28 \cdot 10^5$	$1.21 \cdot 10^7$
473.16	$6.32 \cdot 10^4$	$4.96 \cdot 10^6$
493.16	$1.39 \cdot 10^4$	$2.18 \cdot 10^6$
513.16	$3.45 \cdot 10^3$	$1.02 \cdot 10^6$
533.16	$9.51 \cdot 10^2$	$5.08 \cdot 10^5$
553.16	$2.88 \cdot 10^2$	$2.66 \cdot 10^5$
573.16	$9.45 \cdot 10^1$	$1.45 \cdot 10^5$
593.16	$3.35 \cdot 10^1$	$8.27 \cdot 10^4$
613.16	$1.24 \cdot 10^1$	$4.88 \cdot 10^4$
633.16	$5.10 \cdot 10^0$	$2.98 \cdot 10^4$

Fig. 4 Lifetime values *vs.* temperature for the not immersed and immersed in HCl during 30 days systems

Figure 4 shows lifetime values as a function of the temperature in a logarithm scale for the system not immersed and immersed in HCl during 30 days.

As it can be seen, lifetime value at 373.16 K is lower for the system immersed during 30 days in HCl than for the not immersed system but the difference is not important in order to apply the protective coating because lifetime values are around 2000 years [15].

If the rest of the values are compared, Table 1 shows that at the other temperatures ($\geq$393.16 K) the lifetime values for epoxy system immersed in the agent are higher than the values corresponding to the system not immersed. Therefore, the attack does not have a great influence on the properties of the material and it can be used as a protective coating in extreme conditions. For example, to protect the underlying soil from the leachates migration.

It can be considered the possible application of this material for the coating of basins designed for the collection of the lixiviates originated in sanitary landfills and municipal waste landfill in order to avoid soil contamination [17].

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