The Influence of Lixiviates on the Thermal Degradation of Diglycidyl Ether of Bisphenol A n=0/1,2-Diaminecyclohexane Studied by Dynamic Mechanical Analysis and Thermogravimetry-Fourier Transform Infrared Spectroscopy

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ABSTRACT: The influence of the lixiviates 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 dynamic mechanical analysis. Storage modulus (E'), loss modulus (E''), and glass transition temperature were measured to make a comparative study between the samples before and after being exposed to the chemical compounds in the lixiviate agents. 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. Thermal stability of the system diglycidyl ether of bisphenol A/1,2-diaminecyclohexane exposed to the attack of lixiviates has also been studied by thermogravimetric analysis. A quantitative study of the gases originated during thermal degradation of the epoxy/diamine system made by infrared spectroscopy. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 443-453, 1999

Key words: lixiviates; epoxy resin; DMA; FT-IR; thermogravimetry

INTRODUCTION

Thermosetting systems, in which epoxy resins are included, have been the subject of a multitude of studies. The broad interest in epoxy resins originates from the versatility of their potential uses. Depending on the chemical properties of the hardener and on the curing conditions, it is possible to obtain a final material in a wide range of attainable properties going from extreme flexibility to high strength and hardness, good heat resistance, as well as chemical resistance. In this study, we pretend to measure mechanical properties of the system diglycidyl ether of bisphenol A (BADGE) (n = 0)/1,2-diaminecyclohexane (DCH) to consider its possible application for the coating of basins designed for the collection of lixiviates originated in sanitary landfills and municipal waste landfills.

Leachates (lixiviates) are the contaminated liquids draining from a sanitary landfill. Their compositions vary widely, depending on the age of the landfill and the type of waste it contains. Leachate production is equal to the precipitation falling, less the amount of this precipitation lost from the landfill. Until the landfill becomes satu-

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rated, water entering the landfill is also reduced by the amount of moisture the landfill retains in the soil and refuse.

Once the capacity of the refuse to absorb liquid has been reached, leachate migrates through the underlying soil toward the groundwater table. To avoid contamination, it is necessary to protect the underlying soil from this leachate migration using long-life lixiviate-proof materials that must keep their mechanical properties.

Thermal degradation of the polymer system after it has been exposed to the attack of lixiviates during different periods of time (2, 7, 15, and 30 days) was studied by dynamic mechanical analysis (DMA), comparing samples before and after being exposed to the previously described chemical agents. These kind of studies need the knowledge of storage modulus (E'), loss modulus (E''), and glass transition temperature (T_{σ}) . DMA shows as a useful tool for the investigation of transitions in polymer structures. Dynamic mechanical tests, in general, give more information about a material than other tests.¹ Dynamic tests over a wide temperature and frequency range are especially sensitive to chemical and physical structures of polymer materials. In some cases, the dynamic mechanical tests are the most sensitive tests for studying glass transitions, as well as the morphology of crystalline polymers. Several factors related to chemical structure are known to affect T_g . The most important factor is chain stiffness or flexibility of the polymer. To build flexibility into a polymer is related to a decrease in T_{σ} .

INTERPRETATION OF A DYNAMIC MECHANICAL CURVE

A dynamic mechanical curve gives information about the evolution of polymer stages during a mechanical experiment. The temperature dependence of dynamic properties can be investigated by varying the temperature at constant frequency.² These curves show the behavior of dynamic mechanical properties (E', E'', and tan δ) as a function of temperature. Knowledge of these mechanical properties leads to the value of the T_g , which can be defined as the temperature corresponding to the maximum values of either E'' or tan δ . However, the maximum in the E'' curve occurs at a slightly lower temperature than the peak in the tan δ curve.

Plots of log E' vs. T show the existence of up to five different regions of viscoelastic behavior, depending on the nature of the polymeric system being studied.

Two different behaviors, one corresponding to linear polymers and other to crosslinked polymers, need to be distinguished.

When the polymer is linear, the modulus will drop off slowly. For crosslinked polymers, only three regions can be distinguished: the glassy region, the glass transition region, and the rubbery plateau region; this last region remains up to the decomposition temperature of the polymer.³ The rubber elasticity improves and the elastic modulus follows the equation E = nRT, where *n* is the number of active chain segments in the network, *R* the gas constant, and *T* the absolute temperature.

VISCOELASTIC BEHAVIOR

Viscoelastic properties of a polymeric system depend very much on molecular structure, molecular weight, molecular weight distribution, temperature, crosslinking, and other variables. Because viscoelastic phenomena always involve the change of properties with time, the measurements of viscoelastic properties of solid polymers are known as dynamic mechanical properties. There are many experimental techniques to measure dynamic mechanical properties. The mechanical properties of polymers are of interest in all the applications where polymers are used as structural materials. Mechanical behavior involves deformation of a material under the influence of applied forces. Polymers display both elastic and viscous properties; because of that, their behavior is termed viscoelastic. If the elastic behavior can be described by Hooke's law, and the viscosity relationship is Newtonian, then the material is termed linear viscoelastic. In this case, both strain and rate of strain are infinitesimal, and the time-dependent stress-strain relations can be described by linear differential equations with constant coefficients. In a given experiment, the ratio of stress to strain is a function of time (or frequency) alone, and not of stress magnitude.⁴ If the viscoelastic behavior is linear, a sinusoidal stress will originate a sinusoidal strain, but this will be out of phase with the stress. Let us consider a periodic (or dynamic) experiment.

pH	$\begin{array}{c} 6.32 \\ (mg \ L^{-1}) \end{array}$
Suspension solids	14.68
Dry residue	220.00
Na	12.84
K	1.50
Ca	5.97
Mg	1.90
NH_4^+	0.05
Cl^{-2}	12.45
SO_4^{-2}	6.42
CO_{3}^{-2}	
$CO_{3}H^{-}$	24.07
NO ₂	0.10
NO3	9.38
PO_4^{-3}	0.05
S^{-2}	< 0.01
Fe	0.22
Cu	0.02
Ni	0.01
Zn	0.34
\mathbf{Cr}	0.03
Cd	0.01
Hg	< 0.01
Pb	0.02
Al	0.01
Mn	0.12

Table ILixiviates Physical-ChemicalCharacteristics

The stress may be given by

$$\sigma = \omega_0 \cos \omega t \left[\frac{\omega}{3} \int_0^\infty E(s) \sin \omega s ds \right]$$
$$- \gamma_0 \sin \omega t \left[\frac{\omega}{3} \int_0^\infty E(s) \cos \omega s ds \right] \quad (1)$$

where s is t' - t.

It is clear that the term in $\sin \omega t$ is in phase with γ , and the term in $\cos \omega t$ is 90° out of phase. The quantities in parentheses are frequency-dependent, so eq. (1) can be written in the form

$$\sigma = \gamma_0(E' \cos \omega t - E'' \sin \omega t) \tag{2}$$

The stress may be written in an alternative form displaying the amplitude $\sigma_0(\omega)$ of the stress and the phase with $\delta(\omega)$ between stress and strain. In this way

 $\sigma = \sigma_0 \cos(\omega t + \delta)$

 $= \sigma_0(\cos \omega t \cos \delta - \sin \omega t \sin \delta) \quad (3)$

Comparison of eqs. (2) and (3) leads to

$$E' = \left(\frac{\sigma_0}{\gamma_0}\right) \cos \delta$$
 (storage modulus) (4)

$$E'' = \left(\frac{\sigma_0}{\gamma_0}\right) \sin \delta$$
 (loss modulus) (5)

with a quotient

$$\tan \delta = \frac{E''}{E'} \tag{6}$$

that is termed the loss coefficient, tan δ , which is the ratio of energy dissipated per cycle to the maximum potential energy stored during a cycle. At low frequencies, tan δ is large for all of the uncrosslinked polymers and becomes inversely proportional to the frequency. In the glass transition region, tan δ goes through a pronounced maximum for uncrosslinked polymers of high molecular weight. It is of interest that the maxima in E'' occur to the right of those in tan δ on the frequency scale.

The loss tangent determines such macroscopic physical properties as the damping of free vibrations and the frequency width of a resonance response. It can often be more conveniently measured than any other viscoelastic function. However, its theoretical interpretation becomes more difficult than the other functions.



Figure 1 Log E' vs. T curves of the samples immersed in lixiviates for different periods of time.

Immersion Time (days)		Frequency (Hz)					
		1	5	10	15	20	25
0	T_{g} (°C) $E'(imes 10^{9}$ Pa)	$\begin{array}{c} 162.1 \\ 0.268 \end{array}$	$\begin{array}{c} 168.2 \\ 0.282 \end{array}$	$165.3 \\ 0.290$	$\begin{array}{c} 173.6\\ 0.183\end{array}$	$\begin{array}{c} 174.8\\ 0.120\end{array}$	$\begin{array}{c} 176.6\\ 0.204\end{array}$
2	T_{g} (°C) $E'(imes 10^{9}$ Pa)	$\begin{array}{c}158.5\\0.492\end{array}$	$\begin{array}{c} 166.6\\ 0.405 \end{array}$	$\begin{array}{c} 170.2 \\ 0.426 \end{array}$	$\begin{array}{c} 170.1 \\ 0.295 \end{array}$	$\begin{array}{c} 170.8\\ 0.406\end{array}$	$\begin{array}{r}173.8\\0.409\end{array}$
7	$T_{g}^{}(^{\circ}\mathrm{C}) \ E'(imes 10^{9} \mathrm{Pa})$	$\begin{array}{c} 149.5\\ 0.336\end{array}$	$151.7 \\ 0.266$	$\begin{array}{c} 147.2 \\ 0.346 \end{array}$	$155.1 \\ 0.265$	$\begin{array}{c} 155.6\\ 0.240\end{array}$	$\begin{array}{c} 157.5\\ 0.215\end{array}$
15	T_{g} (°C) $E'(imes 10^{9}$ Pa)	$\begin{array}{c} 141.6\\ 0.306\end{array}$	$\begin{array}{c} 146.6\\ 0.311\end{array}$	$150.5 \\ 0.255$	$\begin{array}{c} 153.8\\ 0.184\end{array}$	$\begin{array}{c} 152.8\\ 0.237\end{array}$	$\begin{array}{c} 152.0\\ 0.211\end{array}$
30	T_{g} (°C) $E'(imes 10^{9}$ Pa)	$\begin{array}{c} 142.8\\ 0.220\end{array}$	$\begin{array}{c} 142.0\\ 0.292\end{array}$	$\begin{array}{c} 146.1 \\ 0.197 \end{array}$	$\begin{array}{c}151.0\\0.142\end{array}$	$\begin{array}{c} 150.5\\ 0.153\end{array}$	$\begin{array}{c}152.4\\0.117\end{array}$

Table II T_g and E' Values for Second DMA Scanning at Various Frequencies and Immersion Times

THERMOGRAVIMETRIC (TG)-FOURIER TRANSFORM INFRARED (FTIR) ANALYSIS

In TG analysis (TGA), the weight loss or gain of a material is measured as a function of temperature variation or at an isothermal regime as a function of time. With this aim, an extremely sensitive microbalance is used.

One of the most important applications of TGA technique is the study of thermal stability of materials. Comparison of decomposition curves can be used as a method for classifying materials according to their relative thermal stability.

The TG-FTIR system is used to obtain infrared (IR) spectra of the different gases evolved from a material during a TGA experiment. By doing this, the composition of the gas emission can be known.



Figure 2 Tan δ *vs. T* curves of the samples immersed in lixiviates for different periods of time.

EXPERIMENTAL

Materials

The thermosetting system was a stoichiometric mixture of epoxy resin/diamine. The epoxy resin was a commercial BADGE (n = 0, Resin 332; Sigma Chemical Co., St. Louis, MO). The epoxide equivalent of the resin was on the label 172–176 (173.6 as determined by wet analysis).^{5,6} The curing agent was DCH (supplied by Fluka, Ulm, Switzerland; >98% pure), with an amine hydrogen equivalent weight of 28.5. Both were used as received.

Sample Preparation

Epoxy resin and cure agent were carefully and homogeneously mixed, at a stoichiometric ratio, before being introduced in a cylindrical frame.

Table III T_g Values Obtained Using DMA and DMTA

	T_g (°C)				
Frequency (Hz)		DMA	DMTA		
1	1Sc 2Sc	$123.0 \\ 162.1$	$\begin{array}{c} 118.0\\ 164.4\end{array}$		
5	1Sc 2Sc	168.2	 168.1		
25	1Sc 2Sc	176.6			
30	1Sc 2Sc	_	 175.1		

1Sc, first DMA scanning; 2Sc, second DMA scanning.

Curing reaction was programmed according to a TTT diagram described for this material.⁷ It consists of two stages: a first step at 23° C for 24 h and a second one, in a stove, at 70°C for 16 h. After curing, samples were removed from the frame.

For DMA, 15- to 20-mm length samples were used. IR TGA used 5 to 15 mg size samples. Once cut, the samples were introduced in flasks containing lixiviates and kept there for different chosen times before being studied.

Leachates were collected from a municipal landfill situated in Santiago de Compostela (Spain). Some of their physical and chemical characteristics are given in Table I.

Techniques

DMA

Dynamic mechanical properties were measured by a Perkin–Elmer DMA7 operated in the 3-point bending horizontal measuring system. DMA was calibrated using indium as a standard. Experiments were conducted in a temperature range from 30°C to 250°C.

Experimental conditions were: dynamic force (700 mN), static force (750 mN), number of points to be determined in the temperature range (500), and heating rate $(10.0^{\circ}\text{C min}^{-1})$. Before starting every experiment, the equipment was stabilized at 30°C. Frequency-fixed values used in the different experiments were 1, 5, 10, 15, 20, and 25 Hz.

TG-FTIR Measurements

Simultaneous measurements of weight loss of the material and identification of the gases evolved



Figure 3 TG curves of the various samples studied.



Figure 4 Decomposition temperatures (T_d) as a function of immersion time.

from it during every experiment were conducted using a TG-IR system from Perkin–Elmer.

The system comprises a TGA-7 Thermogravimetric Analyzer, the TG-IR interface, and a power supply. The TGA-7 is coupled, by means of a transfer line, to a heated gas cell that is located inside the TG-IR interface, together with a temperature controller. The interface can be accommodated in any of the four sample areas of the system 2000 FTIR spectrometer.

Experiments were conducted using 10-15 mg samples. Samples were stored in a desiccator and then stabilized inside the TG for 30 min at 30°C under a nitrogen atmosphere, before being heated up to 900°C, at a heating rate of 40°C min⁻¹ (see ref. 8). In all experiments, a weight loss close to 94% was determined.



Figure 5 Residue at 890°C as a function of immersion time.



Figure 6 FTIR of volatile products of a thermal degradation for differents immersion times: (a) 0 days; (b) 2 days; (c) 7 days; (d) 15 days; and (e) 30 days.

The TGA7 analyzer requires two purge gas lines: one to purge the balance chamber and the other to purge the sample-furnace area. Gases evolved from the samples during the experiments are swept by the purge gases to the FTIR cell. To achieve a good resolution of the IR spectra, it was found, after a great number of experiments using calcium oxalate as a standard, that the optimum gas flow rates were: balance purge gas, 25 mL min⁻¹; sample purge gas, 35 mL min⁻¹; and purge gas to the IR cell, 45 mL min⁻¹. The temperature of the transfer line between the thermobalance and the FTIR light pipe was kept at 200°C.

RESULTS AND DISCUSSION

The behavior of the E' of the nonimmersed cured epoxy system (0 days) and of the same material after being immersed in lixiviates for different periods of time (2–30 days) is shown in Figure 1.



Figure 6 (Continued from the previous page)

In our study, we have considered T_g and E' values corresponding to the second DMA scanning, because T_g values are > 146.0°C, the T_g value measured for this epoxy system by differential scanning calorimetry.⁷ It can be seen that, at a given temperature and frequency, the elastic modulus decreases with immersion time. This fact can be considered as a plasticizing effect, as reported by Lee and Peppas,⁹ when studying water transport in epoxy composites. However, if we focus our study to the glass transition region and consider the inflection point of the log E' vs. T curve, which corresponds to the tan δ vs. T peak (that many authors have considered as T_g), at the

different frequencies experimented, we found data listed in Table II. It may be observed that, in all the cases, the largest values of the elastic modulus correspond to samples immersed in the lixiviates for 2 days, and then generally decrease with immersion time. The possible causes for these observed changes in dynamic mechanical properties could be related with a postcuring effect, because E' is directly proportional to crosslink density. This postcuring could be provocated by some of the components in the lixiviates. One other interpretation could be given in terms of hydrogen bonding or polarity that, as it is known, increases the modulus of some polymer



Figure 6 (Continued from the previous page)

systems. The presence in the lixiviates of metal ions such as zinc or sodium can make the polymer behave as though it were crosslinked. After 2 days, E' decreases with the time of residence in the lixiviates. This may arise as a plasticizing effect caused by water sorption.

Table II also shows an obvious trend of increasing T_g with increased frequency. However, at > 15 Hz, the T_g 's keep practically constant at each frequency. On the other hand, T_g 's decrease with the time the samples were immersed in the lixiviates. This agrees with the fact that E' also decreases with immersion time. Analysis of Table II shows that, in all the cases, E' shows the largest values after 2 days of the samples to be immersed. As previously described this probably arises as a consequence of a postcuring like behavior. However, T_g values are lower for the material immersed for 2 days than for the nonimmersed material, so suggesting plasticization is due to water sorption. This plasticization goes on with the time the samples are immersed in lixiviates, because it can be justified by the decrease of T_g 's with immersion time. The increases of E'could be a consequence of an increase of the crosslink density owing to some compounds existing in the lixiviates. Also, for samples immersed for 2 days, E' shows a significant decrease at 15



Figure 6 (Continued from the previous page)

Hz, thus indicating that this frequency is very close to the resonance value for this material. The behavior of the material immersed in lixiviates depends on two sources: one that is chemical and the other that is physical. The former results from chemical interactions between compounds dissolved in the lixiviates, and penetrating water, and some of the chemical groups of the epoxy resin. Chemical interactions include hydrolysis of polymer bonds and reaction with compounds of the lixiviates. The physical source of interactions is reflected in the plasticization of the epoxy/diamine systems resulting in the reduction in T_g . There are two competitive interactions: one of

them increasing the elastic modulus, E' (stiffness), and a second one decreasing T_g values (plasticization). The first type of interactions are more favored up to 2 days of immersion, whereas plasticization is favored for immersion times for > 2 days. It must be considered, however, that even E' decreases after > 2 days. E' values are always greater than those corresponding to the nonimmersed cured system, thus suggesting a postcuring effect.

A similar discussion could be given using E'' peak and/or tan δ peak values. Figure 2 shows a tan δ vs. T plot at a frequency of 1 Hz. The curve shows an increase of tan δ after 2 days of the



Figure 6 (Continued from the previous page)

material to be immersed in the lixiviates. The tan δ peak decreases with the immersion time, but keep higher than the peak corresponding to the nonimmersed material.

To check our measurements, some values of T_g were measured by a dynamic mechanical thermal analyzer (DMTA) in the laboratories of the Instituto de Polímeros, CSIC, Madrid (Spain), using a DMTA MKII from Polymer Laboratory Ltd., thus obtaining the values that are shown in Table III. As it can be seen, the results fairly agree with those measured in our laboratories using a P-E DMA7.

Thermal degradation curves (Figure 3) show that the material, immersed or not, starts thermal decomposition at ~ 300°C. From these curves, decomposition temperatures of the different samples were calculated. The decomposition temperature (T_d) is defined as the temperature at the point before the main decomposition step (where the curve is horizontal) and from the point of inflection of the main step. 10,11

Figure 4 shows T_d values as a function of the time the samples were immersed in lixiviates. It can be observed that T_d shows its highest value at 2 days of immersion and then decreases to a practically constant value. This increase in T_d could be related to the observed increase in E' corresponding to T_g at 2 days of immersion, thus showing a certain relationship between dynamic me-

chanical properties and decomposition temperatures of the material. The residue at 890°C can also be determined from Figure 3. Figure 5 shows the value of the residue as a function of immersion time in lixiviates. This residue shows its lowest value at 2 days of immersion, which agrees with the clear discontinuities showed in E' and T_d values.

TG-FTIR measurements of the different samples were simultaneously conducted to investigate the thermal degradation of the system. Temperature range was 30°–900°C, using nitrogen as an inert atmosphere. The FTIR spectra of the volatile compounds evolved during degradation experiments are shown in Figure 6(a-e). All IR spectra show the same shape and exhibit all the characteristic peaks of the starting materials in the IR range of $400-4000 \text{ cm}^{-1}$, thus indicating that immersion in lixiviates does not modify the internal structure of the polymer system, and any modification should take place on the surface. To check this assumption, we are starting different tests and measurements of microhardness of the material.

CONCLUSIONS

Thermal degradation of the epoxy system BADGE n = 0/1,2-DCH immersed in lixiviates for different periods of time has been studied by DMA and TG-FTIR. From these studies, it may concluded that immersion in lixiviates does not affect the

internal structure of the epoxy system and that the attack is only on the polymer surface.

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Finally, we think that the epoxy system studied herein can be used to build tanks designed for collecting these draining liquids.

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