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# The Effect of Phase Morphology on the Thermal Stability of Epoxy/Poly(L-lactide) Blends Before and After Curing

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**Summary:** Diglicidylether of bisphenol A (DGEBA) was blended with poly(L-lactic) acid (PLLA) and cured with diaminodiphenylmethane (DDM). The uncured blends were miscible but became immiscible upon curing. The relationship between phase morphology and thermal stability was investigated. It was found that the thermal degradation of uncured DGEBA, PLLA and their blends occurred mainly through one step. PLLA and uncured DGEBA were mutually destabilized. This is probably due to chemical effects, such as some sort of interaction between the products of degradation of DGEBA and PLLA in the miscible blend. On the other hand, the biphasic cured DGEBA/PLLA blends displayed two degradation stages associated to decomposition of two phases, one rich in PLLA and the other in DGEBA. The temperature at which weight loss begins in the blend is intermediate to the temperature of the neat components. This was attributable to physical effects.

**Keywords:** DGEBA/PLLA blends; miscibility; morphology; thermal properties; thermogravimetric analysis (TGA)

## Introduction

Polymer blends are usually subjected to high temperatures during their preparation and/or use. Thus it is important to know the influence of one component on the thermal stability of the other. In polymer blends, the thermal stability depends on chemical effects such as the interactions between their components or between their degradation products, and/or physical effects, such as the diffusion rate of the species evolved. These effects may also be influenced by the level of dispersion of the components.[1]

In thermosetting-thermoplastic blends, the level of dispersion and the morphology of the system can be tailored by controlling the curing conditions. On curing, the initially miscible thermoplastic/thermosetting prepolymer mixture, usually becomes multiphasic.

The purpose of this article is to investigate the effect of the level of dispersion and morphology on the thermal stability of poly(L-lactide) (PLLA) blended with an uncured and an amino-cured epoxy resin, diglycidylether of bisphenol-A (DGEBA) respectively. Poly(L-lactide) is a semicrystalline, biodegradable and biocompatible polymer, which is produced from renewable resources.[2] There are numerous studies on hydrolysis and biodegradability of PLLA[3–6] but very little information is known about its thermal stability or that of its blends, in spite of the fact that PLLA is very sensitive to thermal degradation.

## Experimental Part

### Materials

DGEBA epoxy resin, DER 332, from Dow Chemical, with an epoxy equivalent weight of 175 as measured by titration, was kindly

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supplied by Quimidroga (Spain). Diaminodiphenylmethane, (DDM), was purchased from Aldrich and used as received without further purification. Poly(L-lactide) (PLLA) was purchased from Polysciences Inc. It had a weight average molecular weight $\overline{M_w} = 55\,000$ as measured by Gel Permeation Chromatography using chloroform as eluent at 30 °C.

### Sample Preparation

Uncross–linked DGEBA/PLLA blends, covering the full composition range, were prepared by solvent casting from dichloromethane solutions. Solvent was evaporated under the heat of an infrared lamp, and the blends were finally dried overnight in a vacuum oven at 80 °C.

Cured blends were obtained from the uncured ones, which were firstly melted at 190 °C for 7 min, cooled down to 130 °C, and then, DDM in epoxy:amine stoichiometric amount was added and stirred for 1 min. These mixtures were poured into aluminum moulds, cured in an oven at 140 °C for 40 min, and post-cured at 190 °C for 20 min. Blends containing 5, 10, 20 and 30 wt % PLLA were studied, since only those compositions in which the epoxy-rich phase constitute the matrix remained solid at temperatures above PLLA's melting temperature. In order to simplify, samples were named EP5, EP10, EP20 and EP30, according to their DGEBA/PLLA ratio, without considering the amount of DDM added. EP0 and EP100 denote amino-cured DGEBA and neat PLLA, which were submitted to the same thermal treatment as the cured samples, respectively.

### Characterization and Measurements

The miscibility of DGEBA/PLLA blends was studied in a Perkin Elmer, Pyris 1 Differential Scanning Calorimeter (DSC), equipped with a Perkin Elmer, Intracooler 2P liquid nitrogen cryogenic system. Temperature was calibrated with an indium standard. Samples of about 7 mg were sealed in aluminum pans and heated, under nitrogen atmosphere, at 10 °C/min from −40 °C to 200 °C. The samples were kept at 200 °C for 10 min to erase thermal history effects. Then, the uncured samples were quenched to −40 °C and then reheated to 200 °C at 10 °C/min, while the cured samples were cooled down to 20 °C at −10 °C/min.

The morphology of cured samples was observed using a scanning electron microscope, SEM, Hitachi S-2700, at an acceleration voltage of 15 kV. In order to remove the thermoplastic-rich phase, the cryogenically fractured surface samples were kept in dichloromethane for 24 h, then, repeatedly washed with fresh dichloromethane, and finally dried in a vacuum oven. Before observation, samples were sputter-coated with a thin gold layer using a Fine Coat Jeol Ion Sputter JFC-1100.

Thermogravimetric analysis (TGA) was carried out with a Thermogravimetric Analyzer, TA, model Q500, in the temperature range from 50 °C to 800 °C at a heating rate of 10 °C/min, under a nitrogen flow rate of 40 mL/min. Specimen weight was about 7 mg. The instrument was calibrated in temperature by the Curie method using a nickel standard, and the weight was calibrated with a calcium oxalate standard.

## Results and Discussion

The miscibility of the system was studied by measuring the glass transition temperature, $T_g$, recorded at the half–height of the corresponding heat capacity jump. For uncured mixtures, the $T_g$ was taken from the second calorimetric scan, registered after quenching the samples heated on the first scan. Figure 1 shows the $T_g$ vs composition plot both for uncured and cured blends. For uncured blends, a single $T_g$ monotonically changing with PLLA content was obtained. This result indicates that DGEBA and PLLA are miscible over the whole composition range.

For cured blends, the melting endotherm associated to PLLA's melting appeared in the same temperature range where the $T_g$ for a cured epoxy-rich phase

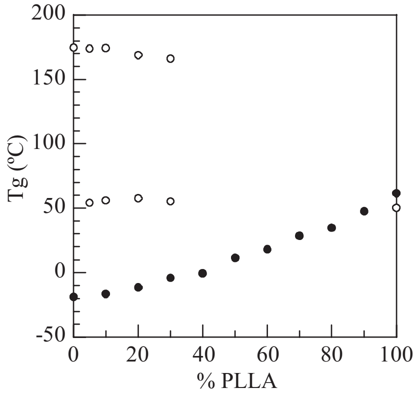

**Figure 1.**
Composition dependence of $T_g$, for uncured (•) and cured (o) blends.

would appear. Thus, in order to avoid experimental uncertainty for these cured samples, the $T_g$s were measured in a cooling scan recorded after the first heating scan. In this way, because of the relatively slow crystallization rate of PLLA, two $T_g$s at around 61 °C appeared almost independent on the PLLA content. One can be assigned to the PLLA-rich phase and the other to the epoxy-rich phase. These results suggest that phase separation has taken place upon curing and that the initially miscible DGEBA/PLLA system has become immiscible, multiphasic.

The morphology of cured DGEBA/PLLA blends with 10% and 20% of PLLA, as observed by SEM, is shown in Figure 2. From the micrographs it is evident what two phases exist, and that the resultant morphology depends on the blend composition. In fact, for EP10 and EP5 (not shown) blends a continuous matrix with spherical holes uniformly distributed is seen. The matrix is a cross-linked epoxy phase, while the holes correspond to the PLLA phase, which was removed with dichloromethane. However, EP20 and EP30 (not shown) blends display a phase inverted structure with large and irregular globules of cross-linked epoxy embedded in a PLLA matrix, which was removed by the solvent.

The micrographs and DSC results reveal that for cured blends two phases exist but they are not pure; nevertheless, the uncured blends were completely miscible. This change in the dispersion level of the components upon curing allows us to relate the miscibility and the morphology of the phases with the thermal degradation behaviour of the system.

### Thermal Degradation of Uncured Epoxy/Poly(L-lactide) Blends

TG and the derivative of the percentage of weight loss (DTG) curves for uncured blends are shown in Figure 3a and 3b. It is evident that PLLA decomposes in a one-step process, between 246 °C and 367 °C, while DGEBA degrades mainly through one step between 189 °C and 342 °C. However, also a small mass loss, difficult to observe, could be detected above 342 °C.

All blends apparently also show a single decomposition step, but only curves for

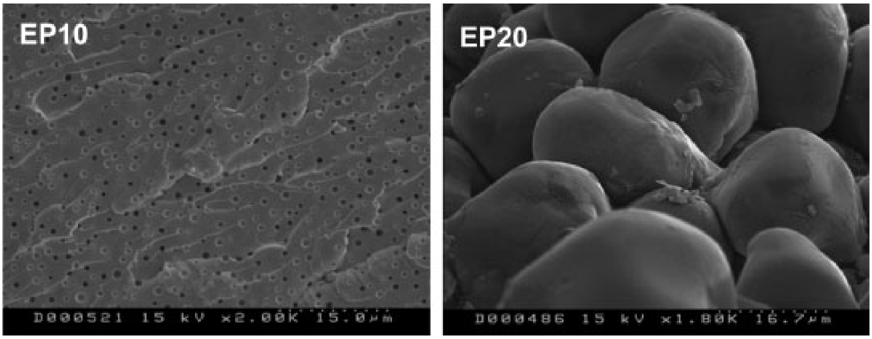

**Figure 2.**
SEM micrographs of the fractured surface of cured EP10 and EP20 blends.

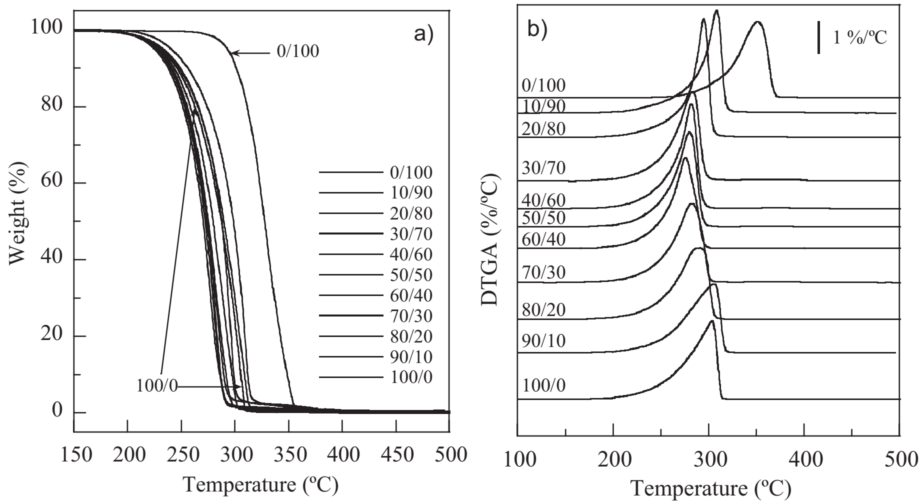

***Figure 3.***
TG (a) and DTG curves (b) for DGEBA/PLLA blends heated at 10 °C/min.

10/90 and 90/10 samples lie between those of PLLA and DGEBA. For the other blends the curves appear at lower temperatures than DGEBA. However, at temperatures between 350 °C and 425 °C another very small stage, difficult to observe, could be detected, thus indicating the presence of some degradation processes leading to a slight weight loss step. A detail of this step is shown in Figure 4.

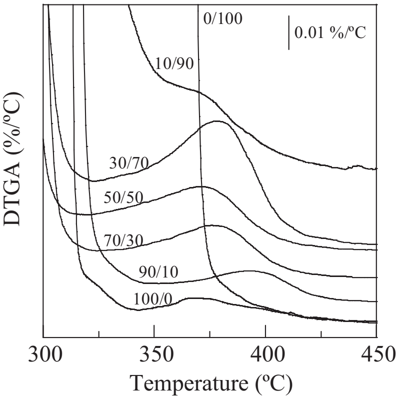

***Figure 4.***
Detail of the DTG curves for DGEBA/PLLA blends heated at 10 °C/min. Thermograms have been shifted vertically for clarity.

These results indicate that DGEBA destabilizes PLLA. Since DGEBA begins to decompose at 189 °C and at 246 °C, the initial decomposition temperature ($T_i$) of PLLA, it has lost about 10% of its initial weight. Therefore, it can be assumed that some sort of interaction exists between PLLA and the initial products of degradation of DGEBA.

With regard to the second degradation stage, which for neat DGEBA only represented a 0.2 wt% weight loss, as far as we know, no references have been published in the open literature. However, it is known that, at high temperatures, DGEBA is able to homopolymerize via etherification reactions yielding polycondensates. This reaction can be catalyzed by acids or tertiary amines. This stage in neat DGEBA could be related with the degradation of this polycondensate. For the blends, increasing the amount of PLLA increased the weight loss associated with this stage up to 4.5 wt% for the 20/80 blend. To explain this trend, the degradation mechanism of DGEBA and of PLLA must be considered.

For PLLA, it was suggested[7–9] that above 200 °C, degradation includes intramolecular transesterification leading to lactide and cyclic oligomers, cis-elimination leading to acrylic acid oligomers, and fragmentation producing acetaldehyde and $CO_2$.

For uncured DGEBA, it has been proposed that the thermal degradation proceeds along several concurrent pathways.[10,11] The first one was reported as the homolytic cleavage of the bisphenol-A unit to yield isopropenylphenol, ethylphenols, cresols and phenol; while the second one was the heterolytic cleavage of the bisphenol-A unit to yield isopropenylphenol and phenol; the last one was postulated to be the cyclization product of the glycidylether side chain to yield $C_6H_5$-O-$C_3H_3$ or $C_6H_4$-O-$C_3H_4$.

According to these mechanisms, it can be suggested that the acidic monomers and oligomers released during PLLA degradation may enhance the homopolymerization reaction of DGEBA at high temperatures. In this way, by increasing PLLA contents in the blends the second degradation stage is more pronounced.

### Thermal Degradation of Cured Epoxy/Poly(L-lactide) Blends

TG and DTG curves for cross-linked EP5, EP10, EP20 and EP30 blends, together with those for EP0 and EP100, are given in Figure 5a and 5b, respectively. Both EP100 and EP0 degrade in a single stage. The stability of EP0 is higher than that of EP100. Cross-linked DGEBA degrades mainly at temperatures between 350 °C and 625 °C, which are clearly higher than those of the uncross-linked DGEBA resin.

For the blends all TG curves are comprised between those of the neat components. Furthermore, in the DTG curves, a shoulder can be seen on the low temperature side of the main peak of the EP10 blend, which progressively becomes more apparent, when increasing PLLA content. Finally, it appears as a separated peak in the EP30 blend. These results show two degradation stages in most of the blends, symbolized as $P_1$ for the low temperature stage and $P_2$ for the high temperature one. If we consider at the weight fraction volatilised in P1, the fact that the weight loss is 7.0, 15.9 and 24.5 wt% for EP10, EP20, and EP30, respectively, and that these values coincide with the real percentage of PLLA in the total mass of amine-epoxy, then this suggests that $P_1$ arises from the decomposition of PLLA in the cross-linked blend.

Moreover, PLLA starts decomposing at lower temperatures than cross-linked DGEBA and it would be expected for $T_i$ in the multiphasic blends to be constant,

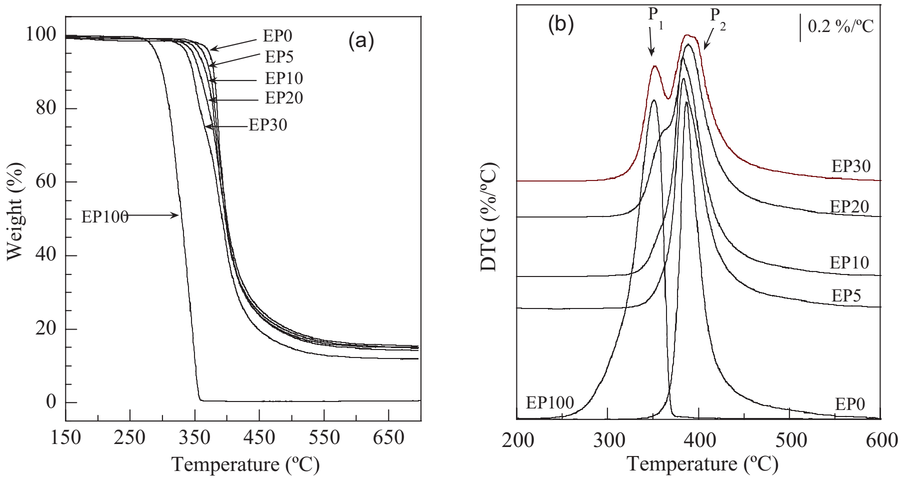

**Figure 5.**
TG (a) and DTG curves (b) for cross-linked DGEBA/PLLA blends heated at 10 °C/min. Thermograms have been shifted vertically for clarity.

and equal to $T_i$ of neat PLLA. However, the experimental results showed that $T_i$ for the blends is higher than that for neat PLLA. This behaviour seems to indicate some chemical or physical effect delaying the onset of degradation.

Peterson-Jones[12] investigated the mechanism of thermal degradation of amino-cured epoxy resins. He proposed that at low temperatures (300–350 °C) a series of dehydration reactions and homolytic scission of the chains, mainly around the nitrogen atoms, coming from the hardener takes place. At higher temperatures, a radical mechanism was proposed to produce phenolic products and aniline derivatives. However, these reactions occur at temperatures higher than $T_i$ of PLLA, so no interaction between the products of degradation of the cross-linked DGEBA with those of PLLA that give rise to such behaviour can be expected.

Since the chemical effects are not possible, physical effects, such as the diffusion rate of the species evolved, which in turn would depend on the degree of dispersion of the phases, may be responsible for this behaviour. Thus, this increase in $T_i$ with the cross-linked DGEBA content would indicate that the evolved gases have more difficulty to escape when increasing cross-linked DGEBA contents.

## Conclusion

It has been shown that PLLA is totally miscible with uncross-linked DGEBA over the entire composition range, and the thermal degradation of their blends depend on chemical effects, such as some sort of interaction between the products of degradation of DGEBA and PLLA. On the contrary, the cross-linked blends were multiphasic and their degradation behaviour could be attributed to physical effects, which in turn would depend on the degree of dispersion of the phases coexisting in the immiscible blend.

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