

ESSENTIAL WORK OF FRACTURE OF POLI(LACTIC ACID) MODIFIED BY REACTIVE EXTRUSION

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RESUMEN

En este trabajo se han evaluado las variaciones en el comportamiento mecánico y a fractura de láminas de 1 mm de espesor de dos grados de PLA con contenidos diferentes de enantiómero D (2 y 4.5 % mol), procesadas mediante extrusión reactiva-calandrado (one-step REX-Calendering). Como agente reactivo se ha empleado un oligo-copolímero de estireno-glicidil-acrilato, el cual promueve durante el procesado reacciones de extensión y/o ramificación de cadenas. De acuerdo con los parámetros mecánicos a tracción evaluados, la modificación en la arquitectura molecular obtenida hace disminuir substancialmente la velocidad de envejecimiento físico, provocando los mayores cambios en el PLA con mayor contenido de enantiómero D. En cuanto al comportamiento a fractura, el término esencial de trabajo específico de fractura (w_e) no presenta modificaciones sustanciales, pero sí el término no-esencial (βw_p) relacionado con la resistencia a la propagación de grieta. En el caso del grado con menor contenido de enantiómero se observó un aumento, mientras que en el de mayor contenido se observó una clara disminución.

ABSTRACT

In this work it has been evaluated the variations in the mechanical and fracture behaviour of sheet 1 mm thick with two commercial grades of PLA with different contents of D-enantiomer (2 and 4.5 mol%), processed by a "one-step REX-Calendering method. As reagent has been used a styrene-glycidyl acrylate copolymer, which promotes chain extension and / or chain branching reactions. According to tensile mechanical parameters, the change in the molecular architecture substantially decreases the rate of physical aging, causing the biggest changes in the PLA with a higher content of D-enantiomer. As for the fracture behaviour, the essential specific work of fracture (w_e) showed no substantial changes, but the term non-essential (βw_p), associated with resistance to crack propagation.

PALABRAS CLAVE: PLA, Reactive extrusion, EWF.

1. INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable and biocompatible polymer available from renewable resources, that finally have found a commercial use in single use packaging and not only in medical applications.

The degree of crystallinity that can be developed in PLA depends on the proportion of the D-lactic enantiomer, as well as the molecular weight. Proportions of as little as 4% mol of the D-lactic enantiomer (typical in commercial grades) reduce the rate of crystallization to such levels that, in typical processing conditions, the product is practically amorphous and has brittle behavior [1-3]

At room temperature, due to the proximity to T_g and the structural characteristics of its chain, PLA exhibits an accelerated ageing process, which causes a significant

decrease in free volume (densification) as well as an increase in the density of molecular entanglement and tie molecules [4]. Both factors limit molecular mobility to a great extent, reducing storage capacity and energy dissipation under a mechanical stimulus, which in itself generates ductile–brittle transition behavior [5].

It is well known that this physical ageing is a reversible process, which can be reverted by applying a thermal treatment at temperatures close to its T_g , followed by quenching. In this way, the high molecular mobility provoked by heating causes a reduction in the proportion of 'densified domains', which favours ductile behaviour [5, 6].

This brittle nature, together with its poor melt strength and high thermo-degradation sensitivity, reduces its use to very limited applications and limits specific processing methods such as film blowing or foaming.

To overcome these drawbacks, chain modification by reactive extrusion (REX) has become an attractive way by using various chemical reactions such as grafting, branching and functionalization [7]. Pilla et al. [8] reported that chain topology modification by branching is an attractive way to enhance melt properties for PLA. Chain branching degree depends on the functionality of the chain extender (CE) and generally leads to an increase in the molecular weight.

Our research group works in a project that aims to assess the final properties (thermal, mechanical, fracture behaviour and biodegradability) of sheets obtained by one step REX-calendering, that could be used in the fabrication of thermoformed packaging.

This paper presents a study of the fracture behaviour of two thermally treated amorphous PLA commercial grades that exhibits ductile behaviour. The objective is to assess possible changes in the Essential work of fracture as a result of the modification induced during reactive extrusion process.

2. EXPERIMENTAL

2.1. Materials

Two PLA extrusion grades from NatureWorks were used: PLA 4032D and PLA 2002D with a nominal molar content of 2% and 4.5% of D-enantiomer and MFI 6.4g/ 10 min \pm 0.3 and 5.8g/ 10 min \pm 0.2 (210°C/2.16Kg), respectively. The chain-extender (CE) was a styrene-acrylic multi-functional-epoxide oligomeric agent (SAMfE), supplied by BASF (Joncryl-ADR-4300F) in flack form with a molecular weight of 5443, an epoxy equivalent weight of 433 g/mol and Tg = 56°C. Figure 1 shows the generic structure of the CE used. [9]

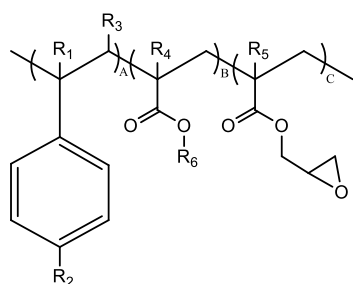


Figure 1. Structure of SAMfE (CE). R1-R5 are H, CH₃, a higher alkyl group, or combinations of them; R6 is an alkyl group, and A, B and C are each between 1 and 20.

2.2. One step Reactive extrusion-calendering

It was performed in a co-rotating twin screw extruder 25 mm (L/D=36), (KNETER 25X24D, COLLIN) at 40 rpm under nitrogen atmosphere and the temperature profile ranging from 150°C (Feeding zone) until 175°C (die). Prior to processing, PLA pellets were dried at

80°C for 3 hours in a PIOVAN (DSN506HE) hopper-dryer (dew point = -40°C) and kept during all the extrusion process under the same conditions. The CE was powdered and dried at 55°C under vacuum.

In order to obtain a nominal dosage of **0.5 weight % of CE**, the dosing rate was adjusted and fed during 120 min to ensure stable regime and obtain enough length of calendered sheet. Furthermore, vacuum was applied in prior die zone to remove any gas created by the reaction. The sheets were calendered (Techline CR72T, COLLIN) with 1 mm nominal width and the chill rolls temperature was set to 50°C. Table 1 shows the sample identification codes used along this study: PLA-X, where X indicates the D-enantiomer content.

Table 1. Sample identification codes used.

Formulation	Sample code.
PLA 4032D neat	PLA-2
+ 0.5% w/w CE	PLA-2M
PLA 2002D neat	PLA-4
+ 0.5% w/w CE	PLA-4M

It should be noted that under these processing conditions the sheets obtained showed a low degree of crystallinity (< 3%, according to DSC analysis), and that the modifications induced by the SAMfE promote an increase in mass molecular average, as shown in Table 2.

Table 2. Average molecular weights and molecular weight distributions according to SEC in HFIP at 25°C.

Sample	Mn (kg/mol)	Mw (kg/mol)	PDI
PLA-2	84.2	179.5	2.1
PLA-2M	119.5	297.3	2.5
PLA-4	98.1	181.8	1.8
PLA-4M	118.7	246.8	2.1

2.3. Mechanical and fracture characterization

All the tests were carried out using a GALDABINI SUN 2500 universal testing machine in tensile configuration equipped with a 5 kN load cell. The testing conditions were a constant crosshead speed of 10 mm/min and room temperature (23°C). Local deformation was measured with a video extensometer, a Mintron OS-65D CCD video camera in conjunction with Messphysik Windows-based software.

The tensile behaviour of the sheets was determined in the machine direction flow (MD) following the ISO 527-2 standard. The test specimens were obtained using a cutting press with a die conforming to type 5B of the ISO 527-2 standard. The thickness of each individual specimen was measured. The load-displacement curve for each specimen was recorded. From these curves, the

elastic modulus (E), yield stress (σ_y), strain at yield (ϵ_y) and at break (ϵ_b) were calculated.

Prior to all mechanical and fracture tests, a thermal treatment for “de-ageing” was applied: heating to 60 °C for 90 min in an oven followed by rapid cooling in iced water (≈ 0 °C) for 30 min and dried. All the tests were then carried out within 50 min in order to avoid the beginning of the ageing process. The de-aged condition was verified by DSC and Dynamic Thermo-mechanic (DMTA) tests. In this last case a clear decrease and higher thermal sensitivity of the storage modulus (E') was observed in all thermal treated samples was observed.

For tensile tests, an additional group of aged samples were evaluated. In this case, after “de-ageing” heat treatment the samples were stored for 1 weeks at 25 °C and subsequently tested.

For the Essential work of fracture tests, Deeply double edge-notched samples (DDENT, Mode I) were prepared by cutting the sheets into rectangular coupons of total length $L=100$ mm, width $W=60$ mm and distance between grips $ZG=60$ mm. Deformation was followed with a video-extensometer following the procedure described in a previous work [10]. For every case, at least 12 specimens with ligament lengths varying between 5 and 25 mm were prepared. The ligament length range was selected according to the ESIS recommendations [11]. The notches were sharpened after the “de-ageing” heat treatment with a fresh razor blade (razor pushing) before testing. The resulting ligament lengths were precisely measured with a travelling binocular lens microscope.

3. RESULTS AND DISCUSSION

3.1. Tensile properties: Effect of chain architecture modification and physical aging.

Figure 2 shows typical engineering stress-strain curves ($\sigma-\epsilon$) for all studied systems. For physical aged samples it can be appreciated that traces correspond to a typical “semi-ductile” polymers, necked unstable after passing the yield point and with limited ductility, giving rise to a fracture with brittle features. Table 3 shows the characteristics mechanical parameter from these curves.

A visual inspection of the calibrated zone of the tested samples (Figure 3), reflect that in the case of neat PLA 2002D (PLA 4) there is a greater proportion of crazes even outside the rupture zone combined with micro-shear bands, being less in number and confined in the rupture zone for other cases. This seems to indicate that the molecular mobility is highly restricted.

Another interesting aspect is the whitening observed in both PLA 4032D systems (i.e., neat and modified), which is attributed to the strain-induced crystallization

which is showed by its greater structural regularity as a result of lower content of D-enantiomer.

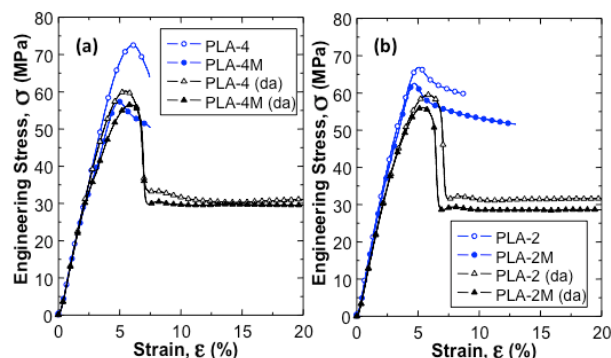


Figure 2. Typical stress-strain curves obtained for (a) PLA 2002D (PLA-4) and (b) PLA 4032D (PLA-2) before and after chain modification and in “physical aged” and “de-aged” (da) conditions.

Table 3. Mean values (7 samples) of the tensile properties of aged sheets. Values in brackets are the standard deviation of the mean.

Material	E (GPa)	σ_y (MPa)	ϵ_y (%)	ϵ_b (%)
<i>Physical aged</i>				
PLA 4032D				
PLA-2	3.5 (0.1)	67.1 (0.4)	2.5 (0.1)	8 (1)
PLA-2M	3.6 (0.1)	59 (3)	2.1 (0.1)	12 (3)
PLA 2002D				
PLA-4	3.5 (0.1)	72.3 (0.3)	2.8 (0.1)	8.5 (0.6)
PLA-4M	3.4 (0.1)	56 (2)	2.1 (0.1)	10 (1)
<i>De-aged</i>				
PLA 4032D				
PLA-2da	3.4 (0.1)	55 (2)	2.9 (0.1)	125 (27)
PLA-2Mda	3.1 (0.1)	53 (2)	2.8 (0.1)	107 (9)
PLA 2002D				
PLA 4da	3.4 (0.1)	65.5 (0.2)	2.82 (0.03)	135 (12)
PLA 4Mda	3.2 (0.1)	53.0 (0.6)	2.7 (0.1)	108 (9)

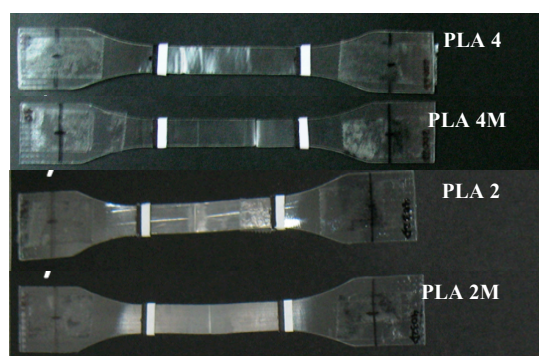


Figure 3. Aspect of the calibrated zone after tensile tests of physical aged samples.

By analyzing in detail the mechanical parameters obtained (Table 3) and considering the standard deviations, virtually no differences are observed in elastic behavior (E) or ductility (ϵ_b) resulting from the modification induced during reactive extrusion. However, clear differences in the yield point,

particularly in the yield stress (σ_y), could be observed. As can be seen in table 3, both PLA show a decrease in σ_y after the modification, being much more in PLA 2002D (about 23 %, Table 4). It is noteworthy that both modified PLA (PLA 2M and 4M), the values do not show differences between them.

As previously reported [12], due to the multifunctionality of the chain extender used (SAMfE), the molecular topology achieved is quite complicated, being a mixture of linear, single branched and star-like chains. The existence of these “star-like” chains could be increasing the free volume, facilitating the conformational changes of the chains during mechanical solicitation. In this way less stress is required to reach the yield point.

Table 4. Variation (%) on the yield stress (σ_y) as a consequence of chain architecture modification and physical aging.

Condition	Material	
	PLA 2002D (PLA 4)	PLA 4032D (PLA 2)
<i>Effect of chain architecture modification</i>		
Physical aged	-23	-12
De-aged (da)	-19	-4
<i>Effect of physical aging</i>		
Neat	+10	+22
Modified (M)	+6	+11

Figure 2 and Table 3 also shows typical curves of engineering stress-strain and mechanical parameters obtained for “de-aged” samples (da). Compared to the “aged” ones, it can be seen a significant increase in elongation at break ($> 100\%$), decrease of σ_y and increase of non-linear elastic region (viscoelastic component) before the yield point. These trends can be expected as a result of “de-aging” heat treatment, due to the reduction of “densified domains” [13,14].

Looking in detail at the calibrated zone after tests in “de-aged” samples it can be seen that for PLA4032D the whitening is substantially decreased in the modified system (Figure 4). This would indicate a decrease in the ability of strain-induced crystallization, which is expected as the structural changes induced during reactive extrusion increases structural irregularity of the chains (branches) that suppress the possibility of crystallization. This aspect has been verified by DSC analysis.

Taking as reference σ_y in de-aged conditions, one can see that the largest changes due to aging are shown for PLA4032D (increase of 22%, see table 4). This trend is to be expected when considering the molecular mass of the system. As shown in table 2, for neat PLA 4032D (PLA -2) has a lower M_n , indicating a higher proportion of short chains, which have greater mobility, offering fewer restrictions on the conformational changes induced by physical aging.

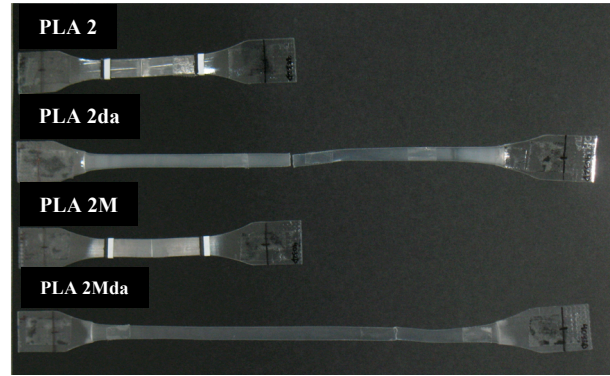


Figure 4. Aspect of the calibrated zone after tensile tests of neat and modified PLA 4032D (PLA 2), prior and after de-aging heat treatment (da).

Aging effects are diminished after the chain architecture modification, tending to be similar to each other. In principle, this may be indicating that the kinetics of physical aging process is being affected, slowing down or at least its consequences as a result of the change in molecular architecture induced by the SAMfe via chain branching.

3.2. Specific work of fracture: Effect of chain architecture modification.

As mentioned, the evaluation has been carried out on samples rejuvenated. Figure 5 shows typical curves of stress- “normalized” displacement (dividing by the ligament length). These traces show characteristic features of initiation of crack propagation after complete plastic collapse and necking of the ligament zone, similar to PET [15], and checked during the tests.

Table 5 shows the numerical values of the analysis. It is important to note the good fit of experimental data obtained (high correlation coefficients). As can be seen, in the case of PLA4032D (PLA-2) the essential term (ω_c) associated with the work required for the onset of crack propagation [16], shows no significant variations (considering the error involved).

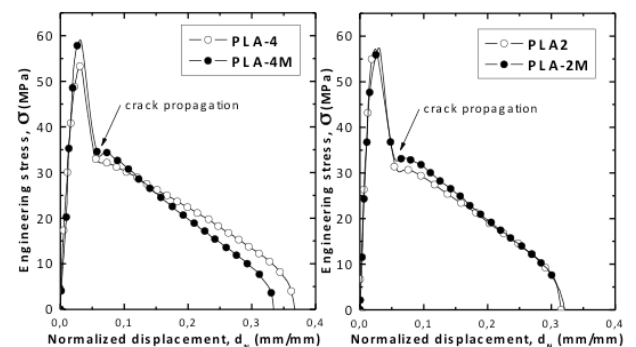


Figure 5. Typical stress-normalized displacement curves obtained for (a) PLA 2002D (PLA-4) and (b) PLA 4032D (PLA-2) after chain modification and in “de-aged” (da) conditions.

Table 5. Essential (ω_e) and non-essential ($\beta\omega_p$) terms from the specific work of fracture analysis. R^2 : correlation coefficient. with 95 % of confidence band.

Material	ω_e (kJ/m ²)	$\beta\omega_p$ (MJ/m ³)	R^2
PLA 4032D			
PLA-2da	43 (1)	4.0 (0.1)	0.9978
PLA-2Mda	39 (2)	4.4 (0.1)	0.9965
PLA 2002D			
PLA 4da	36 (2)	6.0 (0.1)	0.9980
PLA 4Mda	44 (2)	4.4 (0.2)	0.9912

However it does seem to be changes in the term related to the resistance to crack propagation once started, the non-essential term ($\beta\omega_p$). The modification appears to induce an increase in this term.

This may be related to the loss of the ability of strain-induced crystallization. In fact, as shown in Figure 6, the plastically deformed region of the ligament has a higher turbidity when the system has no modification (PLA-2). This behavior is similar to PET, which has been observed that this term is usually higher in samples amorphous, since it may undergo more plastic work during fracture, due to the greater deformability of the system[17].

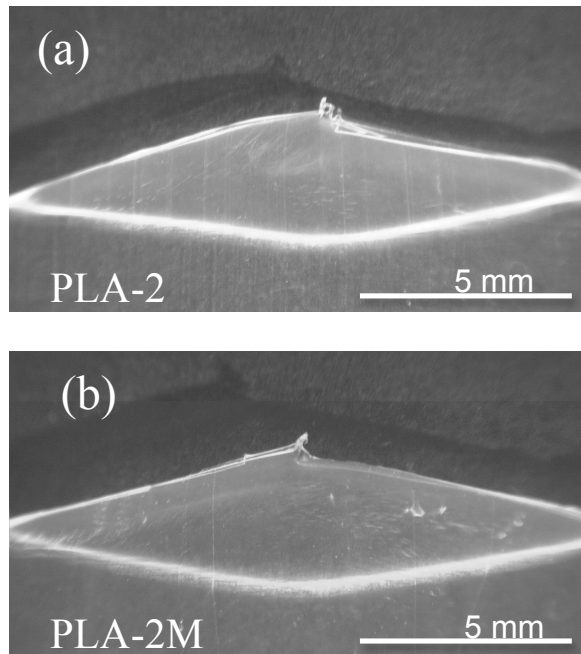


Figure 6. Deformation zone after testing for (a) neat and (b) modified PLA 4032D (PLA-2).

Regarding the PLA 2002D (PLA-4), the results indicate that the chain modifications induced by reactive extrusion seem to affect to a greater extent the evaluated parameters. ω_e shows a considerable increase (about 20%), which may be related to the observed reduction in σ_y .

The fact to start before the yielding process, leads to increased plastic deformation of the system, and therefore greater energy dissipation, prior to initiation of crack propagation. This means that to achieve the necessary local stress for crack propagation, it must be applied greater stress, and therefore further mechanical work.

The same effect causes, once propagation is initiated, that the environment for which it has to be spread is more distorted, close to the maximum possible extension limiting the subsequent deformation of the zone ahead of the propagating crack. Hence, the parameter related to the crack propagation, ie non-essential term ($\beta\omega_p$), decreases.

This aspect may be evidenced by comparing the values of the parameter β , which is related to the plastic zone size, and showed in Table 6. This value is determined, in our case, from the height (h) of the whitened zone after the tests as a function of ligament length, considering a rhomboid type geometry of the zone. Values of h are measured from the plane of the notch.

It can be seen that specific plastic work (ω_p) was not affected, but the plastic zone size, being lower for systems with a greater tendency to crystallize (PLA 4032D). For the case of PLA 2002D, the chain modification causes the plastic zone size decreases, indicative of a limited extensibility after initiating propagation. It is probable that induced topological change increase the number of molecular entanglements, thus hindering the deformability.

Table 6. Essential (ω_e) and non-essential ($\beta\omega_p$) terms from the specific work of fracture analysis. R^2 : correlation coefficient. with 95 % of confidence band.

Material	$\beta \times 10^2$	ω_p (MJ/m ³)
PLA 4032D		
PLA-2da	6.3 (0.3)	64 (4)
PLA-2Mda	6.5 (0.1)	67 (2)
PLA 2002D		
PLA 4da	8.8 (0.2)	66 (3)
PLA 4Mda	7.1 (0.1)	62 (4)

4. CONCLUSIONS

The change in the molecular architecture, induced by reactive processing conditions used in this study, substantially modifies the kinetics of physical aging undergone by the system, reducing its speed. This fact makes the PLA with a higher content of D-enantiomer show the biggest changes as regards yield point.

These topological changes do not alter the mechanical parameters for onset of crack propagation, quantified by

the essential term of the analysis of specific work of fracture (ω_e).

However, these changes do alter the behavior in terms of resistance to crack propagation. In the case of PLA 4032D, with greater ability to crystallization, the change in the molecular architecture that resistance increases as a result of loss in the ability of crystallization, favoring a higher deformability of the environment of the crack propagation plane.

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