Material Behaviour

Poly(lactic acid) and acrylonitrile – butadiene – styrene blends: Influence of adding abs – g – mah compatibilizer on the kinetics of the thermal degradation

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ABSTRACT

Square plates (nominal thickness: 3mm, nominal width: 100mm) of different rheologically modified PLA/ABS blends were manufactured through injection molding, with or without adding ABS grafted with maleic anhydride (MAH). During processing, the properties of the melt were stabilized and enhanced by the addition of a styrene-acrylic multi-functional-epoxide oligomeric reactive agent (SAMfE). PLA-REX was obtained by reactive extrusion of PLA. A general analytical equation was used in order to evaluate the kinetic parameters of the thermal degradation of PLA – REX/ABS and PLA – REX/ABS/ABS – g – MAH blends through thermogravimetric analysis. The thermal degradation of these blends occurred through two different reaction steps. Various empirical and theoretical solid-state mechanisms were tested to elucidate the best kinetic model. In order to reach this goal, plots of standardized conversion functions were constructed. Given that it is not always easy to visualize the best accordance between experimental and theoretical values of standardized conversion functions, a recently proposed index was determined to quantitatively identify the best mechanism. By doing that, it has been possible to determine the right activation energy of the thermal degradation. It has been demonstrated that the best mechanisms for these materials were random scission for the first step ($\alpha < 60\%$) and F3 (*i.e.* three order reaction) for the second one ($\alpha > 70\%$). The thermal stability of PLA – REX/ABS blend was greatly improved by adding the ABS – g – MAH compatibilizer. These findings were also confirmed by means of morphological characterization through scanning electron microscopy.

1. Introduction

Poly (lactic acid) (PLA) is a well-known biodegradable polyester derived from renewable resources that, due to its biodegradable condition, has attracted considerable interest both in academia and industry. Although PLA shows adequate balance of properties, to extend its applications, it is necessary to improve some of them, such as toughness or thermal resistance. The thermal resistance of PLA can be enhanced by increasing its crystalline fraction, for instance, by physical blending with poly-D-lactide (PDLA) to form a highly regular stereocomplex, where PDLA can act as a nucleating agent or by the use of heterogeneous nucleating agents. However, in most cases, the high cooling rate of the injection molding process [1] makes it difficult to obtain molded PLA articles with a high crystallinity level. Therefore, further processing steps, such as annealing treatments, are necessary to increase the crystal fraction [2]. On the other hand, the inherent brittleness is not

changed or is even increased due to the high crystalline level, making the material unsuitable for common uses. Finally, the high cost of PDLA production is probably the most important barrier for the practical application of this solution.

Among the different approaches followed, melt blending probably represents the most straightforward method to modify PLA properties. A review of the different approaches has been summarized by Kfoury et al. [3]. Most of the attempts to modify PLA properties, through melt-blending, have been directed to increase toughness, basically combining PLA with flexible polymers, including poly (ϵ -caprolactone) [4], poly (ether)urethane [5] or polybutylene adipate-co-terephthalate (PBAT) [6]. However, these solutions yield a decrease in the maximum allowable temperature that the blends can withstand. On the other hand, fast PLA degradation during melt blending is an undesirable side effect that needs to be controlled [7].

Previous research carried out in our group showed that the presence of a multifunctional epoxide-type oligomer during melt blending

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contributed to minimize PLA degradation via chain extension [8,9]. In this work, this oligomer was introduced by reactive extrusion and the resultant material was taken as a base matrix for this research and denoted as REX – PLA.

Blending PLA with heat-resistant tough polymers is an appealing way to increase both toughness and thermal resistance. Acrylonitrile-butadiene-styrene (ABS) is a heterogeneous polymer composed of a styrene-acrylonitrile copolymer (SAN) matrix phase with grafted polybutadiene particles. Some of the ABS properties, such as toughness, heat deflection temperature or tensile and flexural strength, may counterbalance those of PLA. However, PLA and ABS are thermodynamically immiscible and, therefore, compatibilizing agents, such as grafted or reactive copolymers miscible in the blend, are used to reduce interfacial tension, increase adhesion and obtain adequate phase morphology. Different coupling agents have been used in the past to compatibilize PLA/ABS blends. One of the first works was done by Li and Shimizu [10]. They used a reactive styrene–acrylonitrile–glycidyl methacrylate copolymer (SAN–GMA) coupled with a catalyst to induce an in-situ reaction during the melt blending between the epoxide group of the SAN–GMA and the PLA end groups (i.e. carbonyl or hydroxyl groups). The results indicated a shift in the glass transition and an improved impact strength and elongation at break with only a slight loss in Young's modulus. Later, Choe et al. [11] used the same compatibilizer to generate PLA/ABS composites, modified with clay and cellulose pulp as well as different additives, such as antioxidants or lubricants. The results indicated that fillers decreased the impact strength, but some of the blends were considered to exhibit an acceptable balance between mechanical properties and thermal resistance for automotive applications. In a similar way, Sun et al. [12] used epoxy-functionalized grafted ABS–g–GMA particles to improve the toughness of PLA. Crosslinking reactions took place in the blends with PLA during the melt-blending, increasing miscibility and impact strength. The effect of different compatibilizers on the mechanical properties of PLA/ABS blends was studied by Jo et al. [13]. Although in this case ABS was partially replaced with PLA, the use of compatibilizers caused a great increase in impact strength. The best performance was found with glycidyl–methacrylate grafted in styrene–acrylonitrile copolymer SAN–g–GMA and the incorporation of an antioxidant which contributed to the stabilization of PLA during the compounding process. In this case, it is expected that the remaining epoxy reactivity of the PLA–REX and the end groups of PLA (–COOH, –OH) were capable to react with the maleic anhydride grafted onto the ABS, enhancing in this way the PLA/ABS compatibility.

Despite the previous work done on PLA/ABS blends, to the best of our knowledge very little work has been devoted to the study of the thermal degradation mechanisms of these blends and the role of the coupling agent on it. The understanding of the thermal degradation behavior of the PLA/ABS blends is of significant importance in order to increase the in-service life of these blends under relative harsh thermal environments. Therefore, the kinetic modeling of the decomposition process plays a central role, being crucial for accurate prediction of the material's behavior under different working conditions [14–19]. Precise prediction requires knowledge of the so called kinetic triplet, namely, the activation energy, the pre-exponential factor and the kinetic model, $f(\alpha)$. This latter parameter, also known as conversion function, is an algebraic expression that is associated with the mathematical model that describes the kinetics of a solid-state reaction.

For these reasons, the aim of this paper is to determine the thermal stability of PLA–REX/ABS and PLA–REX/ABS/ABS–g–MAH blends in order to ascertain the effect of adding ABS–g–MAH. Moreover,

empirical (n-order and autocatalytic), conventional theoretical (R1, F1, D1, R2, F2, D2, R3, F3 and D3) and non-conventional theoretical (random scission) kinetic models have been tested, by means of a general analytical equation, in order to elucidate the best mechanism describing the thermal degradation of these blends.

2. Theoretical background

The reaction rate of a solid-state reaction is usually described by the following equation:

$$\frac{d\alpha}{dt} = k f(\alpha) = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where k is the kinetic constant, A is the Arrhenius frequency factor, R is the gas constant, E the activation energy, α the reacted fraction or conversion, T is the process temperature and $f(\alpha)$ accounts for the reaction rate dependence on α .

When integrating Eqn. (1) for experiments carried out at constant heating rate (β), the linear form of the general analytical equation, developed by Carrasco in 1993 [20], is obtained:

$$\ln \left[\frac{\beta \int_0^\alpha \frac{d\alpha}{f(\alpha)}}{T^2 \sum_{i=1}^{\infty} (-1)^{i+1} i! \left(\frac{RT}{E}\right)^{i-1}} \right] = \ln \frac{AR}{E} - \frac{E}{R} \frac{1}{T} \quad (2)$$

It was demonstrated that this infinite series can be truncated at the third term when activation energy is higher than 90 kJ/mol. Therefore, the equation to be used is the following:

$$\ln \left[\frac{\beta \int_0^\alpha \frac{d\alpha}{f(\alpha)}}{T^2 \left(1 - 2\frac{RT}{E} + 6\left(\frac{RT}{E}\right)^2\right)} \right] = \ln \frac{AR}{E} - \frac{E}{R} \frac{1}{T} \quad (3)$$

It must be taken into consideration that the calculation of activation energy, through Eqn. (3), requires an iterative procedure given that E is needed to evaluate the left hand side of the equation. The E value determined from the slope was introduced in the first member. The new E value obtained from the slope was again included in the first member and so on, until to reach a constant E value. In addition, the effect of truncating the series at a given i will be discussed later.

The most commonly solid-state theoretical mechanisms found in literature (R1, R2, R3, F1, F2, F3, D1, D2, D3 and random scission) have been analyzed. The random scission mechanism has been applied to $L = 2$, where L is the minimum length of the polymer that is not volatile. For $L \geq 3$, there is no symbolic solution and an iterative procedure is needed. The conversion functions [7], $f(\alpha)$, assume idealized models which may not be necessarily fulfilled in real systems. In order to overcome this limitation, empirical kinetic models have been proposed: n-order and autocatalytic kinetic models. The exponents $n = 0.550$ (for n-order kinetics), and $n = 0.771$ and $m = 0.244$ (for autocatalytic kinetics) have been previously optimized for the thermal degradation of PLA [21]. For comparison purposes, the same exponents will be assumed for the thermal degradation of PLA–REX/ABS and PLA–REX/ABS/ABS–g–MAH blends. By using Eqn. (3), it was possible to evaluate the values of activation energy and frequency factor for each kinetic model.

3. Materials and methods

3.1. Materials

In order to facilitate industrial applications, the materials used in our research work were of commercial type. A PLA extrusion grade (Ingeo 4032D®), purchased from NatureWorks (Arendonk, Belgium), was used. Its main properties are: D-lactide content = 2%, $M_n = 77 \pm 1$ kg/mol, $M_w = 165 \pm 4$ kg/mol, melt flow index = $6.5 \pm 0.3/10$ min (210 °C, 2.16 kg), $T_g = 60 \pm 1$ °C, $T_m = 167 \pm 1$ °C. A styrene-acrylic multi-functional-epoxide oligomeric agent (Joncryl-ADR-4300F®, referred to as SamfE in this study) was kindly supplied by BASF (Ludwigshafen, Germany) in flake form and was used as reactive agent for PLA. It features a functionality, $f_n = 12$, $T_g = 56$ °C, M_w of 5443 g/mol, and an epoxy equivalent weight of 433 g/mol. An ABS injection grade (Terluran GP-22®), purchased from Styrolution Group (Frankfurt am Main, Germany), was used, with a melt flow index of 19 ± 1 g/10 min (220 °C, 10 kg). Fourier transform infrared spectroscopy (FTIR) gave the following weight composition: 61% of PS, 18% of AN and 21% of PBD. Finally, a commercial ABS grafted maleic anhydride (ABS-g-MAH), under the trade name of Bondyram 6000, was purchased from Polyram Group (Israel). The content of grafted maleic anhydride, as previously determined through a FTIR calibration curve, was 0.6 molar.

3.2. Processing conditions

Prior to processing, raw PLA was dried at 8 °C for 3 h in a Pi-ovan (DSN506HE, Venice, Italy) hopper-dryer (dew point = -40 °C). Pre-dried raw PLA pellets and SamfE agent were melt compounded in an intermeshing co-rotating twin-screw extruder COLLIN Knetter 25×24D (COLLIN GmbH, Ebersberg, Germany) with a screw diameter of 25 mm (L/D = 36) in order to melt-strengthen PLA, as already reported elsewhere [22,23]. The extruder heating zones were set at 45, 165, 165, 170, 180, 190, 190 °C from the feeding zone to the die, respectively. The screw speed was set to 35 rpm and the mean residence time was 4 min. Once the extrusion line was started and stabilized with raw PLA, PLA and SamfE were introduced simultaneously in the hopper of the feeding zone under a N₂ blanket. The feeding rate of SamfE was

adjusted to PLA resin in order to obtain a nominal dosage of 0.5%. The extrudate (referred to as PLA-REX) was water-cooled, pelletized and placed in a convection oven at 90 °C for 4 h in order to supply crystallized pellets.

Crystallized PLA-REX pellets, ABS and ABS-g-MAH were dry-mixed and subsequently dried at 80 °C for 3 h. Two blends were manufactured: PLA-REX/ABS, by mixing 70% wt of PLA and 30% of ABS, and PLA-REX/ABS/ABS-g-MAH, by mixing 70% of PLA, 24% of ABS and 6% of ABS-g-MAH. A similar extruder process, as described above, was used for the homogenization procedure of the blends. The heating zones were set in this case at 150, 170, 180, 190, 195, 200, 200 °C from the feeding zone to the die, respectively.

Finally, square plates of 100 mm × 100 mm × 3 mm were injected in an Engel Victory 1100 kN injection molding machine. Before processing, each blend was dried at 80 °C, as above reported. The selected injection flow rate of all specimens was 45 cm³/s.

3.3. Thermal and morphological characterizations

TGA data were obtained on a Mettler Toledo thermogravimetric analyzer, model TGA-SDTA851. Samples of 20 mg were heated at nominal heating rates of 2.5, 5, 10 and 15 K/min from room temperature to 600 °C, under a dry nitrogen gas flow rate of 40 cm³/min. Two replicates were scanned and errors were lower than 1%.

Cryo-fractured surfaces of selected samples, located in the middle of injection-molded plates, were analyzed by Scanning Electron Microscopy (SEM) (JEOL, JSM-7001F, Tokyo, Japan). Experiments were performed under vacuum with an accelerating voltage of 2 kV. Samples were previously coated with gold/palladium.

4. Results and discussion

As an example, Fig. 1 shows the experimental curves recorded for the thermal degradation of PLA-REX/ABS and PLA-REX/ABS/ABS-g-MAH blends, under a nominal linear heating rate of 10 K/min. TG curves of both blends clearly exhibit two different zones of decomposition: a first step at $\alpha < 60\%$ and a second step at $\alpha > 70\%$. For this reason, two values of activation energy will be assessed for each blend. It must be taken into consideration that the manufacture of

Fig. 1. TG curves for PLA-REX/ABS and PLA-REX/ABS/ABS-g-MAH blends.

blends consisted of four treatments (reactive extrusion for the preparation of PLA-REX, PLA recrystallization, extrusion for blending PLA-REX and ABS with or without ABS-g-MAH, and further injection). From Fig. 1, it was possible to obtain various decomposition temperatures: onset decomposition temperature (T_5 ; temperature at which 5% of mass is lost) and other temperatures at various conversions (T_{50} and T_{95} ; temperatures at which 50% and 95% of mass is lost), as shown in Table 1. The onset decomposition temperatures, T_5 , of blends without and with ABS-g-MAH compatibilizer were 303.3 and 330.4 °C, respectively. Therefore, the onset decomposition temperature of blend containing ABS-g-MAH was 27.1 °C higher. Hence, the addition of compatibilizer is very relevant in order to increase the blend's thermal stability. On the other hand, the final decomposition temperatures, T_{95} , of blends without and with ABS-g-MAH compatibilizer were 462.5 and 553.4 °C, respectively. Therefore, the final decomposition temperature of blend containing ABS-g-MAH was 90.9 °C higher, thus indicating its excellent thermal resistance.

As an example, Figs. 2 and 3 show conversion and conversion derivative curves for the thermal degradation of PLA-REX/ABS and PLA-REX/ABS/ABS-g-MAH blends (at a nominal heating rate of 10K/min). From these plots, it was possible to evaluate various thermal parameters: conversion (α_m), conversion derivative ($(d\alpha/dT)_m$) and temperature (T_m) at the maximum decomposition rate, as shown in Table 1. It is clear that the presence of ABS-g-MAH slightly modified the values of conversion at the maximum rate: $\alpha_m = 49.2\%$ for PLA-REX/ABS and 46.4% for PLA-REX/ABS/ABS-g-MAH, as well as those of conversion derivative at the maximum rate $(d\alpha/dT)_m$: $2.68 \cdot 10^{-2}$ and $2.99 \cdot 10^{-2} K^{-1}$, respectively. Table 1 also contains the values of temperature ($T_{0.5}$) and conversion derivative ($(d\alpha/dT)_{0.5}$) at $\alpha = 0.5$. These values will be used to construct plots of standardized conversion functions, $f(\alpha)/f(0.5)$.

Table 1
Decomposition temperatures of PLA-REX/ABS and PLA-REX/ABS/ABS-g-MAH blends.

	T_5 (°C)	T_{50} (°C)	T_{95} (°C)	T_m (°C)	α_m	$(d\alpha/dT)_m$ (K^{-1})	$T_{0.5}$ (°C)	$(d\alpha/dT)_{0.5}$ (K^{-1})
PLA-REX/ABS	303.3	351.6	462.5	350.8	0.492	$2.68 \cdot 10^{-2}$	351.1	$2.68 \cdot 10^{-2}$
PLA-REX/ABS/ABS-g-MAH	330.4	356.5	553.4	354.6	0.464	$3.02 \cdot 10^{-2}$	355.8	$2.99 \cdot 10^{-2}$

Fig. 2. Variation of conversion with temperature for PLA-REX/ABS and PLA-REX/ABS/ABS-g-MAH blends.

As an example, Figs. 4 and 5 show the results of the general analytical equation (GAE) for three theoretical conventional mechanisms (F2, R2 and D2) corresponding to the first and second steps of the thermal degradation of PLA-REX/ABS/ABS-g-MAH blend (at a nominal heating rate of 10K/min). The fit of experimental data was excellent ($r^2 > 0.99$) for the three models.

Table 2 contains the average activation energy values (for the four heating rates used in this study) when using the general analytical equation (eqn. (3)) for the first step of the thermal degradation of PLA-REX/ABS and PLA-REX/ABS/ABS-g-MAH blends. During this first step, the degradation mainly corresponds to the PLA matrix. When comparing the activation energy values for both blends, it is clear that the material containing ABS-g-MAH was more thermoresistant (higher activation energies) for all mechanisms. Activation energy values for PLA-REX/ABS ranged in the interval of 155–456 kJ/mol and those for PLA-REX/ABS/ABS-g-MAH, in the interval of 199–579 kJ/mol.

When summarizing the results of linear regressions, most of the mechanisms led to regression coefficients higher than 0.99, except for the second step of the thermal degradation of PLA-REX/ABS/ABS-g-MAH ($r^2 = 0.97$ – 0.98). This means that almost all the mechanisms are quite adequate, from a mathematical point-of-view, to represent the kinetics of the thermal degradation of the blends considered in this study. Therefore, it is necessary to employ a method able to identify the best mechanism (and then it will be possible to evaluate the right activation energy responsible for the split of macromolecules leading to the thermal degradation of the polymer matrix). The standardized conversion functions have been successfully used to serve this goal. Theoretical values are determined by using the conversion functions. On the other hand, experimental values are calculated by means of the following equation:

Fig. 3. Variation of conversion derivative with temperature for PLA – REX/ABS and PLA – REX/ABS/ABS – MAH blends.

Fig. 4. Integral kinetic analysis by means of the general analytical equation (GAE) for the first step of the thermal degradation of PLA – REX/ABS/ABS – MAH blend by using three conventional theoretical mechanisms (F2, R2 and D2).

$$\frac{f(\alpha)}{f(0.5)} = \frac{\left(\frac{d\alpha}{dT}\right)}{\left(\frac{d\alpha}{dT}\right)_{0.5}} \exp \left[\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_{0.5}} \right) \right]$$

where $f(0.5)$, $\left(\frac{d\alpha}{dT}\right)_{0.5}$ and $T_{0.5}$ are conversion function, conversion derivative and temperature at $\alpha = 0.5$. These values are shown in Table 1 for both blends. Conversion derivative and temperature at $\alpha = 0.5$ are experimental values and E is the activation energy previously evalu-

ated for each of the mechanisms considered through the general analytical equation.

As an example, Fig. 6 shows the standardized conversion functions for the first step of the thermal degradation of PLA – REX/ABS/ABS – g – MAH (at $\beta = 10$ K/min), corresponding to one non-conventional theoretical mechanism (random scission) and two conventional theoretical conventional mechanisms (F1 and D2). Among these three mechanisms, it can be concluded that random scission mechanism is appropriate within the conversion interval of $\alpha = 0.2$ – 0.4 , whereas F1 mechanism is adequate for $\alpha < 0.3$. Moreover, it is clear that D2 mechanism is not appropriate at all, because there are high divergences be-

Fig. 5. Integral kinetic analysis by means of the general analytical equation (GAE) for the second step of the thermal degradation of PLA – REX/ABS/ABS – MAH blend by using three conventional theoretical mechanisms (F2, R2 and D2).

Table 2

Mean activation energy values, obtained by using the general analytical equation, for the first step of the thermal degradation, at various heating rates, of PLA – REX/ABS and PLA – REX/ABS/ABS – g – MAH blends.

Mechanism	E (kJ/mol)	
	PLA – REX/ABS	PLA – REX/ABS/ABS – g – MAH
n-order	196 ± 4	276 ± 3
Autocatalytic	176 ± 2	226 ± 4
RS (L = 2)	155 ± 2	199 ± 2
F1	242 ± 3	310 ± 4
R1	184 ± 3	238 ± 3
D1	380 ± 5	487 ± 5
F2	303 ± 6	395 ± 4
R2	212 ± 3	272 ± 3
D2	419 ± 7	530 ± 5
F3	379 ± 5	494 ± 5
R3	221 ± 3	284 ± 3
D3	456 ± 8	579 ± 6

tween experimental and theoretical values of the standardized conversion function. Similar results were found for the other heating rates. These plots give valuable information about the most suitable mechanisms. However, this information is only qualitative.

In order to elucidate the most appropriate kinetic model, it is absolutely necessary to develop a quantitative procedure. For this reason, a new index was proposed in a previous work, the integral mean error (IME) [24], defined as follows:

$$IME (\%) = \frac{\int_0^\alpha |\Delta_{f(\alpha)/f(0,5)}| d\alpha}{\int_0^\alpha d\alpha} \cdot 100 \quad \text{where} \quad |\Delta_{f(\alpha)/f(0,5)}|$$

Table 3 contains IME values for all the mechanisms studied in this paper corresponding to the thermal degradation of PLA – REX/ABS and PLA – REX/ABS/ABS – g – MAH blends. For the first step of the thermal degradation, the best mechanism was R2 for both materials, with IME values of $6.1 \pm 0.3\%$ and $5.4 \pm 0.2\%$ for PLA – REX/ABS and PLA – REX/ABS/ABS – g – MAH, respectively. On the other hand, for the second step of the thermal degradation, the best mechanism was F3 for both materials, with IME values of $3.0 \pm 0.2\%$ and $3.8 \pm 0.2\%$. The IME values for the other mechanisms were considerably higher, thus indicating worse fitting between experimental and theoretical values of standardized conversion functions. The worst mechanisms were: F3 for the first step (IME = 66-69%) and R1 for the second step (IME = 82-88%) for both blends.

In addition, an isoconversional kinetic analysis was carried out, by using the well-known method proposed by Kissinger-Akahira-Sunose:

$$\ln \left[\frac{\beta_i}{T_{\alpha,i}^2} \right] = Const - \frac{E_\alpha}{R} \frac{1}{T_\alpha} \quad (6)$$

From this method, it is possible to evaluate isoconversional values of the activation energy without assuming or determining any particular form of the reaction model. The results shown that both blends (with and without ABS – g – MAH compatibilizer) degraded into two steps, with an activation energy which was almost constant in each step. This was true for the TG experiments carried out at the four heating rates used in this study. For the thermal degradation of PLA – REX/ABS, the average activation energy values were: 215 ± 1 kJ/mol (first step for $\alpha = 5$ -60%) and 94 ± 1 kJ/mol (second step for $\alpha = 70$ -95%). For the thermal degradation of PLA – REX/ABS/ABS – g – MAH, the average activation energy values were: 270 ± 2 kJ/mol (first step for $\alpha = 5$ -60%) and 126 ± 2 kJ/mol (second step for $\alpha = 75$ -90%). These values are in accordance with the activation energy values determined by means of the general analytical equation: 212 ± 3 and kJ/mol and 272 ± 3 kJ/mol for the first step of the thermal degradation of

Fig. 6. Standardized conversion functions for the first step of the thermal degradation of PLA-REX/ABS/ABS-g-MAH blend. Points: experimental data; lines: two conventional theoretical mechanisms (F1 and D2), and a non-conventional theoretical mechanism (random scission for $L = 2$).

Table 3

Integral mean error (IME) between experimental and theoretical $f/f(0.5)$ for various mechanisms for the thermal degradation of PLA-REX/ABS and PLA-REX/ABS/ABS-g-MAH blends.

Mechanism	IME (%)			
	PLA-REX/ABS (1st step)	PLA-REX/ABS (2nd step)	PLA-REX/ABS/ABS-g-MAH (1st step)	PLA-REX/ABS/ABS-g-MAH (2nd step)
n-order	14.8 ± 0.4	48.1 ± 0.5	16.8 ± 0.4	44.1 ± 0.5
Autocatalytic	15.4 ± 0.3	43.1 ± 0.5	14.3 ± 0.3	41.1 ± 0.5
RS ($L = 2$)	16.4 ± 0.4	34.1 ± 0.3	14.3 ± 0.4	36.2 ± 0.3
F1	14.5 ± 0.3	30.5 ± 0.3	16.1 ± 0.3	33.3 ± 0.3
R1	11.6 ± 0.4	88.1 ± 0.6	12.7 ± 0.4	82.1 ± 0.7
D1	17.1 ± 0.4	52.1 ± 0.4	18.2 ± 0.4	50.3 ± 0.5
F2	36.5 ± 0.5	10.2 ± 0.3	33.2 ± 0.5	15.5 ± 0.3
R2	6.1 ± 0.3	51.1 ± 0.5	5.4 ± 0.2	53.0 ± 0.5
D2	19.6 ± 0.5	34.3 ± 0.4	18.7 ± 0.5	32.3 ± 0.4
F3	68.9 ± 0.9	3.0 ± 0.2	65.9 ± 0.8	3.8 ± 0.2
R3	13.7 ± 0.5	43.6 ± 0.6	14.5 ± 0.4	46.7 ± 0.7
D3	36.8 ± 0.6	29.1 ± 0.4	34.9 ± 0.6	28.3 ± 0.4

PLA-REX/ABS and PLA-REX/ABS/ABS-g-MAH, respectively, and 95 ± 2 and 128 ± 2 kJ/mol for the second step. Therefore, these results confirm what was found by means of IME values.

By summarizing our results, the best theoretical mechanisms for both blends (with and without compatibilizer) were R2 for the first step of the thermal degradation and F3 for the second one. The activation energy for the first step was 60 kJ/mol higher (+28%) and that for the second step was 34 kJ/mol higher (+36%) when adding ABS-g-MAH. These findings clearly prove the protective effect of ABS-g-MAH against thermal degradation.

In order to check the validity of the best activation energy values obtained for the thermal degradation of PLA-REX/ABS and PLA-REX/ABS/ABS-g-MAH, the theoretical conversion can be evaluated by using the following equations for R2 and F3 mechanisms:

$$\alpha = 1 - \left[1 - \frac{A R T^2}{\beta E} \left(1 - 2 \frac{R T}{E} + 6 \left(\frac{R T}{E} \right)^2 \right) \exp \left(- \frac{E}{R T} \right) \right]^2 \quad (7)$$

$$\alpha = 1 - \left[1 + \frac{2 A R T^2}{\beta E} \left(1 - 2 \frac{R T}{E} + 6 \left(\frac{R T}{E} \right)^2 \right) \exp \left(- \frac{E}{R T} \right) \right]^{-1}$$

Fig. 7 shows the comparison between experimental and theoretical values of conversion as a function of temperature for the thermal degradation of PLA-REX/ABS/ABS-g-MAH. From this plot, it is clear that the conventional theoretical R2 mechanism is completely appropriate to describe the first step of the thermal degradation of PLA-REX/ABS/ABS-g-MAH as well as it did for F3 mechanism in the second step. Only at very high conversion values ($\alpha > 90\%$), were some slight divergences detected. Similar conclusions were obtained when simulating the thermal degradation of PLA-REX/ABS.

Fig. 8 shows SEM micrographs of the cryogenic fracture surfaces of samples taken from the central zone of injected plate. The biphasic character of the obtained materials was clearly shown, the smoothest phase being that of PLA-REX and the more “porous” or “rough”, that of ABS. Two aspects are worth highlighting: (a) It was observed the refinement of the size of the dispersed or minor phase (ABS) after ABS-g-MAH addition (Fig. 8-b), being arranged in a “stratified-laminar” mode and oriented in the flow direction of the material during the

filling of the mold cavity; (b) The degree of decohesion between both phases decreased after the addition of ABS-g-MAH, thus indicating a higher degree of interaction or mechanical coupling between the phases. Both observations demonstrate the emulsifying/compatibilizing action exerted by the MAH contained in ABS-g-MAH compatibilizer, thus being responsible for a more thermally resistant blend.

5. Conclusions

A reactive extrusion-calendering process (REX) was used in order to manufacture square plates with a nominal thickness of 3mm of poly (lactic acid) (PLA) and its blends with acrylonitrile-butadiene-styrene (ABS) with or without adding ABS grafted with maleic anhydride (MAH) as a compatibilizer agent. During processing, the properties of the melt were stabilized and enhanced by the addition of a styrene-acrylic multi-functional-epoxide oligomeric reactive agent (SAMfE). The onset decomposition temperatures of PLA-REX/ABS and PLA-REX/ABS/ABS-g-MAH PLA-REX were 303 and 330 °C, respec-

Fig. 7. Comparison between experimental (curve) and theoretical (points) values of conversion as a function of temperature for the thermal degradation of PLA-REX/ABS/ABS-g-MAH blend.

Fig. 8. SEM micrographs of the cryogenic fracture surfaces of a) PLA-REX/ABS blend and b) PLA-REX/ABS/ABS-g-MAH blend, extracted from the central zone of the injected plates. The arrow indicates the direction of the filling flow of the cavity. Scale bar: 1 μm. Magnification: 10,000x.

tively. Therefore, the onset temperature increased 27°C when adding the ABS-g-MAH compatibilizer. On the other hand, the final decomposition temperatures were 463 and 553°C, respectively (90°C higher when adding the compatibilizer). The general analytical equation (GAE) was used in order to evaluate the kinetic parameters of the thermal degradation of polymer blends. Various empirical and theoretical solid-state mechanisms have been tested to elucidate the best kinetic model. In order to reach this goal, master plots were constructed by means of standardized conversion functions. Given that it is not always easy to visualize the best accordance between experimental and theoretical values of standardized conversion functions, a recently proposed index was determined to quantitatively discern the best mechanism. By doing that, it was possible to determine the right activation energy of the thermal degradation. The blend thermal degradation occurred in two steps. It was demonstrated that, for both blends, the best mechanism for the first step of the thermal degradation ($\alpha < 60\%$) was R2, with activation energies of 212 ± 3 kJ/mol and 272 kJ/mol, in the absence and presence of ABS-g-MAH, respectively. On the other hand, the best mechanism, also for both blends, for the second step of the thermal degradation ($\alpha > 60\%$) was F3, with activation energies of 95 ± 2 and 128 ± 2 kJ/mol, in the absence and presence of ABS-g-MAH, respectively). Therefore, the addition of ABS-g-MAH led to higher activation energies, thus proving its protective effect against thermal degradation. Finally, SEM micrographs demonstrated the emulsifying/compatibilizing action exerted by the MAH contained in ABS-g-MAH compatibilizer, thus being responsible for a more thermally resistant blend.

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