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PLA/ABS BLENDS: PREPARATION BY REACTIVE EXTRUSION AND MORPHOLOGICAL AND THERMOMECHANICAL CHARACTERIZATION.

MEZCLAS PLA/ABS: PREPARACIÓN POR EXTRUSIÓN REACTIVA Y CARACTERIZACIÓN MORFOLÓGICA Y TERMOMECÁNICA

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ABSTRACT

This paper focuses on the preparation and characterization of PLA/ABS blends by reactive extrusion. The study aims to increase the use of PLA by modifying its structure. The materials used include PLA, a diluent chain called Joncryl ADR-4300 F, and two types of ABS. The methodology involves compounding the materials by extrusion and injection molding, followed by characterization to evaluate their properties. The study found that the addition of ABS-g-MAH improved the stability and temperature of the blends, as well as their thermal and mechanical performance.

Keywords: PLA/ABS blends, reactive extrusion, morphological characterization, thermomechanics, specific mechanical energy.

RESUMEN

Este artículo se centra en la preparación y caracterización de mezclas de PLA/ABS mediante extrusión reactiva. El estudio pretende aumentar el uso del PLA modificando su estructura. Los materiales utilizados incluyen PLA, una cadena diluyente llamada Joncryl ADR-4300 F, y dos tipos de ABS. La metodología consiste en componer los materiales mediante extrusión y moldeo por inyección, seguido de una caracterización para evaluar sus propiedades. El estudio descubrió que la adición de ABS-g-MAH mejoraba la estabilidad y la temperatura de las mezclas, así como sus prestaciones térmicas y mecánicas.

Palabras Claves: mezclas PLA/ABS, extrusión reactiva, caracterización morfológica, termomecánica, energía mecánica específica.

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INTRODUCTION

The use of bio-based materials is constantly increasing. From the first synthesis of poly-lactic acid (PLA) to the present day, significant progress has been made with regard to PLA. A general problem of our times is to change consumption and production habits towards sustainable patterns, and a first step in that direction is to increase and massify the use of PLA. PLA has some limitations, but with the modification of this polymer (improving its structure), the applications of this material can be increased.

The experimental phase of this thesis was developed in a research center in Terrassa (Spain), called Centro Catalán del Plástico, under the supervision of the tutor belonging to the Politecnico di Torino. The argument of this thesis is framed in a wider project developed by the mentioned research center, which is promoted by the Spanish Ministry of Economy and Competitiveness (MINECO), whose name is: Bioblends of Pla prepared by reactive extrusion (project code MAT2013-40730-P). The objectives of this thesis are aligned with those of the project, and the results obtained are an important part of the research.

The main objective of the project is the production of a stable polymer blend containing different elements in an optimal ratio. The addition of the chain extender (JONCRYL® ADR-4300 F) to PLA (Ingeo 4032D), mixing with the compatibilizer acrylonitrile-butadiene-styrene with maleic anhydride grafts (ABS-g-MAH Bondyram 6000) and tests with two different types of acrylonitrile-butadiene-styrene (Styron Magnum 8434 and Terluran GP-22) are the basis for determining the ideal mixture for the for subsequent phases: extrusion and injection molding.

METHODOLOGY

Materials

Poly (lactic acid): Ingeo ™ PLA 4032D

The growing interest in this polymer is due to the natural origin of the monomer and the enormous potential of this material. The monomer of the polymer chain is lactic acid, whose IUPAC name is 2-hydroxypropanoic acid. PLA is classified as a bio-based polymer because it can be synthesized through classical processes using monomers of biological origin. One of the main sources to obtain the monomer is through the carbohydrate fermentation process, using corn, beet or rice as raw materials in conjunction with different microbial consortia of lactic acid bacteria (LAB) to produce lactic acid.

The main disadvantage that is present when working with PLA is the various degradation reactions that can affect the material. Because of the hydroxyl group and the carboxylic group, there is a risk of intra- and intermolecular esterification reactions. In addition, in the presence of moisture hydrolysis of PLA chains can occur and at a certain temperature thermal degradation also occurs. All these factors make the processing of this material complex, but the aim is to compensate part of the degradation effects by modifying the PLA.

Chain Extender (CE): JONCRYL® ADR-4300 F

To improve the stability of PLA, and consequently its properties, it was decided to use the chain extender marketed as BASF Joncryl ADR- 4300 F. The Joncryl molecule is a casual oligomer of styrene-acrylic-epoxy resin that provides reactive groups (epoxy) , which are responsible for the PLA branching process.

This branching of the polymer matrix, which takes place inside the extruder (during the process called "reactive extrusion", improves some properties of natural PLA and the product obtained is called REXPLA (Reactive EXtruded PLA). The main objective of this agent, According to the producer, it is to restore the original molecular weight, the intrinsic viscosity and the viscosity of the fluid state that vary during processing due to degradation reactions. The epoxy groups, provided by the chain extender, reconnect the PLA chains and thereby increasing the molecular weight of the product.

For this Thesis project, PLA and Joncryl are introduced into a co-rotating twin-screw extruder in a nominal proportion of 98.5:1.5 by mass respectively and the mixing and reaction of the components was ensured by a minimum residence time in 4 minute extruder.

Acrylonitrile-Butadiene-Styrene (ABS Terluran GP-22 and Styron Magnum 8434)

Acrylonitrile-Butadiene-Styrene is an amorphous thermoplastic polymer. It is a copolymer (terpolymer) combining acrylonitrile, 1,3- butadiene and styrene to blocks, with ratios typically ranging from 15-30% acrylonitrile, 5-30% butadiene and 40-60% styrene. The composition of each commercial ABS varies in terms of the percentage of each polymer and this has an impact on some ABS properties, such as impact resistance, viscosity, surface appearance, reactivity and heat resistance.

The use of ABS is widespread in the world, and this material is present in thousands or millions of commercial products. One of the most relevant applications of this polymer is the automotive industry, where ABS is used for the manufacture of internal and external parts of vehicles. One of the main drawbacks of ABS is the fact that its synthesis is based on fossil fuels (non-renewable, from petroleum through petrochemical processes to obtain the monomers), and that its recyclability is very limited. The two types of ABS selected to be evaluated in this project are: BASF Terluran GP-22 and TRINSEO Styron Magnum 8434, both targeted at “general purpose.”

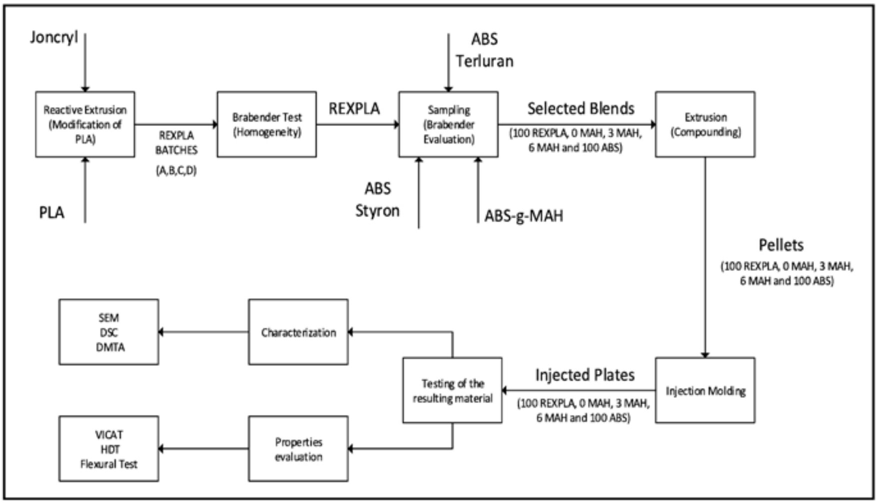
Maleic anhydride grafted on ABS (Bondyram 6000)

This is a polymer that has an ABS matrix with maleic anhydride (MAH) groups that have been grafted onto the structure (ABS-g-MAH). The grafting process can be performed through different mechanisms and the type of mechanism can influence the final properties obtained. A commercially produced ABS-g-MAH, known as BONDYRAM 6000, was used for this project. This compound is generally used to serve as a coupling or compatibilizing agent between ABS and polar resins, polycarbonates (PC) or polyamides (PA). According to the manufacturer’s technical specifications, the amount of maleic anhydride present in the polymer is 0.6-1%. The addition of this compound is intended to increase the interaction or favor compatibility between the two main phases to be used: REXPLA and ABS.

Experimental Procedure

The experimental procedure of this study begins with the production of REXPLA (Reative EXtruded PLA) and this is the basis for the other phases because the main compound of the mixtures is REXPLA. The amount of this material produced is approximately 50 kilograms, which was used in different areas of research and in the development of this project. After the production of REXPLA, a sampling phase was carried out, in which two important parameters were sought to be determined: the amount of compatibilizer (ABS-g-MAH) to be used and which type of ABS is most suitable for preparing the mixtures. The next step was the processing of the mixtures, which contains an extrusion phase (Compounding), with the purpose of mixing the materials and producing homogeneous pellets, and an injection molding phase to produce the final pieces of interest. The final part of the experimental procedure is the characterization of the materials obtained and the evaluation of certain relevant properties. The selected methodology, explained above, is represented in Figure 1.

Figure 1. Diagram of the experimental procedure



The main materials and techniques are indicated in the figure, which shows succinctly the steps followed to meet the objectives of this project.

Material processing

Brabender

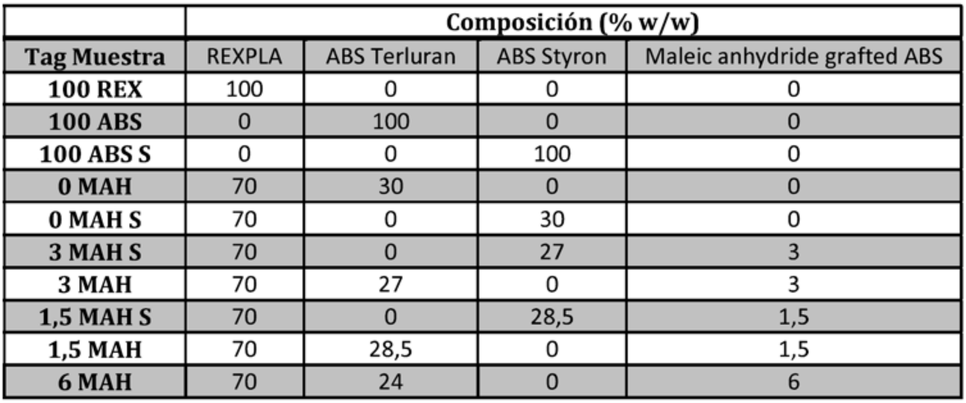
The Internal Mixer Test provides important information that makes it possible to carry out a comparative rheological study. The main use of this equipment for this project is to evaluate the resistance that each sample exerts on the rotating spindles of the Brabender. The equipment results in a “Plastogram”, where torque and temperature are reported as a function of time. Torque measurements are an indirect indicator of viscosity and serve to evaluate phenomena such as structural changes, cross-linking effects, remaining reactivity or degradation.

Many analyses were performed on this equipment, which can be grouped into two main categories: those performed to evaluate the homogeneity of the REXPLA and those aimed at verifying the feasibility of the mixtures (sampling phase).

For this project, the samples tested in the Brabender were labeled and the coding is represented in Table 1, where the composition of each sample is also shown. This labeling is used and maintained throughout the Thesis project, up to the Results and Discussion section.

The use of two different types of ABS is aimed at selecting the most appropriate for the operations to be performed, evaluating possible reactions or changes in viscosity. On the other hand, the variation of the percentage of compatibilizer (ABS- g-MAH) is based on the search for an optimum ratio for the mixtures.

Table 1. Coding of the sampling phase



	Composición (% w/w)			
Tag Muestra	REXPLA	ABS Terluran	ABS Styron	Maleic anhydride grafted ABS
100 REX	100	0	0	0
100 ABS	0	100	0	0
100 ABS S	0	0	100	0
0 MAH	70	30	0	0
0 MAH S	70	0	30	0
3 MAH S	70	0	27	3
3 MAH	70	27	0	3
1,5 MAH S	70	0	28,5	1,5
1,5 MAH	70	28,5	0	1,5
6 MAH	70	24	0	6

Through the data obtained in the Brabender, it is also possible to calculate the Specific Mechanical Energy (SME), which is used to study the amount of energy consumed during the internal mixer test and to compare the performance of each formulation.

Extrusion

Extrusion is a widely used technique for the production of plastic materials. For this project, the starting point is pellets of each pure matrix, which during the extrusion process are melted and processed under a certain temperature profile. The material is “extruded”, that is, it is passed through a hole of defined geometry, and at the end of the extruder a continuous “extrusion thread” is obtained that is cooled (in a water bath at room temperature) and Cut into desired shape. The configuration, geometry and elements of the extruder can be changed depending on the type of material to be worked. Typically, extruders may have one or more screws, which are responsible for transporting and moving the molten polymer within the extruder. For this project, a co-rotating double screw equipment was used because it provides intensive agitation and mixing, which are very favorable for the required objective.

Modification of PLA through reactive extrusion

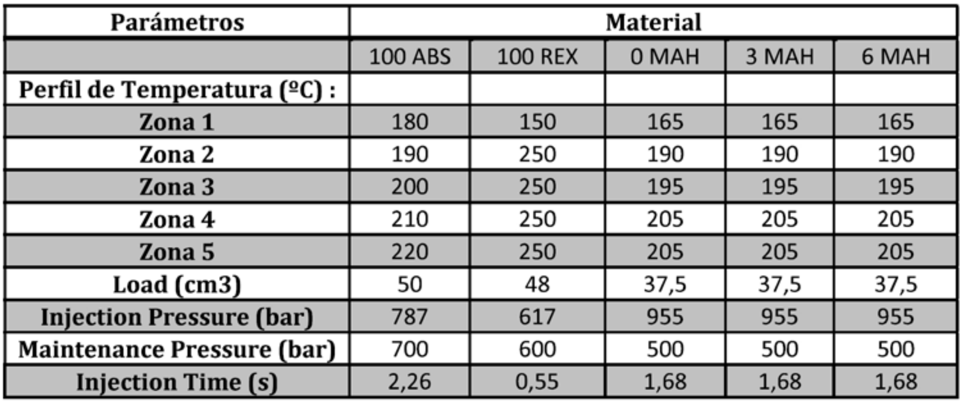
The twin-screw extruder is used as a reactor (in the process known as reactive extrusion) because it has some features that are useful for this purpose. Extruders can be modeled as a real reactor, which has a modest reaction volume, a variable Residence Time Distribution (RTD), a short average residence time and a modelable reaction time.

For PLA extrusion, standard operating conditions were established that allowed homogeneous batches of REXPLA to be produced. To avoid significant pressure changes, which could influence homogeneity, the Joncryl dosing system was carefully calibrated and controlled before extrusion. The Joncryl dosage was calibrated in such a way as to maintain a constant ratio with the PLA fed.

Injection molding

The starting material and the process conditions during injection are responsible for the final result of the injected parts. In this case, the extrusion of REXPLA and ABS is done to produce pellets from the mixture but, due to the inherent conditions of the injection process, there is a risk of phase separation. The injector has only one screw inside that works as a piston, so the shear and mixing are different from the extrusion and internal mixer values. Some conditions such as cycle time, temperature profile and pressure are initially estimated and then adjusted to optimize the process. The conditions for each material are reported in Table 2. It should be considered that REXPLA is not a commercial product and that it was produced on a medium scale in the laboratory and that it is a thermo-reologically complex polymer, whose interaction with ABS has not been fully described.

Table 2. Conditions used during injection molding



Parámetros	**Material**				
	100 ABS	100 REX	0 MAH	3 MAH	6 MAH
Perfil de Temperatura (ºC) :					
Zona 1	180	150	165	165	165
Zona 2	190	250	190	190	190
Zona 3	200	250	195	195	195
Zona 4	210	250	205	205	205
Zona 5	220	250	205	205	205
Load (cm3)	50	48	37,5	37,5	37,5
Injection Pressure (bar)	787	617	955	955	955
Maintenance Pressure (bar)	700	600	500	500	500
Injection Time (s)	2,26	0,55	1,68	1,68	1,68

The mold selected for this process is a square mold, with a side of 100 mm and a thickness of 3 mm, and it also has a cooling system with water circulation at room temperature. This mold was used for the five formulations, so it has a common geometry and cooling conditions for all materials.

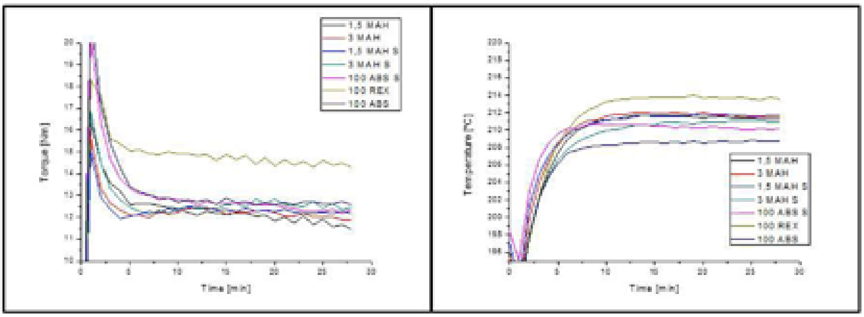
RESULTS

Brabender

The first phase of the project was the preparation of REXPLA. Since the required quantity of this material was 50 kilograms, production was carried out on different days and in different batches. A small sample was taken from each batch to study the behavior and compare the properties of the material. The resulting results were obtained by means of a Brabender test, which reported the values of* stability under shear and temperature for each batch.

After these tests, the sampling phase is carried out, where the samples were prepared with different percentages of ABS-g-MAH and with the two types of ABS. The REXPLA phase is kept fixed at 70 % and 1.5 % and 3 % of ABS-g-MAH are evaluated, completing the rest with ABS. The values of the mixtures are compared with the pure REXPLA samples and the two types of ABS. The action of the compatibilizing agent can be observed in Figure 2, where the stability under shear and temperature improves when the amount of ABS-g-MAH is increased.

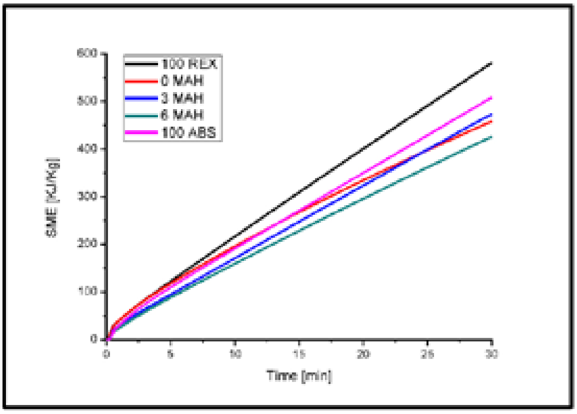
Figure 2. Thermal and shear stability of the different samples.



To select the most suitable type of ABS, a test was carried out at the Brabender and it was decided to use the ABS commercially known as TERLUARAN GP-22, since the torque and temperature values were more convenient. After having selected the ABS and studied the effect of ABS-g-MAH, it was decided to increase the amount of ABS-g-MAH to 6%, and to discard the 1.5% formulation because it had a very similar behavior to the 3% formulation. Therefore, the samples selected to go through the injection process are 100 REX, 0 MAH, 3 MAH, 6 MAH and 100 ABS.

Finally, the value of the Specific Mechanical Energy was calculated from the data obtained in the Brabender, which provides additional information on the materials under study such as, for example, the rheological behavior of the system. The trend of the SME for each compound can be seen in Figure 3, and is as follows linear for all materials except for the 0 MAH sample (composed only of 70% REXPLA and 30% ABS without ABS-g-MAH).

Figure 3. Specific Mechanical Energy values of the selected materials



These selected formulations will be produced on a larger scale in the extruder (compounding phase) and the materials obtained will be injection molded. Then, the characterization and evaluation of certain properties of interest will be carried out on the injected specimens.

Morphological Analysis (SEM)

The starting point for the characterization of the final product is the morphological analysis. For this section, the two most representative mixtures were selected to provide a first idea of the resulting structure: 0 MAH and 6 MAH. For this analysis, different points and directions of cut and observation were selected to determine if there are significant differences in morphology. The morphological study of the materials aims to evaluate four main factors concerning the resulting structure: the influence of the MAH (See Figure 4A), the ABS-butadiene-REXPLA morphology (Figure 4B), the consequences of the metallic coating (Figure 5A) and the differences between the core and near-wall areas of the injected plates (Figure 5B).

Figure 4. Electron microscopy images for different sections of the specimens.

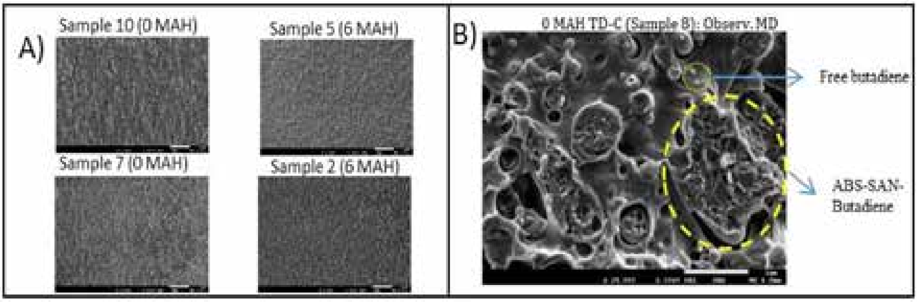
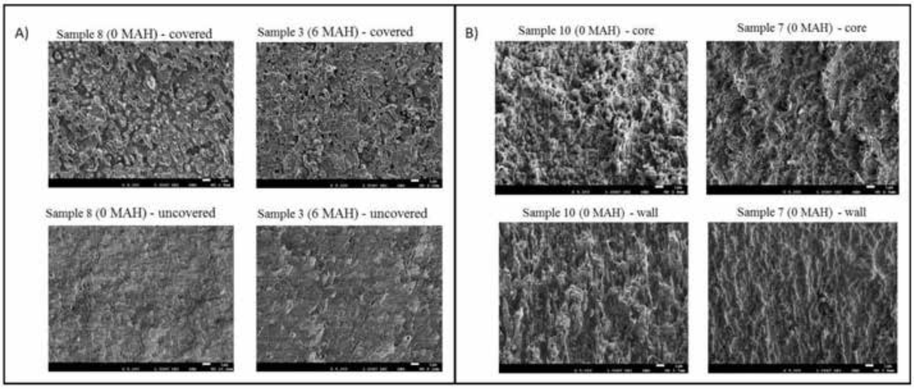


Figure 5. Electron microscopy images for different sections of the specimens.



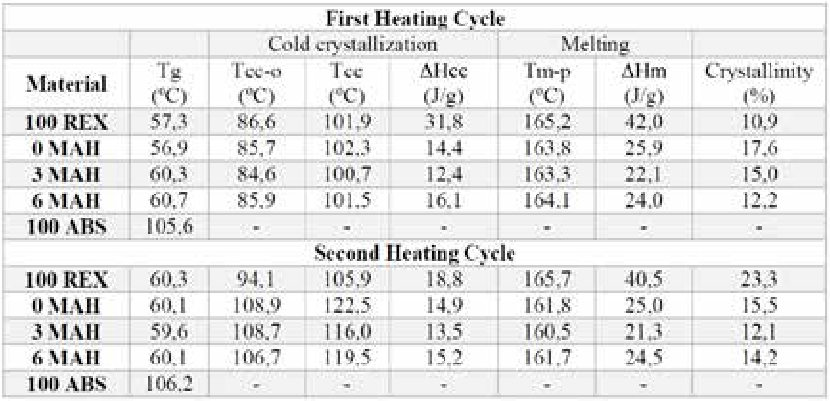
It can be intuited that the addition of ABS-g-MAH seems to have an emulsifying effect, because a reduction of the discontinuous phase within the matrix under study is observed. When a larger magnitude was performed (Figure 4B), the two phases present (REXPLA and ABS) and small domains that can be attributed to free butadiene were observed. It was determined that the coating attacks the samples (similar to a chemical attack) and that there are differences between morphology.

From the different observations, it was possible to intuit that the plates present a stratified morphology, with lamellar strata in the form of parallelepipeds, which have the longest side oriented in the transverse direction to the injection direction. In addition, these strata decrease in thickness from the core towards the plate walls. These features may be induced by the injection model (source type), where the material comes elongated and produces the structures visualized with the SEM.

Differential Scanning Calorimetry (DSC)

The data of interest in this test correspond to a first heating cycle, a cooling cycle and a second heating cycle. During the heating cycles, the typical signs of the glass transition and melting temperature of the REXPLA matrix and the glass transition of ABS are observed. In addition, for REXPLA and blends, the phenomenon of cold crystallization, which occurs simultaneously with the glass transition of ABS, is developed. From the thermal data, the crystallinity of the resulting materials was also calculated from this test. The addition of ABS-g-MAH seems to influence the crystallinity of the mixture, decreasing the value (See Table 3). For the first heating, a lower crystallinity value was obtained for REXPLA than for the blends, but in the second heating, the trend was the other way around.

Table 3. DSC data for the first and second heating cycle

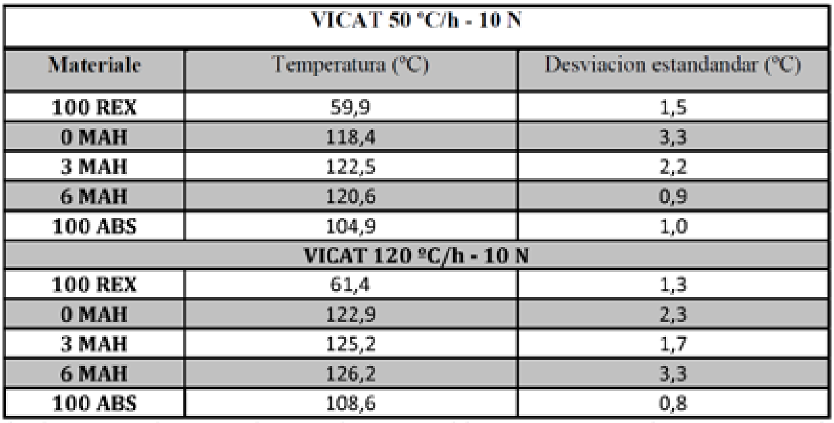


First Heating Cycle							
		Cold crystallization			Melting		
Material	Tg (°C)	Tcc-o (°C)	Tcc (°C)	ΔHcc (J/g)	Tm-p (°C)	ΔHm (J/g)	Crystallinity (%)
100 REX	57,3	86,6	101,9	31,8	165,2	42,0	10,9
0 MAH	56,9	85,7	102,3	14,4	163,8	25,9	17,6
3 MAH	60,3	84,6	100,7	12,4	163,3	22,1	15,0
6 MAH	60,7	85,9	101,5	16,1	164,1	24,0	12,2
100 ABS	105,6	-	-	-	-	-	-
Second Heating Cycle							
100 REX	60,3	94,1	105,9	18,8	165,7	40,5	23,3
0 MAH	60,1	108,9	122,5	14,9	161,8	25,0	15,5
3 MAH	59,6	108,7	116,0	13,5	160,5	21,3	12,1
6 MAH	60,1	106,7	119,5	15,2	161,7	24,5	14,2
100 ABS	106,2	-	-	-	-	-	-

VICAT Softening Temperature (VICAT)

This thermomechanical property was measured at two different heating rates, since this parameter can influence the result obtained. At low speeds, the material has more time available to develop the transformations in its structure.

Table 4. VICAT temperature for both heating rates



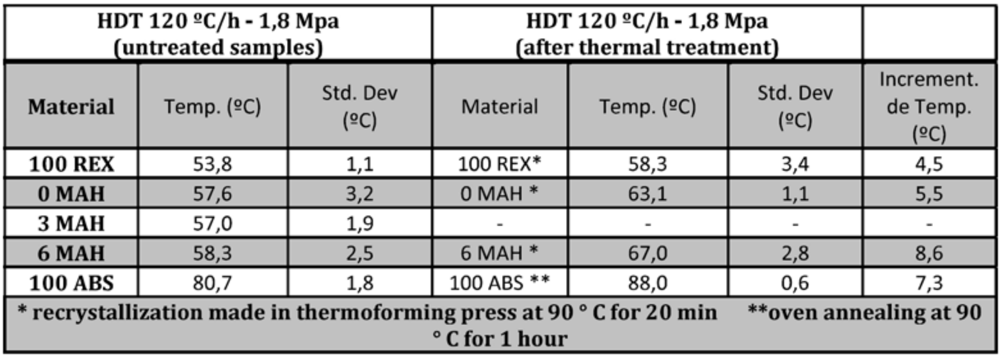
VICAT 50 °C/h - 10 N		
Materiale	**Temperatura (°C)**	**Desviacion estandandar (°C)**
100 REX	59,9	1,5
0 MAH	118,4	3,3
3 MAH	122,5	2,2
6 MAH	120,6	0,9
100 ABS	104,9	1,0
VICAT 120 ºC/h - 10 N		
100 REX	61,4	1,3
0 MAH	122,9	2,3
3 MAH	125,2	1,7
6 MAH	126,2	3,3
100 ABS	108,6	0,8

One fact that stands out is that the blends (see Table 4) have a higher VICAT value than the two starting materials (REXPLA and ABS). This is a thermomechanical advantage, but to evaluate that this is true, the heating rate values must be carefully observed. Another important result is that the addition of ABS-g-MAH increases the obtained VICAT temperature value for the blends.

Thermal Deflection Temperature (HDT)

By means of this experimental technique, two types of samples were analyzed: a first set containing the material at ambient conditions and a second group that was heat treated before the test. The results of this test indicate that the addition of ABS- g-MAH increases the value of the deflection temperature under load, as does the heat treatment in each case. In addition, it was observed that the values of the mixtures are in a range within the pure matrices (ABS and REXPLA).

Table 5. HDT temperature for both groups of samples

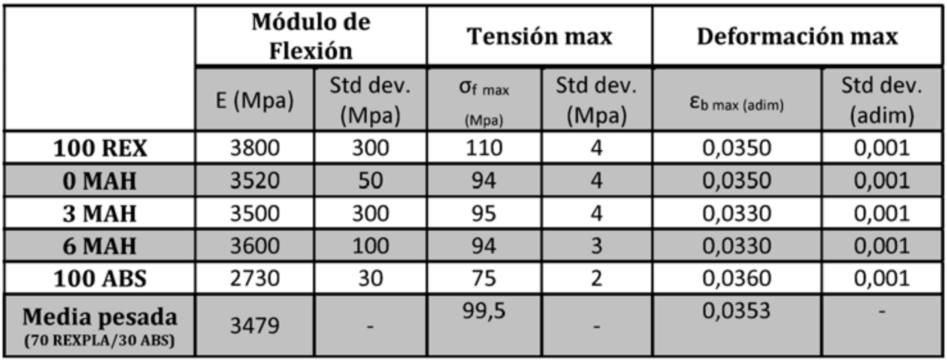


HDT 120 ºC/h - 1,8 Mpa (untreated samples)			**HDT 120 ºC/h - 1,8 Mpa (after thermal treatment)**			
Material	Temp. (ºC)	Std. Dev (ºC)	Material	Temp. (ºC)	Std. Dev (ºC)	Increment. de Temp. (ºC)
100 REX	53,8	1,1	100 REX*	58,3	3,4	4,5
0 MAH	57,6	3,2	0 MAH *	63,1	1,1	5,5
3 MAH	57,0	1,9	-	-	-	-
6 MAH	58,3	2,5	6 MAH *	67,0	2,8	8,6
100 ABS	80,7	1,8	100 ABS **	88,0	0,6	7,3
*** recrystallization made in thermoforming press at 90 ° C for 20 min **oven annealing at 90 ° C for 1 hour**						

Three-point bending test

With the values obtained from this test, the stress-strain graph was plotted, the flexural modulus was calculated for each material and the stress-strain point was located maximum. The mixtures have a flexural modulus value between REXPLA and ABS, located closer to REXPLA.

Table 6. Results of the three-point flexion test



	Módulo de Flexión		**Tensión max**		**Deformación max**	
	E (Mpa)	Std dev. (Mpa)	$\sigma_{f\ max}$ (Mpa)	Std dev. (Mpa)	$\varepsilon_{b\ max\ (adim)}$	Std dev. (adim)
100 REX	3800	300	110	4	0,0350	0,001
0 MAH	3520	50	94	4	0,0350	0,001
3 MAH	3500	300	95	4	0,0330	0,001
6 MAH	3600	100	94	3	0,0330	0,001
100 ABS	2730	30	75	2	0,0360	0,001
Media pesada (70 REXPLA/30 ABS)	3479	-	99,5	-	0,0353	-

The theoretical value of a 70 REXPLA/30 ABS mixture was calculated (see Table 6) and the value coincides with that obtained experimentally for the 3 mixtures. Furthermore, the addition of ABS-g-MAH does not seem to significantly influence the mechanical behavior of the mixtures.

CONCLUSIONS

The process of reactive modification of PLA, through reactive extrusion was carried out under the specified conditions, without major inconveniences, following the control of the proposed variables.

The study of SEM images suggests that ABS-g-MAH has an emulsifying effect on the obtained materials. The reduction of the dispersed phase indicates that there is an interaction between the maleic anhydride groups and REXPLA and ABS. Furthermore, the observations highlight the importance of considering the given flow pattern during injection, because it conditions the resulting structures.

For our process, the “source type” model generates lamellar strata whose influence extends to the measurement of certain parameters such as, for example, the VICAT and HDT values, because each one is related to different areas of the specimens (which have a different).

The analytical thermal study of the materials, through the DSC and DMTA techniques, provided valuable information on the transformations that occur within the material when the temperature is varied. The injection conditions influence the crystallinity obtained (especially in the case of REXPLA) and the emulsifying effect of ABS-g-MAH is also appreciated because the addition of MAH decreases the crystallinity (indicating that the chains are larger, with more interactions and therefore a less crystalline structure is achieved). The VICAT test indicates that the blends have a thermomechanical advantage over REXPLA and ABS, due to the phenomenon of cold crystallization, which develops for these materials and provides greater strength. With respect to the HDT test, the working conditions do not allow the phenomenon to develop before the HDT test.

However, it is found that ABS-g-MAH improves the HDT values as does the application of a heat treatment prior to the samples.

Finally, the mechanical behavior of the materials under bending indicates that the blends have a good performance, coinciding with what is expected theoretically. In addition, the flexural modulus of the blends is higher than that of ABS, which would imply a mechanical advantage of these composites.

Bibliography

A. Jiménez, M. Peltzer, and R. Ruseckaite, Poly(lactic acid) Science and Technology: Processing, Properties, Additives and Applications. Royal Society of Chemistry, 2014.

L.-Prog. Polym. Sci., vol. 33, no. 8, pp. 820 852, 2008.

tafor 2014 Ingeo TM Ind. Biotechnol., vol. 11, no. 3, pp. 167 180, 2015.

H. T. RAFAEL AURAS, LOONG-TAK LIM, SUSAN E. M. SELKE, Ed., POLY(LACTIC ACID) Synthesis,Synthesis, Structures, Properties, Processing, and Application. New Jersey: John Wiley & Sons, Inc., 2010.

F. Carrasco, P. Pagès, J. Gámez-Pérez, O. O. Santana, and M. L. Maspoch, Polym. Degrad. Stab., vol. 95, no. 2, pp. 116 125, 2010.

F. Carrasco, J. Cailloux, P. E. Sánchez-Jiménez, and M. L. Maspoch, Polym. Degrad. Stab., vol. 104, no. 1, pp. 40 49, 2014.

J. Cailloux, O. O. Santana, E. Franco-Urquiza, J. J. Bou, F. Carrasco, J. Gámez-Express Polym. Lett., vol. 7, no. 3, pp. 304 318, 2012.

R. Alrheological and mechanical properties of PLA, PBAT and their blends by reactive Polym. Degrad. Stab., vol. 97, no. 10, pp. 1898 1914, 2012.

S. W. Hwang, S. B. Lee, C. K. Lee, J. Y. Lee, J. K. Shim, S. E. M. Selke, H. Soto- Valdez, L. Matuana, M. Rubino, and R. Aur poly(L- Polym. Test., vol. 31, no. 2, pp. 333 344, 2012. [11] montmorillonite intercalant and anhydride maleic grafting on polylactic acid Appl. Clay Sci., vol. 107, pp. 62 69, 2015.