The effect of pine resin derivatives on the structural, thermal and mechanical properties of Mater-Bi® type bioplastic

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Abstract

The effect of three additives derived from pine resin: gum rosin (GR) and two pentaerythritol ester of gum rosin, Lurefor (LF) and Unik Tack (UT) in 5, 10 and 15 wt.%, on the properties of Mater-Bi®, based on plasticized starch, poly(butylene adipate-co-terephthalate) (PBAT) and poly(ε-caprolactone) (PCL) obtained by injection moulding processes was studied. The mechanical, microstructural and thermal properties were evaluated. LF had a cohesive behaviour with the components of Mater-Bi®, increasing the toughness of the material up to 250% accompanied by an increase of tensile modulus and tensile strength. UT had an intermediate behaviour, conferring cohesive and plasticizing effects, allowing an increase of 105% in impact resistance. GR had a more marked plasticizing effect. This allows processing temperatures of about 50 ºC lower than those used for neat Mater-Bi®. Also, an increase of the elongation at break, toughness and impact resistance in 370%, 480% and 250%, respectively, was achieved.

Keywords: Biodegradable polymers; Thermoplastic starch; Gum rosin; Pine resin derivatives, Compatibilizer; Plasticizer.

1. Introduction

The consumption of the "commodities" plastics has been growing during the last decades. In fact, the worldwide consumption in 2016 of only thermoplastics, polyurethanes and thermosets was 335 million tonnes and 60 million in Europe.[1] The worldwide concern for the generation of high amounts of plastic waste, added to the

environmental impact caused by traditional plastics after their useful life has motivated the research on more environmentally friendly materials.[2] Not only in those plastics that are biodegradables, but also in those that comes from renewable sources.[3-5] As a consequence, bio-polymers are gaining interest in several industrial applications. Thus, the research on polymeric materials that combine both properties, biobased sources and biodegradable character, such as polylactides (polylactic acid, PLA), the family of poly(hydroxyalkanoates) (PHAs), proteins (caseinates, soya) as well as polysaccharides (i.e.: chitosan, pectins, ligno-cellulosic products, gums, starch, etc.) among others, has been increasing in recent years.[3,6-11] Among the bio-based polymers currently commercialized, those derived from agro-resources, such as starch and in particular in its thermoplastic form, are the most widespread and economic bio-polymers.[12-14] In fact, the introduction of starch in the plastic sector has been motivated by its low cost due to the fact that it is available in large quantities. However, starch cannot be processed through conventional processing plastic techniques without further modification since its degradation begins at a temperature lower than its melting point.[8] Therefore, its thermoplastic form, thermoplastic starch (TPS), has gaining considerably interest in several industrial sectors in which biodegradability is a key factor, including the packaging industry, disposable products for hygienic and sanitary uses, etc.[15] However, the development of TPS-based materials is still limited due to its fragility, low water resistance and dependence on the mechanical properties on the environmental moisture.[16,17] In fact, it is widely known that, bioplastic materials may have lower performance than traditional synthetic plastics due to their inherent characteristics.[6,18-20] This is why TPS has also been blended with other polymers with a view to widening its range of applications[13,21], as in the case of bags produced in association with PCL by extrusion displaying low-density polyethylene-like mechanical performance.[14]

Therefore, to obtain real alternatives to traditional synthetic polymers it is essential to improve their overall performance, so that novel formulations based on biopolymers will compete with traditional synthetic ones.[20] The plastic processing industry frequently modified the final properties of the polymers with additives, which are gradually replaced by natural ones, due to their advantages in terms of their lower environmental impact.[22-24] In this sense, Novamont commercializes blends based on TPS with biologically degradable polyesters under the trade name Mater-Bi®. Moreover, from both technical and environmental points of view, there is an increased interest on the use of agricultural biomass resources for the development of high-tech materials.[2]

On the other side, materials with natural origin such as resins derived from pine trees, that has been used since prehistory,[25] result interesting for the bioplastic industry.[22,23] In this sense, gum rosin and its derivatives has gained a renewed attention for the plastic field during the last years, as a source of monomer for polymer synthesis[26] and as additives (i.e.: stabilizers, plasticizers, viscosity increasing agents, nanoparticles modifiers, etc.).[10,22,23,27] Two products can be obtained after the resin, or gum, first distillation: "gum rosin" and "gum turpentine". Resin production is a defensive response of the conifers to external factors such as bark boring insects and fungal pathogens, that can be induced by external factors (i.e.: mechanical wounding, abiotic stress, hormones and chemical stimulants or insect attack.[25] Most of gum rosins are composed mainly by abietic, levopimaric and pimaric acids,[24,28,29] which are monocarboxylic acids with the empirical formula $C_{20}H_{30}O_2$ and have conjugated double bonds and carboxylic acids.[29,30] However, gum rosin shows relatively low thermal stability for the plastic processing industry. In this sense, some chemical modifications, such as hydrogenation and esterification confer to gum rosin higher thermal stability.

Most common alcohols used to stabilize the gum rosin are pentaerythritol, triethylene glycol and glycerol.[24,28,31] Resin and its derivatives have been proposed as low-cost, sustainable, and easily obtainable additives for plastic field.[22,30,32,33] In fact, the natural resins have the viability to be used in both, thermoplastic and thermoset polymers, due to their reactivity centres, the carboxyl group and its double bonds.[22,34,35] Particularly, the resins employed in this work, Lurefor (LF) and Unik Tack (UT) have different content of carboxylic groups, so that they posses different acid number which will provide better thermal stability as well as different ability to react with the polymeric matrix. The revalorization of gum rosin derivatives as plastic additives is interesting not only due to their natural origin and their similar structure in rigidity to rigid petroleum chemicals,[34] but also since cleaning activities are required for good forest management practices in terms of fire risk.[22] In this sense, in a previous work a triethylene glycol ester of gum rosin (TEGR) was used as the natural viscosity-increasing agent for polyvinyl chloride (PVC).[22] Several plastisols with tuneable mechanical and thermal performance were obtained depending on the TEGR proportion used, resulting interesting for several industrial applications.

In this work, three natural additives derived from pine resin: gum rosin, and two pentaerythritol ester of gum rosin were used as Mater-Bi® additives in three different compositions to improve the processability of the blends and to obtain materials with a broader spectrum of properties. The formulations were melt-extruded and further processed by injection moulding, to simulate the most typical processing approaches currently used at industrial level for traditional plastics. The effect of pine resin derivatives type and loading on the novel Mater-Bi® based formulations in terms of structural, thermal and mechanical properties was studied to get information regarding the possible applications of these novel formulations at the industrial level.

2. Experimental

2.1. Materials

Mater-Bi® NF 866 based on thermoplastic starch (TPS) and aliphatic aromatic polyesters (PBAT and PCL) was supplied by Novamont SPA (Novara, Italy). As additives, three pine resins derivatives were used: gum rosin (GR), supplied by Sigma-Aldrich (Mostoles, Spain); Lurefor 125 resin (LF, softening point of 125 ºC and acid number 11.9), kindly supplied by LureSA (Segovia, Spain); Unik Tack P100 resin (UT, softening point of 90 ºC and acid number 15), kindly supplied by United Resins (Figueira da Foz, Portugal).

2.2. Preparation of Mater-Bi®-resin formulations

The resin contents added to the Mater-Bi® matrix were 5, 10 and 15 wt.% and ten Mater-Bi®-resin based formulations were obtained, as shown **Table 1**. Initially, all materials were dried at 50 ºC for 24 hours in an air circulation oven. Subsequently, the Mater-Bi®-resin formulations were premixed in plastic containers. Finally, to process the materials the following procedure was followed: (1) extrusion of the material formulations, (2) milling into pellets and (3) injection moulding to obtain test specimens. The materials were processed in a twin-screw extruder (Dupra S.L, Castalla, Spain), with a temperature profile of: 160 ºC, 150 ºC, 140 ºC, 100 ºC (from die to hopper) at 50 rpm. An injection moulding machine (Sprinter-11, Erinca S,L., Barcelona, Spain) was then used to obtain injection moulding test specimens. In this work, the

injection moulding process parameters were varied for each formulation by trial-and-error practice until good quality injected moulded test samples were obtained. Therefore, the injection moulding temperature profiles varied considerably in each group of formulations and are detailed in **Table 1**. The test specimens were standard rectangular specimens (80 x 10 x 4 mm) and standard tensile specimens "1BA" (length ≥ 75 mm, with 10 mm and thickness ≥ 2 mm) according to UNE-EN ISO 527.[36] Starchy materials are water sensitive and it has been observed that TPS based materials performance are influenced by the humidity (i.e.: mechanical[37] and thermal[38] properties). Therefore, all samples were conditioned 24 h at 25±1 ºC and 50±5% HR previous to be characterized.

Table 1. Mater-Bi®-resin formulations and their injection moulding temperature profiles

Formulation labelling	Resin content in each formulation (wt.%)	Injection moulding temperature profiles (from die to hopper) (ºC)
Mater-Bi®	0	165, 160, 160
MaterBi-5LF	5	165, 160, 160
MaterBi-10LF	10	150, 150, 145
MaterBi-15LF	15	145, 140, 135
MaterBi-5UT	5	150, 145, 140
MaterBi-10UT	10	150, 145, 140
MaterBi-15UT	15	120, 115, 105

MaterBi-5GR	5	130, 125, 115
MaterBi-10GR	10	117, 112, 100
MaterBi-15GR	15	117, 117, 105

2.3. ATR-FTIR characterization

All developed materials as well as the starting raw materials (pine resins and Mater-Bi®) were characterized by Attenuated total reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR), using a Perkin Elmer – Spectrum BX (FT-IR system) within the range of 4000 to 650 cm^{-1}, with a resolution of 4 cm^{-1} and 32 scans. FTIR of resins were recorded using KBr discs made by blending the resins and KBr powder in transmission mode. FTIR of Mater-Bi® and Mater-Bi®-resin formulations were obtained from the injected samples.

2.4. Mechanical characterization

The tensile and flexural properties of the Mater-Bi®-resin based formulations were assessed in a universal test machine Ibertest Elib 30 of SAE Ibertest (Madrid, Spain) at room temperature, according to ISO 527[36] and ISO 178,[39] respectively. The tests were performed with a loading cell of 5 kN and a test speed of 10 mm min^{-1}. At least five specimens from each formulation for both, tensile strength as well as for flexural measurements, were tested. In addition, to analyse the toughness of the materials, the area under the typical stress-strain curve and the increase of toughness with respect to the neat Mater-Bi® were calculated. For each sample, one curve was

chosen to be representative of the average behaviour of each formulation.[20] The area was calculated using the OriginPro2015 program.

The resistance to the Charpy Impact by drop of pendulum was measured in a Metrotec S.A. machine (San Sebastian, Spain), using a 1 J pendulum and notched specimens under the ISO 179[40]. The geometry of the notch was type A, with a background radius of 0.25 ± 0.05 mm, the remaining width of 8.0 ± 0.2 and the notch angle was 45º ± 1º. At least five specimens were tested, and the mean was reported.

Shore D hardness of samples with 4 mm thickness was measured on a durometer Model 673-D from Instrument J.Bot S.A. (Barcelona, Spain), under the ISO 868.[41] The mean of at least 20 measurements was reported as the hardness values.

Significance in the mechanical data differences were statistically analyzed with OriginPro 8 software. One-way analysis of variance (ANOVA) was carried out and significant differences among formulations were recorded at 95% confidence level according to Tukey's test.

2.5. Microstructural characterization

Scanning electron microscopy (SEM) micrographs from the fracture surface of the impact specimens were obtained using a Phenon SEM equipment of FEI (Eindhoven, The Netherlands) with a voltage of 5 kV and using a working distance for 1000 X and 5000 X of 241 µm and 48 µm, respectively. Previously, the samples were coated with a gold-palladium alloy to make their surface conductive, on a Sputter Mod Coater Emitech SC7620, Quorum Technologies (East Sussex, UK).

2.6. Thermal characterization

DSC experiments were conducted in a DSC 2000 calorimeter TA Instruments (New Castle, USA) under nitrogen atmosphere (50 mL min^{-1}). Samples were subjected to a thermal cycle consisting in a first heating stage from -60 ºC to 190 ºC, to remove thermal history; followed by a cooling process down to -60 ºC and subsequent heating up again to 190 ºC, all scans at a heating rate of 10 ºC min^{-1}. The degree of crystallinity (Xc) of the formulated materials was evaluated according to equation 1 and considering PBAT the most abundant polymeric fraction in Mater-Bi® of 70 wt.%.[5]

$$X_c(\%) = \frac{\Delta H_m - \Delta H_{CC}}{f \times \Delta H_m^c} \times 100 \quad (1)$$

Where $\Delta H_m m$ is the melting enthalpy and ΔH_{CC} is the cold crystallization enthalpy of PBAT. ΔH_m^c is the calculated melting enthalpy of purely crystalline PBAT, being 114 J/g.[42]

Thermogravimetric analysis (TGA) was conducted in TGA Q500 thermal analyser TA Instruments (New Castle, USA). Samples were heated under TGA dynamic mode from 55 ºC to 700 ºC at 10 ºC min^{-1} under nitrogen atmosphere (flow rate 50 mL min^{-1}). The onset degradation temperatures ($T_{5\%}$) were determined at 5% of mass loss, while temperatures of the maximum decomposition rate (T_{max}) were calculated from the first derivative of the TGA curves (DTG).

The Heat Deflection Temperature (HDT) was determined using a VICAT/HDT station DEFLEX 687-A2, Metrotec SA (San Sebastián, Spain) according to ISO 75 (method A)[43] applying a force of 1.8 MPa with a heating rate of 120 ºC h^{-1}.

Dynamic mechanical thermal analysis (DMTA) in torsion mode was done on rectangular samples sizing 40 × 10 × 4 mm, in an oscillatory rheometer AR G2 from TA Instruments (New Castle, USA) equipped with a special clamp system for solid samples. The temperature of the test was from -50 ºC to 110 ºC at a heating rate of 2 ºC min^{-1} at a frequency of 1 Hz and 0.1% of maximum deformation.

3. Results

3.1. Processing behaviour

The determination of the process parameters for injection moulding is highly skilled task and it is mainly based on a intuitive sense during the preparation of the formulations by the skilled operator's "know-how" acquired through long-term experience.[44] In this work, as reports **Table 1** during the samples preparation with each pine resin derivative, it was necessary to change the temperature profile to achieve optimal fill of the mould for the injection moulding process. Although to scale up the injected moulded materials developed here for their commercial production the process optimization is required, including a proper experimental design instead of trial-and-error practice, some interest aspects were observed during materials processing. For instance, the profile of temperature on the injection moulding process vary considerably, from 165 ºC in die of the machine for neat Mater-Bi®, to 145 ºC, 120 ºC and 117 ºC for MaterBi-15LF, MaterBi-15UT and MaterBi-15GR, respectively. Hence, it is possible to point out the effect of pine resin derivatives on the injection moulding processing properties of the Mater-Bi®. This drop of temperature is related to the reduction of softening point of resins and it could help to save energy when processing, very interesting for their processing at industrial level. Moreover, this effect could be

interesting in materials that have a narrow processing window or when high processing temperatures are not allowed, to prevent the materials thermal degradation.[3,6,33]

3.2. FTIR characterization

Figure 1 shows the FTIR spectra of all developed materials as well as the starting raw materials (pine resins and Mater-Bi®). Mater-Bi® exhibits a peak at 2915 cm^{-1} corresponding to C-H stretching in aliphatic and aromatic groups; others at 1724 cm^{-1} and 1250 cm^{-1} due to the carbonyl groups (C=O) and the C-O link respectively, found in the ester linkage.[14] A group of peaks reported at 1578, 1504, 1458 and 1022 cm^{-1} attributed to stretching of phenylene groups and at 728 cm^{-1} a peak attributed to four or more adjacent methylene (-CH_2-) groups. Finally, bending peaks of the benzene substitutes are located between 900 and 700 cm^{-1}. All these groups are attributed to PBAT portion.[5,45,46] The plasticized starch portion of the Mater-Bi® results in peaks between 3900 - 3300 cm^{-1}, attributed to O-H stretching; 1445 - 1325 cm^{-1}, due to C-H bending and wagging and peaks between 1250-900 cm^{-1} attributed to C-O stretching and hydrogen bonding peaks. The peaks at 1180 and 1104 cm^{-1} correspond to C–O stretching of the C–O–H group (the starch group which mainly participates in hydrogen bonding). The peak at 1022 cm^{-1} corresponds to C–O stretching of the C–O–C group of the starch anhydroglucose ring which also can participate in hydrogen bonding.[47,48] There are also PCL characteristic peaks which are due to C=O stretching (1724 cm^{-1}), symmetric CH_2 stretching (2853 cm^{-1}) and asymmetric CH_2 stretching (2952 cm^{-1}).[49,50] Thus, the commercial Mater-Bi® used in this study is based on PBAT, plasticized starch and PCL as well as other additives in less proportion, in well accordance with the

literature.[5,45,46,48,49] According to Borchani et al., the content of each polymer is about 70, 20 and 10 wt.%, respectively.[5]

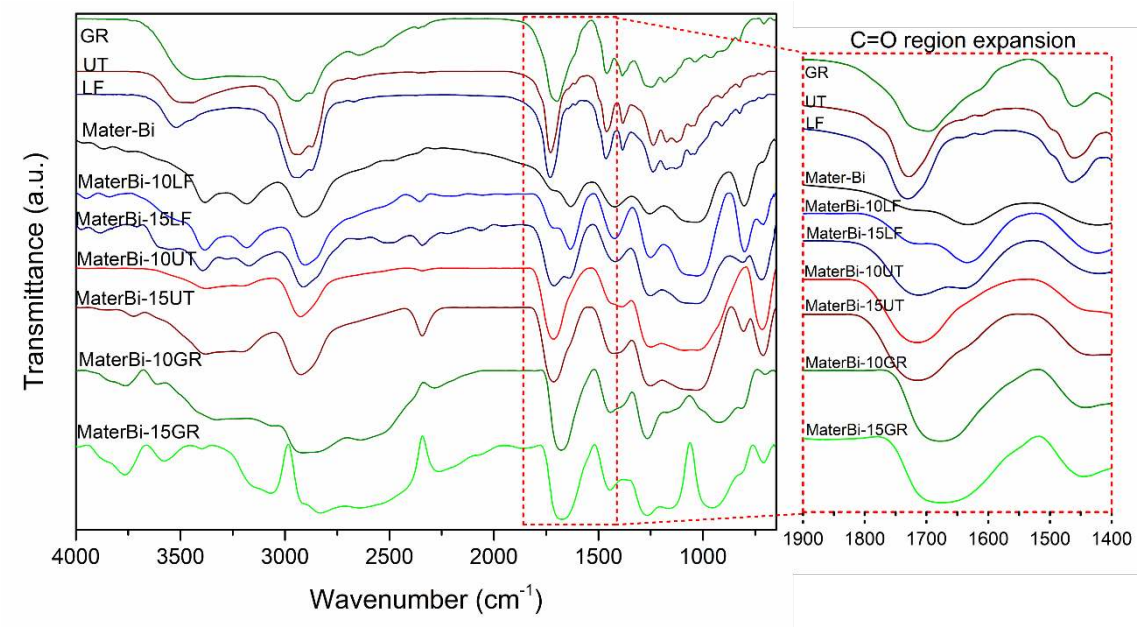


Figure 1. FTIR spectra of gum rosin (GR), pine resin derivatives (UT, LF), Mater-Bi®, and studied materials

FTIR spectra of gum rosin (GR) and its derivatives (LF and UT) shows common peaks around 3500 cm^{-1} attributed to rosin, which after esterification in LF and UT showed two shoulders attributed to the appearance of O-H stretching of COOH in the resins, suggesting the presence of acids stabilizers in pentaerythritol ester resins and/or somewhat amount of resin in the form of gum rosin due to the incomplete reaction of pentaerythritol esters.[29] There are two peaks at 2944 cm^{-1} and 2872 cm^{-1} because of the C-H stretching. Also one peak at 1698 cm^{-1}, attributed to hydrogen bonded acid dimers of gum rosin and to the C=O stretching of the gum rosin. This peak corresponding to the carboxylic acids groups has been slightly shifted to 1730 cm^{-1} in LF and UT. Peaks at

1450 cm^{-1} are due to CH_2 bending mode, 1362 cm^{-1} are due to CH_3 bending, while those at 1225 cm^{-1} and 1215 cm^{-1} are due to the C-O stretching of acid groups. Finally, some peaks from 1000 to 650 cm^{-1} correspond to C-H out of plane bending. [30,51,52]

Regarding formulated materials, the peaks observed for the raw starting materials are also observed in the formulations. In LF based formulations, the peak at 3390 cm^{-1}, attributed to O-H stretching of TPS,[12] increase its intensity. Meanwhile the peaks at 2915 cm^{-1} and 1724 cm^{-1} of TPS were shifted to 2890 cm^{-1} and 1710 cm^{-1}, respectively suggesting somewhat positive interaction between the polymeric matrix and the resin. The intensity of the peak corresponding to C-H stretching in aliphatic and aromatic groups (2915 cm^{-1}) decrease when the content of resin increase. As expected, the intensity of the carbonyl groups (C=O) and the C-O link increase with the resin content, due to the increment of the esters linkage coming from the resin, while the shift to lower wavelengths suggest hydrogen bonding interactions (see the expansion of the spectra in the C = O stretching region in Figure 1). Moreover, the intensity of peaks between 1250 and 800 cm^{-1} increase their value when the resin content increase, due to the increment of C-O stretching and also probably due to the formation of hydrogen bonding interaction between Mater-Bi® hydroxyl groups and the resin carbonyl groups. Finally, the peak corresponding to benzene substitutes (718 cm^{-1}) also increase with the resin content due to the chemical structure of the resin, then again confirming the correct incorporation of the LF resin into the polymeric matrix. Similar findings have been found for UT based formulations, because both resins are gum rosin esters. For instance, the peak corresponding to the carbonyl group (C=O) was shifted from 1724 cm^{-1} to 1716 cm^{-1} suggesting hydrogen bonding interactions (see the expansion of the spectra in the C = O stretching region in Figure 1). On the other hand, the main difference with GR based formulations is that the peaks at 1710 and 1638 cm^{-1} are

merged in a bigger one centered at 1680 cm^{-1}, probably due to the less hydrogen bonding interactions previously commented for other additives (see the expansion of the spectra in the C = O stretching region in Figure 1).

These FTIR spectra revealed that the molecular structure of the additives (gum rosin and its derivatives) interacts with that of the Mater-Bi® during the formulation of materials. The spectra of both materials, that is the polymeric matrix and the resin, are well merged in the studied formulations. This phenomenon suggests a good chemical interaction such as the formation of hydrogen bonds between each resin and the components of the polymeric matrix, particularly in the case of pentaerythritol esters of gum rosin, as it has been previously observed when using gum rosin derivatives as polymer additives.[22,23,30,52]

3.3. Mechanical properties

The tensile properties of materials were evaluated, and it was observed that neat Mater-Bi® has a tensile strength of 8.2 MPa, tensile modulus of 239 MPa and an elongation at break of 18.4%. **Figure 2-a** and **2-b** represents the variation of Young's modulus and tensile strength in terms of percentage and type of resin. The incorporation of LF and UT resins up to 10 wt.% in the blend, did not significantly ($p < 0.05$) modify the Young's modulus while the tensile strength slightly increased ($p > 0.05$), around 13% in MaterBi-10LF, compared to neat Mater-Bi®. This behaviour could be explained because of the modified resins make easier the compatibilization between the resin and the polymeric matrix,[5] in good accordance with the already commented hydrogen bonding interactions. For larger contents, that is 15 wt.% of LF, a significant increment of 14% of the modulus was reached ($p > 0.05$). However, the maximum strength,

although higher than neat Mater-Bi®, did not show significant changes when LF resin content increases.

With UT resin, an intermediate effect between plasticizing and compatibilization was observed. As the resin content increases, the Young's modulus of the material tends to decrease, up to 20% lower in MaterBi-15UT ($p > 0.05$) compared to the neat Mater-Bi®. The tensile strength for the MaterBi-5UT and MaterBi-10UT presented a slight significant ($p > 0.05$) increment respect to neat matrix, showing the positive interaction between Mater-Bi® and UT resin probably due to the already commented hydrogen bonding interactions. However, a saturation effect is observed from contents of 5 wt.% of UT, where the higher value of tensile strength was achieved. The same effect was observed by Ferri et al. when using maleinized linseed oil as Mater-Bi® and PLA compatibilizer in ternary blends.[6] This effect makes that the maximum resistance significantly ($p > 0.05$) drops from 9.3 MPa in the MaterBi-5UT to 7.6 MPa in MaterBi-15UT, which represents the maximum decrease (7.3%) of Mater-Bi® tensile strength. Borchani et al. also reported and increment in Young's modulus and tensile strength in Mater-Bi® by using Alfa fibers for the development of biocomposites, and they attributed this result to the good interfacial adhesion between Mater-Bi® and the fibers [5]. Therefore, it is possible to establish that the modified pine resins used in this work have a good compatibilization effect among the Mater-Bi® components, in good agreement with FTIR results.

A very different behaviour was observed in unmodified resin (GR) based formulations. The Young's modulus and maximum strength had a significant loss ($p > 0.05$). Even though, the loss of tensile strength was not proportional to the resin content, since all three formulations experienced a loss of 28% with respect to the strength of the neat Mater-Bi®. In contrast, the Young's modulus showed a linear decrement

behaviour, reporting a loss of Mater-Bi® Young's modulus from a 40% up to 70% in the MaterBi-5GR and MaterBi-15GR, respectively. This effect caused by GR in tensile properties was also observed by Narayanan et al., in PLA/rosin materials.[23]

The elongation at break (**Figure 2-c**) increased regardless the type or content of pine resin suggesting a plasticizing effect, particularly in the case of the gum rosin. It is important to observe that with a content of 10 wt.% of any type of resin, the elongation at break was similar in all formulations, with a value of about 30%. This property remains constant with 15 wt% in the blends with LF and UT ($p < 0.05$), while it increased in GR based formulations ($p > 0.05$). In fact, MaterBi-15GR showed a significant increase of the elongation at break, from 18.4% in neat Mater-Bi® to 85.7% in MaterBi-15GR. This is an indicative of a plasticization effect, which let the reduction of processing temperature, as it was already discussed in the processing behaviour of Mater-Bi® and its blends. In all formulations, an increase in the cohesion of the material was observed, although this behaviour is different depending on the pine resin derivative. The LF and UT resins contribute to cohesion and higher resistance values. This is due to the compatibilizing effect they produce on the Mater-Bi® components.[5,20] In contrast, GR confers lower strength and Young's modulus and a longer elongation at break, an indicative of a marked solubilizing, compatibilizing and plasticizing effect, thus providing a greater ductility to the Mater-Bi®. Moreover, the solubility of GR with the polymeric matrix is considerably higher than the one for modified rosins, which allows a greater movement of the polymer chains and, consequently, a greater deformation and easier processability. In fact, in GR based formulations saturation is not reached as shown in **Figure 2-c**.

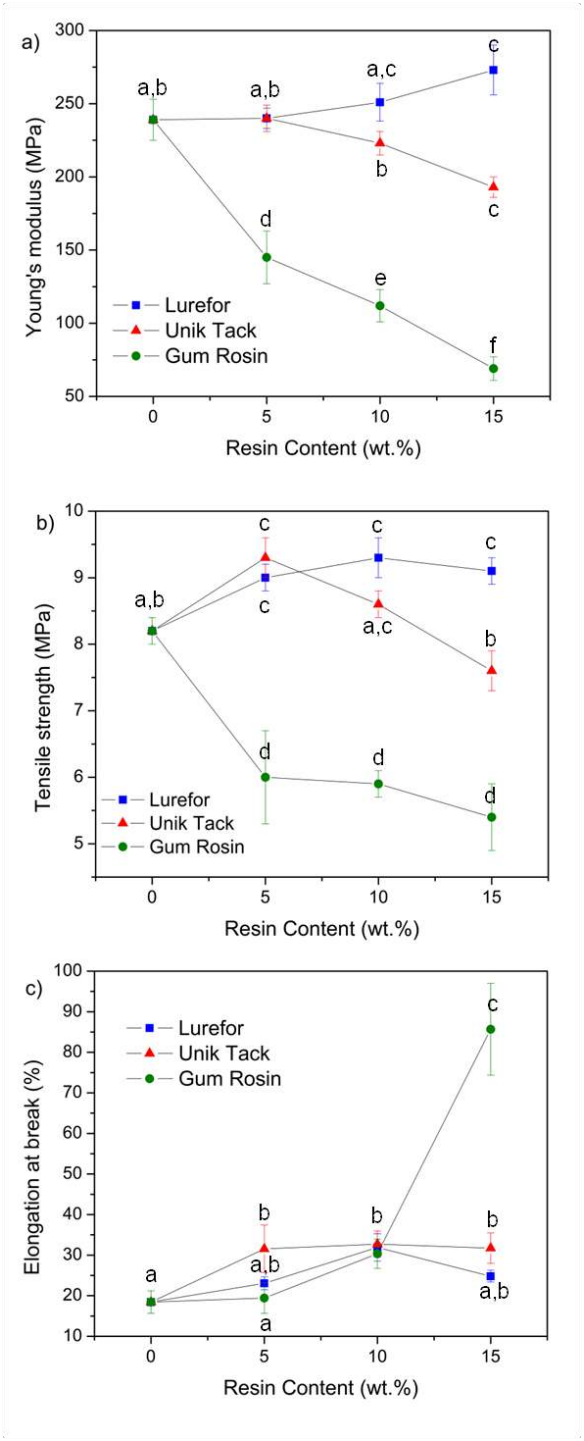


Figure 2. Effect of increasing amount of pine resin derivatives on the tensile properties of Mater-Bi®-based formulations a) Young's modulus, b) tensile strength and c) elongation at break.

[a-f] Different letters within the same graph indicate statistically significant differences between formulations ($p < 0.05$).

Analysing the flexural properties, charted in **Figure 3**, materials formulated with LF did not showed significant ($p < 0.05$) changes either in flexural modulus **(Figure 3-a)** or in maximum flexural strength **(Figure 3-b)**. In contrast, the formulations with UT and GR experienced a significant ($p > 0.05$) loss of both properties as their content increases. Specifically, flexural modulus and maximum flexural strength decreased by 38% and 72% respectively, compared to neat Mater-Bi® for materials containing 15 wt.% of UT ($p > 0.05$); while decreased 27% and 54% respectively, for materials containing 15 wt.% of GR. This behaviour is due to the increase of the ductility, more marked in GR based formulations, produced thanks to the good solubility of this resin in the Mater-Bi® polymeric matrix. Such solubility promotes the lubricity of the polymer chains and therefore, an improved ductility. This phenomenon, also reported by Narayanan et al. in materials containing GR, plays an effective role in enhancing the elongation at break, providing suitable materials for industrial applications such as biodegradable films.[23]

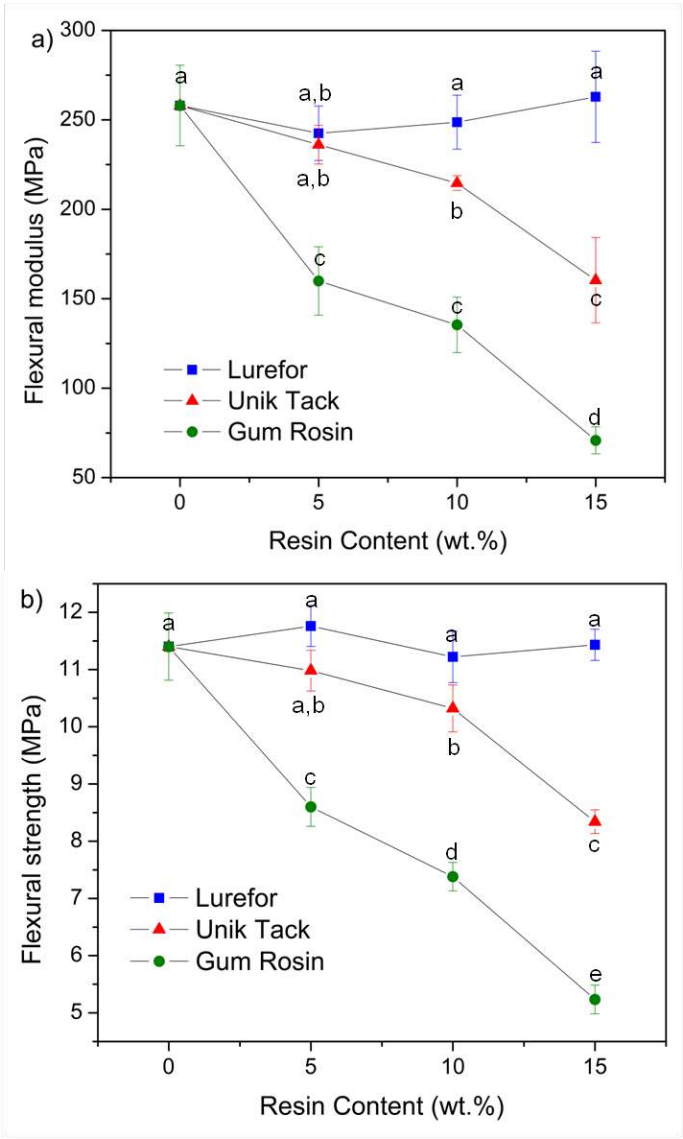


Figure 3. Effect of increasing amount of pine resin derivatives on the flexural properties of Mater-Bi®-based formulations a) flexural strength and b) flexural modulus.

[a-e] Different letters within the same graph indicate statistically significant differences between formulations ($p < 0.05$).

Regarding the toughness of materials (*T*), which is shown in **Table 2**, the toughness of all formulations increased considerably compared to neat Mater-Bi®, except for the MaterBi-5GR formulation, which remains similar to Mater-Bi®. However, results for MaterBi -15GR stands out because it showed an increase of toughness more than 450%

higher than the neat matrix. Regarding UT and LF, these resin derivatives provided greater cohesion to the Mater-Bi®, thus increasing their mechanical performance due to the interaction of the polar groups of the resins with the aliphatic and aromatic groups presents in the Mater-Bi®[24] as it was previously observed by Arrieta et al. in PVC-resin based materials.[22] UT resin seems to have a significant higher cohesive effect at lower contents (5 wt.%) than the LF resin, although with 10 wt.% of LF, MaterBi-10LF achieved greater toughness and ductility than MaterBi-10UT. Moreover, with GR addition, an increase of the ductility was also obtained, as a consequence of its greater plasticization effect.[17]

Table 2. Area of stress-strain curve (toughness) and its comparison with neat Mater-Bi® toughness.

Formulation	Toughness T (kJ.m^{-3})	Increase of toughness (%)
Mater-Bi®	745	-
MaterBi-5LF	1388	86
MaterBi-10LF	2657	257
MaterBi-15LF	1514	103
MaterBi-5UT	2287	207
MaterBi-10UT	2141	187
MaterBi-15UT	1950	162
MaterBi-5GR	741	0
MaterBi-10GR	1227	65
MaterBi-15GR	4304	478

A deeper analysis of the stress-strain curve (**Figure 4**) shows that with a 10 wt.% of resin, the gain of Mater-Bi®-resin properties is much greater than that of the neat Mater-Bi®, since its earning rate of elongation, without losing Young's modulus. This behaviour is very outstanding for LF which showed the higher softening point, while it decreased for UT and GR based formulations in that order.

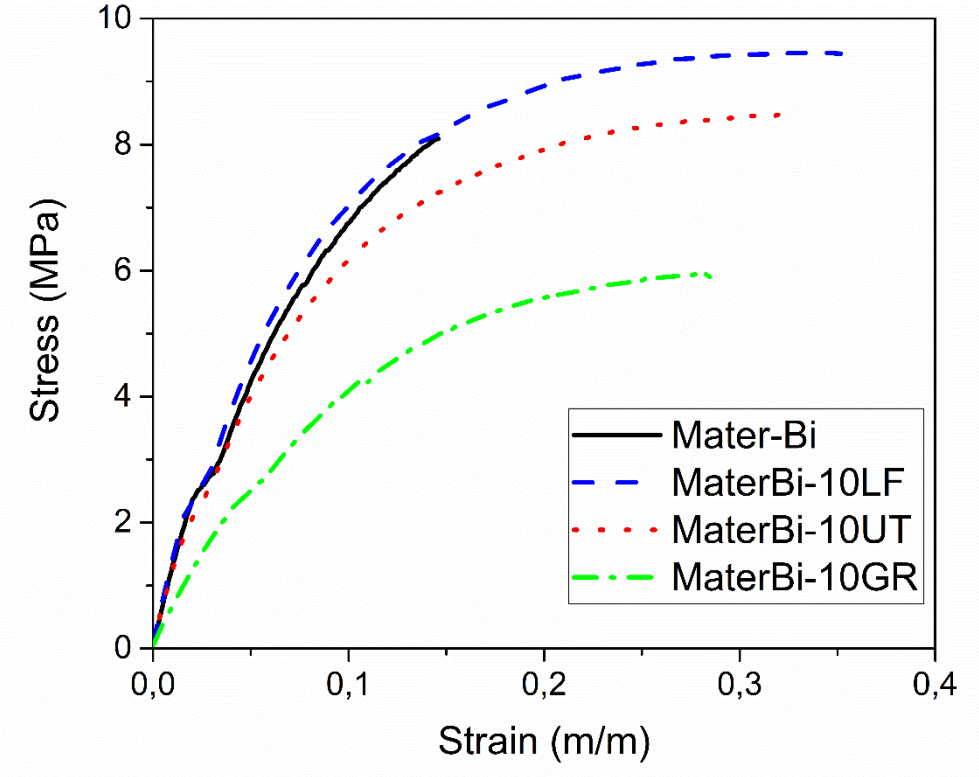


Figure 4. Stress-strain curve of neat Mater-Bi® and formulations with 10 wt.% of resin

Another property of the materials that gives an idea of the variation of the ductile properties is the impact absorption per unit area. As shown in **Table 3**, there are two clear trends: formulations added with UT and LF experienced a considerable significant ($p > 0.05$) gain of energy absorbed at impact, although its saturation point is at low contents (5 wt.%). Whereas, formulations added with GR underwent a larger

increase than those provided by pentaerythritol esters of gum rosin (LF and UT). The increment is linear as the GR content increases, up to 250 % for MaterBi-15GR ($p > 0.05$) respect to neat Mater-Bi®. This behaviour is related with the higher solubility of GR with Mater-Bi® resulting in a high increase of the ductility. This interaction confers high cohesion to the formulated material but low solubility of the resin in the Mater-Bi® matrix. The solubility behaviour between pine resin derivatives with the Mater-Bi® will be also confirmed by SEM observations, where it is possible to advise the reduction of the materials porosity (see section 3.4).

Regarding the hardness properties (**Table 3**), LF did not significant modify ($p < 0.05$) Shore D hardness of the neat Mater-Bi®, regardless the content of resin. On the other hand, when using UT and GR, the hardness significant decreased ($p > 0.05$), being very low in MaterBi-15GR in about 17% (lower compared to neat matrix).

Table 3. Variation of Charpy's impact energy, Shore D harness and HDT of neat Mater-Bi® and Mater-Bi-resin formulations

	Charpy's impact energy (kJ/m^2)			Shore D hardness			Heat deflection temperature HDT (ºC)		
Mater-Bi®	3,9±0.4[a]			50.3 ± 0.6[a]			35.6		
Rosin content (wt.%)	LF	UT	GR	LF	UT	GR	LF	UT	GR
5	7,8 ± 0.4[b]	8.0 ± 0.8[b]	3.8 ± 0.2[a]	50.3 ± 1.0[a,b]	50.0 ± 0.5[a,c]	46.4 ± 0.6[e]	33.8	34.5	32.8
10	6,9 ± 0.4[b,c]	6.8 ± 0.3[c,d]	8.0 ± 0.8[b,c]	50.4 ± 1.0[a,b]	49.6 ± 0.8[b,c]	46.1 ± 0.6[e]	31.3	25.6	*
15	5,2 ± 0.4[d,e]	5.1 ± 0.3[a,e]	13.8 ± 1.1[f]	50.7 ± 0.7[a]	48.7 ± 0.9[d]	42.0 ±0.8[f]	34	*	*

* HDT lower than room temperature (25 ºC)

[a-f] Different letters within the same property indicate statistically significant differences between formulations ($p < 0.05$).

3.4. Scanning electron microscopy

The effect of pine resin derivatives on the microstructure of Mater-Bi® was studied by SEM. **Figure 5** and **Figure 6** show the SEM images of the fractured surface of neat Mater-Bi® and formulations blended with pine resin derivatives at low and high concentrations (5 wt.% and 15 wt.%), respectively.

A characteristic material with a lack of phase's cohesion is observed for neat Mater-Bi® (**Figure 5-a** and **Figure 6-a**). In addition, large discontinuities with flakes shape are observed, confirming this lack of cohesion due to a low miscibility between the components of the Mater-Bi® polymeric matrix (PBAT, plasticized starch and PCL). This morphology is also characteristic of ductile fractures in poor cohesion materials, mainly observed in binary or ternary blends with low miscibility (**Figure 5-a**).[6,19] Specifically, small spheres attributed to the minor portion of PCL are observed.[53,54] As well, plasticized starch domains are also observed and as a major component the PBAT portion.

In **Figure 5-b** and **c**, corresponding to the SEM micrographs of MaterBi-LF formulations, small domains of homogeneously distributed LF are observed. This morphology is due to the low solubility of this resin within Mater-Bi® matrix (**Figure 5-b** and **Figure 6-b**), showing some "empty" interface between the two polymeric phases, suggesting a poor interfacial adhesion.[54] These domains increased with the increment of LF content (15 wt.% of resin, **Figure 5-c** and **Figure 6-c**). However, it is observed that the porosity of the material decreased considerably (**Figure 6-b**) with respect to neat Mater-Bi® (**Figure 6-a**). In addition, flakes due to lack of cohesion fracture were still observed, but these were smaller than those observed in the SEM images of Mater-Bi® matrix (**Figure 5-a** and **Figure 6-a**). Although the modified pine

resins were not completely miscible with the components of Mater-Bi® (PBAT, plasticized starch and PCL), they may have a good interaction with some of those components and, consequently, they increase the cohesion of these components.[3] Therefore, it seems that LF confers a compatibilizing (cohesive) effect on the Mater-Bi®-based material, which was previously corroborated by the increase in tensile modulus and tensile strength, being higher for higher LF contents.

In **Figure 5-d** and **Figure 5-e** as well as **Figure 6-d** and **Figure 6-e**, the effect of the UT resin on the Mater-Bi® matrix is observed. As with LF, less porosity and smaller flakes were detected. In general, UT formulations show fewer discontinuities than the Mater-Bi® matrix (**Figure 5-a** and **Figure 6-a**). The morphology showed greater cohesion, which may be due to chemical interactions between UT resin and the components of the Mater-Bi® matrix.[3,6,22] This double effect, cohesive and plasticizing, can be corroborated with the evolution of the mechanical properties previously discussed; which, at low UT contents higher values in modulus and resistance were found, with respect to Mater-Bi®. However, for high UT contents (**Figure 5-e** and **Figure 6-e**), signs of a plasticizing effect were observed, in accordance with the increased elongation at break and reduced strength, Young's modulus and hardness, as reported in mechanical properties results.

Finally, in **Figure 5-f** and **Figure 5-g** as well as **Figure 6-f** and **Figure 6-g**, corresponding to the MaterBi-GR formulations, a very marked plasticizing effect confer by GR was observed. In these images, it is impossible to identify the different domains previously observed in neat Mater-Bi® (**Figure 5-a** and **Figure 6-a**), even more difficult for higher resin content (**Figure 5-g** and **Figure 6-g**). Thus, from the microstructure analysis it is possible to state that MaterBi-GR based formulations resulted in the most compatibilized samples. The discontinuities of the material are

considerably reduced. This behaviour results from the high affinity of the GR with the Mater-Bi® components. The small size of the GR molecules together with its reactivity centres, the carboxyl group and its double bonds[22,35] allowed GR to be solubilized in the intramolecular free volume of the Mater-Bi® polymeric matrices. In addition, the free volume increases and this behaviour contributes to an important increase in the miscibility between the components of the Mater-Bi® (PBAT, plasticized starch and PCL) and GR.[6] Thus, GR shows a plasticizer-compatibilizing effect, as it was also reflected in the reduction of the processing temperature as well as the mechanical performance, characterized by an increase in elongation at break, a significant decrease in strength and hardness, as well as an important increment in the impact energy.

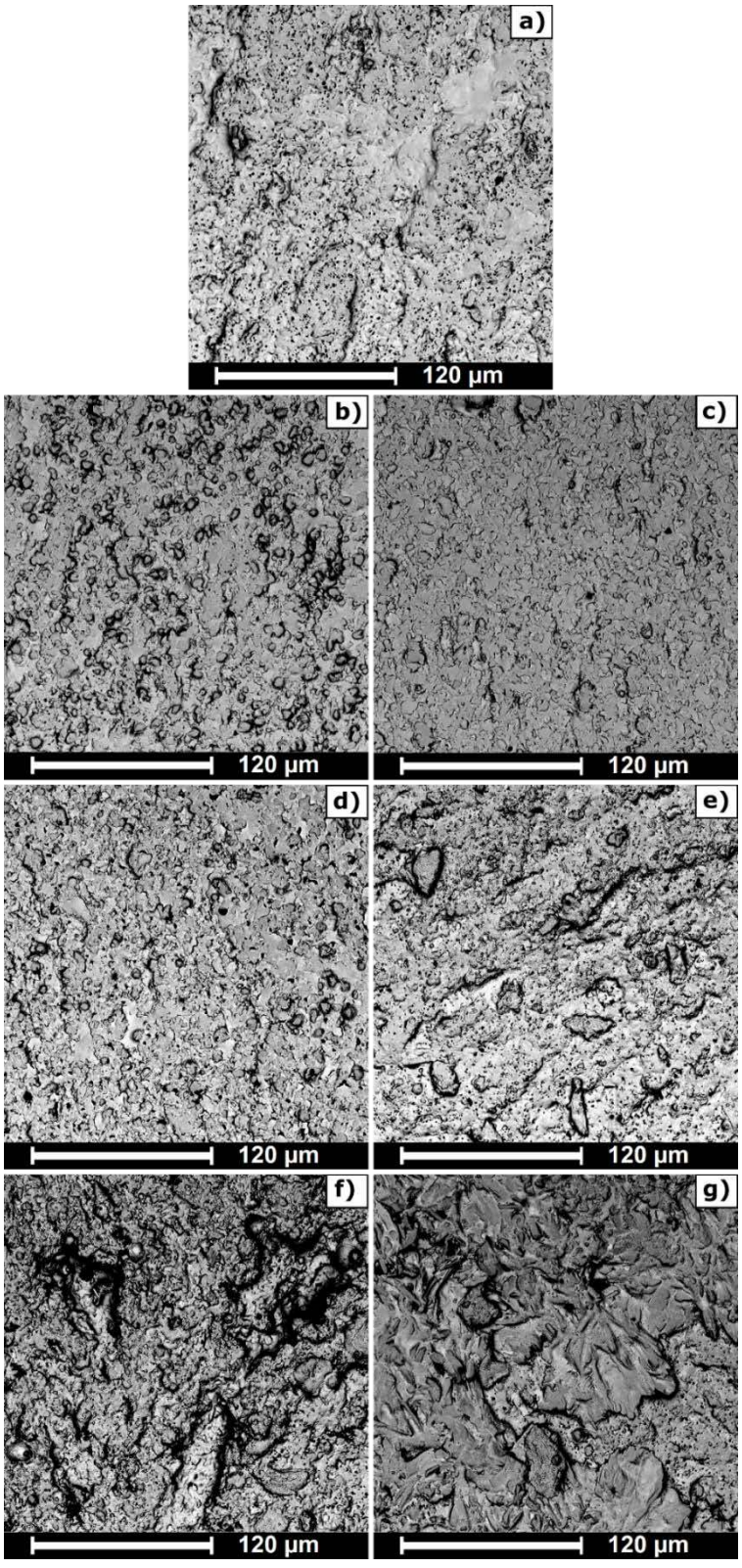


Figure 5. SEM images from impact fracture surface at 1000 X of: **a)** neat Mater-Bi®, **b)** MaterBi-5LF, **c)** MaterBi-15LF, **d)** MaterBi-5UT, **e)** MaterBi-15UT, **f)** MaterBi-5GR and **g)** MaterBi-15GR

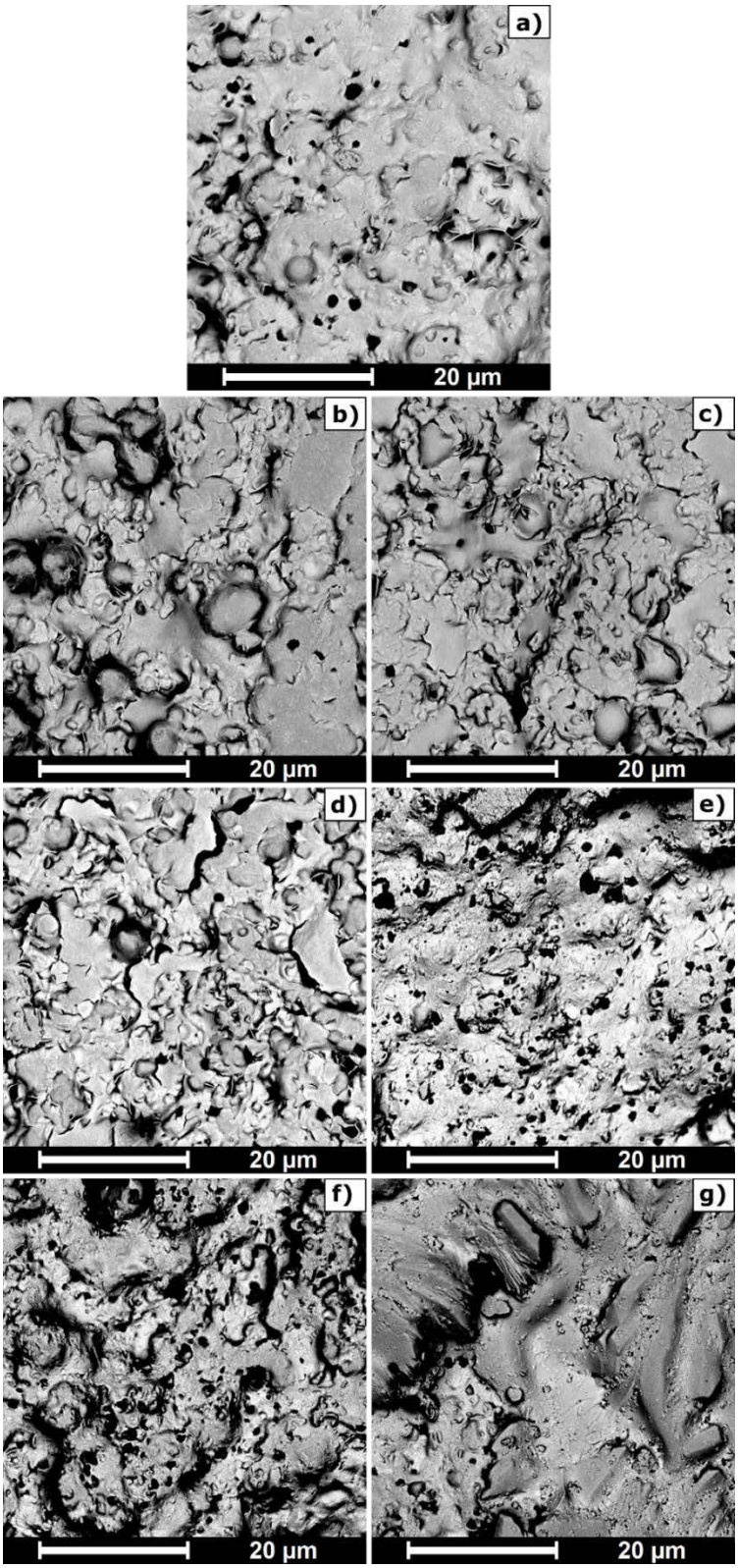


Figure 6. SEM images from impact fracture surface at 5000 X of: **a)** neat Mater-Bi®, **b)** MaterBi-5LF, **c)** MaterBi-15LF, **d)** MaterBi-5UT, **e)** MaterBi-15UT, **f)** MaterBi-5GR and **g)** MaterBi-15GR.

3.5. Thermal properties

Figure 7 shows the DSC second heating curves as well as the DSC cooling curves of samples added with 15 wt.% of pine resin as example to show the DSC changes more clearly. In addition, the thermal data of all formulations are summarized in **Table 4**. Mater-Bi® exhibited a thermal transition at -32 ºC, corresponding mainly to the glass transition of the PBAT fraction (T_{gPBAT}) with a combination of the T_g of the plasticized starch fraction ($T_{gplasticized\ starch}$) of the Mater-Bi®.[5,55,56] In addition, Mater-Bi® presents a thermal transition at 56.3 ºC, attributed to the PCL melting.[50,53,57] Due to the PCL content in Mater-Bi® is estimated to be less than 10 wt.%,[5] this thermal transition is very trivial, and no melting peak is observed. Moreover, the calorimetric curve of Mater-Bi® presents a cold crystallization peak at 107.3 ºC, attributed to the cold crystallization of the PBAT portion. Finally, it is possible to determine two groups of melting peaks: one at 124.7 ºC, corresponding to the melting of PBAT fraction,[55] and other two peaks centred at 150.3 ºC attributed to the melting of the plasticized starch fraction.[18] The DSC cooling assessment in Mater-Bi®, shown in **Figure7-b**, exhibits a peak at 92.5 ºC attributed to the crystallization of the PBAT fraction. This peak was also observed by Borchani et al., who used a similar Mater-Bi® in their study,[5] and by Lendvai et al.[19] and Muthuraj et al.[55], who worked with TPS-PBAT blends and with an hydrolytically degraded PBAT, respectively. The T_{gPCL}, established between -40 and -60 ºC,[50,53,58] could not be observed, possibly due to the low content of PCL in the Mater-Bi® (estimated to be less than 10 wt.%).[5]

Regarding the changes in the glass transition temperature, results showed that the effect of resins in Mater-Bi® is to slightly increase it. LF and UT resins increased the T_g in about 5 ºC when using 15 wt.% content of resin. Meanwhile, GR increased the T_g in

about 10 ºC at the same percentage. Due to this T_g is attributed to the PBAT portion of Mater-Bi® the trend suggests that all additives used in this work are thermodynamic compatible with this component of the Mater-Bi®.[59] Moreover, the shift of T_g to high temperatures could show that PBAT interacts with the plasticized starch portion of the material with the aid of pine resins; thus, it increases the miscibility of these two portions confirming the compatibilizing and plasticizing effect of resins.

Regarding the melting temperature corresponding to PCL portion (T_{mPCL}), typically in the range of 40 and 60 ºC,[50,53,60] the pine resin derivatives slightly modify it. A shift to low temperatures was detected, due to the interaction of the resins with the PCL portion of Mater-Bi®. The PCL is also plasticized with the pine resin derivatives; even if this effect is light detectable in DSC, because the content of this portion is lower than 10 wt.%.[5] In addition, it is possible to notice that GR has an important effect on the PCL portion as showed the decreasing trend of the T_{mPCL}.

The cold crystallization peak present in neat Mater-Bi® (T_{cc}) disappeared in all the formulations studied, suggesting that all the resin based formulations were able to promote the complete crystallization of the PBAT fraction at the low cooling rate applied. In fact, while the ΔH_c and the ΔH_m of PBAT was mainly maintained in neat MaterBi®, the degree of PBAT crystallinity increased for all resin based formulations. Concerning the melting temperature of PBAT portion (T_{mPBAT}) there was a noticeable decrement of this temperature with all resin derivatives, mainly when using UT and GR. The variation on this temperature reaches 16 ºC in MaterBi-15GR formulation. Moreover, analysing the tendency of the melting enthalpy of the PBAT portion (ΔH_{mPBAT}), it increased as the pine resin content increased in the formulation, regardless of the type of additive used. All these behaviours show that pine resin derivatives cause an important plasticizing effect on the base polymeric matrix, more specifically with the

PBAT portion of the Mater-Bi®. Furthermore, this behaviour suggests that all the pine resin derivatives studied are compatible with PBAT fraction of the Mater-Bi®.[5,18,19,59] Analysing the melting temperature ($T_{m\ plasticized\ starch}$) and the melting enthalpy ($\Delta H_{m\ plasticized\ starch}$) linked to the plasticized starch fraction, it is possible to verify a slight interaction between pine resins derivatives and the plasticized starch fraction of the formulations. The melting temperature decreased in about 4 ºC for the formulations that contains LF and UT, and 7 ºC in the MaterBi-GR based formulations. This is an indicative that GR has a better plasticizing effect on the Mater-Bi®, than the chemically modified resins (LF and UT). The melting enthalpy has a similar behaviour, which trends to decrease more evidently in the UT and GR added formulations. This explains the difference between the interactions of LF and UT, and the interaction of GR with the Mater-Bi® matrix. On one hand, LF has mainly a marked cohesive effect on Mater-Bi®, and UT has both effects, plasticizing and cohesive, already advised on the mechanical properties. On the other hand, GR confers a marked plasticization/compatibilizing effect, even greater than the other resins derivatives, with influence in the mechanical, thermal and morphological properties of the formulations based on MaterBi-GR blends.

Finally, regarding the crystallization temperature (T_c), it is possible to observe that ormulations show a noticeable decrement in this transition temperature that reaches 5.6, 10.8 and 16 ºC with LF, UT and GR at 15wt.%, respectively. Meanwhile, no significant changes were observed on the crystallization enthalpy (ΔH_c) for all formulations.

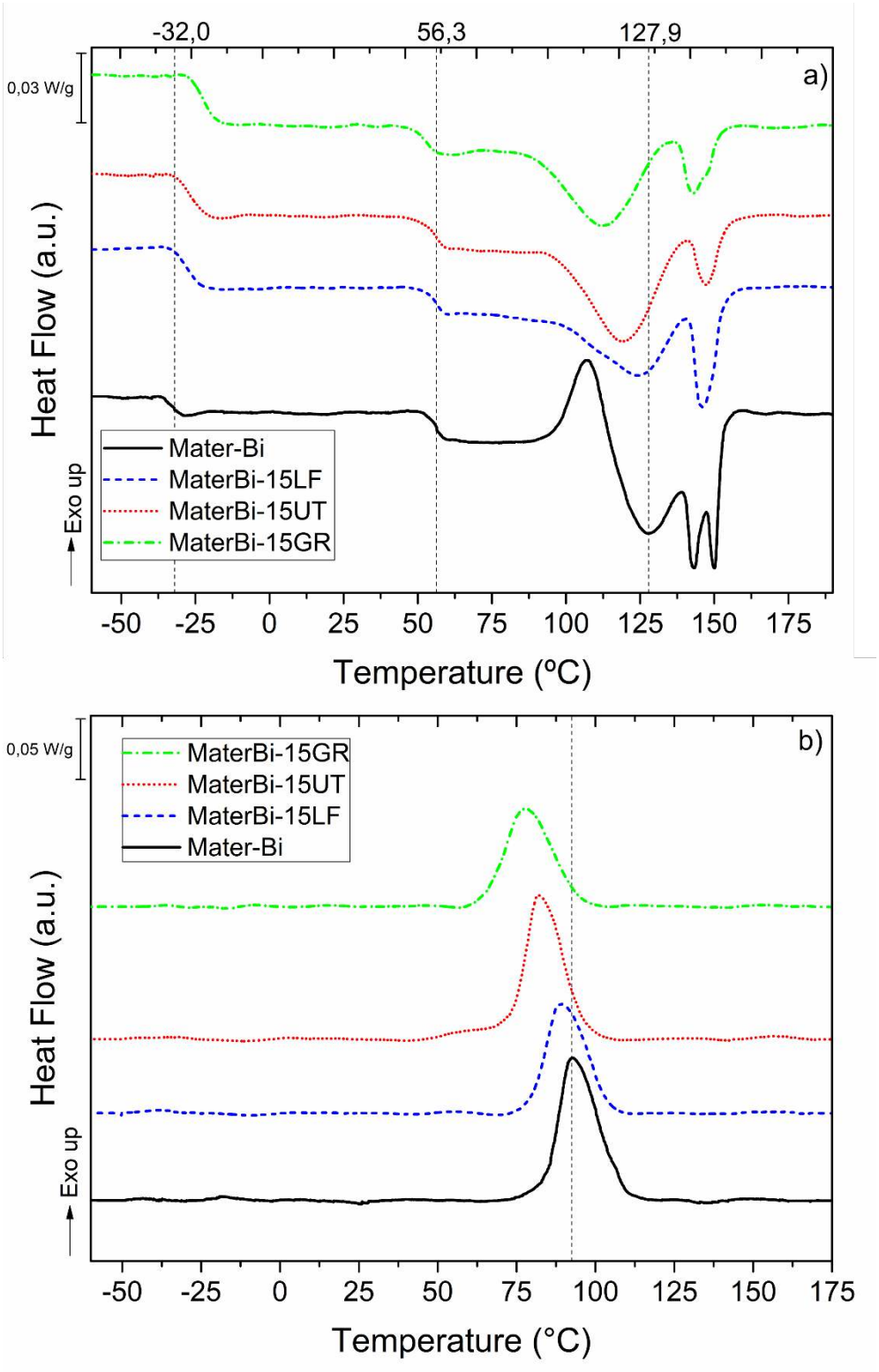
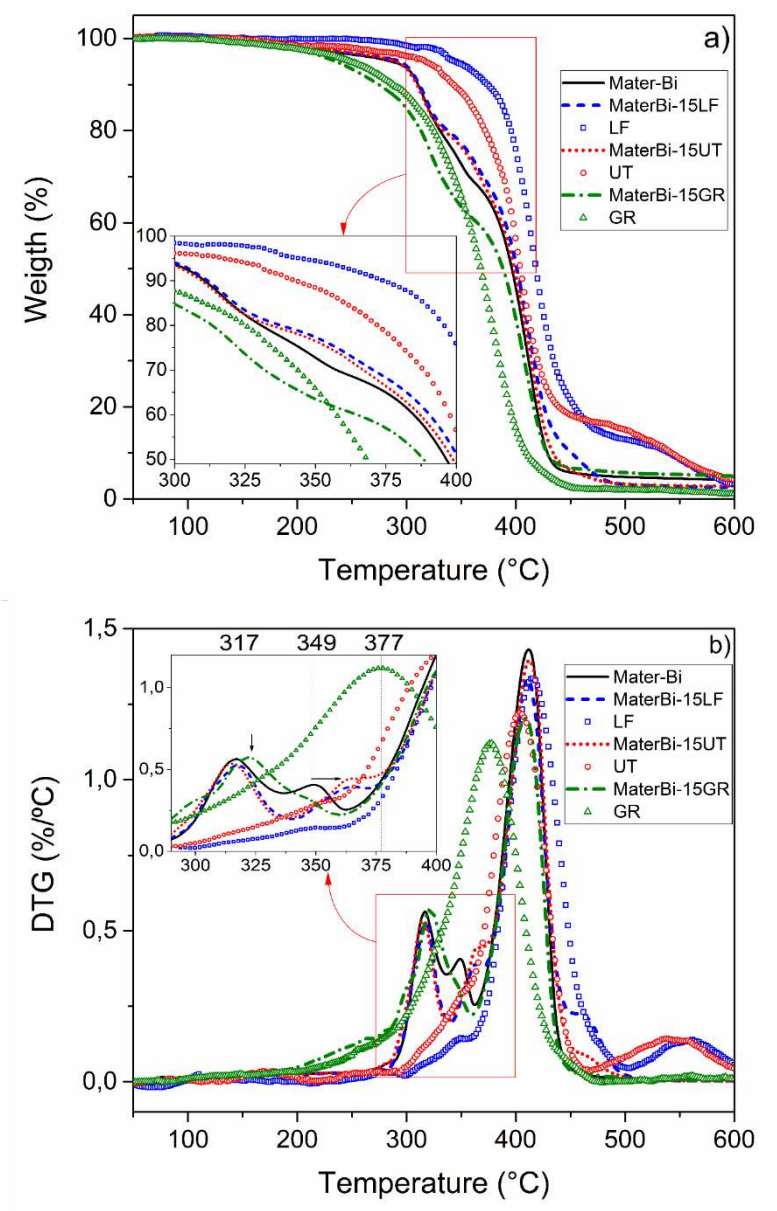


Figure 7. a) DSC second heating and b) DSC cooling of neat Mater-Bi® and formulations with 15 wt.% of pine resin derivatives

147 **Table 4.** DSC thermal properties of neat Mater-Bi® and Mater-Bi®-pine resin derivatives formulations

	DSC second heating								DSC Cooling		
Formulation	T_g (ºC)	T_{mPCL} (ºC)	T_{cc} (ºC)	ΔH_{cc} (J/g)	T_{mPBAT} (ºC)	ΔH_{mPBAT} (J/g)	$T_{m\ plasticized\ starch}$ (ºC)	$\Delta H_{m\ plasticized\ starch}$ (J/g)	X_c (%)	T_c (ºC)	ΔH_c (J/g)
Mater-Bi®	-32.0	56.3	107.3	2.2	127.9	2.3	150.3	2.5	0.1	92.5	9,2
MaterBi-5LF	-31.0	56.3	-	-	126.4	3.0	146.1	2.6	1.8	88.0	10.2
MaterBi-10LF	-29.1	56.5	-	-	123.9	3.6	146.6	2.1	2.0	86.9	11.1
MaterBi-15LF	-27.7	56.6	-	-	123.7	3.5	146.6	2.1	1.8	88.2	8.5
MaterBi-5UT	-29.7	57.3	-	-	124.2	3.7	147.4	2.1	2.2	86.6	9.5
MaterBi-10UT	-27.0	56.6	-	-	119.9	6.0	148.5	1.1	3.3	83.3	10.7
MaterBi-15UT	-27.0	56.4	-	-	118.9	5.9	147.6	1.0	3.1	81.7	9.5
MaterBi-5GR	-28.6	56.2	-	-	123.9	1.8	144.6	3.1	1.1	84.6	12.3
MaterBi-10GR	-25.3	54.1	-	-	122.4	2.6	142.8	2.5	2.4	82.9	9.9
MaterBi-15GR	-22.3	53.6	-	-	111.6	5.4	143.0	1.3	2.8	76.6	8.2

148 Regarding TGA analysis, **Figure 8-a** shows the thermogravimetric curves of
149 neat Mater-Bi® and the formulations added with 15 wt.% of resin. Meanwhile, **Table 5**
150 summarizes the thermal data of the initial degradation temperature (5% of weight loss,
151 $T_{5\%}$) as well as the maximum degradation peaks (T_{max}), extracted from the TGA and
152 DTG curves, respectively.
153



154
155 **Figure 8. a)** TGA and **b)** DTG curves of Mater-Bi® and formulations with 15 wt.% of
156 pine resin derivatives.

157 The results showed that the polymeric matrix used in this study (Mater-Bi®) presents a
158 three step degradation process: the first step centred at 317 ºC, corresponding to the
159 plasticized starch degradation.[19,21,48,61] The second step centred at 349 ºC, attributed to
160 either the degradation of the compatibilizing agents usually present in Mater-Bi®
161 formulations, or to interpenetrating networks formed by starch with the aliphatic
162 aromatic polyesters.[61] The third step, with a maximum degradation peak at 412 ºC,
163 corresponding to the degradations of the PBAT.[19] This peak could be overlapped with
164 the degradation peak of PCL, because it has similar degradation temperature[53] and also
165 because its fraction on Mater-Bi® is less than 10 wt.%.[5] The $T_{5\%}$ increased up to 4 ºC
166 and 7 ºC in formulations added with UT or LF, respectively. On the contrary, in GR
167 added formulations, the onset degradation temperature had a noticeable decrement
168 between 14 ºC (in MaterBi-5GR formulation) and 51 ºC (in MaterBi-15GR formulation)
169 compared to neat Mater-Bi®. This behaviour is attributed to the inherent thermal
170 characteristics of each pine resin derivative, where GR started the degradation at lower
171 temperatures than LF or UT, because pentaerythritol esters of gum rosin present a more
172 thermally stable chemical structure and also interact better with the polymeric matrix by
173 hydrogen bonding interactions leading to a stabilizing effect which protect the
174 polymeric matrix from thermal degradation.

175 As discussed for the neat Mater-Bi®, all formulations exhibit a three-step
176 degradation. The maximum degradation temperatures (T_{max}) presented the following
177 behaviours: T_{max1} increased their values in MaterBi-GR formulations, while LF and UT
178 did not modify these temperatures. Besides, T_{max2} tend to increase its values up to 18 ºC
179 in MaterBi-10LF and MaterBi-5UT. In contrast, for GR added formulations, the peak
180 corresponding to T_{max1} was overlapped with the peak corresponding to T_{max2}. This
181 behaviour reveals that GR had somewhat interaction with the plasticized starch portion

of the Mater-Bi® than LF and UT. However, the thermal stability of the formulations added with GR tends to decrease, and those with chemically modified resins, LF and UT, tends to increase. On the other hand, the addition of resins did not influence the degradation step corresponding to PBAT portion of the polymeric material (T_{max3}), even though the tendency of this temperature is to decrease in higher GR resin contents. As well in the DTG curves, shown in **Figure 8-b**, it is important to notice that MaterBi-15LF and MaterBi-15UT curves presented a peak near to 460 ºC due to the resin remainder in the formulations, as can be seen from the DTG of neat pentaerythritol ester of colophony.[31]

Table 5. Onset degradation temperature ($T_{5\%}$), temperatures of the maximum decomposition rate (T_{max1}, T_{max2} and T_{max3}) for all formulations studied

Formulation	$T_{5\%}$ (ºC)	T_{max1} (ºC)	T_{max2} (ºC)	T_{max3} (ºC)
Mater-Bi®	286	317	349	412
MaterBi-5LF	286	317	346	411
MaterBi-10LF	292	316	366	411
MaterBi-15LF	293	318	365	411
LF	345	-	415	561
MaterBi-5UT	287	316	367	410
MaterBi-10UT	290	317	358	411
MaterBi-15UT	290	315	365	412
UT	317	-	404	545
MaterBi-5GR	272	320	-	411
MaterBi-10GR	253	321	350	411
MaterBi-15GR	235	322	-	409
GR	248	-	377	-

Finally, **Table 3** shows the Heat Deflection Temperature (HDT) where is possible to verify that this property followed the same tendency of the already discussed properties. LF resin did not change significantly the HDT. In fact, Mater-Bi® chains did not have easy movement, due to the low compatibilizing effect of the LF resin. This behaviour also allowed confirming the lack of the plasticizing effect of LF. Whereas, adding 10 wt.% of GR or 15 wt.% of UT, the HDT at room temperature was reduced,

confirming their important plasticizing effect, since those resins facilitates the free movements of the polymer chains.

3.6. Dynamic-Mechanical properties

The effect of pine resin derivatives on the dynamic-mechanical properties of Mater-Bi® was also studied. **Figure 9** presents the trend of storage modulus of Mater-Bi®-based formulations respect to the resin type and content **(Figure 9-a),** the evolution of storage modulus (G') and the gap between the loss modulus (G'') and G', represented by the tangent of the gap (*tan δ*), plotted against the temperature (**Figure 9-b** and **Figure 9-c**, respectively). Considering the amount of resin added, the storage modulus determined at 25 ºC follows the same trend than Young's modulus (**Figure 2-a**) and flexural modulus (**Figure 3-a**). As discussed, LF and UT resins has a compatibilizing effect between the resin and the polymeric matrix, while UT resin also shows a plasticizing effect. On the other hand, increasing the amount of GR there is a linear decrement in the storage modulus values, suggesting a solubilising, compatibilizing and plasticizing effect. Plus, if the trend of storage modulus (G') with temperature (**Figure 9-b**) is observed, in the curve corresponding to the neat Mater-Bi®, two important losses of G' are observed.[17] The first one corresponds to the combination of the glass transition of the PBAT and the one of the plasticized starch portion of the Mater-Bi® (T_{gPBAT} and $T_{g\ plasticized\ starch}$) having associated a peak in *tan δ* at -28 ºC.[19] The second major loss of G' is associated with a peak of *tan δ* at 60 ºC, corresponding to the PCL and additives portion which represents the 10% of the Mater-Bi® polymeric matrix, as discussed before on FTIR and DSC analysis.[55] Thus, in these dynamic mechanical analyses it was observed a peak around 60 ºC that coincides with

226 the melting temperature of the PCL.[18,57] Below the first T_g (T_{gPBAT} and $T_{g\ plasticized\ starch}$),
227 Mater-Bi® formulations with 15 wt.% of UT, LF and GR have a higher G' value than
228 the neat Mater-Bi®. In addition, above this T_g, the formulations containing 15 wt.% of
229 UT and LF provide higher G' values, increasing the values of the elastic component of
230 polymeric matrix. This is due to the chemical interaction between resin derivatives and
231 Mater-Bi® components. Moreover, this behaviour contributes to a greater cohesion
232 between the components of the Mater-Bi®, already observed in other properties. This
233 interaction may be due to the molecules of both chemically modified resins act as
234 compatabilizer agent, hindering molecular movement of the polymeric chains.
235 However, the formulation with 15 wt.% of GR showed values of G' below to those
236 obtained for neat Mater-Bi®. In this case, GR acts as a compatibilizing agent between
237 the components of matrix (plasticized starch, PBAT and PCL), increasing the
238 intramolecular free volume and the solubility between them.[6,19] This causes a lower
239 interaction between the functional groups of the polymer chains and increases the
240 viscous component of the Mater-Bi® and consequently its fluidity. Moreover, the
241 processability of the Mater-Bi®-resin based formulations is easier than that of neat
242 Mater-Bi®, standing out the MaterBi-GR based formulations.

243 Analysing the effect of *tan δ* peaks (**Figure 9-c**) of Mater-Bi® added with pine
244 resin derivatives it is possible to corroborate the effect of the LF, UT and GR resins on
245 the matrix. As observe from DSC results, LF and UT act as cohesive agents, probably
246 as a consequence of the chemical interactions between the functional groups of the
247 polymer components and the functional groups of the modified resin derivatives
248 commented in FTIR analysis.[3,5,22] In fact, the peak of T_{gPBAT}-$T_{gplasticized\ starch}$ (between -
249 20 and -25 ºC) was well defined and separated from that corresponding to the melting of
250 PCL (around 60 ºC).[57] In contrast, the MaterBi-GR based formulations exhibited a very

different behaviour: firstly, the peak corresponding to T_{gPBAT}-$T_{g\ plasticized\ starch}$ was shifted to higher temperatures (15 ºC in the MaterBi-15GR). These shifts indicate an improvement in the interfacial adhesion between the components of the neat Mater-Bi® and the resins.[19] Secondly, the peak of PCL component at 60 ºC disappeared. The second peak of the MaterBi-15GR curve correspond to the melting of GR. The disappearance of the melting peak is due to the greater compatibilizing effect of the GR resin on the components of Mater-Bi®. Furthermore, said effect results in a large increase in the solubility of the three polymeric fractions of the Mater-Bi®, which increased their miscibility between them due to the GR presence in addition to an important plasticizing effect. Finally, these results are in good agreement with the easier processability of the Mater-Bi®-resin based formulations, the lower Shore D hardness as well as the lower melting temperature of the MaterBi-GR based formulations which are indicatives of the compatibilizing-plasticizer effect of the GR in the Mater-Bi® matrix.

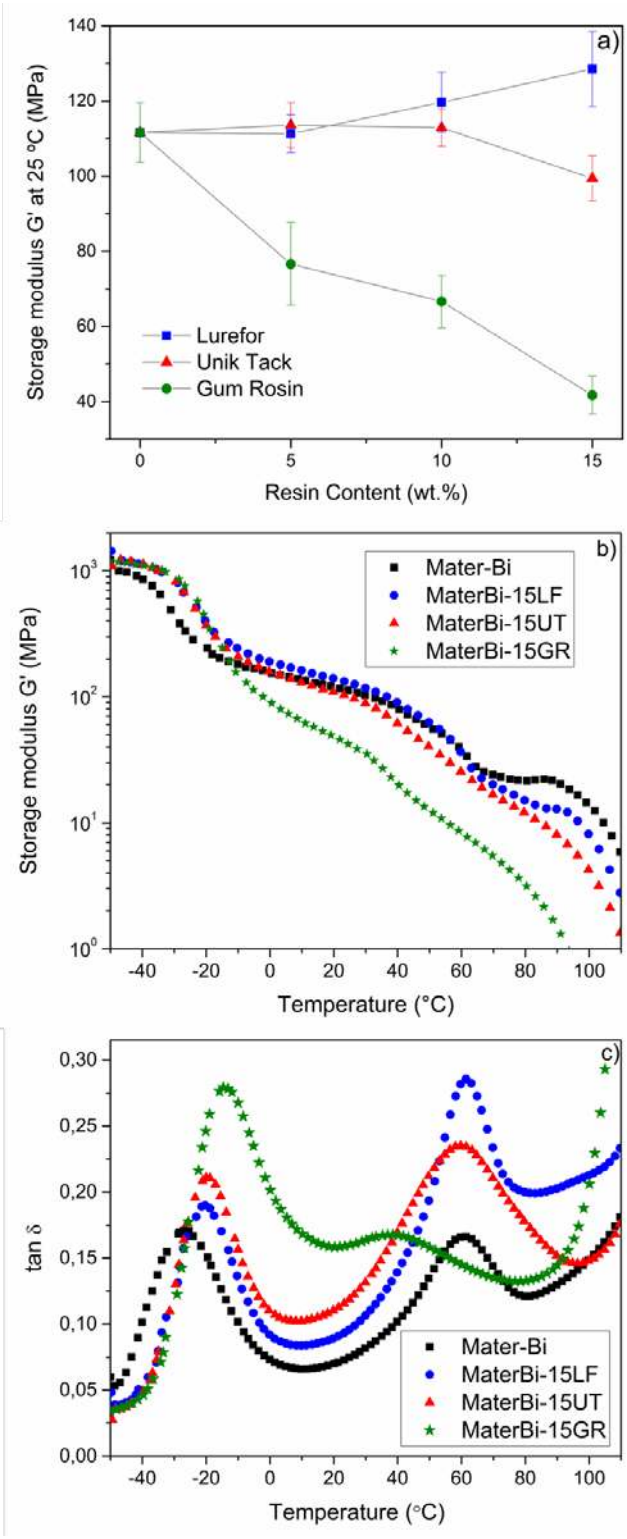


Figure 9. DMA analysis: a) Effect of increasing amount of pine resin derivatives on the storage modulus of Mater-Bi®-based formulations at 25 °C; b) storage modulus and c) loss factor curves for neat Mater-Bi® and 15 wt.% of pine resin derivatives formulations

4. Conclusions

Mater-Bi®-resin based formulations were successfully processed by melt extrusion followed by injection moulding process. Mater-Bi® was blended with three pine resin derivatives which act in three different ways. GR exerts a marked plasticizing, solubilizing and compatibilizing effect on the Mater-Bi® polymeric matrix. That means, an increase of 365% in maximum elongation at break, 480% in toughness and 250% in the Charpy's impact energy, in material formulated with 15 wt.% of GR. There is also a significant decrease on the processing temperatures, up to 50 ºC lower than the processing temperatures of neat Mater-Bi®. On the other hand, chemically modified resins showed different behaviour. LF acts as a compatibilizer between the components of Mater-Bi® (PBAT, plasticized starch and PCL), contributing up to 250% more toughness to the material, 5% more Young's modulus and 13% more tensile strength in formulations with 10 wt.% of LF resin, with respect to neat Mater-Bi®. Meanwhile, UT acts as a compatabilizer/plasticizer agent, which confers greater cohesion to the components of the Mater-Bi®, improving its processability performance by decreasing the processing temperature up to 45 ºC and increasing the maximum elongation at break by 72% in formulations with 15 wt.% of UT resin. Additionally, SEM micrographs and the changes in thermal transitions corroborated the plasticizing solubilising and cohesive behaviour observed in each formulation. Moreover, pine resins and their derivatives are a viable alternative as natural additives for Mater-Bi® (composed by plasticized starch, aliphatic/aromatic polyesters and aliphatic polyesters as components). Finally, the processability properties conferred by the rosin resins studied here opens the possibility of using these formulations in several industrial applications such as food packaging, agricultural mulch films or greenhouse plastics.

Acknowledgment

This work has been supported by the Spanish Ministry of Economy and Competitiveness, PROMADEPCOL (MAT2017-84909-C2-2-R). M.P. Arrieta thanks Complutense University of Madrid for "Ayudas para la contratación de personal postdoctoral en formación en docencia e investigación en departamentos de la UCM".

References

1. Plastics Europe, Plastics – the Facts 2016. An analysis of European plastics production, demand and waste data" [Online]. Available: http://www.plasticseurope.es/industria-del-plastico/datos-de-mercado.aspx. 2017.
2. Arrieta, M. P.; Peponi, L.; López, D.; Fernández-García, M., Industrial Crops and Products 111, 317 2018.
3. Akrami, M.; Ghasemi, I.; Azizi, H.; Karrabi, M.; Seyedabadi, M., Carbohydrate polymers 144, 254 2016.
4. Arrieta, M. P.; Samper, M. D.; Aldas, M.; López, J., Materials 10, 1008 2017.
5. Borchani, K. E.; Carrot, C.; Jaziri, M., Composites Part A: Applied Science and Manufacturing 78, 371 2015.
6. Ferri, J. M.; Garcia-Garcia, D.; Sánchez-Nacher, L.; Fenollar, O.; Balart, R., Carbohydrate polymers 147, 60 2016.
7. Arrieta, M. P.; López, J.; López, D.; Kenny, J. M.; Peponi, L., Polymer Degradation and Stability 132, 145 2016.
8. Fabra, M. J.; López-Rubio, A.; Cabedo, L.; Lagaron, J. M., Journal of Colloid and Interface Science 483, 84 2016.

9. Makaremi, M.; Pasbakhsh, P.; Cavallaro, G.; Lazzara, G.; Aw, Y. K.; Lee, S. M.; Milioto, S., ACS applied materials & interfaces 9, 17476 2017.
10. Niu, X.; Liu, Y.; Song, Y.; Han, J.; Pan, H., Carbohydrate polymers 183, 102 2018.
11. Mujica-Garcia, A.; Sonseca, A.; Arrieta, M. P.; Yusef, M.; López, D.; Gimenez, E.; Kenny, J. M.; Peponi, L. In Advanced Surface Engineering Materials, 2016.
12. Sessini, V.; Arrieta, M. P.; Kenny, J. M.; Peponi, L., Polymer Degradation and Stability 132, 157 2016.
13. Ferri, J. M.; Garcia-Garcia, D.; Carbonell-Verdu, A.; Fenollar, O.; Balart, R., Journal of Applied Polymer Science 1352018.
14. Trovatti, E.; Carvalho, A. J. F.; Gandini, A., Polymer International 64, 605 2015.
15. Samper-Madrigal, M.; Fenollar, O.; Dominici, F.; Balart, R.; Kenny, J., Journal of materials science 50, 863 2015.
16. Azevedo, V. M.; Borges, S. V.; Marconcini, J. M.; Yoshida, M. I.; Neto, A. R. S.; Pereira, T. C.; Pereira, C. F. G., Carbohydrate polymers 157, 971 2017.
17. Sessini, V.; Raquez, J. M.; Lourdin, D.; Maigret, J. E.; Kenny, J. M.; Dubois, P.; Peponi, L., Macromolecular Chemistry and Physics 2182017.
18. Correa, A. C.; Carmona, V. B.; Simão, J. A.; Mattoso, L. H. C.; Marconcini, J. M., Carbohydrate polymers 167, 177 2017.
19. Lendvai, L.; Apostolov, A.; Karger-Kocsis, J., Carbohydrate polymers 173, 566 2017.
20. Mikus, P.-Y.; Alix, S.; Soulestin, J.; Lacrampe, M.; Krawczak, P.; Coqueret, X.; Dole, P., Carbohydrate polymers 114, 450 2014.
21. Sessini, V.; Arrieta, M. P.; Raquez, J. M.; Dubois, P.; Kenny, J. M.; Peponi, L., Polymer Degradation and Stability 159, 184 2019.

22. Arrieta, M. P.; Samper, M. D.; Jiménez-López, M.; Aldas, M.; López, J., Industrial Crops and Products 99, 196 2017.
23. Narayanan, M.; Loganathan, S.; Valapa, R. B.; Thomas, S.; Varghese, T., International Journal of Biological Macromolecules 99, 37 2017.
24. Wilbon, P. A.; Chu, F.; Tang, C., Macromolecular rapid communications 34, 8 2013.
25. Rodríguez-García, A.; Martín, J. A.; López, R.; Sanz, A.; Gil, L., Industrial Crops and Products 86, 143 2016.
26. Sharma, L.; Singh, C., Polymer Composites 39, 1480 2018.
27. Moustafa, H.; El Kissi, N.; Abou-Kandil, A. I.; Abdel-Aziz, M. S.; Dufresne, A., ACS applied materials & interfaces 9, 20132 2017.
28. Romero, A. in Atelier International de diagnostique de l'indutrie des résineux de seconde transformation: 2012.
29. Yu, C.; Chen, C.; Gong, Q.; Zhang, F. A., Polymer International 61, 1619 2012.
30. Gutierrez, J.; Tercjak, A., RSC Advances 4, 32024 2014.
31. Cavallaro, G.; Lazzara, G.; Milioto, S.; Parisi, F.; Ruisi, F., Cellulose 24, 3367 2017.
32. Arrieta, M. P.; López, J.; Ferrándiz, S.; Peltzer, M. A., Acta Horticulturae 1065, 719 2015.
33. Arrieta, M. P.; López, J.; Hernández, A.; Rayón, E., European Polymer Journal 50, 255 2014.
34. Liu, X. Q.; Huang, W.; Jiang, Y. H.; Zhu, J.; Zhang, C. Z., Express Polymer Letters 62012.
35. López, J.; Arrieta, M. P., Actas del II Simp. Int. Resinas Nat., 206 2013.

371 36. International Standards Organization, ISO 527-1:2012 - Plastics - Determination
372 of tensile properties - Part 1: General. 2012.
373 37. Sessini, V.; Raquez, J. M.; Lo Re, G.; Mincheva, R.; Kenny, J. M.; Dubois, P.;
374 Peponi, L., ACS Applied Materials and Interfaces 8, 19197 2016.
375 38. Samper, M. D.; Bartomeu, D.; Arrieta, M. P.; Ferri, J. M.; López-Martínez, J.,
376 Materials 112018.
377 39. International Standards Organization, ISO 178:2010 - Plastics - Determination of
378 flexural properties. 2010.
379 40. International Standards Organization, ISO 179:2010 - Plastics - Determination of
380 charpy impact properties. 2010.
381 41. International Standards Organization, ISO 868:2003 - Plastics and ebonite -
382 Determination of indentation hardness by means of a durometer (Shore hardness).
383 2003.
384 42. Jost, V., Express Polymer Letters 12, 429 2018.
385 43. International Standards Organization, ISO 75-1:2013 - Plastics - Determination of
386 temperature of deflection under load - Part 1: General test method. 2013.
387 44. Mok, S. L.; Kwong, C. K.; Lau, W. S., The International Journal of Advanced
388 Manufacturing Technology 18, 404 2001.
389 45. Al-Itry, R.; Lamnawar, K.; Maazouz, A., Polymer Degradation and Stability 97,
390 1898 2012.
391 46. Bastioli, C.; Cerutti, A.; Guanella, I.; Romano, G. C.; Tosin, M., Journal of
392 Polymers and the Environment 3, 81 1995.
393 47. Esmaeili, M.; Pircheraghi, G.; Bagheri, R., Polymer International 66, 809 2017.
394 48. Mano, J.; Koniarova, D.; Reis, R., Journal of Materials Science: Materials in
395 Medicine 14, 127 2003.

396 49. Khan, G.; Yadav, S. K.; Patel, R. R.; Kumar, N.; Bansal, M.; Mishra, B.,
397 International Journal of Biological Macromolecules 103, 1311 2017.
398 50. Arrieta, M. P.; Peponi, L., European Polymer Journal 89, 174 2017.
399 51. Jindal, R.; Sharma, R.; Maiti, M.; Kaur, A.; Sharma, P.; Mishra, V.; Jana, A.,
400 Polymer Bulletin 74, 2995 2017.
401 52. Singh, V.; Joshi, S.; Malviya, T., International Journal of Biological
402 Macromolecules 112, 390 2018.
403 53. Garcia-Garcia, D.; Rayón, E.; Carbonell-Verdu, A.; Lopez-Martinez, J.; Balart,
404 R., European Polymer Journal 86, 41 2017.
405 54. Peponi, L.; Sessini, V.; Arrieta, M. P.; Navarro-Baena, I.; Sonseca, A.; Dominici,
406 F.; Gimenez, E.; Torre, L.; Tercjak, A.; López, D.; Kenny, J. M., Polymer
407 Degradation and Stability 151, 36 2018.
408 55. Muthuraj, R.; Misra, M.; Mohanty, A., Journal of Applied Polymer Science
409 1322015.
410 56. Signori, F.; Coltelli, M.-B.; Bronco, S., Polymer Degradation and Stability 94, 74
411 2009.
412 57. Navarro-Baena, I.; Arrieta, M. P.; Sonseca, A.; Torre, L.; López, D.; Giménez, E.;
413 Kenny, J. M.; Peponi, L., Polymer Degradation and Stability 121, 171 2015.
414 58. Salgado, C.; Arrieta, M. P.; Peponi, L.; Fernández-García, M.; López, D.,
415 Macromolecular Materials and Engineering 3022017.
416 59. Zhao, P.; Liu, W.; Wu, Q.; Ren, J., Journal of Nanomaterials 2010, 4 2010.
417 60. Ferri, J. M.; Fenollar, O.; Jorda-Vilaplana, A.; García-Sanoguera, D.; Balart, R.,
418 Polymer International 65, 453 2016.
419 61. Cerruti, P.; Santagata, G.; d'Ayala, G. G.; Ambrogi, V.; Carfagna, C.;
420 Malinconico, M.; Persico, P., Polymer Degradation and Stability 96, 839 2011.

421

422