Thermomechanical Characterization of Polylactic Acid and Its Composites

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Abstract. This paper presents the experimental tests for the thermomechanical characterization of biopolymer polylactic acid, and its composites with beech flour or with nanoreiforcement of modified montmorillonite, with the purpose of applicability in the automotive sector. Tests of torque and traction are executed for the mechanical characterization and the results comparison; dynamical tests are executed for the thermomechanical characterization, determining the elastic modulus and loss factor versus the actual temperature.

Keywords: PLA, beech flour, dellite, montmorillonite, material tests

1 Introduction

The ability to use lightweight materials that increase fuel economy is one of the strengths for car composite development. Replacing parts with heavier components not only contributes to energy savings, but also affects the size of the braking system, engine and fuel tanks that can be reduced. Due to the growing number of environmental problems, interest in biopolymers has grown. Bioplastics can either be recycled through organic recovery or being used as fertilizers, i.e. they are compostable, following the rule EN 13432 [1] [2] [3]. A nanocomposite is a solid multi-phase material where one of the phases has at least one dimension smaller than 100 nanometers [4] [5] [6] [7] [8] [9] and can be used with biodegradable polymers. In this paper, the mechanical and thermomechanical properties of a biodegradable synthetic polymer, PLA (pure polylactic acid), as well as an array for the realization of two composite materials are analyzed: the first material is a microcomposite consisting of a PLA matrix and a reinforcement of wood flour, the second is a nanocomposite with PLA matrix and nanoreinforcement of modified montmorillonite.

2 Used materials and processing

The polymer matrix used in this work is extruded with a melting range of 7 g/10 min (210 °C, 2.16 kg) of PLA (Ingeo™ Biopolymer 4032D, NatureWorks, Minnetonka, Minnesota, USA), density 1, 24 g/cm^3 and melting point at 155-170 °C [10]. Wood flour (mainly from beech) was supplied by La.So.Le (Percoto, Italy), with a particle size varying from 300 to 500 μm [12]. Nanocarriage is a Dellite 72T silicate resin supplied by Laviosa Minerary Chemistry (Livorno, Italy). Montmorillonite is modified with organic alkylammonium salts to improve and enhance the delamination and adhesion of clay with the polymer matrix. Table 1 shows the compositions.

Table 1: Percent composition of prepared composites.

Matrix	Filler
PLA 100%	None
PLA 70%	Beech flour 30%
PLA 95%	Dellite 5%

By comparison, pure PLA was treated under the same conditions as for composites. To expel the residual moisture that would cause the polymer hydrolysis during mixing, the PLA is placed in a vacuum oven (model NSV 9035) at temperature of 80 °C overnight (about 16-17 hours). It is dried in an identical oven to charge Dellite for the same time, but at temperature of 110 °C. Drying of beech flour, however, takes place in a ventilated stove at 80 °C. This device is preferred to prevent condensation on the walls during the process.

Note the maximum volume of the mixer chamber (50 cm^3) and the density of the PLA (1.24 g/cm^3), a mass of 45 g is used for the preparation of the blends. Once the matrix and charge amounts are weighed, PLA grains and the filler were mixed in a beaker before inserting them into the Plasti-Corder Brabender PLE 330 mixer at temperature of 190 °C, to allow the polymer to be melted. The blend is immersed in the chamber with 10 rpm rotation speeds. The loading phase is carried out in 60 seconds, then the speed of rotation of the cams is increased to 60 rpm. Mixing is interrupted when the torque offered by the melt reaches a constant value (after 5 minutes about). This indicates complete polymer fusion and possible homogenization with the charge (if present). A viscous fluid is drawn from the mixer, which quickly solidifies at room temperature. The removal of the material from the mixer in a short time is important to prevent the degradation, while remaining too long at 190 °C. This operation is performed in 120 seconds; all material obtained over this time is discarded. The material taken from the mixer is placed in a vacuum oven at 80 °C, all the night before being pressed into the desired shape. The specimens are obtained from a rectangular mold. To know the amount of material to be entered in each mold, the volume of the latter was measured (14.3 cm^3). 19 g of PLA is weighed and placed in the mold. The weighed quantity is slightly higher than the one needed to be sure that the whole mold will fill. Carver Laboratory Press (Wabash, IN, USA), is used to obtain the films; the material is pressed at temperature of 190 °C, for 2 minutes at ambient pressure and for 1 minute with completely forced plates on the mold. at pressure of 100 bar to ensure complete filling by the material. After this time the electric resistors are switched off and water is circulated at room temperature inside the press plates to cool them down. When a temperature of 40 °C is reached the mold is extracted from the device and the specimens are punched through a lab coil. The dumbbell shape follows the dimensions of the technical standard ASTM D638, in particular it is of type IV [12]. Two films for each material are drawn from six to seven samples to perform traction tests. Changing the die molding shape, three specimens are obtained for each prepared material, 30 mm long and 5 mm wide parallelepiped, used for performing dynamic mechanical analysis. After the numbering of all the samples, the thickness of the same was measured by centimeter caliber; the average of the three point measurement indicates the thickness of each specimen.

2 Thermal and Mechanical Characterization

Tensile tests are performed using a Zwick Roell z005 universal test machine using a 5 kN load cell. The elastic modulus is determined at an initial speed of the crossbar of 1 mm/min. After the acquisition of Young's module, the test speed was increased to 20 mm/min until breaking. The data released by the equipment are processed through a spreadsheet, allowing the recalculation of the elastic module with other data obtained from the test (breakdown stress, yield stress, etc.). The tests are carried out using the Metravib DMA +150 equipment with a capacitive force sensing sensor (maximum load 150 N) and an accelerometer for measuring the displacement. A 0.01 mm traction shift is applied to the frequency of 1 Hz and a temperature ramp from room temperature (25 to 30 °C) up to 130 °C with an increase of 3 °C/min.

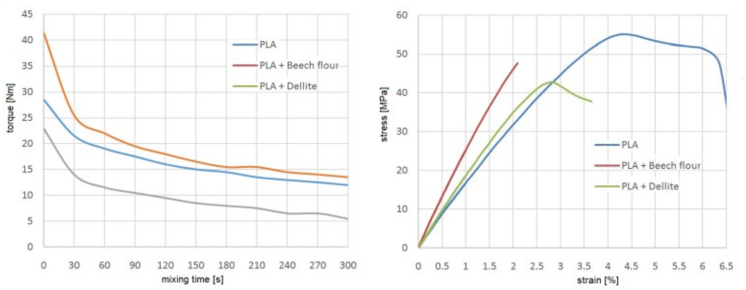

Fig. 1. Left: Torque offered by the blends according to the mixing time. Right: Representative strain-deformation graph.

3 Results and Discussion

The viscosity of the various systems is measured during the mixing phase: the torque offered by the fuselage is measured and the values are set at 30 second time intervals until the end of the operation. Torque values are reported versus the time in figure 1 on the left. After the rapid initial descent due to the blending polymer mix, the curves tend to reach a stationary state for the complete fusion of the polymeric material and homogenization in the presence of the charge. Torque is an indirect measure of viscosity; therefore the PLA + bead mixture has a higher viscosity than PLA alone. Viscosity increase is a well-known phenomenon for the addition of charges that produces a matrix reinforcement effect. This is also expected for the addition of Dellite but it turns out that the viscosity of the nanocomposite is lower than that of the single matrix. PLA viscosity probably decreases due to the degradation of the polymer chain [10]. Scientific literature indicates that this effect is attributed to a remarkable decrease in molecular weight due to various complex processes of degradation such as hydrolysis and radical degradation [13]. This effect is probably due also to the presence of the organic modifier in montmorillonite which could in turn promote degradation phenomena [14]. This event has been observed in many cases, for example in the use of hydrotalcites (HT) as nanoscale [10].

3.1 Thermal and Mechanical Properties

Figure 1 on the right shows the stress-strain curves. The yield stress (σ_y) is calculated conventionally using Jhonson method, which is the stress at a predetermined permanent deformation of 0.2% [15]. The obtained tensile and elongation values are shown in table 2. PLA has ductile behavior with the highest peak stress and elongation at break. The same behavior occurs with the addition of Dellite, while with beech the material is fragile. Compared to pure PLA, both treated composites show an increase of elastic modulus by adding filler. The highest value is achieved with the micro charge of beech flour with an increase of 47%. The use of Dellite as reinforcement also leads, albeit to a lesser extent (9%), to the increase of Young's module. This last mechanical performance is the result of a balance between the positive effect of the introduction of montmorillonite and the negative effect of the matrix degradation phenomena due to the presence of the organic modifier [10] [14].

Table 2 Values obtained experimentally by traction tests

PLA	E [MPa]	σ_{max} [MPa]	σ_y [MPa]	strain σ_{max} [%]	strain Break [%]
pure	1831±37	56.6±1.6	28.0±2.1	4.8±0.7	7.6±2.4
Beech fl.	2689±88	50.3±2.3	36.3±1.3	2.3±0.2	2.3±0.2
Dellite	1989±73	44.7±2.2	35.1±1.1	2.9±0.1	3.8±0.4

With regard to the elongation at break, the presence of charges causes a decrease of this property, due to the different degree of crystallinity. In fact, crystallinity depends not only on the chemical composition and the chain configuration, but also on the cooling rate during the solidification.

Concerning mechanical dynamic analysis, the trend of elastic modulus (E') and loss factor (tan δ) at the actual temperature variation measured are shown in figure 2. The conservation modulus E’ of composite with beech flour keeps a higher value than that with the addition of Dellite, which is just above the pure PLA module. The module E' decreases by increasing the temperature for all prepared materials, with a significant decrease in the temperature range of 50 to 60 °C; the high value of the elastic modulus has not to surprise; it is due to the small size of the specimens used in dynamic tests and the high variation of strain speed.

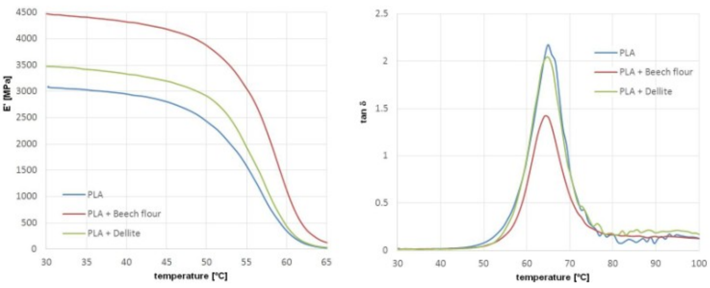

Fig. 2. Left: E' variation versus temperature, Right: damping factor versus temperature

Evolution of the damping factor tan δ versus the temperature shows that the trend for pure PLA is similar to that with the addition of Dellite. A lower peak of tan δ is obtained for beech flour. The incorporation of charges into a polymer matrix influences the damping behavior of the composites, which is due both to the shear stress concentrations at the charge - matrix interface and to the dissipation of the viscoelastic energy in the matrix [16] [17]. Therefore, the damping factor depends on the adhesion between charge and matrix. Therefore, a weak adhesion leads to higher values than tan δ, while good adhesion limits the mobility of the polymer chains by lowering the damping [18] [19]. Low damping value leads to better composite loading capacity. This result is consistent with what is obtained during torque measurement. The glass transition temperature (Tg) is established as the temperature at which the damping factor reaches the maximum value. There is no appreciable variation with the addition of the two charges. Tg is maintained at 65 °C for all the materials tested.

5 Conclusions

Thermomechanical characteristics of the PLA biopolymer are analyzed in order to assess the possible applicability in the automotive sector. In order to improve their performance, they have embedded charges in the polymer matrix. The addition of beech flour leads to an increase in the elastic modulus of 47% due to a polymer infiltration. The nanocomposite with modified montmorillonite maintains ductile behavior of the material by increasing the elastic modulus by 9%. There is the problem of decay of mechanical properties for temperatures above 55 °C to 60 °C. The addition of charges does not cause an increase in glass transition temperature. One of the prerequisites that a polymer needs to have, if used in the interior of a vehicle, is that it has not to lose its mechanical properties until 100 °C. The use of PLA as a composite matrix today is ideal for obtaining fully biochemical polymeric materials, but this need to be strengthened. A charge is required to increase the temperature at which the PLA loses resistance.

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