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Development and Characterization of a Biodegradable Composite Based on PLA Matrix and Date Kernels Powder

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Abstract: In the present study, a biodegradable composite material based on polylactic acid (PLA) and date kernels (DK) is developed by hot pressing. In first, all the raw materials were processed into powders. Then, PLA-50% date kernels (DK) (% vol.) mixtures were hot-pressed at 180°C under 10 MPa pressure during 5 minutes. Microstructural characterization of the obtained composites was performed using Scanning electron microscopy (SEM), Fourier Transform InfraRed spectroscopy (FTIR), and Differential Scanning Calorimetry (DSC) analyzes. The mechanical behavior was evaluated through tribological tests and mass loss measurements were also taken. The results show that the developed composite material exhibits a homogeneous microstructure, with a continuous (polylactic acid) PLA- (date pits) DP interface and chemical bonds of PLA and plant fiber interactions. The tribological tests revealed a low coefficient of friction for this material.

Keywords: Biodegradable composite, Date kernels, PLA, Friction coefficient.

Introduction

Nowadays sustainable development becomes highly important, so researchers and industries are focusing on replacing nonrenewable and fossil based materials with environmentally friendly materials **(**Dicker et al., 2014). Composites with biodegradable matrices reinforced by natural and especially plant-based reinforcements present an interesting alternative to fossil based materials, they have also been introduced in automotive, building and other industries. This has been the focus on different research subjects recently (Fazita et al., 2016)**.** Polylactic acid (PLA) is a biodegradable polymer derived from renewable resources, making it a good replacement to petroleum-based plastics and PLA-based composites are well known for their ecological benefits. PLA polymers offer good thermal stability and high resistance, which makes its applicability wider (Wang et al., 2014)**.** Despite all these advantages, they also have some disadvantages such as their high costs compared to their lower mechanical properties than other polymer-based composites. Advancements in material science and manufacturing techniques are overcoming these limitations, by adding other different reinforcements to the polymer which can allow better properties.

In Algeria where the palm trees are very widespread, the exploitation of its fruit wastes (date kernels) is a very interesting. In order to valorize these date wastes, we used them as natural reinforcements in biodegradable polymer based composite materials (Rahmoune, 2017) They can possibly improve their characteristics. (Nagarjun et al., 2021). Developed biodegradable composites using poly-lactic acid (PLA). The composites were manufactured through compression molding technique. Their tensile results showed that the date seed filler reinforcement has significantly improved the tensile strength of PLA matrix. Moreover, the obtained composites showed 34.68% improvement in micro hardness when compared with neat PLA. The authors revealed that the composition wt.% of fillers has a mojor role in deciding the properties of the PLA composites. Different studies have investigated the wear and friction properties of polymer matrix composites reinforced with vegetal fibers and it is deduced that the incorporation of reinforcements can either improve or decrease the tribological performance of the polymer matrix.

The aim of this work is to develop a fully biodegradable composite material based on PLA matrix and date kernels (DK) powder reinforcement. Thus, the raw materials have been reduced into powders and hot-compacted. Microstructural characterization using Scanning electron microscopy (SEM) was carried out in addition to Differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) analysis. The materials mechanical behavior was evaluated through tribological tests in which coefficients of friction were deduced.

Experimental

Processing of Raw Materials into Powders and Sample Preparation

The PLA powder was obtained by grinding pellets in a grinder-chopper. In order to allow a better yield of this process, the PLA pelletswere previously brought to a temperature of -10 °C, what fragilizes them and facilitates their fragmentation. The powder thus obtained is then sieved to select the particles having upper 200 µm of size. Date kernels was washed and roasted in an oven at 180°C for 2 hours and then processed into powder with the same grinder-chopper. PLA-DK mixtures at the proportion 50% (% vol.) was prepared and homogenized in Turbula® to be compacted at 180°C under 10 MPa during 5 mn.

Samples were characterized by SEM to highlight their microstructure and by Fourier Transform InfraRed Spectroscopy (FTIR) to reveal the possible formation of new chemical bonds between PLA and DK reinforcement. DSC analysis was used to follow the evolution of the structural transformations in the PLA and in the DK of the developed composite. Also, the friction coefficients of the composite were determined by tribological tests.

Results and Discussion

SEM Observations of Raw Materials

Figure 1and Figure 2 show the SEM micrographs of the developed PLA-DK composite. The figure 1, obtained in secondary electron mode reveals a microporous appearance of the sample (pores of sizes less than 2 µmwith illuminated edges; circled in yellow, points 1 and 2) as well as particles presenting a more contrasting dark color but without luminous edges (points 3 and 4) suggesting that these are date kernel particles.

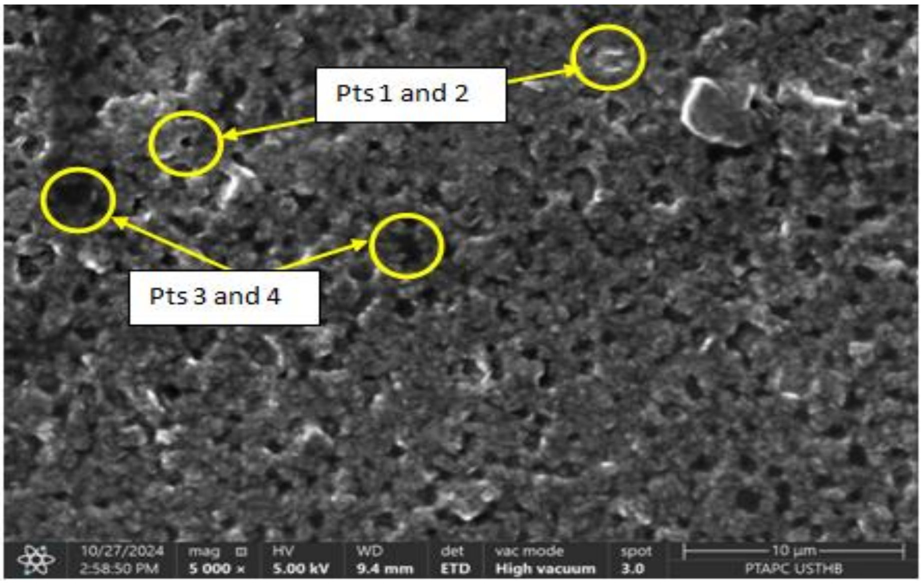


Figure 1.SEM image obtained in secondary electron mode.

Figure 2 represents SEM micrograph in backscattered electrons (CBS) of composite. Compared to that obtained in secondary electrons (Fig. 1), it clearly shows the significant contrast color of a phase contrast. Indeed, the PLA; of chemical formula $(C_3H_4O_2)_n$ has an average atomic number greater than that of the molecules constituting the date kernels (also for cellulose, lignin, etc.). We also notice a difference in the contrast between the particles (in light gray) and the pores (in dark) that we have located (points 1 and 2 in Figure 1).

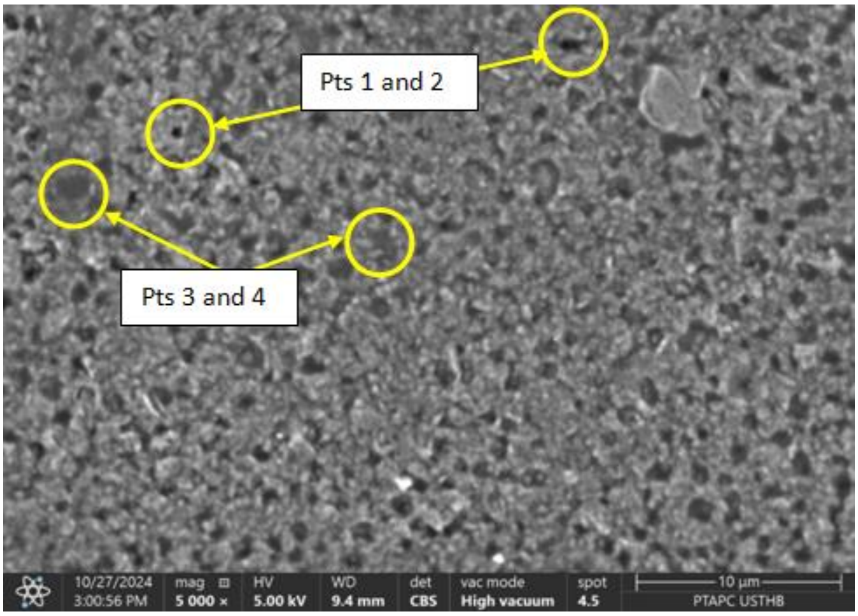
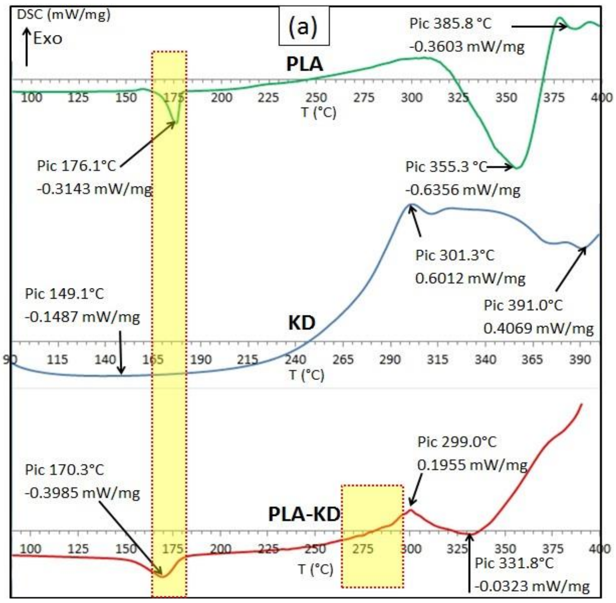


Figure 2. The SEM image obtained in backscattered electrons

Differential Scanning Calorimetry DSC Analysis

To understand PLA behaviour during heating and the influence of the addition of date pits reinforcements on the structural transformations of the obtained composite material, DSC analyzes were carried out starting from the ambient temperature to 400°C under N_2/50%/air atmosphere. The figure below (Fig. 3) shows the obtained curves. For virgin PLA, we observe a peak at 176.1 °C (minima value) which corresponds to the total melting of the PLA powder. At 307°C, the curve shows a significant endothermic peak from the onset of PLA evaporation which ends at 355.3°C. Another endothermic peak appears at 385.8°C which corresponds to the evaporation of residual substances produced by PLA transformations. The evaporation temperature of the composite was determined to start at 299°C. The decrease of PLA's evaporation and melting temperature is due to the chemical bonds formed between PLA and DK components.



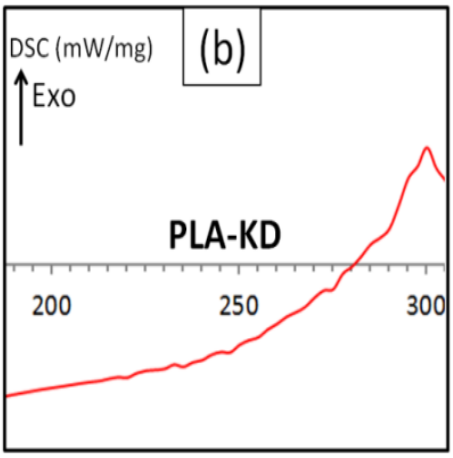


Figure 3 . DSC curves

FTIR Analysis

The FTIR spectra of the obtained PLA-DK composite sample is shown in Figure 4.A, comparison with the obtained result and the FTIR analysis previously carried out on PLA alone is done. For high wave numbers values (up to 3500 cm^{-1}), low-intensity elongation vibrations are observed, which are explained by the presence of alcohols and phenols in the date kernels.

The peaks of 2951 cm^{-1}wavenumbers value (and those in the vicinity) are due to the C-H and C = CH groups of PLA. Peaks around 2340-2360 cm^{-1} corresponding to C≡N nitriles appear with high intensities translating a high probability of formation of chemical bonds between PLA and date kernels compounds. They are less intense in the case of PLA alone. The peak at 1730 cm^{-1}corresponds to the aliphatic aldehydes of PLA, whereas those at 1650-1684 $cm^{-1}$are due to the aromatic aldehydes, alkenes and ketones. The peaks between 1241 and 1149 cm^{-1} correspond to PLA (different alcohols). For values between 1092 and 843 cm^{-1}, these ones occur in the case of date kernels (presence of ethers). At low wavenumbers values, peaks corresponding to the C-C and C = O bonds occur and instead reflect the presence of date kernels.

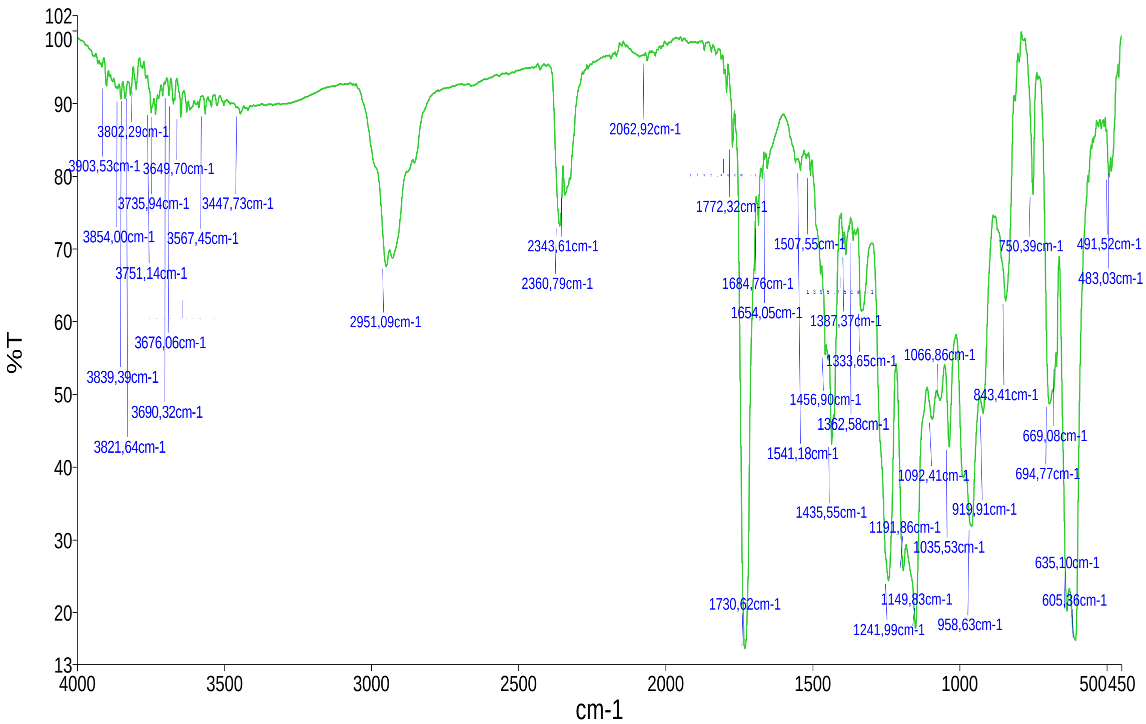


Figure 4.A. Fourier transform infrared spectra of PLA-DK sample

Tribological Tests

PLA alone and PLA-DK samples in the form of thick disks were tribologically tested using a CSM tribometer (Figure 5). The different results are recorded using a data logger with a frequency of 40 Hz.

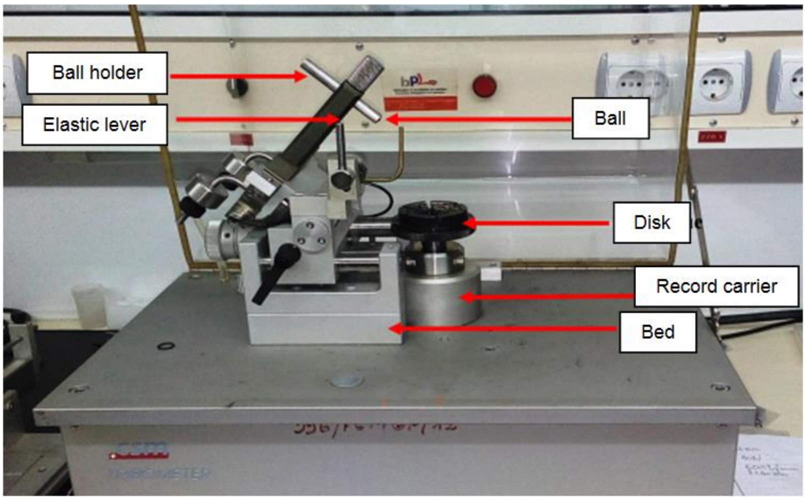


Figure 5. Overview of the tribometer and its instrumentation

A ball of stainless steel 6 mm in diameter rubs on the rotating sample with a distance of 200 m traveled with a speed of 10 cm / s, 20 cm/s and 30 cm/s.The tests are carried out at ambient temperature, under loads of 3, 5,7 and 10 N. They make it possible to determine the variation of the coefficient of friction of the material, and to estimate the rate of wear.Its principle is to apply a vertical load on a stationary ball in contact with the horizontal surface of the sample placed on a rotating disk as shown in Figure 6.

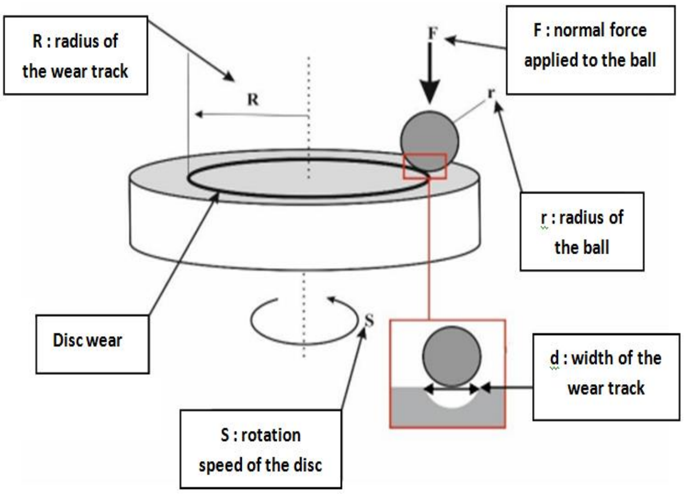


Figure 6. Schematic diagram of the tribometer

Measurement of Friction Coefficient

The contact of two bodies during a rotary movement causes a friction force which opposes the sliding. The coefficient of friction μ is given as a ratio ofthe tangential force (F_t) on the normal force (F_n)

$$\mu = \frac{F_t}{F_n}$$

The tangential force causes a lateral displacement of the resilient arm that supports the ball rod.The elastic deformation of the arm is sensed by an inductive sensor, which allows to deduce the value of F_t.Since the normal force is known (the applied force), the coefficient of friction, μ, is calculated by the data acquisition and processing software. This value is recorded according to the number of revolutions.

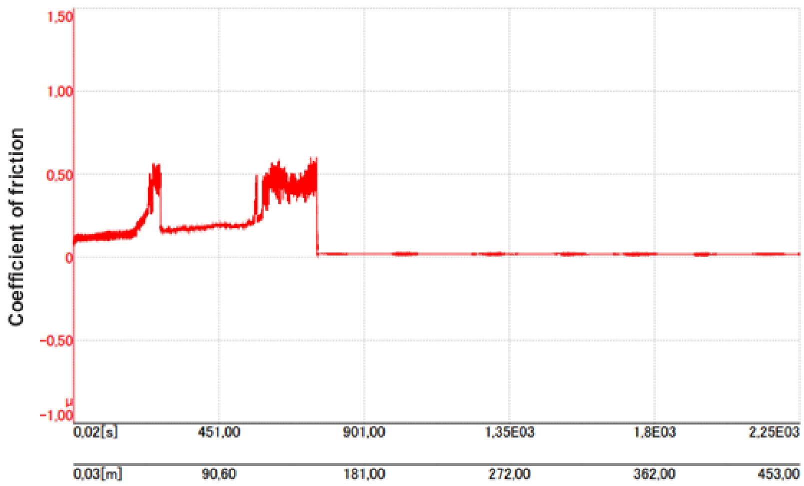


Figure 7. Evolution of the coefficient of friction of PLA alone

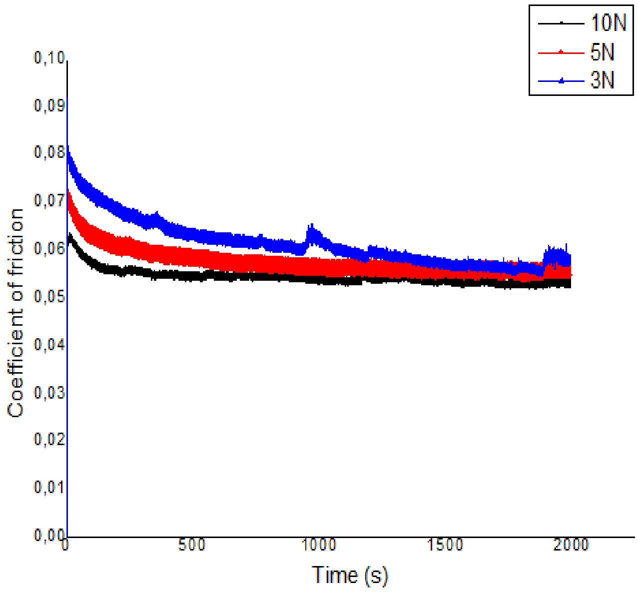


Figure 8. Evolution of the coefficient of friction of PLA –DK composite sample for a linear rotation speed of 10 cm/s

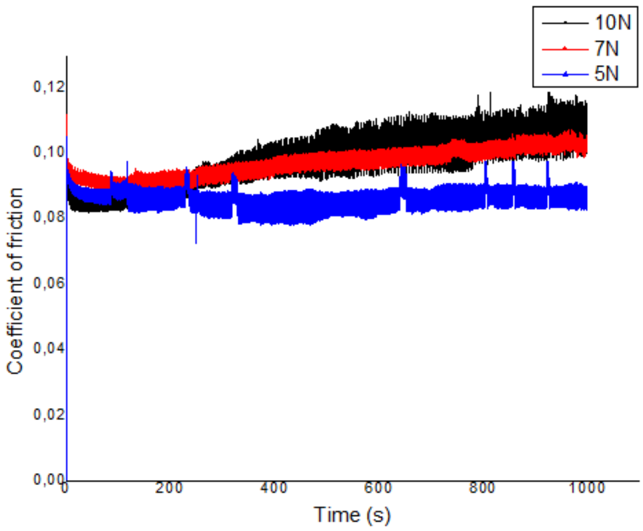


Figure 9. Evolution of the coefficient of friction of PLA –DK composite sample for a linear rotation speed of 20 cm/s

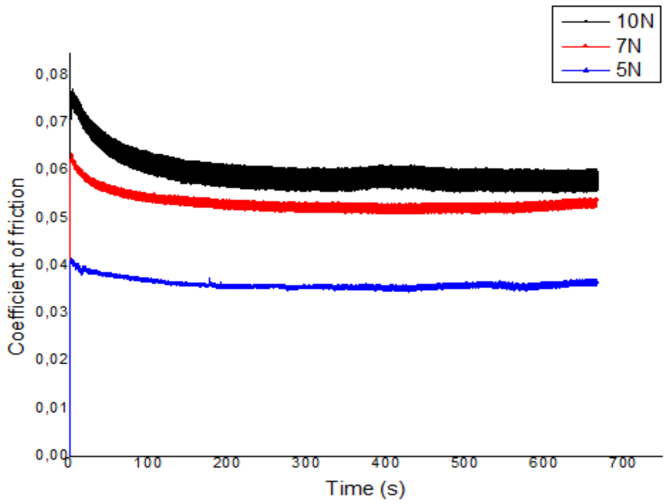


Figure 10. Evolution of the coefficient of friction of PLA –DK composite sample for a linear rotation speed of 30 cm/s

The friction coefficient was recorded periodically during the tribological test for PLA and PLA-DK composite sample. The experimental work was carried out for the composite on the tribometer shown in figure 5, under a normal load of 3,5,7 and 10N and a linear rotation speed of 10, 20 and 30cm/s. We observe a consequent decrease of the coefficient of friction for PLA-DK sample due to the addition of DK particles to the PLA matrix. The possible mechanism behind reduction in friction coefficient is the release of fatty substances contained in the micro-pores of DK particles. Mass loss measurements were also carried out, and the results are summurazied in the table 1,2 and 3.

Table 1. Mass loss measurementsfor a linear rotation speed of 10cm/s

Speed (cm/s)	Load (N)	Mass (g)	M_0 (g)
	3	9.4535	
10	5	9.4534	9.4536
	10	9.4528	

Table2. Mass loss measurementsfor a linear rotation speed of 20cm/s

Speed (cm/s)	Load (N)	Mass (g)	M_0 (g)
	5	9.4692	
20	7	9.4685	9.4697
	10	9.4665	

Table 3. Mass loss measurements for a linear rotation speed of 30cm/s

Speed (cm/s)	Load (N)	Mass (g)	M_0 (g)
	5	9.2413	
30	7	9.2409	9.2417
	10	9.2402	

Figure 11. Overview of the helium pycnometer and its instrumentation

Density Measurements

After carrying analyzes using helium pycnometer for the sample PLA –DK composite and DK alone we obtained density values 1.3317 g/cm^3 and1.4405 g/cm^3 respectively.

Conclusion

A fully biodegradable composite material has been developed from PLA and OK particles using hot-compaction process. SEM observations of this material showed continuous interfaces and particles well embedded in the matrix with a significantly different contrast from a phase contrast. DSC analyses show significant changes in transformation points as well as in the energies characterizing them, indicating the presence of new chemical compounds different from those present in the PLA and in the OK particles alone. The FTIR spectrum of the composite (compared to those obtained for the starting compounds separately) shows some differences. These notably include characteristic peaks of various phenolic compounds and certain ketones, which may be attributed to the formation of new chemical bonds at the PLA-DK interfaces which is consistent with the formation of new interfaces, during hot compaction, consisting of phases formed by the reaction between PLA and DK macromolecules. Tribological tests show that this biodegradable material exhibits sufficiently satisfactory characteristics given the nature of the starting constituents, namely PLA and DK. The interesting values of the coefficients of friction and the low mass losses indicate good tribological performance.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM Journal belongs to the authors.

Acknowledgements or Notes

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