INFLUENCE OF ACCELERATED WEATHERING ON THE PERFORMANCE OF POLYLACTIC ACID BASED MATERIALS

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Dedicated to the 50[th] anniversary of
Cellulose Chemistry and Technology

The interest in materials based on renewable resources has increased due to the need for finding alternatives to synthetic polymers made from petrochemicals. Biocomposites based on polylactic acid and grape seeds were obtained. Their mechanical, surface and antimicrobial properties were evaluated. It appeared that the grape seeds acted as a rigid filler responsible for increasing the stiffness of the polymeric matrix. Also, the addition of grape seeds determined an increase in the hydrophilicity of the materials. All the mechanical properties dropped after exposure of the materials to the combined action of temperature, humidity and UV radiation for 600 h, but the presence of a higher amount of grape seeds embedded in the polylactic acid matrix evidenced a stabilizing effect against UV exposure.

Keywords: PLA, biocomposites, grape seeds

INTRODUCTION

Composites made from a blend of thermoplastic and natural fibres have been a subject of much research and are attractive to manufacturers due to their many advantages.[1] The impetus behind this is that plastic wastes have become a worldwide environmental problem and a solution to it represents a serious challenge to waste management. That is why, the production and the use of environmentally friendly degradable polymers, especially for packaging applications, could be a viable alternative. A large number of studies have focused on totally or partially replacing polyolefin matrices with polylactic acid (PLA) ones to create fully biodegradable composites by using various natural fibres.[2-3] Biodegradable polymers obtained from natural materials, such as polylactic acid, starch, polycaprolactone (PCL), and partially biodegradable polymer composites made of natural and synthetic polymers have been studied.[4-7] As a matrix, PLA offers the advantages of relatively high strength and processability in existing equipment, such as injection molding machines,[8] but reinforcement is usually needed for practical applications due to its brittleness.

Grape seeds produce about 15% of solid waste in the wine industry and contain approximately 60-70% of total extractible grape phenolic compounds.[9] Due their antioxidant properties, grape seeds are used in the pharmaceutical, cosmetic and food industry.

In the present work, different amounts of *Vitis vinifera* Chambourcin grape seeds were embedded into PLA matrices. New green materials were manufactured and their surface, mechanical, morphological and rheological properties were evaluated.

It has been found that the addition of natural fillers has a vital role and a significant impact on the final properties of the natural filler/polymer matrix composites.

EXPERIMENTAL

Materials

The PLA used was NatureWorks 2002D, with the density of 1.24 g/cm^3, MFI of 5-7 g/10 min (at 210 °C/2.16 kg), Tg = 60 °C, and Tm = 150 °C (determined by DSC analysis).

We used seeds of *Vitis vinifera* Chambourcin as fillers in two different amounts. Fractions of ground and sieved seeds greater than 30 µm and smaller than 70 µm were used.

Preparation of composite formulations

PLA was dried at 80 °C before melt compounding for 6 h, while the seeds were dried at 100 °C for 24 h. Compounding was performed at 175 °C for 10 min, at a rotation speed of 60 rpm, using a fully automated laboratory Brabender station. Specimens for mechanical characterization were prepared by compression molding using a Carver press at 175 °C (with a pre-pressing step of 3 min at 50 atm and a pressing step of 2 min at 150 atm).

Sample composition and notation are as follows:
PLA – neat PLA
PLA-GR3 – PLA and 3% grape seeds
PLA-GR10 – PLA and 10% grape seeds

Accelerated weathering

In order to accelerate the weathering of the samples, the neat PLA and the composites were placed in a laboratory chamber (Angelantoni Ind.). The samples were exposed to artificial light of a mercury lamp (200 < 700 nm, incident light intensity of 39 mW cm^{-2}) at a temperature of 30 °C and 60% humidity. The samples were removed from chamber after 600 h of exposure and analyzed. Non-irradiated samples were used as reference.

Characterization methods

Mechanical testing

The specimens were conditioned at 50% relative humidity and 23 °C for 24 h before testing. The tensile strength and Young's modulus were determined according to EN ISO 527:2012. An Instron 1 kN test machine operated at a crosshead speed of 10 mm/min was used for testing the specimens. The Charpy impact strength of the composites was evaluated according to EN ISO 179:2001. A CEAST testing machine with a pendulum of 50 J was used to measure the unnotched specimens.

The presented results represent an average of ten samples both for the tensile and for the impact tests.

Contact angle measurements

The samples were kept for 48 h at 50% RH before being tested under static conditions on an AdveX Instrument. The contact angle was measured by randomly placing 10 drops of distilled water (2.5 µl) on the surface of each film sample using a syringe needle. Six samples were tested for each specimen.

Scanning Electron Microscopy (SEM)

The fractured surfaces of the tensile test specimens were analyzed using a VEGA TESCAN microscope under an accelerating voltage of 20 kV. Sputtering with gold was performed prior to SEM observations.

Dynamic rheological measurements

The rheological properties of the PLA/grape seed composites were measured by means of a stress-controlled rheometer (Anton Paar MCR301) using parallel-plate geometry (upper diameter of 25 mm), with a fixed gap of 1 mm. Oscillatory frequency sweeps were performed at 175 °C both for neat PLA and for the composite samples. Rheological measurements started with the strain sweep mode, performed to find the suitable strain value. A strain of 10%, corresponding to the linear viscoelastic domain (LVE), was chosen to perform dynamic measurements over a frequency range of 0.05 to 500 rad/s.

Antimicrobial activity

The antimicrobial activity of the materials was tested against Gram-negative *E. coli* (ATCC-25922) and Gram-positive *S. aureus (*ATCC-29213) by the viable cell count method. Film samples were shaped into squares (1 x 1 cm) and placed in individual sterile Eppendorf tubes. The bacteria were incubated separately in nutrient broth under aerobic conditions and appropriate humidity levels for 24 hours at 37 °C. The inoculum, consisting of 100 mL diluted with nutrient broth in a ratio of 1:10, was then added under sterile conditions to the flask containing the test films. The inoculum was prepared in order to obtain a concentration of approx. 9 x 10^5 CFU/mL. The control was a cell suspension without PLA film. The tubes were then incubated for another 24 hours at 37 °C. Aliquots of 0.3 mL suspension were taken from the tubes and diluted serially, plated on blood agar. The plates were incubated aerobically for one day at 37 °C and the colony forming units (CFU) were determined.

RESULTS AND DISCUSSION

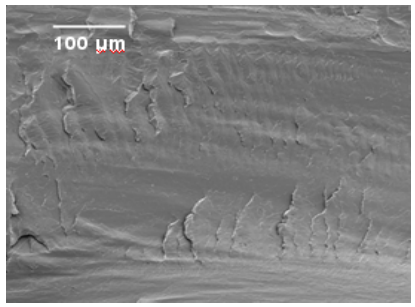
SEM

Scanning electron micrographs in Fig. 1 illustrate the even surface morphology of neat PLA, as well as the homogeneity of the PLA-GR composites surfaces.

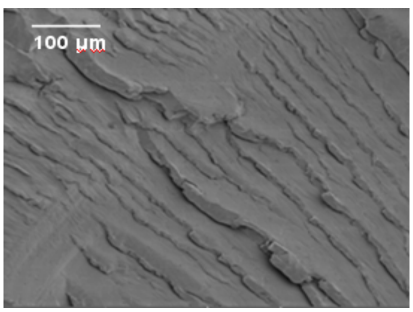
Mechanical properties

Based on the results obtained from the mechanical tests and presented in Table 1, one can observe that the PLA-GR composites are affected by the fiber content.

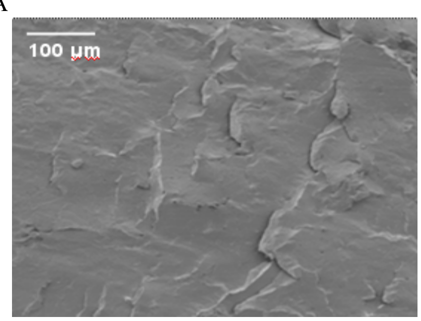
The introduction of grape seeds into the PLA matrix resulted in improved Young's modulus, with a 10.1% increment when 3 wt% grape seeds were added to the PLA matrix, while an increment of about 7.8% was registered for the material comprising 10% of filler. It seems that grape seeds acted as a rigid filler responsible for increasing the polymeric matrix stiffness. Tensile strength slightly decreased when 3 and 10% grape seeds were loaded (Table 1). The elongation at break of the biocomposites was relatively lower at filler contents of 3 and 10 wt%, when compared with that for the PLA, indicating the rigid reinforcement nature of the grape seeds within the PLA matrix. Surprisingly, at the higher filler content (of 10 wt%), the biocomposites exhibited higher elongation at break, as compared to that of the composite comprising 3% of filler.



PLA



PLA-GR3



PLA-GR10

Figure 1: SEM images of neat PLA, PLA-GR3 and PLA-GR10 before ageing

Table 1
Mechanical properties for neat PLA and PLA/grape seed composites

Sample	Young's modulus, MPa	Tensile strength, MPa	Elongation at break, mm	Impact strength, kJ/m^2
PLA	2587.33	58.76	1.50	10.40
PLA-GR3	2848.89	57.47	0.98	9.99
PLA-GR10	2788.68	56.81	1.03	12.54

Contact angle

The data reported in Fig. 2 show that the addition of grape seeds determined an increase in the hydrophilicity of the materials. Thus, the water contact angle has decreased upon filler addition into the PLA matrix.

The hydrophilic effect of the proanthocyanidins contained in grape seeds has been reported,[10] and this is the reason for the drop in the hydrophobicity of the PLA/grape seed biocomposites upon increasing filler addition from 3 to 10%.

Dynamic rheology

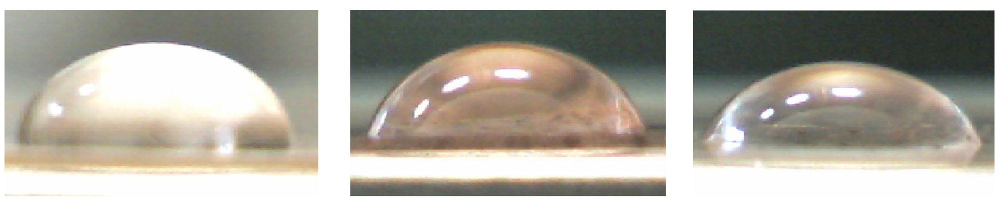
Concerning the effect of the grape seed content on the rheological parameters of the investigated composites, the results highlighted that the presence of grape seeds mainly affected the storage modulus (G′) and complex viscosity at low frequencies, while the loss modulus was almost similar for the composites over the whole frequency testing range. The slopes of G′ and complex viscosity for both PLA blend melts were considerably lower than that for the neat PLA melt, especially at low oscillation frequencies, as observed in Fig. 3.

The decrease of G′ and complex viscosity, compared to the values for the neat PLA, indicates a drop of the viscous component and an improvement of flow with the incorporation of grape seeds and with the increase of the loading from 3 to 10 wt%, possibly due to the essential oils contained in the grape seeds, which act as plasticizers. A Newtonian behavior is observed both for the neat PLA, as well as for the studied composites, especially for that containing 10 wt% grape seeds, a shear-thinning effect appearing at higher oscillation frequencies. The storage modulus decreased progressively with the concentration of grape seeds due to its low viscosity, compared to that of virgin PLA.

Table 2 lists the values registered for the crossover point, ωi, when G′ = G″. The relaxation time (θ) was calculated from the crossover frequency (ωi), as θ = 1/ωi and the resulted data are presented in Fig. 4.

The values of relaxation time decreased for the composites, in comparison with the neat PLA, which is possibly explained by the increased changes in interaction and chain mobility.

The composites comprising grape seeds exhibited the most efficient antimicrobial activity against Gram-positive *S. aureus* (Fig. 5) under specific experimental conditions. It should be noted that the increase of filler addition resulted in an increment of antimicrobial activity toward the investigated Gram-positive microorganisms. The efficacy of these materials should be further tested for food storage applications.



PLA 77.8º | PLA-GR3 75.45º | PLA-GR10 74.33º

Figure 2: Water contact angle of neat PLA and PLA/grape seed biocomposites

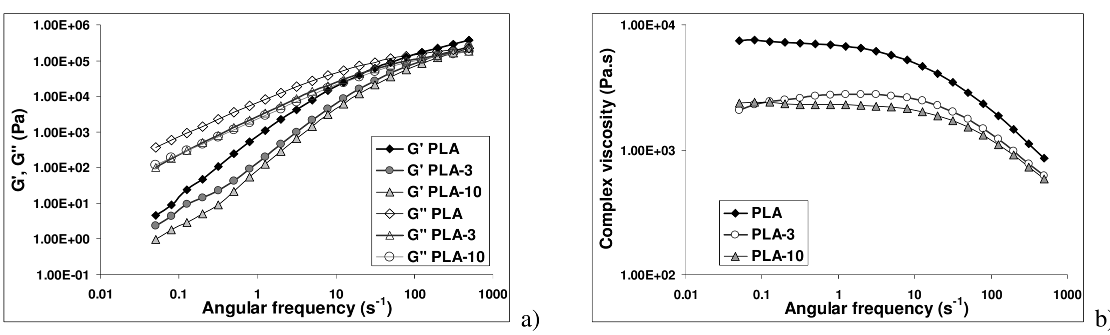


Figure 3: Variation of storage modulus and loss modulus (a), as well as complex viscosity (b) with angular frequency for PLA and PLA/grape seed composites

Table 2
Crossover frequency and modulus values for neat PLA and PLA composites

Sample	PLA	PLA-GR3	PLA-GR10
ωi	96.4	202.1	277.4
G' = G" (MPa)	144.5	139	158

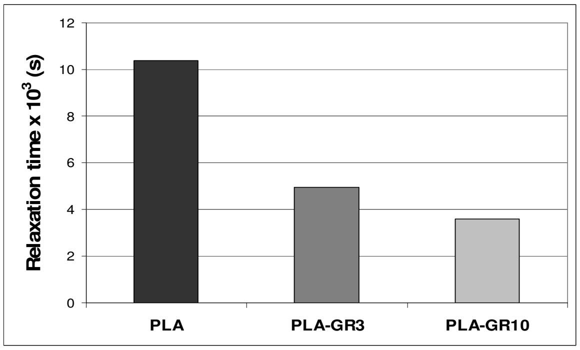


Figure 4: Relaxation time (θ) for neat PLA and PLA composites

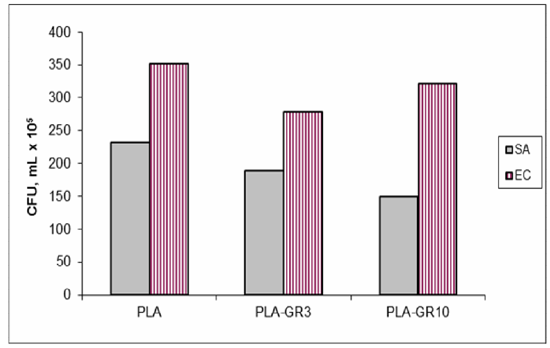
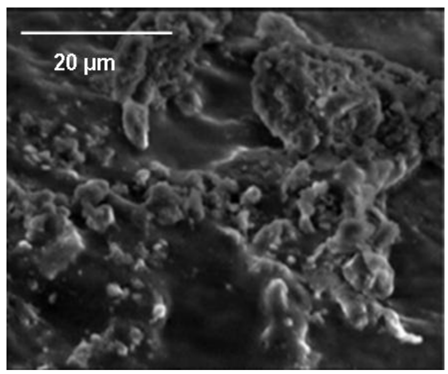
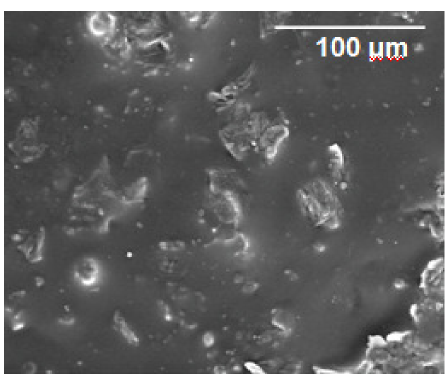


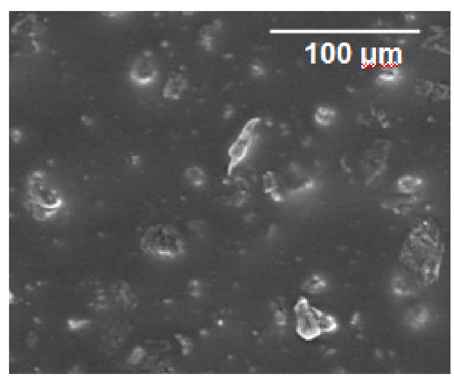
Figure 5: Antimicrobial activity of the studied materials



PLA-600



PLA-GR3



PLA-GR10

Figure 6: SEM images of neat PLA, PLA-GR3 and PLA-GR10 after accelerated weathering

Effect of accelerated weathering

The weathering process influences all properties of composite materials.

SEM

An exposure of 600 hours to accelerated weathering caused the formation of lactic acid with some white surface defects on the PLA. The combined effect of UV, humidity and temperature was also visible on the surfaces of the composites, where roughness increased as compared to the non-aged samples, although the PLA/grape seed biocomposites partially retained their surface homogeneity when compared with the neat PLA surface (Fig. 6).

This morphological observation is correlated with the other studied properties, explaining the performance of the composites after accelerated weathering. The induced morphological changes would significantly influence the material's performance. Decrements of 6.3% in Young's modulus, of 77.7% in tensile strength, and of 82% in elongation at break were registered for PLA upon ageing. As seen in Table 3, the drop of composites' tensile strength was by about 55.2% for PLA-3% and by 20.5% for PLA-10%, while the modification of Young's modulus was less significant. Elongation at break decreased after 600 h to UV exposure as follows: PLA (82%) > PLA-GR3 (75%) > PLA-GR10 (21.3%). It is worth noticing that after accelerated weathering, all tensile properties registered enhanced values when increasing the amount of the grape seeds embedded in the PLA matrix, thus the composites showed a stabilizing effect against UV exposure.

The Charpy impact strength of the PLA composites (unnotched) after accelerated weathering is reported in Table 3. The obtained results show that the impact strength of the PLA drops considerably after weathering (by about 50%). The composite comprising 10% of filler presented a lower impact strength, as compared to that comprising 3% grape seeds, and both were weaker compared to PLA. This reduction of energy absorption is frequently reported in the literature.[11-12]

Table 3
Mechanical properties for neat PLA and PLA/grape seed composites after 600 h of accelerated weathering

Sample	Young's modulus, MPa	Tensile strength, MPa	Elongation at break, mm	Impact strength, kJ/m^2
PLA	2424.67	13.07	0.27	5.34
PLA-GR3	2620.95	25.71	0.56	3.99
PLA-GR10	2887.10	45.15	0.81	1.51

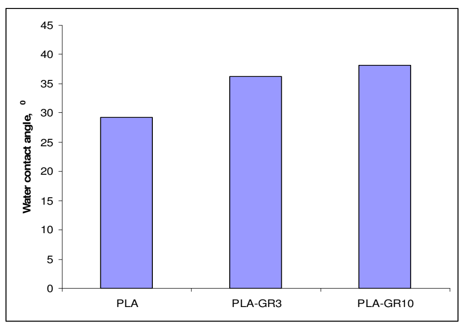


Figure 7: Water contact angles of the studied materials after weathering

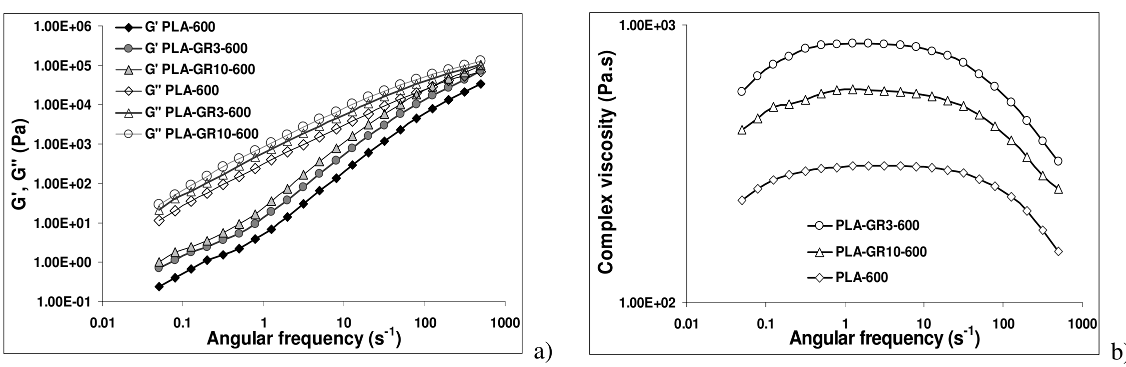


Figure 8: Variation of storage modulus and loss modulus (a), and complex viscosity (b) with angular frequency for PLA and PLA/grape seed composites after accelerated weathering

As expected, the combined action of temperature, humidity and UV radiation resulted in an increment of hydrophilic, as can be noted in Fig. 7.

Dynamic rheology

The viscoelastic behavior of the composites strongly depends on the inter-particle and particle–polymer interactions. The data plotted in Fig. 8a show that the storage moduli have increased values compared with the loss moduli, the trend being similar with that for the non-aged materials, where the viscous component is dominant.

The composites containing 3% and 10% grape seeds show a slight gradual deviation of the G′ slope at low frequencies, indicating a "pseudo solid-like behavior."

Accelerated weathering significantly lowered the rheological parameters compared to the non-aged samples, especially for the PLA matrix. The degradation of the polyester matrix led to a decrease in the molecular weight, PLA-600 showing thus the lowest complex viscosity (Fig 8b). The combined effect of UV radiation, humidity and temperature was less obvious on the dynamic moduli and viscosity of the composites, PLA-GR3-600 and PLA-GR10-600 showing increased values. In conclusion, the addition of grape seeds had a stabilizing effect against the degradation of the materials.

CONCLUSION

New biocomposite materials comprising PLA and grape seeds were obtained by melt blending. The filler content was found to influence the mechanical and surface properties of the biocomposites. It appeared that the grape seeds acted as a rigid filler responsible for increasing the polymeric matrix stiffness. Tensile strength slightly decreased when using 3 and 10% grape seed loadings, while the elongation at break of the biocomposites was relatively lower at filler contents of 3 and 10%, when compared with that of PLA. Also, the addition of grape seeds determined an increase in the hydrophilicity of the materials.

The morphological changes induced by the weathering treatment have influenced the performance of the materials. The drop in the composites' tensile strength was by about 55.2% for PLA-GR3 and by 20.5% for PLA-GR10, while the modification of Young's modulus was less significant. It is worth noticing that after accelerated weathering, all tensile properties registered enhanced values when increasing the amount of the grape seeds embedded in the PLA matrix, the composites thus exhibited a stabilizing effect against UV exposure.

The efficacy of these materials should be further tested for food storage applications.

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