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Dynamic-Mechanical Behaviour of Bio-Composites

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Abstract

PLA-hemp bio-composites with different reinforcement content were manufactured by compression moulding process. Both flexural and impact properties were investigated and compared to the unreinforced polymer. In addition, also the creep behaviour adopting the Arrhenius theory was determined, in order to better understand the industrial application limits of PLA reinforced by natural fibres. For this purpose, DMA tests were carried out, in order to evaluate the activation energy and to apply the Time-Temperature Superposition model to the compliance curves obtained by short-time creep tests.

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Keywords: Bio-Composites; Mechanical Characterization; Dynamic-Mechanical Analysis; Creep

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1. Introduction

In the recent years, the use of renewable resources for the production of composite materials has attached a growing attention because of the increasing demand of environmental friendly materials. Biodegradable materials deriving from renewable agriculture can be competitive with products based on petroleum feedstock. Life cycle assessment of bio-based composites has shown favorable results in terms of environmental impact and energy use compared to petroleum based products [1,2]. Furthermore, for some applications, bio-composites based on biodegradable plastics and natural fibres can be considered an excellent alternative to the traditional polymer composites, for example for interiors application in automotive field [3].

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A great deal of works has been published regarding to the behaviour of composites with natural fibres in terms of, i.e., mechanical [4] and fire properties [5] or how the fibres interact with various thermoset and thermoplastic matrices [6-7].

In this work, laminates of bio-composites in PLA reinforced by hemp woven fabric with different reinforcement content were manufactured by compression moulding and mechanically characterized. Then, their dynamic-mechanical behaviour was investigated. In the specific, DMA and creep tests were carried out, in order to predict the material's long-term mechanical performance by means of TTS.

Nomenclature

PLA	Poly-Lactic Acid
DMA	Dynamic-Mechanical Analysis
TTS	Time-Temperature Superposition model
p	Pressure applied during the compression moulding process
$S(t)$	Creep compliance
ε_c	Creep deformation
σ	Applied stress
T	Testing temperature
T_{ref}	Reference temperature
t	Actual testing time
t_r	Reduced time
$\log a_T$	Shift factor
T_g	Glass transition temperature
ΔH	Activation energy
R	Universal gas constant
f	Frequencies of DMA tests
$\tan \delta$	Ratio of energy dissipated to energy stored
σ_f	Flexural strength
a_{cU}	Impact strength

2. Experimental part

This section describes the materials used, the manufacture of the laminates and the characterization of the bio-composites.

2.1. Materials and laminates manufacturing

Nature work PLA film 4042D was used as thermoplastic matrix and hemp woven fabric, with areal density of 160 g/m^2, supplied by MAEKO srl, was used as reinforcement. The fibres were soaked in 2%wt sodium hydroxide solution at room temperature for 1 hour. After the treatment, they were washed with water to remove any traces of alkali on their surface and dried in an oven at 80°C for 48 hours.

The laminates were manufactured by compression moulding placing alternately PLA films and fabric layers; laminates with three different volume reinforcement content: 20, 30 and 40% (A, B and C in the rest of the text) were manufactured.

The PLA film and fabric layers assembly were pre-pressed at 175°C for 5 min at p=0.2 MPa and, after compacted, at p=1 MPa for 3 minutes.

2.2. Mechanical tests

Both flexural and impacts tests were carried out. Three-point static flexural tests were performed using MTS RT/50 universal testing machine according to the D790-10 standard; the span to depth ratio was 16:1 and the crosshead speed was 1 mm/min. Five specimens of each sample were tested at room temperature.

Charpy impact tests were performed using a CEAST Resil Impactor according to the ISO 179-1 standard; unnotched specimens were tested by imposing a normal direction of blow with respect to the laminate plane. Ten specimens of each sample were tested at room temperature.

2.3. Dynamic-Mechanical and Creep tests

In order to evaluate the limits in application of bio-composites like PLA reinforced by natural fibres, it is necessary to investigate about the changes of mechanical properties with temperature and in particular the creep behaviour. In this regard, the creep deformation ε_c occurs as a result of long-term exposure; it is a monotonically increasing function of temperature and, if the material shows viscoelastic behaviour, may depend either on the magnitude of the applied stress σ and on strain rate. If the dependence on the stress could be neglected, the inverse of the stiffness, called creep compliance S, is time dependent and can be defined by the following expression:

$$S(t) = \frac{\varepsilon_c(t)}{\sigma} \tag{1}$$

In scientific literature, several models can be found in order to consider the long-time behaviour of viscoelastic materials [8-10]. Due to the complexity of these models, empirical approaches were developed to determine long-time behaviour from short-time tests [11-13]. In the specific, TTS exhibits good suitability to composite materials [14,15] resulting widely used. It undertakes that the creep response at a testing temperature is equivalent to the creep response at a different temperature, called reference temperature, if opportunely shifted in the time scale. Considering a reference temperature, the reduced time t_r can be evaluated shifting the actual testing time with an opportune value of a shift factor, $\log a_T$:

$$\log a_T = \log \frac{t}{t_r} \tag{2}$$

This can be determined by hand or calculated by the activation energy method:

$$\log a_T = \frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\log e \tag{3}$$

The activation energy ΔH, which is the energy required to activate the glass transition temperature, can be calculated by DMA tests to determine the frequency dependence of T_g [16,17]:

$$\Delta H = R\frac{d \ln f}{d\left(\frac{1}{T_g}\right)} \tag{4}$$

In the light of the above reported considerations, DMA tests were carried out in order to evaluate, according to TTS, the shift factors of the creep curves for determining the master curve. The TA Instruments Rheometric Series RSA III was used with flexural loading system. Tan δ curves were monitored for four different frequencies (0.1, 1, 20 and 60 Hz) using 1, 2 and 3°C/min as heating rate. Creep tests were conducted at isotherms between 20 and 45°C at intervals of 5°C. A three-point bending mode with a span of 40 mm was used. For each isotherm, a stress level equal to 30 % of σ_f was applied for 1 h.

3. Results and discussion

Table 1 reports both flexural and impact strengths. From the table, it results that hemp fabric always guarantees an increase in strength, compared to the PLA. Moreover, the flexural strength decreases significantly for the C type. Finally, the impact strength increases with the reinforcement content.

Table 1. Flexural and impact strength.

	A	B	C	PLA
σ_f [MPa]	118.6	116.6	77.9	56.2
a_{cU} [kJ/m^2]	20.5	24.9	29.3	8.9

DMA and creep tests were performed only for the A type; this choice is justified by the fact that A and B types show similar mechanical behaviour, in terms of flexural strength, and A presents lower reinforcement content.

Relatively to DMA, Fig. 1 shows tan δ curves at the different test frequencies and a heating rate of 2°C/min. The activation energy was calculated from the slope of the plot ln f versus $1000/T_g$ (in Fig. 2 the case at a heating rate of 3°C/min); an average value of 369.8 kJ/mol was evaluated.

Finally, the results of the creep tests are reported in Fig. 3. They report both unshifted (left) and shifted (right) creep compliances. The last ones are obtained for T_{ref}=25°C. The master curve shows that the compliance doubles after about 2 weeks.

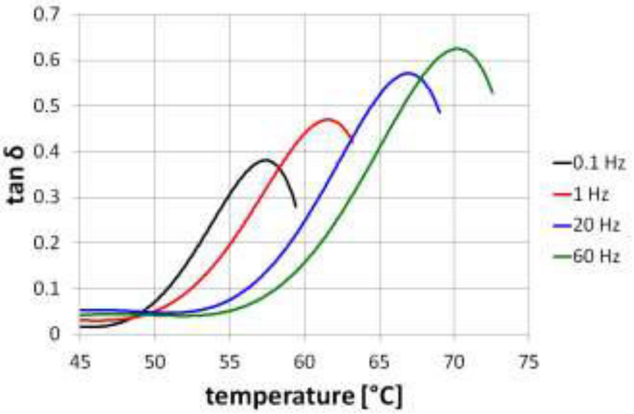


Fig. 1. Tan δ-temperature curves (heating rate of 2°C/min).

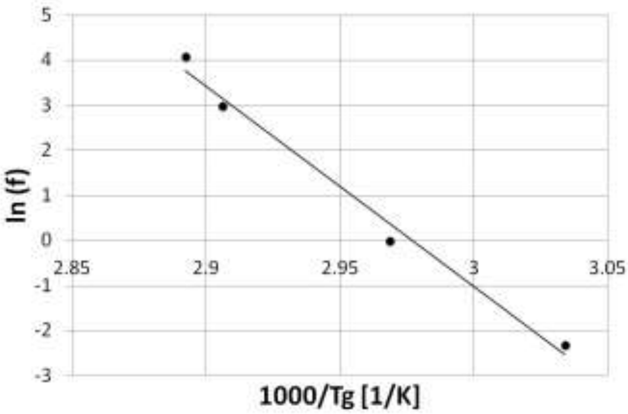
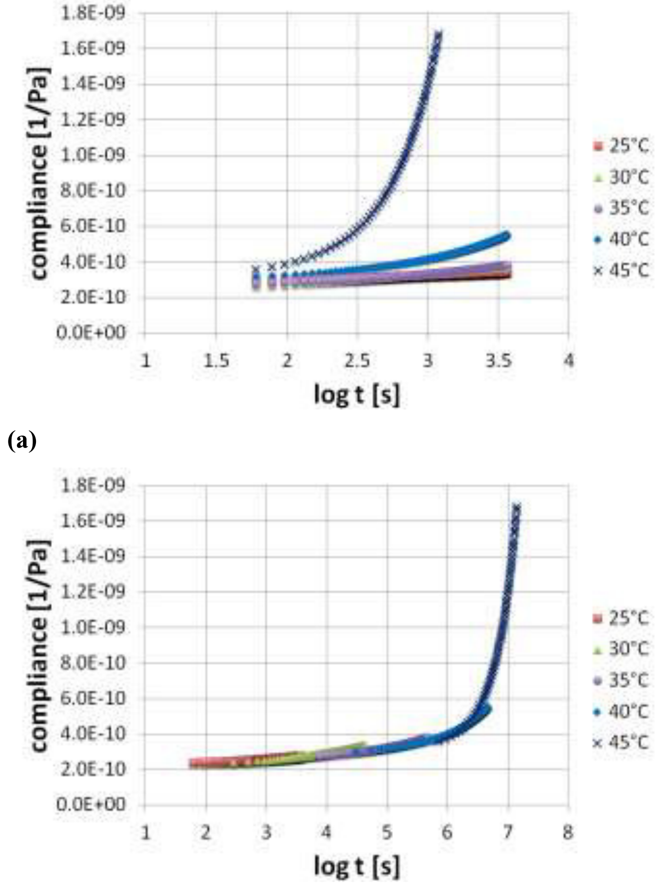


Fig. 2. Frequency (log scale) versus 1000/T_g (heating rate of 3°C/min).



(a)

(b)

Fig. 3. Unshifted (a) and shifted (b) creep compliance of type A bio-composite (T_{ref} =25°C, 30% of σ_f) versus test time (log scale).

4. Conclusions

A typical behaviour of a composite with low adhesion between matrix and reinforcement results by flexural and impact tests on PLA-hemp bio-composites. In particular, the flexural tests show a decrease of strength with the reinforcement content; on the other hand, the impact properties increase with it.

Furthermore, the Arrhenius model was applied determining the shift factors by dynamic-mechanical tests carried out at different heating rates and frequencies. The curves resulting from the short-time creep tests were shifted, obtaining the master curve describing the long-time behaviour.

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