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Soft interface dynamics in flax-fabrics/epoxy composites

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ABSTRACT

In this work, we investigate the thermomechanical behavior of flax-fabric/epoxy composites by means of DMA experiments. Fabrics from flax fibers have undergone different chemical treatments: leaching, bleaching or mercerization. We study the influence of these chemical treatments on the dynamic mechanical relaxation spectra of the composites around the main relaxation mode. We construct master plots for the loss modulus for each sample using the time–temperature superposition (TTS) principle. The master curves were fitted with the Havriliak-Negami model and we show that both interface and interphase of composites are modified as a result of the chemical treatments. Best mechanical properties were found for mercerized treatment.

1. Introduction

Stiffness and damping are among the most important features for advanced engineering composite materials based on polymeric matrix; nevertheless, and contrarily to stress/strain behavior, both material properties attains their maximal performances only in very specific configurations (see for example [1]). The search for the best balance between rigidity and damping has been pursue in different ways considering additionally how to reach the best thermo-chemical and economic performance on the modern composites materials [2]. In this search of new ad-hoc and low expensive composites, the use of new reinforcing geometries and materials, as the case of bio-textile reinforced composites, has opened a panoply of new advantages and challenges. In recent years, textile composites and specially woven fabric (WF) composites have gained much attention by their unique combination of high specific strength and stiffness and more balanced properties in orthogonal directions. These particular features come together with a large versatility in the forming processes, which made of textile composites a very interesting and viable economic alternative. The last is particularly true in the manufacture of complicated geometric shapes as compared with classical unidirectional (UD) composites. The understanding of the complex behavior of textile composites must necessarily take into account the specific fabric's geometries and the particular dimensionality of the reinforcing woven. 2-D WF are characterized by the waviness of the fiber bundles which are woven in specific patterns as plain, twill or satin fabrics, each one with a specific repeating symmetry [3,4]. Fabric laminates on a macroscopic scale, had been defined as quasi homogeneous orthotropic materials, when both yarns, i.e. weft and warn, are in the in-plane directions and the through-thickness correspond to the third principal axis [4]. This particular anisotropy, which is described by nine independent elastic constants, is characterized by a very non linear elastic response to normal stresses [5]. It had been made very important efforts to understand the very unusual mechanical response and deformability of WF composites. In particular, the development of modeling software tools which allows to obtain quite realistic descriptions of the mechanical behavior of textile composites at a meso level, see for example the compendium work of Lomov et al. and the references therein [6] or the book of A.C. Long (Ed.) [7]). These descriptions are supported on the successful construction of a realistic geometrical model of the reinforcement geometry and in the good knowledge of both matrix and bundle fibers properties. The precise understanding of fiber micromechanics of one of the most interesting varieties of WF is a meaningful task since most of the work is done on materials whose properties are rather unpredictable in a regular basis, as is the case of bio-fibers. Actually, a growing part of modern textile composites are based in new eco-friendly engineering materials, which are more compatible with the modern societal expectations about environmental impact. Fully bio-composites or synthetic matrixes reinforced with cellulose based bio-fibers represent one of the new challenges in the composites research an industry and several recent reviews show the significance of this change [8,9].

The objective of this work is the analysis of the characteristics of damping and stiffness on a series of woven fabric composites made of 2/2 twills of linen yarns as a reinforcing agent in a matrix of a

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commercial epoxy resin. Samples with different textile pretreatments are compared, as a way to introduce different chemical and morphological modifications into the fiber structure. The effects of these pretreatments in the composites were analyzed by dynamic mechanical analysis (DMA), as a way to follow the molecular dynamics associated to the mechanical response. All the observed changes were related to the evolution of the relaxation dynamics as can be ascertain with the observation of the main relaxation mode of the epoxy resin, the α mode. This work is a continuation of a previous one developed by one of the authors concerning the effect of textile pretreatment on mechanical and sorption properties of these flax fabrics/epoxy composites [10]. It was observed in the previous work a neat enhancement in the stiffness and strength and a reduction in the water sorption after specific pretreatments. All these improvements were associated to a best interfacial contact between the flax fibers and the epoxy matrix, which was the result of the superficial modification of the original fibers on the fabric. Through the present work, our aim is to investigate how are reflected on the composites relaxation dynamics the effects of the interphase evolution after the chemical treatments, which result in the stiffening and higher damping of the composites.

DMA measurements are a suitable technique for this mechanical study as stress and strain must always remain in a linear regime. In consequence, these results are extensible to the natural molecular correlations functions in the samples and their modifications. Since mechanical relaxation modes spans over spatial correlations from microscopic scales to nanometer domains and even lower, the samplés mechanical response might be investigated at very different scales, going from the pure matrix components to the polymer-fiber interface.

The dynamic mechanical properties refers to the elastic response of a material subject to a periodic stress, σ(ω), or strain, ε(ω), (sinusoidal most of the time), with $\omega = 2\ \pi\ f$ (ω in rad.s^{-1}, f in Hz). Thus, for periodic shear stress, the complex shear modulus is:

$$G^{*}(\omega) = \frac{\sigma(\omega)}{\varepsilon(\omega)} = G'(\omega) + iG''(\omega) \tag{1}$$

where G' and G'' are the real and the imaginary parts of the shear modulus, respectively. The real part of the shear modulus, G', namely the storage modulus, is a measure of the elastic energy stored and recovered; and the imaginary part, G'', namely loss modulus, is a measure of the energy dissipated in the cyclic deformation. The deformation of a viscoelastic body is not in phase with the applied stress. The phase shift,δ, is attributed to the lag necessary for relaxation to occur and is given by:

$$\tan\delta(\omega) = \frac{G''(\omega)}{G'(\omega)} \tag{2}$$

Even though the differences at a formal level, one both $G'(\omega)$ and $G''(\omega)$ gives equivalent information about the relaxation processes as they are not independent according to Kramers-Krönig relationship.

2. Materials and methods

2.1. Materials

The prepregs used to elaborate the composites have been supplied by LINEO NV Company [11]. All four studied prepregs consist of weight controlled 2/2 twill fabric impregnated by an epoxy resin. Transformation of flax fibers into flax/epoxy resin prepregs was made in several steps in a fully continuous process: spinning of flax fibers (258 m^{-1}, 7.2 Nm, diameter 0.58 mm), fabric weaving, textile pretreatment, and impregnation of fabric. During the first step (yarn spinning) the fibers were successively scutched, hackled and spinned to form a yarn. The spinning technique used is the *flax semiwet spinning*, where yarns are only moistened on their external surface. After spinning, all the yarns were woven in the form of 2/2 twill fabric. The weight was set up to 300 g/m^2 for all the fabrics with ten yarns by centimeter for both the warp and the weft direction. After weaving, fabrics were subjected to one of the following pretreatments: leaching, bleaching or mercerization. The linen fabrics reached the impregnate line (in roll form) after the pretreatment. The impregnation steps were the following: drying, compatibilization treatment of the fabric (patented by LINEO NV, similar to the sizing treatment of glass fibers), impregnation of the fabric, and finally insertion of the fabric between two polyethylene films. The only difference between the prepregs is the linen pretreatment.

The fabrics are impregnated by an epoxy resin especially formulated for prepregs (Hunstman Araldite LY5150/Aradur 5021/Hardener XB 3471). Composite materials were prepared with an autoclave process. A six ply laminate was formed by staking prepregs on a highly rigid plate (370 mm × 330 mm) and placed in a vacuum polymer bag. Special care has been taken to align the warp yarns in the main direction. The laminates were cured in the autoclave after a single-stage cycle at 120 °C during 150 min. The applied vacuum and the external pressure are, respectively, set at 2 and 300 kPa. The final thickness varies from 2.7 to 3.2 mm. Before any characterization, samples undergo a post-cure for one hour at 140 °C so as to presumably fully crosslink the epoxy network. No T_g evolution was detected on DMA measurements after post-curing. After elaboration, the volume fraction of the fibers, V_r, and the porosity volume fraction, V_p, were determined from the weight of the composite plate and the reinforcement and matrix theoretical specific weight: $\rho_r = 1.54$ and $\rho_m = 1.2$, respectively. Volume fractions of all the composites are indicated in Table 1.

2.2. Characterization technique

2.2.1. DMA experiments

The dynamic mechanical behavior of flax-fiber reinforced epoxy composites was studied by using a dynamic mechanical analyser (DHR2, TA Instrument). The experiments were performed under torsion mode. Rectangular specimens of $50 \times 10 \times 3\ \text{mm}^3$ were used for the analysis. In the isochronal measurements, the testing temperature ranged from 30 °C to 150 °C; the relaxation spectra were measured during a heating ramp at a rate of 2 °C/min with an oscillation frequency of 1 Hz. In the case of isothermal measurements, the frequencies used were $10^{-2} < f < 60$ Hz in the same temperature range indicated above. The strain amplitude was 0.3%, which is well within the linear viscoelastic regime at all the scanned temperatures.

2.2.2. Resilience tests

To link the DMA analyse with macroscopic behaviors activating interface properties of the composite materials, we chose to make resilience measurements. The test of resilience consists of breaking, by a single shock, a notched specimen or not. By knowing the initial position of the pendulum, its final position and its weight, one can determine the amount of energy absorbed by the material before breaking. The resilience tests were performed on a Zwick 5102 Pendulum Impact Tester equipped with a 4 J pendulum. This impact tester is designed to perform Izod and Charpy impact bending testing on plastics and similar

Table 1
Details of composites and parameters of the mechanical experiments.

	Untreated	Leached	Bleached	Mercerized
Basic fabric weight (g.m^{-2})	300	277	302	267
V_f (%)	39.5	39	38	43
V_p (%)	18.8	11.5	12.2	10.0
G''_{max} (MPa)	131	157	147	184
$T_{G''max}$ (°C)	106.8	104.6	103.2	106.5
C_1	35.6 ± 5.2	23.0 ± 1.9	19.5 ± 1.3	23.7 ± 2.4
C_2 (K)	184 ± 26	144 ± 11	108 ± 7	124 ± 12
z_g	4.2 ± 2.1	6.9 ± 2.3	12.2 ± 3.7	9.3 ± 2.6
Resilience (kJ/m^2)	18.4	13.6	13.0	11.0