TRANSIENT MECHANICAL ANALYSIS OF COMPOSITES PE/AGAVE FIBER. EFFECT OF COMPATIBILIZATION

M. Mendoza[1]*, R. Ibarra[1]
[1*]***Centro de Investigación en Materiales Avanzados, S.C.***
Calle Miguel de Cervantes #120 Complejo Industrial Chihuahua
C.P. 31109, Chihuahua, Chih. México.
monica.mendoza@cimav.edu.mx

Abstract- In this research, two different transient measurements for determining the reinforcement grade in a thermoplastic/blue agave fiber composite were applied. The techniques employed were creep-recovery and stress-relaxation and were carried out in a Dynamical Mechanical Analyzer. The composites were prepared by the incorporation of blue agave fiber in high density polyethylene (HDPE). Before that, the fiber was superficially modified by means of an esterification method for improving the adherence in the interface polymer/fiber. Different contents of modified and unmodified fiber were employed in order to evaluate the effect of both modification and fiber content on the time-dependent mechanical properties of composites. It was found that, in general, samples with modified fibers are more creep resistant and showed a higher recovery than their unmodified counterparts. These results are in agreement with those obtained by stress relaxation tests, in which, modified fiber samples presented a higher relaxation modulus at the end of the experiment, even though the differences observed in this test are minima. Retardation and relaxation times for both transient tests were calculated empirically based in the (1-1/e) and 1/e times the change of the property, respectively.

Introduction

Rheological testing provides precise means for measuring intrinsic mechanical material properties that can be related to a material's processing characteristics and performance.

There are three rheological test modes: *steady*, *dynamic* and *transient*. These methods are distinguished according to the manner in which the strain is applied to the sample. Stress-relaxation and creep-recovery are techniques that correspond to the transient mode in which the response of a material as a function of time is measured after subjecting it to an instantaneous change in strain, strain rate, or stress.

The stress relaxation phenomenon is viewed as the most fundamental manifestation of viscoelasticity of polymers since covers a wide spectrum of molecular rearrangements as a function of time. Stress relaxation tests involve a rapid, pre-selected deformation of the material followed by measurement of the stress required to maintain that strain over time. [1]. Also, Creep-Recovery tests fully complement relaxation experiments even though the former is directly applicable to a product performance [2]. Creep is measured by imposing a constant load on a sample in torsion, tension or compression, and recording the resulting strain over time. [1] Recovery tests look at how the material relaxes once the load is removed. [3].

A few works has been done applying transient analysis for determining the reinforcement grade in a thermoplastic/fiber composite. Typically, static methods like tensile strength are used for this purpose; however, lack of sensitivity often leads to poor results, contrary to viscoelastic analysis as mentioned before, which are very sensitive to microstructural modifications.

Respect to this particular research, blue Agave fiber is a biodegradable hydrophilic lignocellulosic fiber that can improve the toughness and strength of plastics, for this reason the production of thermoplastic composites is becoming important in applications for plastics reinforcement. However, as mentioned above, the hydrophilic nature of lignocellulosics difficult their interaction with most thermoplastic polymers. In order to improve the interaction fiber/polymer the fibers should be superficially modified. A chemical modification reduces the hydrophilicity of the fiber which should solve the problem related to polarity differences between the fiber and the thermoplastic improving the interfacial interaction fiber / thermoplastic.[4]
In the present study Blue Agave fiber was chemically modified for improving its adherence to a polymeric matrix of HDPE. Composites were prepared varying the weight ratio of the Agave fiber/HDPE. The reinforcement grade was evaluated by two different rheological techniques, stress-relaxation and creep-recovery.

Section Experimental

Fiber modification

The fiber modification was performed using acetic anhydride / octanoic acid, as reported in literature [5]. Prior to modification the fiber was washed in order to eliminate dust and sugar remains from the fermentation process. Afterwards, the fiber was dried in an air convection oven at 110 C for 24 hours. Later the fiber was partially milled, in order to favor a possible reinforcement effect. The esterification reaction was carried out in a three-neck-round-bottomed flask of 1000 mL provided with mechanical agitation and a glass condenser. A typical experiment was performed as follows: 2.0 eq of acetic anhydride and 5.6 eq of octanoic acid were mechanically mixed (200 rpm) for 1.0 h at 90ºC. These compounds react to form a so-called mixed anhydride (MAn = CH_3-OCOCO-$(CH_2)_6$-CH_3). Next, the corresponding amount to 2.0 eq of fiber (108.0 g) was added to MAn. The system was allowed to react for 3.0 h at 135 C with mechanical agitation. After the reaction time the modified fiber was cleaned by extraction with acetone. [4]

Composites preparation

Fiber / HDPE composites, with different contents of modified or unmodified fiber, were prepared in order to evaluate the effect of both modification and fiber content on the composites mechanical properties. The ratios fiber/HDPE employed for the compounding were: 10/90, 20/80, 30/70, 40/60 and 50/50. Samples were prepared in a Plasti-corder C.W. Brabender at 180°C and 30 rpm.. Afterwards, plaques (15x15 cm and 2.0 mm wide) were prepared by compression molding at 10 metric tons and 200°C.

Rheological Studies

The viscoelastic properties of the samples were analyzed by Creep-recovery and Stress relaxation techniques. These tests were performed in a Dynamical Mechanical

Analizer of TA Instruments, Inc. (model RSAIII), with a three point bending geometry. The samples of 40 x 12.38 x 2 mm were evaluated at room temperature.
In order to determine applied force and the strain over which linear viscoelasticity prevails, amplitude sweep tests were carried out at the frequency of 1 Hz.
With the results obtained the force and strain amplitude chosen for the next test were 300g and 0.4% respectively.
The creep test was carried out for 30 minutes with an applied force of 300g, and the recovery test was carried out for 60 minutes, both at room temperature.
The stress relaxation test was carried out with a strain amplitude of 0.4% for 30 minutes at 25°C.

Results and Discussion

Creep-recovery results for 10,20 and 30 fiber/HDPE ratios are shown in figure 1 and for the rest of the samples results are recorded in figure 2. It is observed that the fiber by itself increases the resistance to creep of the compound since filler increases the modulus. It is clearly seen that the modification of the fiber improves the resistance to creep for all the fiber/HDPE ratios except for 10% wt of fiber. With respect to the recovery segment it is observed that for 20/80 and 50/50 ratios the percentage of deformation recovered for the modified samples is about 0.07% higher than the unmodified ones, whereas for 30 and 40 %wt of fiber, there is no significant difference.

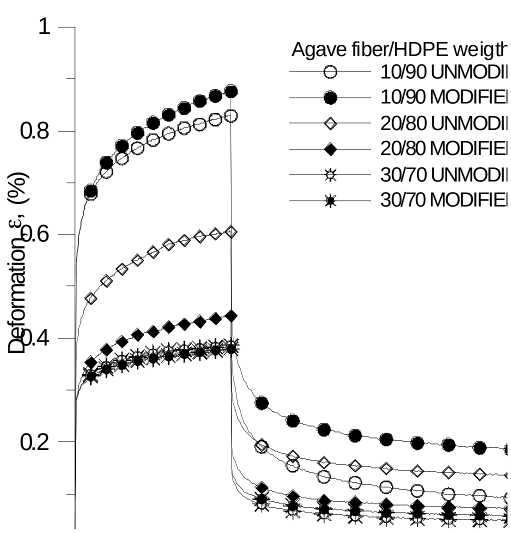


Figure 1. Creep-recovery test for fiber/HDPE ratios of 10, 20 and 30.

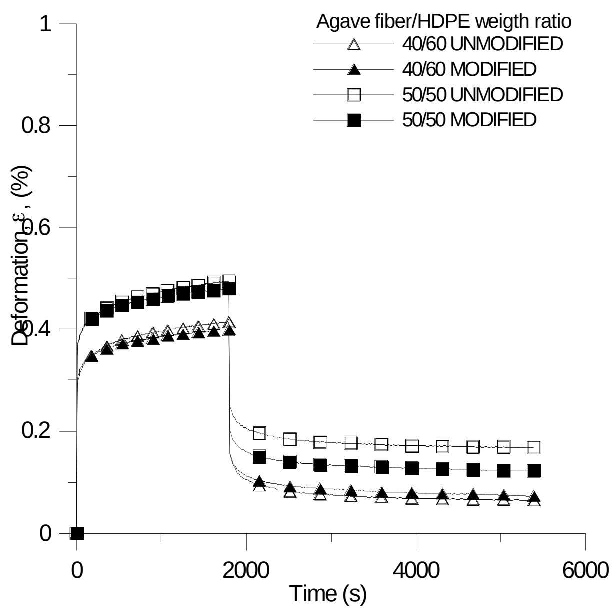
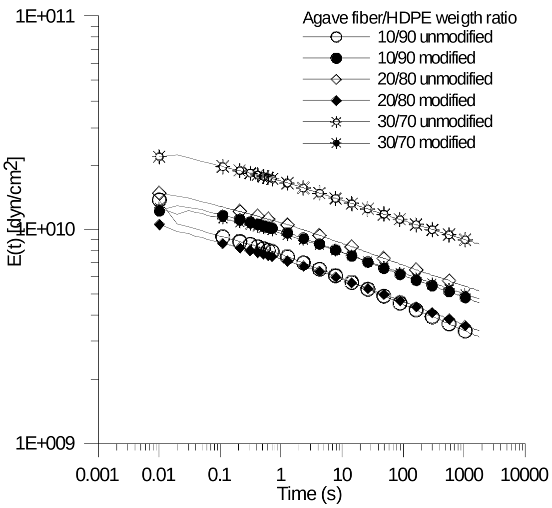


Figure 2. Creep-recovery test for fiber/HDPE ratios of 40 and 50.

Figure 3 shows the stress-relaxation results for 10,20 and 30 fiber/HDPE ratios. Here the 30/70 unmodified composite exhibits a higher modulus than 10 and 20 %wt of fiber do.

In figure 4 results for 40 and 50 %wt of fiber are observed. Here the 50/50 ratio exhibits a high influence of the modified fiber in the elasticity of the composite.
But these results are not too much significant, and it is necessary to calculate their relaxation times for making a conclusion.



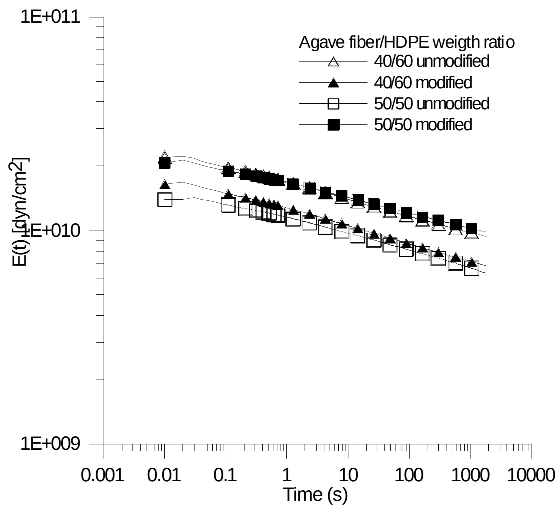


Figure 3. Stress-relaxation results for fiber/HDPE ratios of 10, 20 and 30.

Figure 4. Stress-relaxation resultsfor fiber/HDPE ratios of 40 and 50.

In figure 5 relaxation times of composites are observed. These times are higher for modified composites at fiber concentrations of 30, 40 and 50 % wt of fiber.

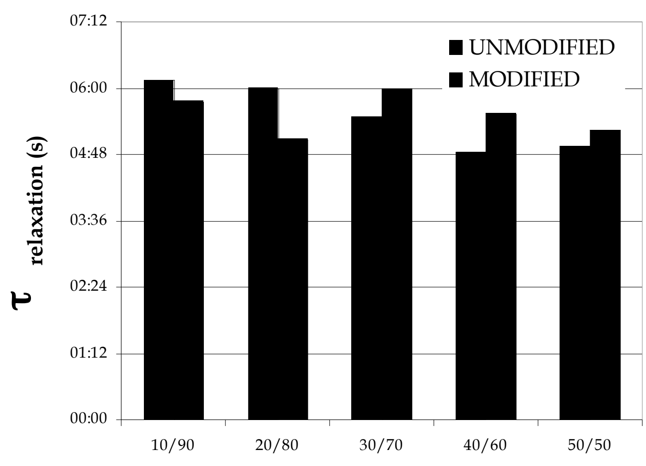


Figure 5.Relaxation times for modified and unmodified samples

According to the results above, it is evident a lack of a tendency within the modified and unmodified composites series. This situation accounts for the fact that creep in thermoplastics is a complex phenomenon, which depend on both material properties (molecular orientation, cristallinity, etc.) and external parameters (applied stress, temperature and humidity). The presence of agave fibers introduces several additional parameters that affect the mechanical and creep behavior of the composites. These include the fiber-volume fraction, the fiber-aspect ratio, the orientation of fibers as a result of processing, and the mechanical properties of fibers. However, in the direction of comparative creep behavior between modified and unmodified composites, differences are evident at the time that favors to the improvement in fiber/matrix adhesion, characterized by the higher creep resistance and recovery for the modified composites. [6]

Conclusions

Creep-recovery tests showed more sensitivity respect to modification effects on fiber/HDPE composites than stress–relaxation. Nevertheless with the last method it is possible the calculation of the relaxation time and relate this to the modification extent. Modified samples presented, in general, the higher resistance to creep, as well as the larger recovery, situation that reflects the effectiveness of coupling treatment. Also, in spite of little differences observed, relaxation times for the modified composites showed a tendency toward higher values than the unmodified ones. In both kinds of transient experiments it could be seen that the mayor influence of modification process is noticeable preferment at large concentrations of agave fiber, suggesting that the increase in surface area of treated fiber favors the improvement of fiber/matrix interaction.

Acknowledgment

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