Use of an Epoxidized Oil-Based Resin as Matrix in Vegetable Fibers-Reinforced Composites

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Received 3 September 2004; accepted 9 June 2005
DOI 10.1002/app.23133
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Hemp fibers were used as natural reinforcement in composites of thermosetting vegetal oil based resin. Boards with fibers content from 0 to 65 vol % were produced by hot pressing. The mechanical properties were investigated with flexural testing. The effect of effect has been observed on both modulus and strength, indicating a good fiber–matrix interfacial adhesion, which was confirmed by means of scanning electron microscopy observations. Dynamic mechanical analysis also showed an important reinforcement effect in the polymer rubbery region, where at 180°C the storage modulus increased from 17 MPa for the neat resin to 850 MPa for 65 vol % fiber content composites. It also revealed an glass transition temperature decrease when fiber amount in the composite increased. Additional experiments based on differential scanning calorimetry show a weakly accelerated cure when fibers content increases, which usually lead to a lower T_g. But, this phenomenon alone cannot explain the observed T_g change. Contact angle on hemp evolution with time for the resin components show that anhydride is totally absorbed after a few seconds, whereas contact angle of epoxydized oil decreases slowly. This indicates probably a preferential anhydride absorption that leads to a lower amount of anhydride in the matrix and as a consequence to a reduced T_g. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4037–4043, 2006

Key words: adhesion; composites; biofibres; thermosets; glass transition temperature

INTRODUCTION

During the last years, an increasing attention has been paid to composite materials from vegetal origin. This interest is justified by the environmental advantages of these substances. They allow a reduction in raw materials from petroleum and/or forest origin consumption and, in the case of agricultural resources, are rapidly renewable. These materials might also constitute new outlets for agriculture and contribute to a sustainable growth.

Among the wide variety of plant fibers available, like flax, hemp, sisal, cereal straws, jute, or bamboo fibers, hemp seems especially promising due to high specific properties close to glass fibers. Despite these interesting properties,[1] hemp production[2,3] decreased continuously since the 19th century due to the disappearing of sailing navy, the development of both cotton and synthetic fibers, and the legislation on drug variety of *Cannabis sativa*. But, since the last 10 years, a growing interest for plant fiber-based composites[4–7] has led to the development of new applications, especially in the field of the automotive industry. The production of inner parts like car door panels, where rather low mechanical requirements and resistance to moisture are necessary, has reached an industrial scale. The low properties obtained are due to a lack of adhesion between the nonpolar matrix employed, mainly synthetic polyolefin like polypropylene, and the polar vegetable fibers.[8] Moreover, the use of these polymers from petrochemical origin reduces the environmental interest for these materials. Therefore, extended applications, requiring higher properties and being more environmentally friendly, could be reached using alternative types of matrix.

In the field of agriculture-based polymers that could be used as matrix in composite materials, oil-based systems seem attractive. Recent studies have been devoted to the development of thermosetting resins based on epoxidized vegetal oils.[9,10] This new type of epoxy resin has already been successfully used for the production of synthetic fiber-based composites[11] for aeronautic applications. The possibility to produce wheat straw, an annual plant fibers whose bonding presents high difficulties, panels[12] has also been demonstrated.

Consequently, this new type of resin was selected within the present study to produce hemp fibers-reinforced composite materials. The purpose of this work is to investigate the structure and properties for these new composite materials, especially the bond quality and compatibility aspects between matrix and fibers.

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Journal of Applied Polymer Science, Vol. 101, 4037–4043 (2006)
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EXPERIMENTAL

Materials

The thermosetting resin so-called PTP® (polymeric material for triglycerides and polycarbonic acid anhydrides) used in this study was elaborated at our facilities and based on epoxidized linseed oil and methyl tetrahydrophthalic anhydride as hardener. 2-Methylimidazole (2%) based on the weight of the resin was added as a catalyst. A DGEBA prepolymer (DER330) from Dow Chemical was used instead of epoxidized linseed oil for comparative tests.

Hemp (*C. sativa* L.) fibers were obtained from La Chanvrière de l'Aube (France). The fiber preparation was realized through retting followed by a mechanical treatment. This allowed to obtain fibers having a 40 μm average diameter without woody core particles. These fibers were then precisely cut to 1, 2, or 6 mm length.

Composites manufacturing

The resin was sprayed onto the hemp fibers in a blender. The fiber content varied from 0 to 65%, based on the dry weight of hemp fibers. A hot press (Carver model M43196) was used to prepare the composite panels. The platen temperature was fixed at 180°C and pressing time at 5 min. The fact that the cure cycle lead to composite maximal properties is linked to a resin full cure. Pressure was adapted from 1 MPa for low fibers content to 4 MPa for 65 vol % fibers content, to fasten the mold closing. The materials manufactured were 200-mm side square and 2-mm thick. Such a thickness is usually employed in vegetal fibers-based composites for automotive industry.

Mechanical tests

Mechanical properties were measured using an INSTRON4204 testing machine. Each measurement presented is the average for eight samples. Three point flexural tests have been carried out according to the NF-EN 310 standard, allows to calculate the modulus of elasticity (MOE), the modulus of rupture (MOR), and deflection at break. Sample size was 130-mm length, 20-mm large, and 2-mm thick.

Differential scanning calorimetry measurements

Thermograms were obtained using a Setaram DSC92. Runs were carried out under a nitrogen atmosphere, in aluminum pans. The sample (around 25 mg) was heated from ambient temperature to 280°C, at the scanning rate of 10°C/min. The extent of cure α was calculated as:

$$\alpha = \Delta H / \Delta H_T$$

where ΔH is the partial heat of reaction (J/g of resin) and ΔH_T is the total heat of reaction (J/g of resin).

Thermomechanical analysis

The dynamic mechanical properties (DMA) of thermosets were determined using a TA Instruments DMA2980, operating in dual cantilever mode. The applied strain was 25 μm. Sample size was $7.5 \times 3.0 \times 60$ mm^3. Measurements were performed from ambient temperature to 180°C, at a heating rate of 3°C/min. The values of storage modulus (E'), loss modulus (E''), and tan δ (E''/E') were followed. The frequency of deformation was 1 Hz.

Contact angle measurements

The contact angles were measured using a goniometer Krüss G40, under standard conditions (50% relative humidity and 23°C). The measurements were carried out on tablets (200 mg) molded at room temperature, using short hemp fibers (2 mm). Contact angle evolution was followed during 30 s.

Scanning electron microscopy

Scanning electron microscopy (SEM) was performed using a ZEISS LEO982 instrument to investigate the interface between fibers and matrix. Samples were both flexural fractured and cut from composites, with a diamond precision saw, and then polished. SEM micrographs were obtained with a voltage of 1.45 kV and the samples were not coated.

Infrared spectroscopy

Infrared characterization of fibers was carried out using a Brücker V22 apparatus, on KBr based tablets. The scanned wave number range was 4000–400 cm^{-1}. Neat and anhydrides-impregnated fibers were pressed under time and temperature conditions similar to composites manufacture. They were then washed with acetone to remove unreacted anhydride and dried at room temperature.

RESULTS AND DISCUSSION

Mechanical properties of the hemp/PTP composites

Figure 1 shows a rise of both stiffness and strength for hemp fibers-reinforced PTP with increasing fibers content until 30 vol %, indicating a good fiber–matrix compatibility. MOE increases from 1750 to 5600 MPa and MOR from 60 to 91 MPa. Beyond 30% fibers content, properties do not increase probably due to the

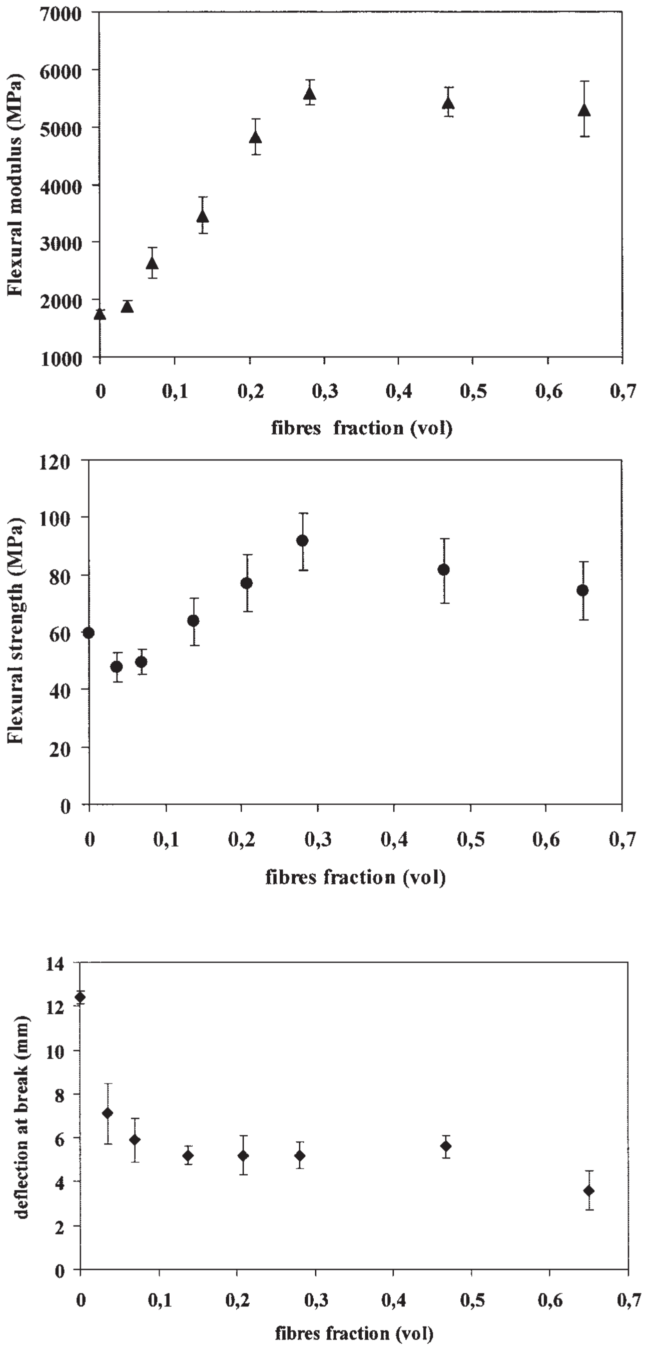

Figure 1 Evolution of flexural modulus (▲), flexural strength (●), and dip at break (◆)versus composite fiber content.

occurrence of fiber–fiber contact that does not participate to the reinforcement effect.

The good compatibility between the material components are confirmed by means of SEM micrographs of composite flexural fracture and composite polished surface, presented in Figure 2. Fiber damage without pull out from the matrix is observed during flexural fracture, which indicates a good level of adhesion. Moreover, no void between fibers and matrix on the polished sample was noticed. This confirms the good compatibility between the material components. The polished surface also shows that no major fiber damage occurs during composite preparation.

At low fiber content, a decrease in MOR is observed. In our materials, hemp fibers have a low elongation at break[1] around 1.5% against 4.5% for the PTP resin. As a consequence, when adhesion between fibers and matrix is high, which is the case in our materials, the composite break is due to fiber failure that occurs before the neat matrix breaking point. This explains, as described in Figure 1, the deflection at break decrease even for low fiber content in the composite.

Strength of composite materials can be described using the following relation[13] between composite tensile strength (σ_c) and fiber fraction (V_f):

$$\sigma_c = \sigma_f V_f (1 - (l_c/2l))K + \sigma_{m(\varepsilon)} V_m$$

where σ_f is the strength of the fibers, l_c is the fibers critical length, l is the fibers length, K is a factor taking into account the fibers orientation, $\sigma_{m(\varepsilon)}$ the strength into the matrix at the composite break for a deformation ε, and V_m is the matrix fraction.

$\sigma_{\mathrm{m}(\varepsilon)}$ has been calculated for the different fiber amount tested. Results are presented in Figure 3. Due to the fragile behavior of the PTP matrix, an decrease (even at low fiber content) similar to composite deflection at break (see Fig. 1) is noticed. Using the aforementioned relation, we can reasonably suppose that at low fiber amount, the decrease of $\sigma_{\mathrm{m}(\varepsilon)}$ is not compensated by the fibers reinforcing effect.

Influence of fiber length is described in Table I. Whatever the fiber length may be, modulus increase is significant. Flexural strength is increased for the 2- and 6-mm fibers only. For the shorter fibers, no significant change is observed, compared with the pure resin. This cannot be linked to a difference in adhesion. Most probably, the fiber critical length, as defined in literature,[14] from which a reinforcement effect on the composite strength can here be observed. That critical length is probably between 1 and 2 mm for our composites.

The properties measured at room temperature seem promising. Nevertheless, the use of an epoxy resin as matrix can be justified only if properties remain acceptable at higher temperatures.

Thermomechanical determination

Evolution of mechanical properties from DMTA experiments at different fiber levels in the composite is presented in Figures 4 and 5. For each sample tested, a peak in the tan δ curve, correlated to the large fall of storage modulus at high temperature, is observed. It was previously identified[10] as the PTP α relaxation, linked to the glass transition temperature (T_g) of the

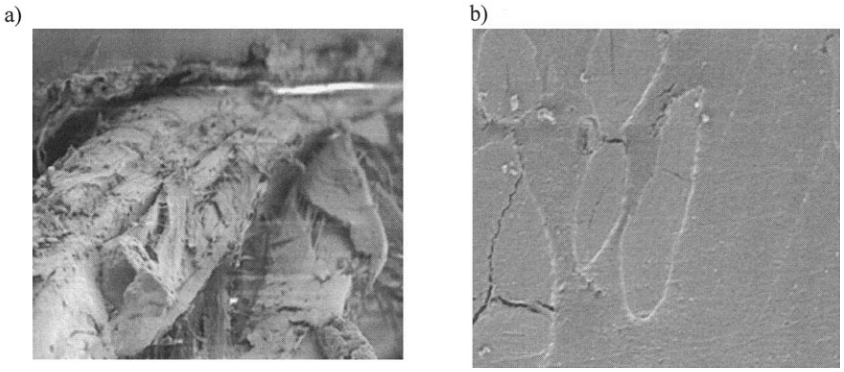

Figure 2 SEM micrographs of flexural fracture (a) and polished surface (b) for PTP filled with 15 vol % hemp fibers.

thermoset. Then, in the rubbery region, the storage modulus remains rather stable from 30°C over the maximum of α relaxation.

A consequence of the introduction of hemp fibers into the matrix is an important reduction of the modulus decrease. Neat resin storage modulus decreases from 1700 MPa at 30°C to 17 MPa at 180°C. The decrease is only from 4700 to 815 MPa for 65% fiber content in the composite, indicating a high reinforcing effect in the rubbery region. This result is usually observed for fiber-reinforced composites. Figure 4 shows that the relaxation intensity decreases with increasing fiber amount. This is due the lower storage modulus fall when hemp is added to the epoxy resin. An decrease in peak temperature from 109°C for the neat resin to 50°C for 65% fiber content is also observed, which is a quite unusual result in fiber-reinforced plastics.

Analysis of t_g decrease

The aforementioned decrease in glass transition temperature has been reported elsewhere[15] on flax fibers-reinforced epoxy–anhydride resins, but not been explained. On the other hand, research works reported on fiberglass-reinforced epoxy–amine systems[16] do not show any important glass transition temperature change linked to the introduction of the fibers. This phenomena seems specific for the interaction between vegetable fibers and the epoxy–anhydride system used.

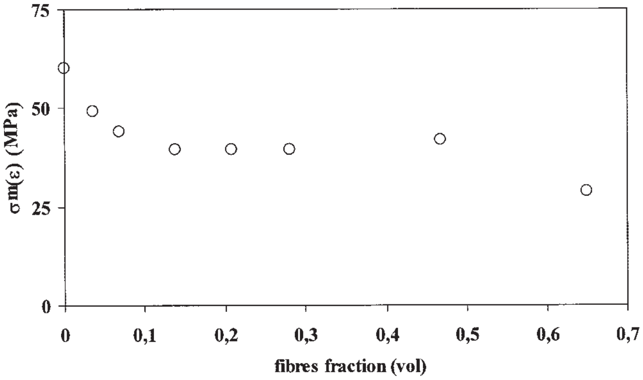

Figure 3 Evolution of flexural strength in the matrix at the composite break $\sigma_{m(\varepsilon)}$ for different fiber content.

In a previous paper,[10] we have reported that PTP glass transition temperature depend both on anhydride/epoxy ratio and catalyst amount. The higher the catalyst amount or the lower the ratio anhydride/epoxide are, the lower the T_g is, due to reduction in polymer crosslinking density. The influence of hemp fibers on PTP cure has been explored by means of differential scanning measurements. Results expressed in Figure 6 show a weak accelerated cure when fibers are present in the resin. As described in Table II, exothermic peak temperature is a little lowered from 164°C for the neat resin to 160°C when 20% fibers are added. According to the literature,[17–18] hydroxyl groups take part in epoxy–anhydride catalysis. In our materials, hydroxyl groups from vegetable fiber components could explain the cure mechanism change observed. Influence of catalyst amount on neat resin T_g and exothermic peak temperature is described in Figure 7. Assuming a linear evolution for these parameters we observe that a 4°C decrease in the peak temperature is correlated with a 7°C decrease in the polymer T_g. In the mean time, for a composite comprising 20% fiber, T_g decrease would be around 40°C. Taking into account these results, the effect of fibers on

TABLE I
Evolution of Flexural Properties for 28 vol % Fiber Content Composites with Fiber Length

Fiber length (mm)	Modulus (MPa)	Flexural strength (MPa)
Reference neat resin	1750	59.5
1	3900	56.5
2	4600	72.5
6	5600	91

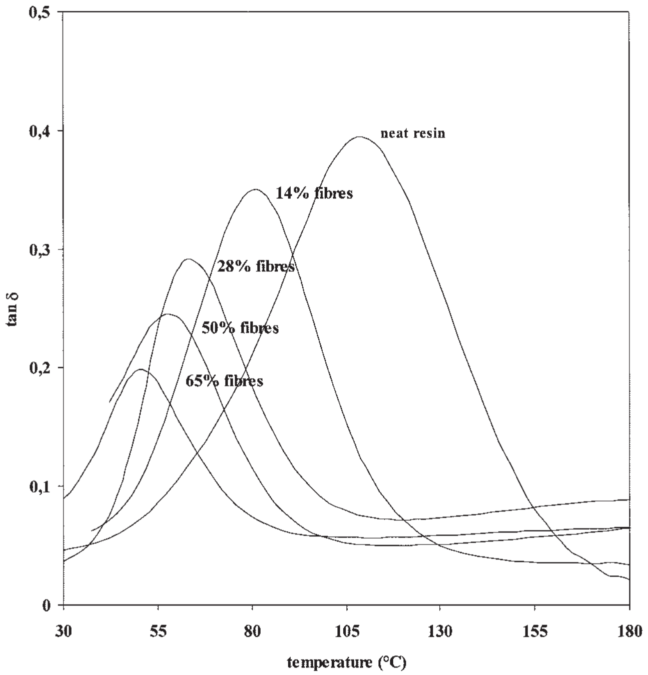

Figure 4 Temperature dependence of tan δ at 1 Hz for different fiber amounts in the composite.

reaction kinetic is not sufficient to explain alone the important T_g decrease observed. Another possibility mentioned earlier is a change in the anhydride/epoxy ratio. In fact anhydride and vegetable fibers have a great affinity that is usually taken into account in fiber surface treatments,[19,20] where anhydride might react with fibers hydroxyl group to form covalent bonding. In the case of our resin, such a reaction would consume anhydride and result in a lowered network density and T_g. Infrared spectra of both the neat fibers and fibers impregnated with anhydride are shown in Figure 8. No change in the IR spectra indicating a fiber–anhydride reaction has been observed. Additional experiments based on contact angles measurements on hemp tablets, expressed in Figure 9, show that anhydride is absorbed very rapidly, whereas epoxidized linseed oil contact angle decreases slowly, indicating a much lower absorption. The situation for the resin contact angle evolution is between its two components. On the basis of this experience, it can reasonably be assumed that during the material manufacture, an preferential anhydride absorption (without grafting reaction) into the fibers occurs. This leads to a reduced amount of anhydride in the matrix and as a consequence to a reduced T_g.

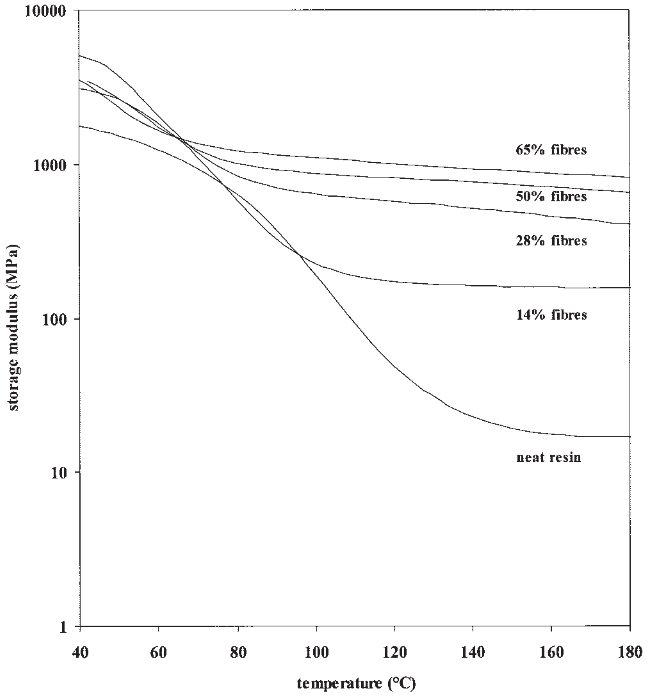

Figure 5 Temperature dependence of storage modulus at 1 Hz for different fiber amounts in the composite.

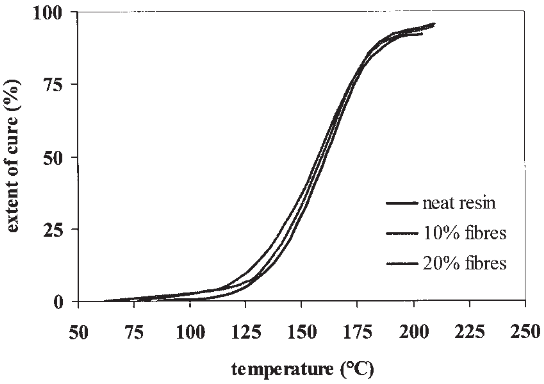

Figure 6 Influence of hemp fiber amount on PTP cure kinetic.

Thermomechanical properties of DGEBA-based composites

Complementary experiments were carried out using a DGEBA-based resins formulated with the same anhydride and catalyst rather than PTP. Results described in Figure 10 indicate a much lower T_g decrease from 121°C for the neat resin to 99°C for 65% fiber content than that in the case of PTP resin, where the T_g de-

TABLE II
DSC Determination on Influence of Hemp Fibers on PTP Curing

Amount of fibers (wt %)	Exothermic peak temperature (°C)
0	163.9
10	161.5
20	160.1

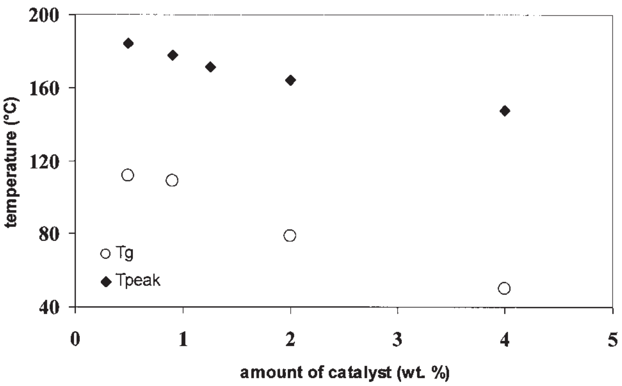

Figure 7 Influence of catalyst amount on glass transition temperature and exothermic peak temperature (cure cycle 15 h at 150°C + 1 h at 170°C).

crease reaches about 60°C. Figure 11 describes the evolutions of T_g with both the anhydride/epoxy ratio for the neat resin and the amount of fibers in the composite. T_g for DGEBA-based resin increase from 90 to 110°C when anhydride/epoxy ration increases from 0.4 to 1, whereas for PTP T_g rises from 45 to 106°C. The lower T_g decrease for the DGEBA-based resin seems to be linked to its lower sensitivity to changes in anhydride/epoxy ratio.

CONCLUSIONS

Composites based on PTP and hemp fibers exhibit interesting mechanical properties. Reinforcement effect on both modulus and strength is significant, indicating a good compatibility between resin and fibers, confirmed by means of microscopic determinations. Hemp fibers seem to preferably absorb the anhydride component of the resin and to modify the cure mechanism, leading to a reduced glass transition temperature. But, despite that negative effect of hemp fibers on resin thermomechanical properties, an important reinforcement effect is observed at high temperature. Therefore, industrial applications can reasonably be foreseen.

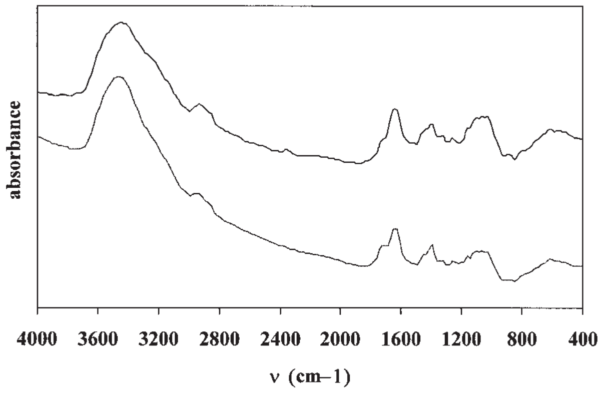

Figure 8 IR spectra for untreated and anhydride-treated hemp fibers.

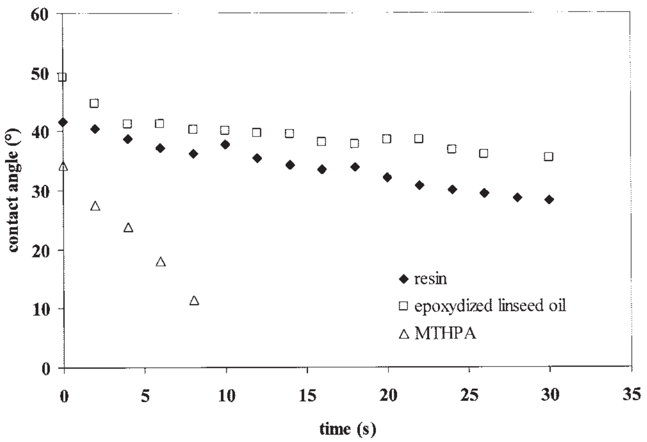

Figure 9 Contact angle versus time between the resin and its components and hemp tablets.

In this study, optimized fibers have been used that are not representative of industrially available raw materials. Additional experiments using such industrial fibers will be carried out to clearly identify the technical and economical potential of these new composites. Moreover, our results are being transferred at industrial scale using technologies like resin transfer molding or semiproducts like prepregs.

The author wish to thank Europol'Agro (Reims, France) for financial support.

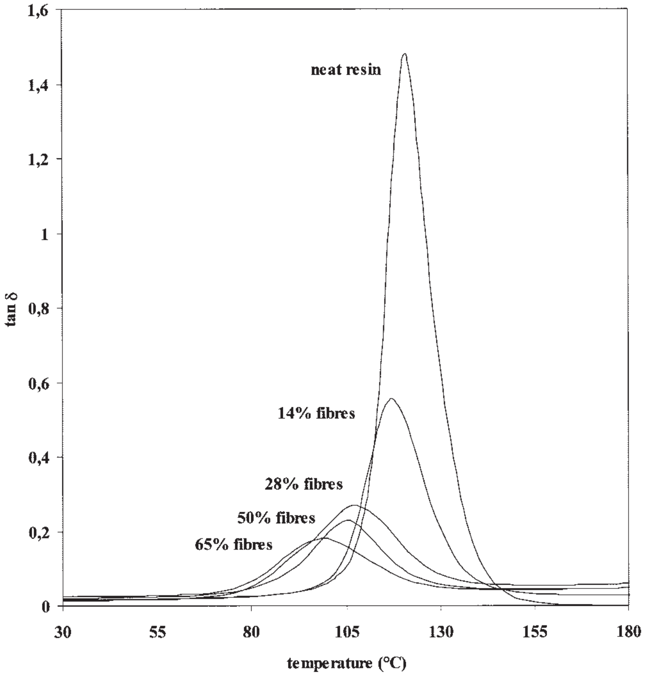

Figure 10 Temperature dependence of tan δ at 1 Hz for different fiber amounts in the composite.

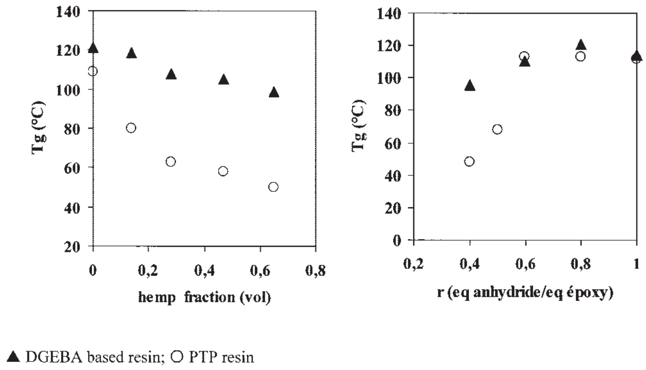

Figure 11 Influence of anhydride/epoxy ratio and amount of fibers in the composites on T_g for both PTP (○) and DGEBA (▲) matrix.

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