

SHORT DATE PALM TREE FIBERS / POLYEPOXY COMPOSITES PREPARED USING RTM PROCESS: EFFECT OF TEMPO MEDIATED OXYDATION OF THE FIBERS

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Short date palm tree lignocellulosic fibers were used as a reinforcing phase in a polyepoxy thermoset commodity resin. Unmodified fibers as well as counterparts chemically oxidized using TEMPO catalyst mediation were used as fillers for composite materials prepared in a Resin Transfer Molding process. The preparation was facilitated in the case of the composites based on oxidized fibers. During the process, the front displacement of injected resin was more regular, more homogeneous, and faster in the case of oxidized fibers. The morphology, thermal and mechanical properties of the resultant composites were characterized by SEM, DSC, DMA, as well as three-point bending and Charpy impact tests. An elevated reinforcing capability of the oxidized fibers as compared to their unmodified counterparts was demonstrated, particularly by a high strain test in the glassy state. This confirmed the enhanced filler/matrix interface observed in such materials during the process and in the final composite as analyzed by SEM. No significant difference in reinforcing capability of the two kinds of filler was observed in the DMA analysis.

Keywords: Date palm tree fibers; Composite; TEMPO-mediated oxidation; Interface; Mechanical properties

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INTRODUCTION

Lignocellulosic fibers display many well-known advantages as compared to their synthetic counterparts, including their being ecologically and toxicologically harmless, biologically degradable, and carbon dioxide (CO₂) neutral. Furthermore, natural fibers are characterized by a huge degree of variability and diversity in their properties. They are available in various forms, give a feeling of warmth to the touch, and have a pleasant appearance. None of these properties are offered by other non-wood engineering fibers. Over the last two decades, a great deal of work has been dedicated to composites reinforced with natural fibers. However, only few studies have dealt with polymers reinforced with lignocellulosic fibers obtained from palm trees (Abu-Sharkh and Hamid 2004; Wan Rosli et al. 2004; Kaddami et al. 2006; Bendahou et al. 2008 ; Sbiai et al.

2008; Bendahou et al. 2009). In the previous investigations (Kaddami et al. 2006; Bendahou et al. 2008; Sbiai et al. 2008), the reinforcing capability of palm tree fibers in thermoset or thermoplastic polymer matrices was demonstrated. In the case of epoxy-based composites, expected and strong interactions gave rise to enhanced mechanical and thermal characteristics. An increase in the glass transition temperature and an improvement of the thermo-mechanical properties, bending moduli, stress at break values, and maximum absorbed energies were reported for composites based on fibers modified with acetic anhydride (Kaddami et al. 2006). The size of the fibers was also found to have an effect on the properties (Sbiai et al. 2008).

Reinforcement is the physical expression of the microscopic balance at the matrix/filler interface that makes up a filler network. Thus, the adhesion filler/matrix is the most important parameter governing reinforcement. This adhesion can be enhanced through chemical or physical modification of the polymer and/or the filler. Natural fibers bear hydroxyl groups from cellulose and lignin, and the literature is full of contributions regarding the modification and the use of coupling agents to promote the adhesion between the filler surface and the matrix. Such modifications depend on the physico-chemical nature of the matrix.

Among modifications used to improve interfacial adhesion in natural fiber/polymer composites, oxidative treatments have received much attention during the seventies and eighties. Corona and plasma treatments were found to effectively enhance the interface in epoxy-based composites (Sakata et al 1993a,b), and chemical oxidative treatments have been widely reported in several studies for numerous composites of natural fiber and polymers. Many types of oxidants have been employed, e.g. dichromate/oxalic acid, ozone, potassium ferricyanide, ferric chloride, nitric acid, hydrogen peroxide, dicumyle peroxide, etc. (Sapieha et al 1989; Felix et al 1994; Cousin et al 1989; Kaliński et al. 1981; Raj et al. 1990; Felix and Gatenholm 1991; Flink et al. 1988; Young 1978; Moharana et al. 1990; Gardinera and Cabasso 1987; Zang and Sapieha 1991; Iwakura et al. 1965; Jutier et al. 1988; Michell et al. 1978; Coutts and Campbell 1979; Tzoganakis et al. 1988; Sung et al. 1982; Philippou et al. 1982; Manrich et al. 1989; Sapieha et al. 1991).

More recently, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation of polysaccharides bearing primary alcohols has been intensively studied. This type of oxidation makes it possible to selectively oxidize, in aqueous medium, primary alcohol groups into carboxyl groups in natural polysaccharides (Isogai, and Kato 1998; Isogai and Saito 2005; Isogai et al. 2005; Davis and Flitsch 1993; De Nooy et al. 1995; Fukuzumi et al. 2009; Chang and Robyt 1996; Tahiri and Vignon 2000; Habibi et al. 2006).

In all of our previous studies the composites materials were prepared using the compression technique. For the present study our composites materials were prepared using the resin transfer molding technique (RTM), which has been widely used for composites processing (O'Flynn 2007; Oceau 2001; Chu 2003). The purpose of this process was to improve the quality (dry spots, voids) and processability and to minimize the material wastage. The interaction between matrix and reinforced fiber is particularly important to the RTM process (Nguyen-Thuc and Maazouz 2004).

Our most recent work explored the kinetics of oxidation of date palm tree fibers (Sbiai et al. 2010). These fibers are more complex as compared to those generally described in the literature, since natural fibers are a mixture of macromolecules (cellulose, hemicellulose, and lignin) with different kinetic reactions toward oxidation. As a continuation, the present paper describes an investigation of the effect of this oxidation on the RTM process and on the interfacial adhesion between the oxidized fibers and an epoxy matrix.

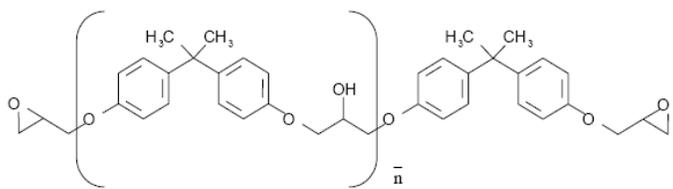
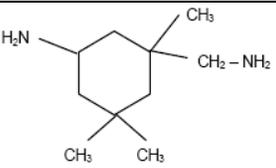
EXPERIMENTAL

Materials

Polymer Matrix

The polyepoxy matrix was obtained through a polymerization reaction of an epoxy prepolymer with an amine curing agent. The selected epoxy resin was di-glycidyl ether of bisphenol A (DGEBA) (Ref.: LY 556) supplied by Ciba-Geigy, and the curing agent was isophorone diamine (IPD) supplied by Fluka-Chemika. The characteristics of these components are presented in Table 1. The curing was carried out according to the following setup: 2 h at 80 °C, 2 h at 120 °C, and 2 h at 160 °C.

Table 1. Chemical Characteristics

Component	Chemical structure	Characteristics
Prepolymer DGEBA		Ciba Geigy LY 556 n = 0.15 M = 380 g/mol d = 1.169 g/cm ³ f = 2
isophorone diamine		Fluka-Chemika M = 170 g/mol d = 0.92 g/cm ³ g = 4

Reinforcement fiber preparation

The lignocellulosic fibers were obtained by cutting date palm tree leaves into small pieces of approximately 5 cm long and 10 mm wide. The fibers were then extracted for 24 h in a Soxhlet reflux of a solvent mixture composed of acetone/ethanol (75/25). Subsequently, the discolored fibers were dried at room temperature. The used fibers were denoted as unmodified. The length and width of these fibers ranged from 2 to 10 mm, and 0.2 to 0.8 mm, respectively. They were obtained by grinding and sieving the bleached fibers in a 0.1mm-hole sieve to eliminate particles designated as fines, after which they were further sieved through 0.8 mm holes to eliminate bigger fibers.

Fibers oxidation experiments were made under the following conditions. The following samples were oxidized separately. Samples (fiber, cellulose, lignin, and

hemicellulose) (2 g, i.e., 12.35 mmol of anhydroglucose units) were dispersed in distilled water (200 ml) for 1 min with a mechanical agitator. TEMPO (32 mg, 0.065 mmol) and NaBr (0.636 g, 1.9 mmol) were added to the suspension, which was maintained at 4 °C. The sodium hypochlorite solution (10 %, 32.17 ml, 43.21 mmol) with pH adjusted to 10 by addition of a 0.1 M aqueous HCl was set at 4 °C by means a thermocontrolled bath. The mixture was then added to the suspension, which was stirred mechanically.

The pH was maintained at 10 during the reaction by addition of a 0.5-M NaOH solution. The temperature of the suspension was maintained at 4 °C by means of a thermocontrolled bath during the oxidation reaction. When the reaction time exceeded 12 h, the kinetics became very slow and the solution turned a yellowish white. The reaction was stopped by adding 5 ml of methanol.

The reaction mixture was neutralized to pH 7 with 0.1 M HCl. The oxidized sample was washed with distilled water, after which it was filtered and dried at room temperature. The fiber oxidation was characterized by various methods (IR, conductimetry, solid-state NMR, XPS, MEB, EDX, X-ray diffraction) (Sbiai and al 2010). In the following, the oxidized fibers are referred to as modified fibers.

Composite Processing

Composites were processed using the resin transfer molding (RTM) method. This process can be divided into four stages: preforming, mould filling, curing, and demoulding. The epoxy resin was stored in container A while container B contained the curing agent IPD. The resin mixtures were preheated at approximately 60 °C to reduce the viscosity. The resin was degassed for 20 min to prevent voids from forming during pumping. In container B, IPD was kept at room temperature under an argon atmosphere in order to avoid evaporation and carboxylation. A good circulation of the resin throughout the pump and pipes was necessary. A mold (100 × 60 × 6 mm³) made of a composite material, was preheated at 80 °C for 2 h before injection. A continuous mat of date palm tree fibers (either unmodified or modified (oxidized)) used as reinforcement was placed in the mold cavity under isothermal conditions. To observe the flow of the resin during the injection process, a transparent mold made of glass was used under equivalent conditions. A camera was employed to observe the process, which was deemed to have come to an end when the resin was seen to exit from the vent at the other side of the mold. Upon completion of the cure cycle, the solid composite parts were ejected and post-cured under the same conditions as the pure matrices.

Methods

Chemical composition of the fiber

The chemical compositions of the dried date palm tree fibers were determined according to French Standards (NFT12-011). It was thus possible to assess the weight fraction of cellulose, hemicelluloses, and lignin.

Scanning Electron Microscopy (SEM)

SEM was used to investigate the morphology of the different types of materials, as well as the filler/matrix interface. The microscope was an ABT-55. The specimens

were frozen in liquid nitrogen, fractured, mounted, coated with gold/palladium, and observed using an applied voltage of 10 kV.

Differential Scanning Calorimetry (DSC)

A Mettler TA3000 calorimeter was used to measure the glass transition temperature, T_g , which was taken as the onset temperature of the specific heat increment. The heating rate was fixed at $10\text{ }^\circ\text{C min}^{-1}$, and scans were recorded under an argon atmosphere (flowrate 10 mL min^{-1}) in a temperature range between -100 and $+200\text{ }^\circ\text{C}$.

Dynamic Mechanical Analysis (DMA)

DMA experiments were performed with a Rheometrics RDAII device, equipped for rectangular samples and working in shear mode. Values of the shear storage, G' , and shear loss, G'' , moduli as well as the tangent of the loss angle, $\tan\delta = G''/G'$, were determined. This apparatus was especially dedicated to the study of films and composite materials. The average typical dimensions of the composite samples were $20\times 4\times 1\text{ mm}^3$. The tests were performed under isochronal conditions at 1 Hz, and each sample was heated from -120 to $+200\text{ }^\circ\text{C}$ at a heating rate of 2K/min . The maximum shear strain was equal to 0.2%.

Non-Linear Mechanical Properties

Three-point bending tests were performed according to the international ISO178 standard to determine the flexural strength (MPa), the flexural modulus (GPa), and the total absorbed energy (J) of the composites. The testing machine was a 2/M type supplied by MTS (load cell: 10kN). The samples were parallelepiped bars with dimensions close to $60\times 10\times 5\text{ mm}^3$ and the distance between the supports was fixed at 50 mm. Tests were carried out at room temperature, and the data collected on five samples was averaged.

RESULTS AND DISCUSSION

Chemical Analysis of the Fibers

Results of the chemical composition of the different fibers are presented in Table 2. It can be clearly seen that the chemical oxidation induced a significant decrease of the lignin content and an increase of that of the cellulose and hemicelluloses. This was explained by the oxidation followed by the dissolution of lignin during the TEMPO-mediated oxidation.

Fiber oxidation, i.e. the creation of carboxylic groups on the fibers, was characterized by various methods (FTIR, conductimetry, solid-state NMR, XPS, MEB, EDX, X-ray diffraction) (Sbiai et al. 2010). These various methods provided additional qualitative or quantitative information on the modification. According to these analysis, the oxidation degree (DO) was 12% (Sbiai and al 2010).

Observation of Resin Flow during Composite Preparation

With regard to the observation of front displacement in the mat during the RTM experiments, there was a large difference between the two kinds of fibers. In fact, in the

case of unmodified fibers, the front displacement was slow and heterogeneous, whereas in the case of the oxidized fibers, it was faster and homogeneous. This difference is portrayed in Fig. 1, presenting the photos of the fronts taken after 15 seconds of resin injection. In fact, the distance covered by the resin front was higher in the case of the oxidized fibers. On the other hand, the mat of oxidized fibers was homogeneously traveled by the resin, as compared to the mat of unmodified fibers.

Table 2. Chemical Composition of Date Palm Tree Fibers Before (raw dried palm tree fibers) and After (modified (oxidized) fibers) the Chemical Oxidative Treatment (Sbiai et al. 2010).

Constituent	Raw dried palm tree fibers (wt %)	Oxidized fibers (wt %)
Cellulose	35 %	46 %
Hemicelluloses	28 %	34 %
Lignin	27 %	12 %

These differences could be explained by variations in compatibility between the resin and the filler in the two systems, giving rise to a difference of interaction at the resin/fiber interface. In fact, the carboxylic groups at the fiber surface, in addition to the low amount of lignin in the case of the modified fibers, helped increase the affinity of the epoxy resin with the oxidized fibers. These observations were very important for the control of the process. On the other hand, one can predict some effects of the fiber oxidation on the morphologies and the properties.

Morphological Investigation of the Interfaces

Figures 2 and 3 show SEM micrographs of freshly fractured surfaces of composite materials based on the polyepoxy matrix filled with unmodified and modified fibers, respectively. Reinforced materials were investigated. For each composite material, at least three magnifications were used to reveal the effect of the fiber treatment on the interfacial adhesion. For the unfilled material, i.e. the thermoset matrix (Fig. 2-a), the fracture surface was rather smooth, as could be expected for brittle polymers. By comparing these micrographs with those of the composite materials (Fig. 2 b, c, d and e), the fibers could be clearly identified. The SEM micrographs in Fig. 2 indicated that the interfacial adhesion between the filler and the matrix was not very strong in the case of composites based on unmodified fibers. In fact, the fibers were pulled out from the matrix and their surface remained practically clean (see Figs. 2-b and 2-c). On the other hand, fracturing the samples did not lead to the palm tree fibers breakage (Figs. 2-d and 2-e). However, it is worth noting that the interaction between the unmodified fibers and the matrix was superior to that of the composite constituted of a hydrophobic matrix filled with unmodified fibers, such as unsaturated polyesters, polypropylenes or polyethylenes.

In contrast, for the composites containing modified fibers, the micrographs in Fig. 3 are evidence of a better adhesion between the matrix and the filler. One can observe the absence of holes around the fillers on the fractured surface, i.e. no debonding occurred. Nor was there any breakage of fibers during fracture (See Fig. 3-d and 3-e). On the other hand, the area surrounding the cellulosic filler seemed to be continuous with the matrix phase, and the epoxy resin appeared to be polymerized within the fiber lumens (see Figs.

3d and 3-e). This variation in interfacial adhesion between the composites based on unmodified and modified fibers is attributed to difference in the nature of physico-chemical interactions that can be created at the interface. This difference can be explained from the stronger interaction developed by the carboxylic groups created on the modified fibers. On the other hand, the dissolution of lignin after fiber oxidation gave rise to an increase of the hydrophilic character of the fibers. As a consequence, the wettability of the fiber surface with regard to the epoxy resin - a necessary condition for good interfacial adhesion - was superior in the case of the modified fibers. The introduction of the epoxy resin within the lumen was evidence of this higher thermodynamic affinity between the fibers and the polyepoxy matrix.

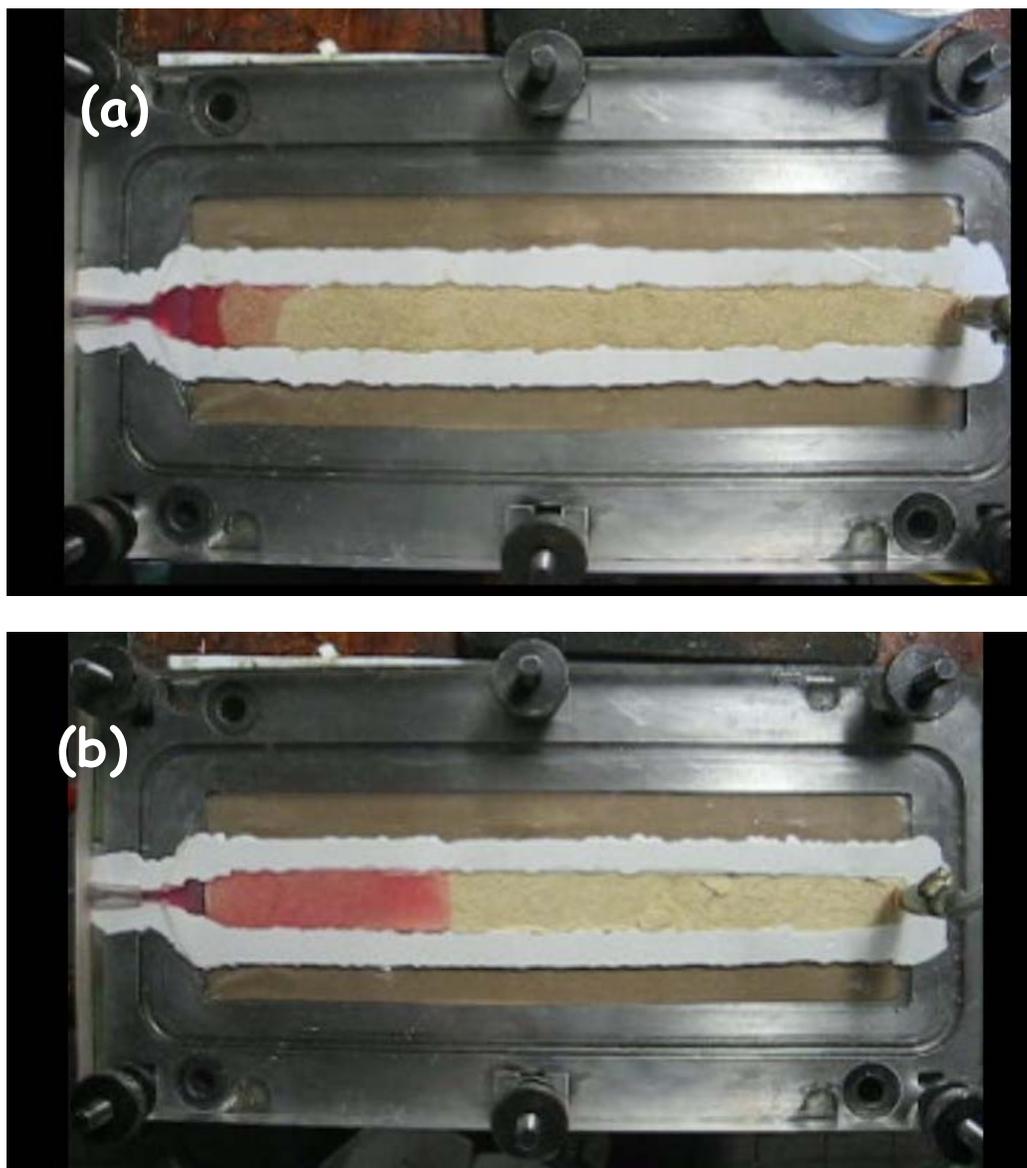


Fig. 1. RTM experiment: the resin front after 15 second of injection (at $T^{\circ} = 25^{\circ}\text{C}$ and $P = 1.5$ bar) on a mat of (a) unmodified and (b) TEMPO-mediated oxidized date palm tree fibers

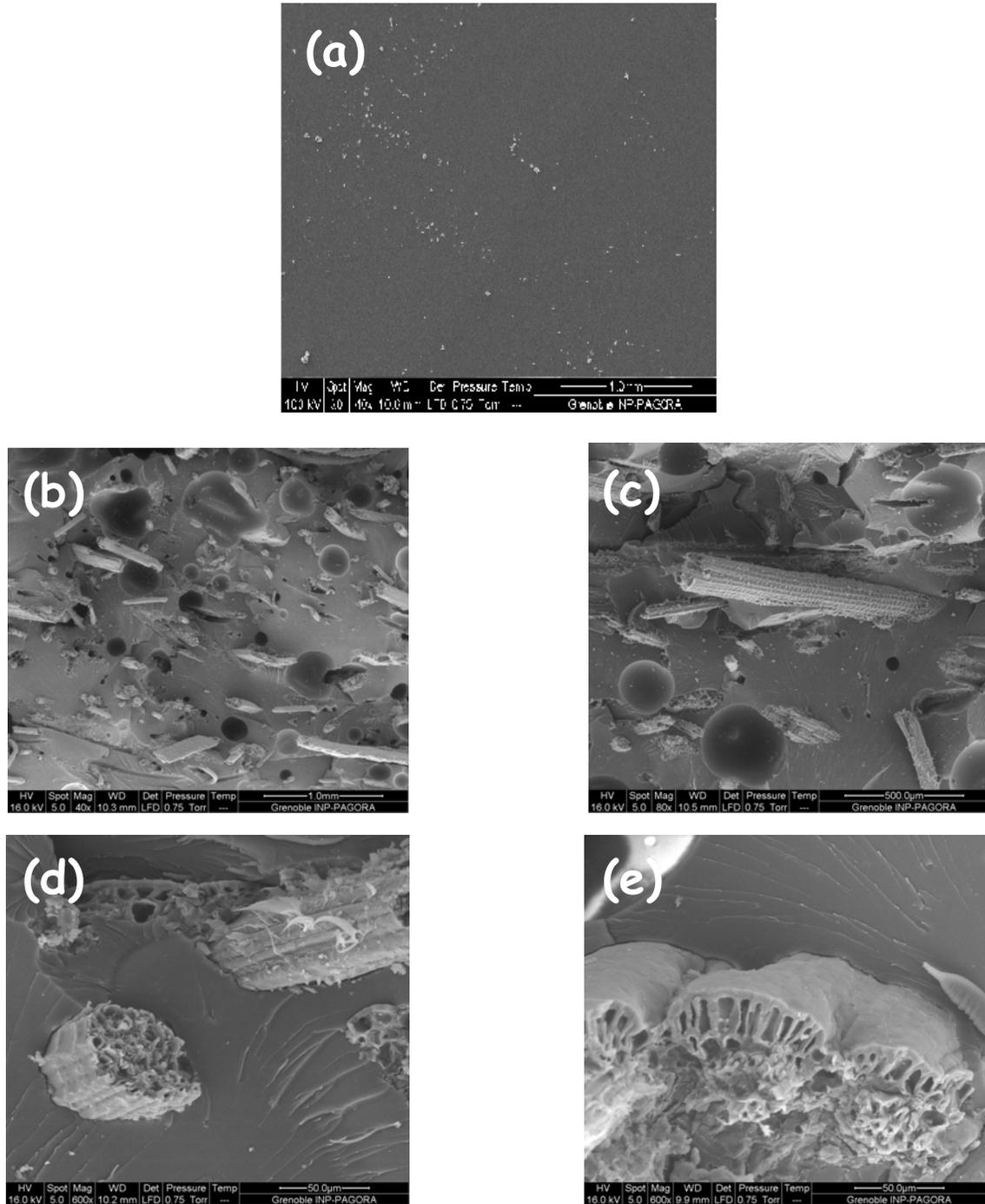


Fig. 2. Scanning electron micrographs of freshly fractured surfaces of polyepoxy /unmodified fiber composites with (a) 0 wt%, and (b, c, d, e) 10 wt % of unmodified date palm tree fibers at various magnifications

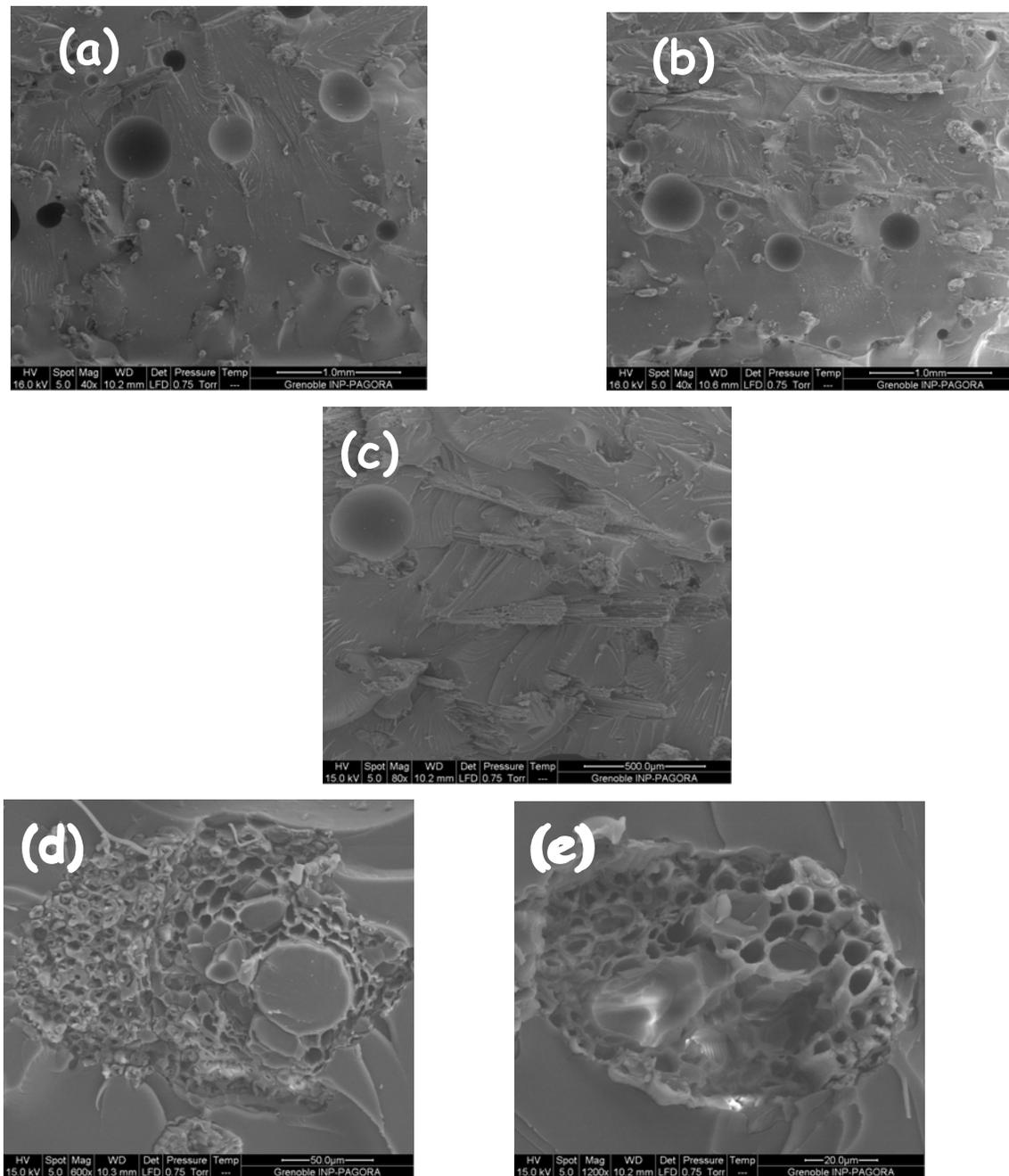


Fig. 3. Scanning electron micrographs of freshly fractured surfaces of polyepoxy /modified fiber composites with 10 wt % of modified date palm tree fibers at various magnifications.

Thermal Behavior of Palm Tree Fiber-Based Composite Materials

As mentioned, the thermal behavior of date palm tree fiber-based composites was investigated by DSC. The glass transition temperatures, T_g 's, of these materials are listed in Table 3. The T_g of the unfilled epoxy matrix was around 155°C. Table 3 clearly shows that the introduction of the lignocellulosic fibers led to a decrease in T_g . This decrease was more pronounced in the case of composites based on unmodified fibers.

The decrease in T_g could be explained by an unbalance of the stoichiometric ratio in the matrix as well as in the vicinity of the fibers after mixing with fibers. The fibers could have more affinity with one component as opposed to with another. This resulted in a hindering of the cross-linking process of the polyepoxy resin.

These results were completely opposite to those obtained in the case of composites based on an industrial epoxy matrix (DGEAB (AW106)/Jeffamin (HV953U)) supplied by CIBA-Geigy. For the latter composites, an increase in T_g was observed after the introduction of the lignocellulosic filler (Kaddami et al 2006; Sbiai et al 2008). This difference could be attributed to the difference of resin and polymerization kinetics.

Table 3. The Glass Transition Temperature, T_g , Determined from DSC Measurements, the Main Relaxation Temperature, T_α , the Rubbery Storage Shear Modulus at $T_g + 50$ °C, the G'_c , of the Composite Materials and the Relative Shear Modulus, G'_c/G'_m (where G'_m refers to the rubbery shear storage modulus of the neat epoxy) Determined from DMA Experiments

Sample		T_g °C	T_α °C	G'_c Mpa	G'_c/G'_m
Neat epoxy		155	150	9.69 (G'e)	1
Composites based on unmodified fibers	5 wt%	147	148	14.4	1.49
	10 wt%	148	148	22.2	2.29
	15 wt%	145	149	25.9	2.67
Composites based on oxidized fibers	5 wt%	147	146	11.5	1.19
	10 wt%	137	145	17.8	1.84
	15 wt%	137	148	16.4	1.69

Mechanical Behavior

The mechanical behavior of all specimens was investigated under both linear (DMA measurements), non-linear conditions (three-point bending experiments), and Charpy impact tests.

Dynamical mechanical analysis

The dependence of $\log G'$, i.e. the logarithm of the shear storage modulus, and the loss factor $\tan \delta$, vs. the temperature at 1Hz are displayed in Figs. 4 and 5, for composite materials based on unmodified and modified fibers, respectively.

All materials exhibited a relaxation process that was associated with the glass-rubber transition of the matrix, displayed as a sharp decrease in modulus and a concomitant maximum of the loss factor. This relaxation process, denoted α , involved the release of cooperative motions of the chains between crosslinks. The relaxation temperature, T_α , corresponding to the maximum of the loss factor is listed in Table 3, and was found to be approximately 150°C for all materials. A slight decrease in T_α was observed for the composites based on modified fibers; however it was less significant than the one observed for the T_g , as obtained by DSC.

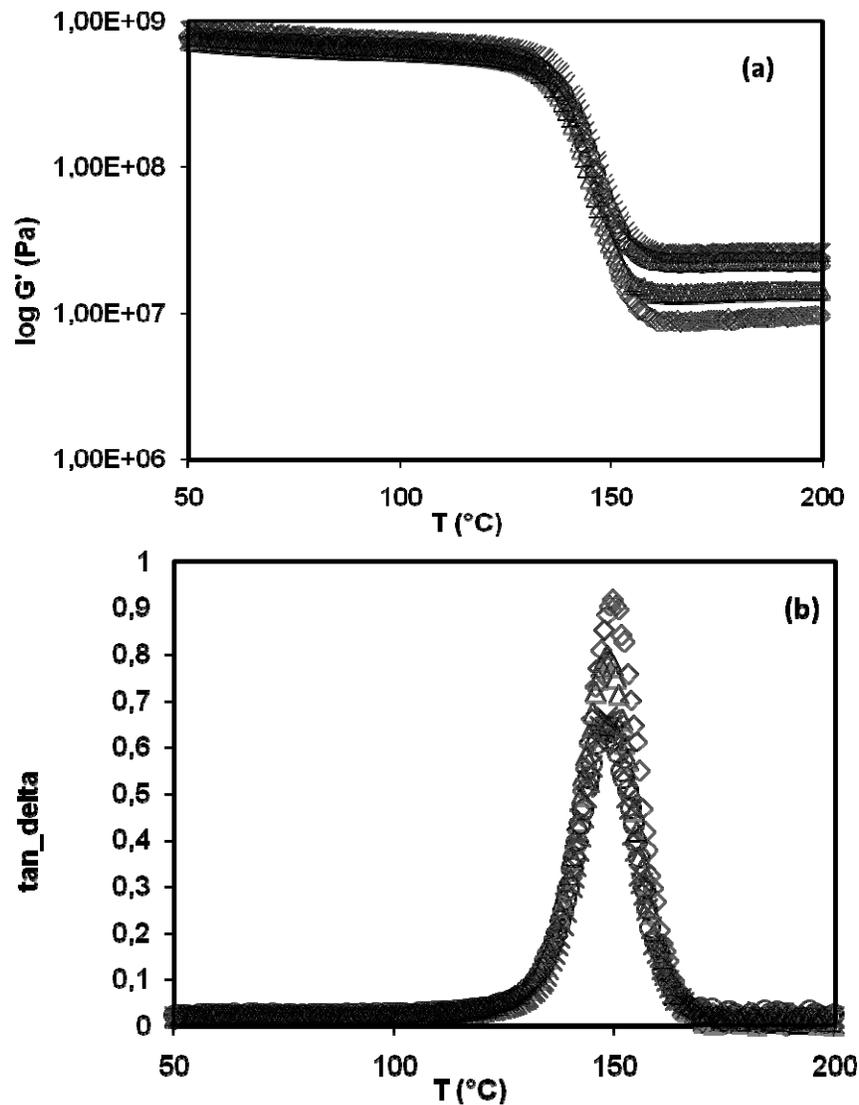


Fig. 4. (a) The shear storage modulus G' , and (b) the loss factor $\tan \delta$ vs. temperature at 1 Hz for composites based on unmodified date palm tree fibers with (\diamond) 0, (Δ) 5, (\circ) 10 and (\times) 15 wt.-% of filler

From the dependence of $\log G'$ vs. temperature, it was clear, for both kinds of fibers (oxidized and not oxidized), that the modulus at the rubbery state increased with the fibers content. However, it was difficult to observe any significant effect of the filler at low temperature, i.e. in the glassy state. A simple mixing rule rendered it possible to account for this fact. As is well known, the exact determination of a sample's glassy modulus depends on the precise knowledge of the sample dimensions. On the other hand, the water absorption could affect the exact determination of the glassy modulus. Therefore, the reinforcing effect of the filler was estimated in the rubbery region of the polymer matrix. The values of the rubbery shear modulus are reported in Table 3, as are the relative rubbery modulus values corresponding to the ratio of the rubbery modulus of the composites, G'_c , divided by that of the neat matrix, G'_m . Since the modulus was not

perfectly constant as a function of the temperature, the G' values reported in Table 3 correspond to averages.

For all the composites, the reinforcement effect of the lignocellulosic filler (modified or unmodified) was observed in the rubbery state. It could be quantified through the values of the relative rubbery modulus, which increased up to 1.84 and 2.67, respectively, for the composites based on the modified and unmodified fibers. The increase in modulus upon filler addition was ascribed to the difference between the modulus of the neat matrix (polyepoxy) and that of the lignocellulosic fibers, as well as to the decent interactions at the interfaces of these composites. No significant effect of the fiber modification was observed on the rubbery modulus despite the fact that TEM microscopy demonstrated the presence of better interactions at the interface in the case of the composites based on modified fibers.

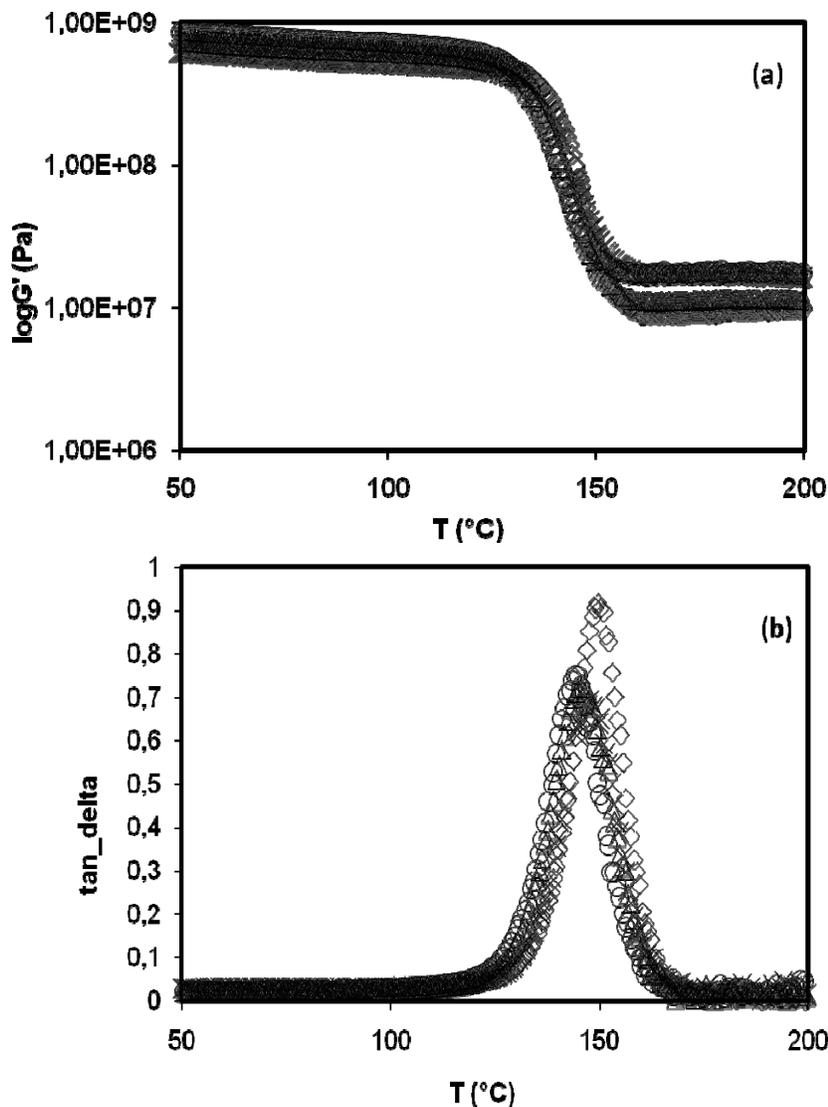


Fig.5. (a) The shear storage modulus G' , and (b) the loss factor $\tan \delta$ vs. temperature at 1 Hz for composites based on modified date palm tree fibers with (\diamond) 0, (Δ) 5, (O) 10, and (X) 15 wt.-% of filler.

High strain behavior (three-point bending test)

Storage shear modulus values measured through DMA experiments were determined at room temperature. High strain experiments should provide information on the mechanical properties at the glassy state. Figure 6 gives typical load vs. displacement curves obtained from the three-point bending experiments for the neat polyepoxy matrix and composites filled with 15 wt.-% of modified and unmodified date palm tree fibers. These curves were obtained in the glassy state of the matrix, and the tests were conducted for all materials filled with 5, 10, and 15 wt.-% of modified and unmodified date palm tree fibers. The mechanical properties derived from these experiments are presented in Fig. 7.

Panels a and b of Fig. 7 show the evolution of the shear modulus and the upper yield stress as a function of the filler content. The data were obtained from the three point bending tests. As expected, the composites were more brittle than the neat matrix. The composite material reinforced with the modified filler displayed higher mechanical properties as compared to the composite filled with the unmodified filler. In fact, the composites with modified fibers showed a higher modulus and a higher upper yield stress.

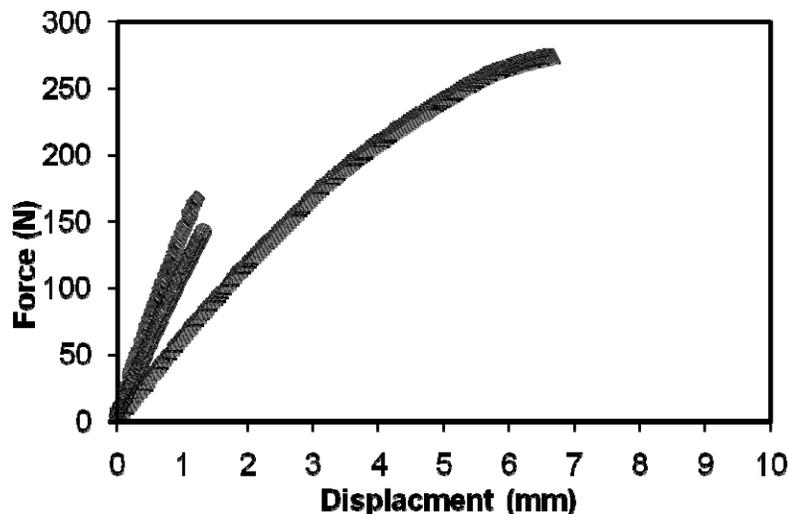


Fig.6. Load versus displacement curves obtained from three-point bending tests performed at room temperature (25 °C) for epoxy-based composites filled with : (Δ) 0, (O)15wt% of non-modified fibers and (◇)15 wt % of oxidized palm tree fibers.

Charpy impact tests

Figure 8 shows the results of Charpy impact tests. The absorbed energy at break is presented as a function of the filler content. These tests confirmed that the composites were brittle. In fact, a lower energy was required for breaking the composite materials as compared to the neat matrix. On the other hand, and within the error margins, no significant difference was observed between the composites based on modified and unmodified fibers.

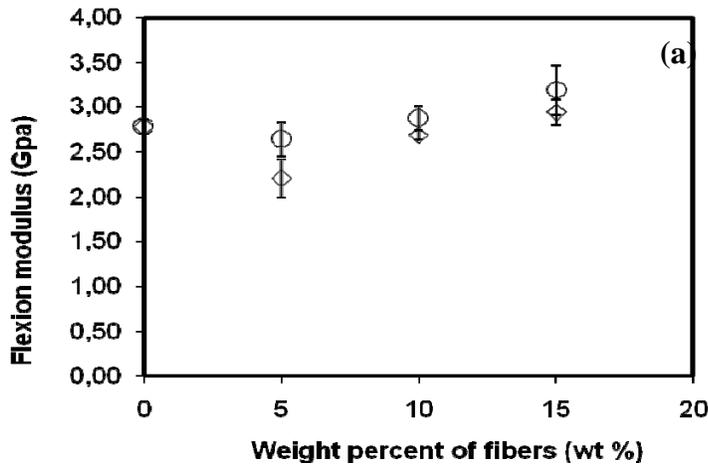


Fig. 7a. Mechanical properties as functions of the filler content, obtained from three-point bending tests of epoxy based composites filled with modified and unmodified fibers. a) shear modulus; b) upper yield stress

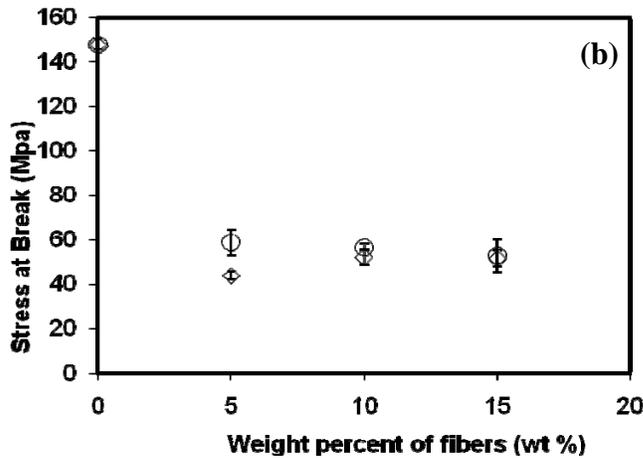


Fig. 7b. Mechanical properties as functions of the filler content, obtained from three-point bending tests of epoxy based composites filled with (O) modified and (◊) unmodified. a) shear modulus; b) upper yield stress

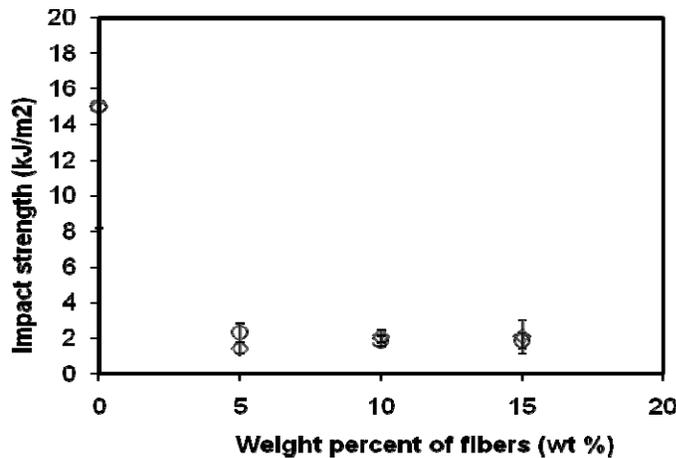


Fig. 8. The absorbed energy as a function of the filler content, obtained from Charpy impact tests of epoxy based composites filled with (O) modified and (◊) unmodified fibers

CONCLUSIONS

1. The results obtained from this study show that the preparation of composites using an RTM process was facilitated in the case of composites based on oxidized fibers. During the process, the front displacement of injected resin was regular, homogeneous, and faster in the case of oxidized fibers. The morphology, thermal, and mechanical properties of polyepoxy reinforced with lignocellulosic fibers extracted from date palm trees were also investigated.
2. Thermal properties from DSC measurements showed that the glass transition temperature of the composites, mainly those based on oxidized fibers, was lower than that of the neat matrix.
3. Dynamic mechanical analysis showed a significant increase of the rubbery modulus when lignocellulosic, unmodified and oxidized fibers were introduced into the polymer. No significant difference of the rubbery modulus between the two families of composites was observed.
4. Analysis of the high-strain mechanical proprieties (three-point bending tests) demonstrated some reinforcement of the oxidized fibers as compared to their unmodified counterparts. This confirmed the microscopic analysis, which pointed at a better adhesion at the fiber/matrix interface in the case of the composites comprising the oxidized fibers.

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