

Chemical modification of jute fibers for the production of green-composites

F. Corrales*, F. Vilaseca, M. Llop, J. Gironès, J.A. Méndez, P. Mutjè

Group Lepamap, Department of Chemical Engineering, University of Girona, Girona 17071, Spain

Available online 30 January 2007

Abstract

Natural fiber reinforced composites is an emerging area in polymer science. Fibers derived from annual plants are considered a potential substitute for non-renewable synthetic fibers like glass and carbon fibers. The hydrophilic nature of natural fibers affects negatively its adhesion to hydrophobic polymeric matrices. To improve the compatibility between both components a surface modification has been proposed.

The aim of the study is the chemical modification of jute fibers using a fatty acid derivate (oleoyl chloride) to confer hydrophobicity and resistance to biofibers. This reaction was applied in swelling and non-swelling solvents, pyridine and dichloromethane, respectively. The formation of ester groups, resulting from the reaction of oleoyl chloride with hydroxyl group of cellulose were studied by elemental analysis (EA) and Fourier Transform infrared spectroscopy (FTIR). The characterization methods applied has proved the chemical interaction between the cellulosic material and the coupling agent. The extent of the reactions evaluated by elemental analysis was calculated using two ratios. Finally electron microscopy was applied to evaluate the surface changes of cellulose fibers after modification process.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Jute fibers; Chemical modification; Wettability; Compatibility; Composites

1. Introduction

Nowadays, one of the high attractive research lines is the development of natural fiber reinforced composites. The leading geographic market in the use of natural fibers-based composites is Europe [1]. Polymers have replaced many of the conventional materials because of their advantages in ease processing, in better productivity and possible cost reduction. Properties of polymers may be modified using fillers and fibers to suit high strength/high modulus requirements. Composites reinforced with glass fibers have found applications in many fields, but their non-recyclability becomes a significant disadvantage at the end of their lifetime.

Natural fibers provide with interesting properties the final composite, especially those related to the protection of the envi-

ronment such as their capacity to be recyclable, renewable raw material, and less abrasive and harmful behavior [2]. Thus, some advantages associated to the use of natural fibers as reinforcement in plastics are their non-abrasive nature, biodegradability, low energy consumption and low cost. Additionally, natural fibers have low density and high specific properties. The specific mechanical properties of natural fibers are comparable to those of traditional reinforcements [3]. Thus, the intrinsic properties of natural fibers can satisfy the requests of the global market [4] especially for those industries concerned in weight reduction (i.e. automotive [5], aerospace). That is why they can be potential substitute for non-renewable synthetic fibers [6].

However, the hydrophilic nature of natural fibers is a major drawback for their application as reinforcement for composites. The poor moisture resistance of natural fibers leads to incompatibility and poor wettability with hydrophobic polymers, and this reprovves the interaction bonding at fiber/matrix interface [7]. Chemical or physical modifications are usually applied to impart bonding and adhesion affinity to polymeric matrices, and dimensional stability. The use of compatibilizers [8], surface modification techniques such as alkali treatments [9–11], acetylation [12], graft co-polymerisation [13] or the use of maleic-anhydride-polypropylene co-polymer (MAH-PP) [14,15] has been reported to overcome the incompatible surface

Abbreviations: Py, pyridine; dcm, dichloromethane; Mod_{ΔC}, modification degree referred to carbon increment; Mod_{molar}, molar modification degree; Mm, molecular weight for the cellulose monomer (C₆H₁₀O₅)_n; 162 g; *w*, *t*/1 of carbons in the modified fibers obtained from elemental analysis; *w*₁, *t*/1 of carbons in the non-treated fibers (experimental value: 0.4082); Mc_{ri}, carbon weight into the coupling agent: 216 g; Mami, weight of the coupling agent introduced: 265 g; SEM, scanning electron microscopy; OH, hydroxyl group; OCl, oleoyl chloride

* Corresponding author. Tel.: +34 972 41 84 32; fax: +34 972 41 83 99.

E-mail address: farners.corrales@udg.es (F. Corrales).

polarities between the natural fiber and polymer matrix. Surface chemical modification with coupling agents is usually applied to optimize the wetting of the biofibers by the polymeric matrix and to improve the interaction and adhesion between the non-polar matrix and the polar lignocellulosic fibers [16].

Many processing aids and coupling agents [17] have been used to improve dispersion and adhesion. In this sense, several methods have been proposed trying the superficial chemical modification of the fibers and the use of polymers capable of coupling with the hydroxyl groups of the surface cellulosic substrate.

In our laboratory, we have been studying a variety of reagents containing a function able to modify the cellulose hydroxyl groups and a second moiety to be used in the subsequent elaboration of composite to establish continuous covalent linkages at fiber/matrix interfaces.

Jute fiber is one of the most common biofibers used as reinforcement for natural fiber composites. Among all the other lignocellulosic fibers, jute contains a reasonably high proportion of stiff natural cellulose. The aim of this work is to study the surface modification of jute fibers with a reagent able to react with hydroxyl groups of cellulose. Chemical modification with a fatty acid derivate was used to modify the surface properties of jute fibers and to improve the wettability and interface adhesion [18]. Concretely, oleoyl chloride was used to block the majority of accessible hydroxyl groups. Chemical modification was applied in swelling and non-swelling solvents and different extents of modification were obtained. The extent of modification reaction was evaluated by elemental analysis and FTIR techniques.

2. Experimental

2.1. Materials

Jute fibers were supplied by Celulosa de Levante SA (Tortosa, Spain). According to bibliography [19], the specific modulus for jute fibers and the specific gravity were 40 GPa and 1.3 g/cm³, respectively. Chemicals and solvents were used without further purification. Oleoyl chloride from Aldrich Chemical Co. with 85% purity was used as coupling agent and 4-dimethylaminopyridine (DMAP) also from Aldrich Chemical Co. as catalyst. Pyridine and dichloromethane were applied as reaction media for the modification reaction. The solvents supplied by Panreac SA were dry commercial products and thoroughly dried over activated 0.4 nm sieves for a week. For modification reactions in dichloromethane, triethylamine was added as co-solvent which acts as an acceptor for the liberated hydrochloric acid. Commercial grade dichloromethane was used as the washing solvent after quenching the modification reaction.

2.2. Chemical modification reaction

Chemical modification was applied in pyridine or dichloromethane solvents using oleoyl chloride as coupling agent. Jute fibers were vacuum dried at 90 °C for 24 h

before being placed in a flask for chemical modification. Reactions were carried out in a dry nitrogen atmosphere by suspending the fibers in the dry solvent (40 mL/g of fiber). The modification reactions were conducted at 20 °C for both solvents, at 40 °C and 60 °C for dichloromethane and pyridine, respectively, and kept for different reaction times. The working up of the reaction was completed by draining the liquid phase through a sinter glass and washing the solid several times with dichloromethane commercial grade. The modified jute fibers were dried under vacuum at 90 °C for 24 h and kept under nitrogen awaiting characterization.

2.3. Characterization methods

The methods used to evaluate the modification degree were Fourier Transform infrared spectroscopy (FTIR) and elemental analysis (EA).

The FTIR spectra of the non-modified and modified cellulose fibers were obtained to detect the new absorption bands depicted in the chemical modification. The FTIR was performed using a FTIR Matson Galaxy Series 5000 Spectrometer. The spectrometer was used in the transmission mode with a resolution of 4 cm⁻¹ in the range of 4000–400 cm⁻¹.

Elemental analysis was employed to quantify the extent of modification reactions. The elemental analysis was performed using a ThermoQuest Instruments analyzer where 1 mg of ultra-pure sample was burned to determine the percentage of carbon, hydrogen, sulphur and nitrogen contained. Samples were analyzed three times to get the accurate percentage.

Scanning electron microscopy (SEM) was used to examine the fiber surface before and after modification. The SEM observations were made with a Zeiss DSM 960 microscope. Dry samples were coated with a thin layer of carbon before observation under the microscope mark, in order to increase the sample conductivity.

3. Results and discussion

Oleoyl chloride is a fatty acid derivate able to react with the –OH groups of jute fibers to afford ester groups. In this paper, we examine the results of the modification reaction obtained using two solvents, pyridine (Py) and dichloromethane (dcm). The treatment of the lignocellulosic fibers with oleoyl chloride has been undertaken to bring a chemical modification of the substrate by grafting oleoyl moieties on the cellulose backbone according to the reaction in Fig. 1a.

The different swelling capacity of each solvent to the cellulose fiber will lead to different degree of modifications, which measurements were made by means of FTIR spectra and elemental analysis results. The principal characteristic of pyridine is its polar nature and his catalytic capacity for the modification reaction proposed. Thus, the basic character of pyridine allows the molecule to diffuse deeply inside the internal structure of the cellulose fiber increasing its ability to interact with hydroxyl groups and making accessible more hydroxyl groups to the coupling agent. On the opposite side, methylene chloride is a non-swelling solvent for cellulosic

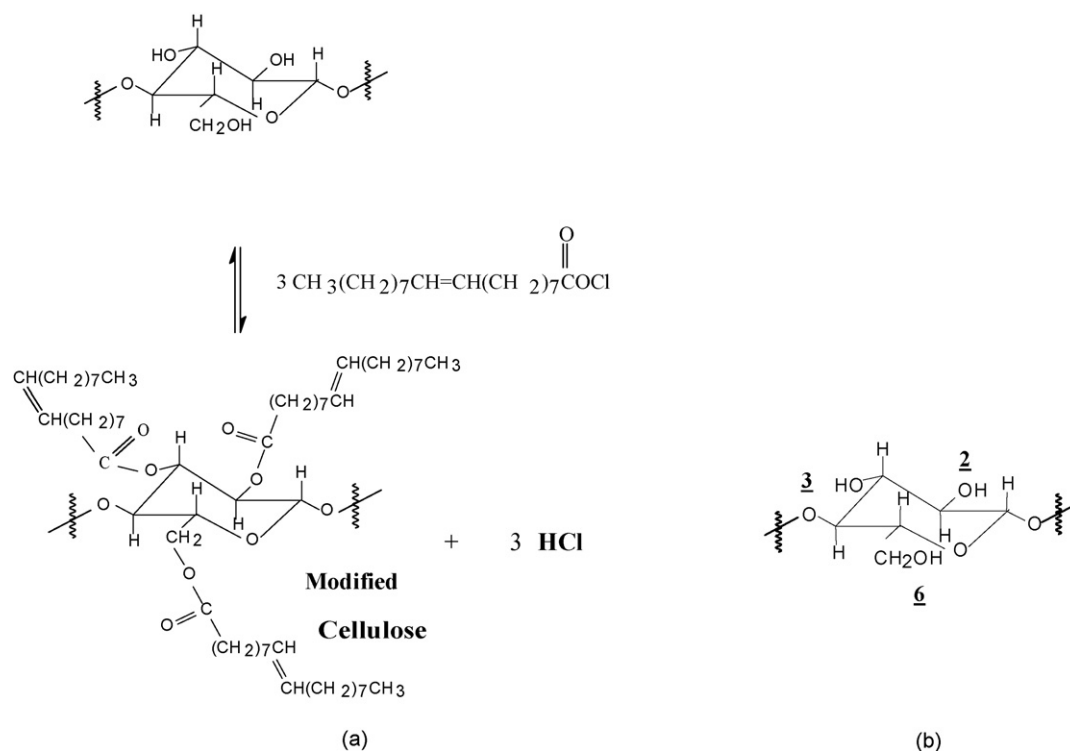


Fig. 1. (a) Scheme of the modification reaction and (b) accessibility of hydroxyl groups [21,22].

fibers, thus the esterification reaction will be limited to the hydroxyl groups located on the external surface of the fiber.

The reactions were carried out in a dry nitrogen atmosphere using 4-dimethylaminopyridine as catalyst (10% of the coupling agent weight) and the amount of the coupling agent equivalent to the number of the estimated hydroxyl group on the cellulosic substrate.

Fig. 2 shows the infrared spectrum of the jute fibers after the modification reaction in pyridine at 20 °C during 24 h, and Fig. 3 shows the spectrum for the same reaction in dichloromethane. It can be observed the great dependence of the extension reaction to the solvent nature. Thus, while the reaction in pyridine leads to a considerable increasing of carbonyl peak, almost no modification could be observed for the reaction in dichloromethane.

However, if the modified jute fibers were submitted to elemental analysis, some significant differences on the carbon percentage could be found between the non-treated jute fiber and the oleoyl chloride modified jute fiber. Therefore, the quantification of the extension reaction was deduced from the elemental analysis results and a molar modification degree was expressed according to Eq. (A.1).

The application of Eq. (A.1) to elemental analysis results gave modification degrees of 29% and 0.4% for the fibers modified in pyridine and dichloromethane, respectively.

Moreover, another expression was deduced from elemental analysis results to estimate the recovering degree achieved with the coupling agent. In this case, the difference between the carbon percentage of modified fibers and the carbon percentage of pure fibers was related with the subtraction between the carbon percentage for the theoretically all-modified fibers (75.42%) and the carbon percentage of pure fibers. This ratio

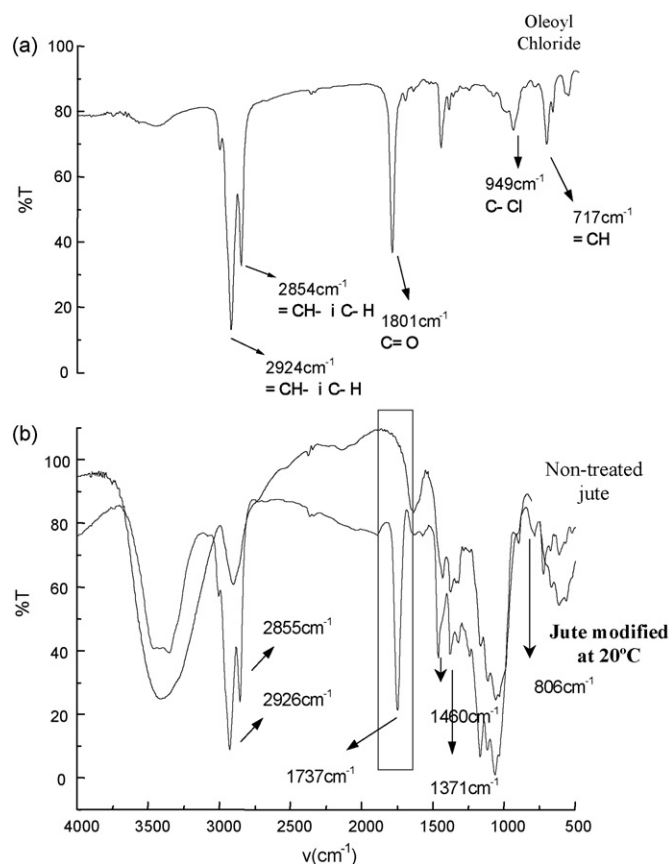


Fig. 2. (a) Oleoyl chloride spectrum; (b) jute fiber non-treated spectrum and jute fiber modified in pyridine 24 h at 20 °C.

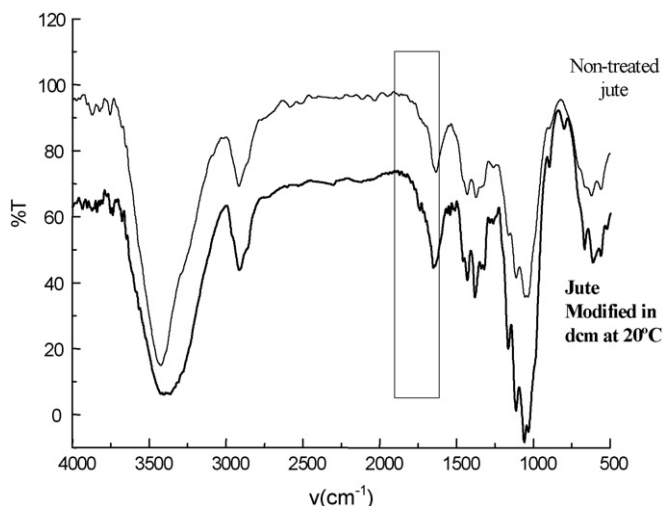


Fig. 3. Jute fiber non-treated spectrum and jute fiber modified 24 h in dichloromethane (dcm) at 20 °C.

was named modification degree referred to carbon increment ($\text{Mod}_{\Delta C}$) and was calculated according to Eq. (A.2). Thus, the modification degrees referred to carbon increment were of 69.4% and 2.3% for the same reactions commented above. When the time reaction was increased up to 48 h, Fig. 4, an increase in molar modification degree of 1.6% was found for the reaction in dichloromethane.

In order to increase the modification degree when using dichloromethane, higher temperature (40 °C) was assayed without any significant improvement. So, triethylamine base was added to the reaction (1.05 equiv. with respect to the oleoyl chloride moles). In this case, the hydrogen cation liberated to the reaction media was neutralized and a displacement of the reaction to the modified fiber was favored. Consequently, higher modification degrees were obtained and significant covalent bonding between the cellulose and the coupling agent was detected by FTIR spectroscopy [20]. The characteristic ester peak at 1737 cm^{-1} (C=O) confirmed the chemical modification. Moreover, the increase of the C–H aliphatic bands at 2918 cm^{-1} and 2852 cm^{-1} corroborated the reaction between the fibers and

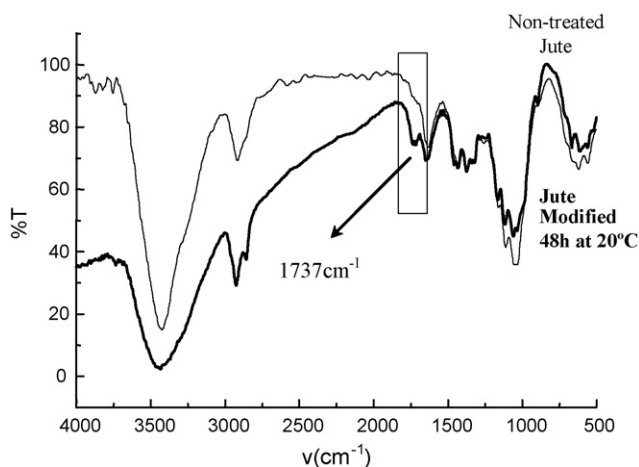


Fig. 4. Jute fiber modified at 48 h reaction.

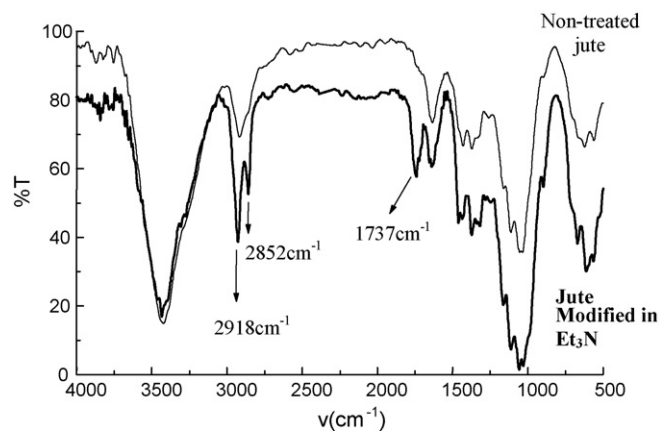


Fig. 5. Jute fibers non-treated spectrum and jute fibers modified 24 h at 40 °C in dichloromethane/triethylamine.

the oleoyl chloride. The spectrum at Fig. 5 shows the modification reaction for the non-swelling solvent, which was stabilized as 22% ($\text{Mod}_{\Delta C}$).

The different behavior between both solvents can be explained on the different swelling capacity of every solvent. Owing the heterogeneous phase of the reaction, the esterification reaction taking place will be a function of the accessibility of the hydroxyl groups. Accessibility is the capacity of coupling agents to achieve the hydroxyl groups in conditions that will occur by means of diffusion mechanism of the coupling agent molecules to the cellulose fiber.

Rowland and Roberts [21] and more recently Joly [22] determined experimentally the accessibility of hydroxyl groups, as shown in Fig. 1b. These authors explained that accessibility is an inverse function of the hydroxyl group capacity to form hydrogen bridges enclases. This indicates that OH in position 3, is more accessible than in position 6, and this are more accessible than the group in position 2. Due to the higher swelling capacity of pyridine, the solvent increases the accessible hydroxyl groups of the fibers, allowing modification not only for the more external hydroxyl groups but also for those in the cavities and in internal layers. Conversely, the use of dichloromethane does not allow the modification below the external layer.

The effect of the catalyser was also investigated and modification reactions using 0%, 1% and 10% of coupling agent were tested. The modification reactions were conducted at 40 °C and 60 °C for dichloromethane and pyridine, respectively, and were kept for 24 h. From the results, it could be said that the presence of catalyser in pyridine solvent did not affect spectacularly the modification degree. It was proposed that the catalytic behavior of the solvent itself was enough for the modification reaction, and any improvement could be observed with additional catalyser (modification degree referred to carbon increment increased from 54% to 80% in presence of 0% and 10% of catalyser). However, for the reactions in dichloromethane, Fig. 6, more significant dependence with the presence of the catalyser was observed. Thus, an increase of the intensity of carbonyl group peak was observed with the amount of the catalyst. This meant that the modification degree enhanced with the amount of catalyser, which gave modification degree referred to carbon

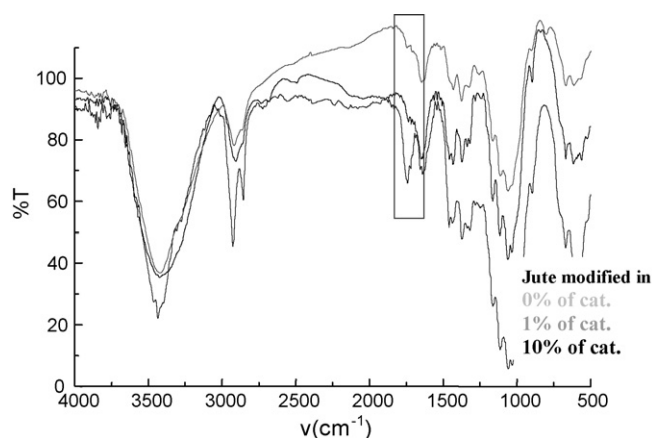


Fig. 6. Modification reactions spectrum in 4-DMAP.

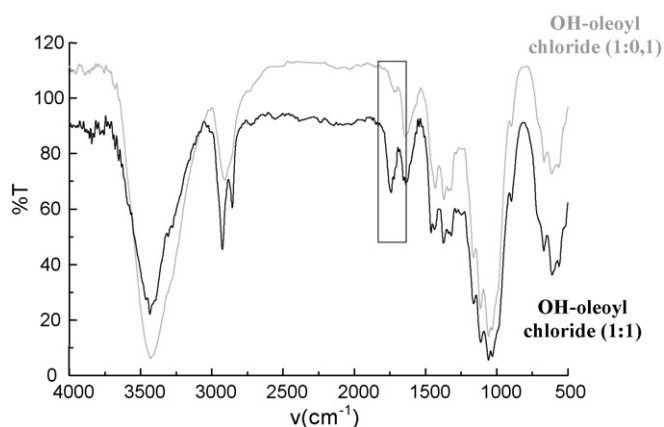


Fig. 7. Modification reactions in two amounts of OCl in dichloromethane.

increment of 5% in absence of catalyser, 8% and 22% in presence of 1% and 10% of 4-DMAP, respectively. It could be concluded that in dichloromethane the catalyst influence was more important. Using catalyser, the reactions took place quickly. For this reason the use of catalyser was essential in posterior reactions. Afterwards, the influence of the reaction time was studied for reactions from 3 h to 168 h. In the case of a non-swelling solvent (40 °C) the modification degree referred to carbon increment

increased from 8% to 49% and the results for the swelling solvent (60 °C) increased from 18% to 84%.

Many authors reported the synthesis of modified fibers using coupling agent in excess with respect to the hydroxyl groups in the cellulose fiber. In this work, the synthesis with two different amounts 1:0.1 and 1:1 molar ratio of hydroxyl groups and coupling agent were studied. The results obtained were noteworthy, especially in pyridine where the molar modification degree increased from 9% to 80%. In dichloromethane the molar modification degree enhanced from 5.6% to 22% for 1:0.1 and 1:1 molar ratio, respectively (Fig. 7).

The volume ratio was also investigated and reactions using 40 mL or 80 mL/g of fiber were carried out. The increase of the solvent amount decreased considerably the modification degree. The effect was less important for pyridine.

Finally, fiber surface was evaluated by scanning electron microscopy (SEM). Higher roughness was observed for the fiber surface after chemical modification with oleoyl chloride (Fig. 8).

4. Conclusions

One of the most important factors in the formation of composite materials is the compatibility of both components at interface. In this paper, the chemical modification of cellulosic fibers with a fatty acid coupling agents in order to improve the wetting and adhesion of the fiber surface by the polymer macromolecules have been studied.

Therefore, oleoyl chloride has been used as coupling agent to turn the hydrophilic surface of jute fibers into hydrophobic, leaving an olefinic residue able to react with the matrix. The esterification of hydroxyl groups during the modification reaction has been evidenced by FTIR spectroscopy, which establishes the development of ester bonds between hydroxyl groups of cellulose fiber and the coupling agent. Elemental analysis was employed to quantify the modification degree. Complementary techniques like scanning electron microscopy (SEM) proved the effectiveness of the modification reaction.

The results confirmed higher modification degrees using pyridine as solvent medium. In this swelling solvent the accessibility of hydroxyl groups was improved. It was assessed that the efficiency of the reaction depends to the solvent polarity and his

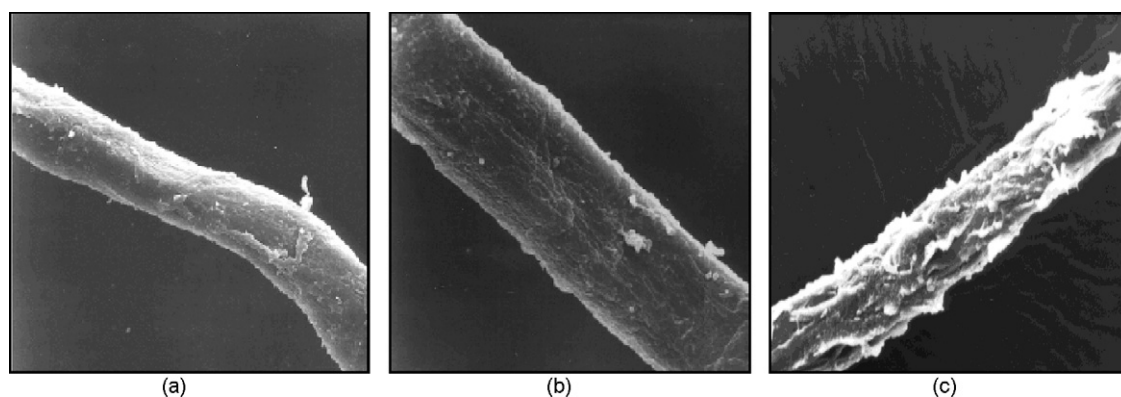


Fig. 8. SEM microphotographies of (a) jute fibers non-treated; (b) jute fibers modified 3 h in pyridine; (c) jute fibers modified 24 h in pyridine.

catalytic capacity; which are two factors governing the extension of the modification reaction. Other factors like temperature, time, and amount of coupling agent, volume ratio and catalyst contribute to the increasing of modification degree.

The carbon chain incorporated with the fatty acid derivate is inducing hydrophobicity to the fiber surface, which might improve its wettability when used as reinforcement for polymeric matrices and decrease the water absorption. The procedure described in this communication is applicable to any substrate bearing hydroxyl groups at their surface.

Acknowledgement

The authors acknowledge the financial support of the Generalitat of Catalonia for the fellowship Ref. 1999TDOC00012.

Appendix A

$$\text{Mod}_{\text{molar}} (\%) = \frac{\text{Mm} \times (w - w_1)}{3 \times (\text{Mcrl} - (w \times \text{Mami}))} \times 100 \quad (\text{A.1})$$

where Mm is the molecular weight for the cellulose monomer ($\text{C}_6\text{H}_{10}\text{O}_5$)_n: 162 g; *w* the t/l of carbons in the modified fibers obtained from elemental analysis; *w*₁ the t/l of carbons in the non-treated fibers (experimental value: 0.4082); 3 the number of hydroxyl groups in the monomer; Mcrl the carbon weight into the coupling agent: 216 g; Mami is the weight of the coupling agent introduced: 265 g.

$$\text{Mod}_{\Delta\text{C}}(\%) = \left[\frac{(\%C_{\text{modified fiber}} - \%C_{\text{fiber}})}{(\%C_{\text{modified cellulose}} - \%C_{\text{fiber}})} \right] \times 100 \quad (\text{A.2})$$

References

- [1] (a) Al. Oliver, H. Joynt, Industrial Hemp Fact Sheet, British Columbia Ministry of Agriculture and Food, Kamloops, British Columbia, Canada, 1999, p. 20;
(b) M. Karus, M. Kaup. Use of natural fibres in the German automotive industry.
- [2] M. Riedel, J. Nickel, Die Angew. Makromol. Chem. 4756 (1999) 34–40.
- [3] H. Hanselka, A.S. Herrmann, VDI Berichte Nr. 1235, 1995.
- [4] A.S. Herrmann, H. Hanselka, H. Nickel, U. Riedel, TECNITEX, Torino, 1996.
- [5] A.K. Mohanty, A. Mubarak, G. Khan, Hinrichsen, Surface modification of jute and its influence on performance of biodegradable jute-fabric, Compos. Sci. Technol. 60 (2000) 1115–1124.
- [6] A. Gandini, W. Botaro, E. Zeno, S. Bach, Polym. Int. 50 (2001) 7–9.
- [7] A.K. Rana, A. Manda, B.C. Mitra, R. Jacobson, R. Rowell, A.N. Banerjee, Short jute fiber-reinforced polypropylene composites: effect of compatibilizer, J. Appl. Polym. Sci. 69 (1997) 329–338.
- [8] V.P. Cyras, C. Vallo, J.M. Henry, A. Vazquez, Effect of chemical treatment on the mechanical properties of starch-based blends reinforced with sisal fibre, J. Compos. Mater. 38 (16) (2004) 1387–1399.
- [9] A.K. Bledzki, H.-P. Fink, K. Specht, Unidirectional hemp and flax EP and PP-composites: influence of defined fiber treatments, J. Appl. Polym. Sci. 93 (2004) 2150–2156.
- [10] S.H. Aziz, M.P. Ansell, The effect of alkalization and fibres alignment on the mechanical and thermal properties of kenaf and hemp bast fibre composites. Part I. Polyester resin matrix, Compos. Sci. Technol. 64 (2003) 1219–1230.
- [11] S. Mishra, M. Mishra, S.S. Tripathy, S.K. Nayak, A.K. Mohanty, Graft copolymerisation of acrylonitrile on chemically modified sisal fibers, Macromol. Mater. Eng. 286 (2) (2001) 107–113.
- [12] S. Mohanty, S.K. Nayak, S.K. Verma, S.S. Triphacy, Effect of MAPP as a coupling agent on the performance of jute–PP composites, J. Reinf. Plast. Comp. 23 (2004) 625–637.
- [13] A.C. Karmaker, J.A. Youngquist, Injection moulding of polypropylene reinforced with short jute fibres, J. Appl. Polym. Sci. 62 (1996) 1147–1151.
- [14] D. Nabi Hahed, J.P. Jog, Adv. Polym. Tech. 4 (18) (1999) 351–363.
- [15] A. Mohanty, K. Mubarak, A. Khan, G. Hinrichsen, Surface modification of jute and its influence on performance of biodegradable jute-fabric, Composites Science Technology 60 (2000) 1115–1124.
- [16] M. Felix, P. Gatenholm, Plasma modification of cellulose fibers, Nordic Pulp Paper Res. J. 51 (1994) 285–295.
- [17] C. Vaca-Garcia, S. Thiebaud, M.E. Borredon, G. Gozzelino, Cellulose esterification with fatty acids and acetic anhydride in lithium chloride/*N,N*-dimethylacetamide medium, JAOCS 75 (1998) 315.
- [18] M. Gou, F. Corrales, F. Vilaseca, Afinidad 61 (513) (2004) 393–395.
- [19] M.L. Lewin, E.M. Pearce, Vol. IV Fiber Chemistry, Marcel Dekker, NY, 1985.
- [20] S.K. Madhuban Gopal, S.K. Bhaduri, K.P. Banerjee, Sao Indian J. Text. Res. 10 (1985) 68–70.
- [21] S.P. Rowland, I.E. Roberts, J. Polym. Sci. Part A1 10 (1972) 2447–2461.
- [22] C. Joly, Thèse, Université Claude Berbard Lyon. I., Mars 1995.